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PLENARY

The heat is on: Power electronics and the challenge of cooling in a changing world

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Keywords: power modules, power electronics, energy conversion, ceramics, direct copper bond

The challenge of global warming (1) (2) has made it essential to improve how we produce and use energy, with a focus on renewable sources like solar and wind power. Efficiently managing this energy is crucial, especially when it comes to transporting and utilizing it in devices that rely on electricity. Modern power electronics play a critical role in this, as they control complex energy conversions and help to distribute energy effectively.

To meet the increasing demand for these technologies, materials science has made significant strides, particularly in the use of advanced ceramics (3)

These materials are critical because they provide both high electrical insulation and excellent thermal conductivity — key features for the next generation of power modules that must operate at high temperatures above 175°C (4) and withstand harsh conditions over extended periods.

Ceramics have proven to be indispensable in this sector due to their durability at high temperatures, resistance to sudden temperature changes, and inertness to chemicals. They are becoming increasingly important for power electronics that are striving for better efficiency and smaller sizes (5).

There's a growing interest in wide bandgap technologies, such as SiC and GaN, which offer compact solutions and increased power density compared to traditional silicon-based power transistors like IGBT (6). The use of wide bandgap technologies also necessitates power electronics that can perform at higher operating temperatures. Although ceramics like AlN and SiN are known for their superior performance, their high cost remains a barrier for widespread application.

To truly transition from fossil fuels to green energy, it's imperative to intensify research and development into new, cost-effective ceramic materials that can conduct heat well. Investing in the innovation of such materials is a crucial step toward a sustainable energy future powered by advanced, efficient, and more affordable power electronics.

Figures

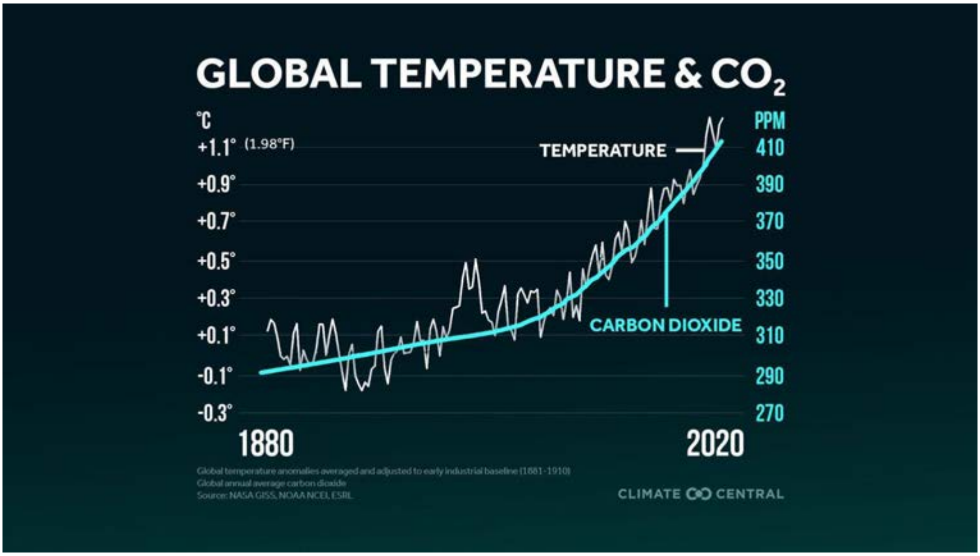

Figure 1: Earth temperature & CO2 development, Source: NASA GISS, NOAA NCEI, ESRL

Figure 2: Current Smart City with examples of energy paths starting from electrical energy creation (e.g. off shore wind, solar panels) to its consumption (e.g. trams/trains, heat pumps, EV charging, factory motors, data centers) and energy storage systems (solid state batteries, water reservoirs).

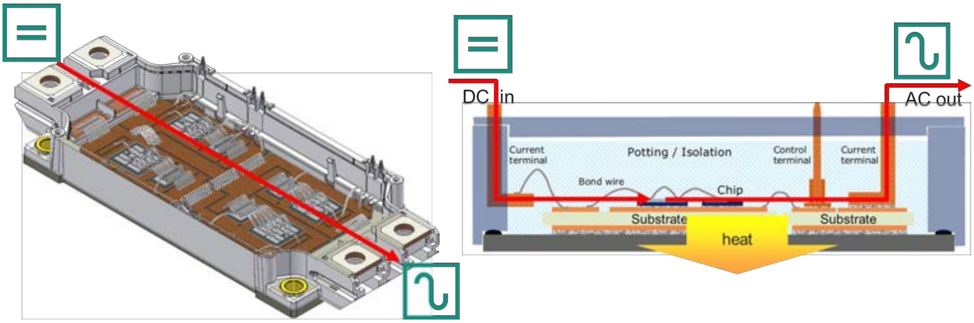

Figure 3: On the left side a 3D drawing of an Infineon Econo2 Power Module including the current path (red) from DC input to AC output. On the right hand side an examplary cross section throuth the same module. The power chips (IGBT or SiC Power Mosfets) are die attached onto a direct copper bond (DCB) here called substrate). The DCB core is typically Al2O3, SiN, AlN. Its most important function is high electrical isolation (to an external heasink) and high thermal conductivity (heat from chips to baseplate and exteranl heatsink, not depicted here).

Acknowledgments

Many thanks to Dr. Jean-Laurent Deborde the ceramic expert from Infineon Technology Warstein and Dr. Marianna Nomann the Head of Engineering at Infineon Cegléd for their contributions and significant support in the creation of this abstract and presentation. Their expertise and their assistance throughout this process has been greatly appreciated.

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Advancements in material selection and optimization for high-efficiency halide perovskite solar cells

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Keywords: halide perovskite solar cells, electron transporting layer, perovskite crystallization, alkylammonium chlorides, TiO_2, SnO_2

Halide perovskite solar cells (PSCs) hold immense promise for next-generation photovoltaic technology, boasting high efficiency and cost-effective fabrication. The architecture of PSCs typically involves a layered structure comprising transparent conductive oxide (TCO), electron transport layer (ETL), perovskite, hole transport layer (HTL), and counter electrode stacks. Meticulous material selection and preparation, particularly focusing on ETLs, HTLs, and perovskites, significantly influence both structural and optoelectronic properties, thereby maximizing performance. Recent advancements in perovskite research have highlighted the efficacy of alkylammonium chlorides (RACl), notably methylammonium chloride (MACl), in modulating perovskite crystallization dynamics, resulting in improved device performance. While TiO_2 stands as one of the most efficient ETL materials, its high-temperature processing poses challenges. Low-temperature processed ETLs, such as SnO_2, have been explored to address this, with novel strategies involving synthesizing SnO_2 colloids in an H_2O_2 solution to reduce oxygen vacancies within the lattice, resulting in enhanced device performance. Furthermore, a hybrid electrode comprising a blend of TiO_2 nanosols and SnO_2 colloidal solution has been introduced, offering superior mechanical reliability and efficiency compared to standalone SnO_2 colloids. Flexible PSCs fabricated with this hybrid electrode demonstrate promising performance, emphasizing the importance of strategic material selection and optimization in achieving highly efficient and stable PSCs. In this presentation, our contributions to optimizing key materials for PSCs will be discussed, encompassing advancements in material synthesis, interface engineering, and device fabrication techniques aimed at pushing the boundaries of PSC efficiency and stability.

Novel oxide ceramic LSI device for the AI age

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Keywords: oxide semiconductor, IGZO

Oxide semiconductor LSI (OSLSI) uses indium–gallium–zinc oxide (IGZO) or indium oxide (IO) as its core material [Ref. 1].

Power saving is an increasingly urgent issue for humanity to mitigate global warming. Servers and other equipment however consume more and more power with the boom of generative AI and its technological innovations, which is raised as a significant issue.

Unlike widely used Si LSI, OSLSI has not been brought into the mass production phase yet, but we have been transferring our OSLSI techhology to achieve its first mass production, which is currently expected to start from the summar of 2024. The first product will be an LSI for OLED/OS/Si displays for AR/VR applications. Our paper on this system display [Figs. 1-2][Ref. 2] is in the top 10% of the downloaded papers among all JSID pepers published in 2022. This leads us to the belief that this product would be suitable as the first OSLSI product.

As a next step, we are developing a highly integrated vertical FET structure for extremely low power consumption computers, which is our true target[Ref.3]. The DRAM active times are set to 1%, 10%, and 90% [Fig. 3], and we aim to achieve nonvolatility of the most power consuming RAM.

In this presentation, we propose a three-dimensional (vertical) oxide semiconductor memory (3D OS memory) as a game changer enabling both global warming mitigation and further spread of AI.

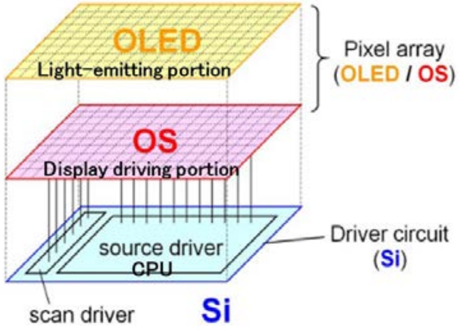

Fig. 1 Conceptuial diagram of the OLED/OS/Si monolithic stack.

Fig. 2 Photograph of the 3 kppi display.

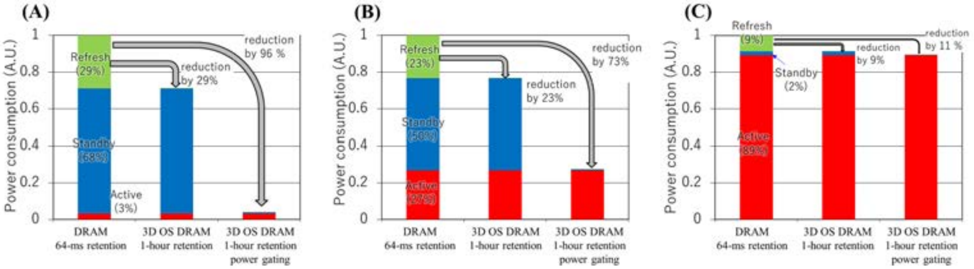

Fig. 3 Power consumption with **conventional DRAM replaced by 3D OS DRAM ((A) 1%, (B) 10%, (C) 90%).**

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KEYNOTE

T1 Ceramics for Energy Conversion, Storage, and Distribution Systems

T1.1 HIGH-TEMPERATURE FUEL CELLS AND ELECTROLYSIS

Status and challenges on Solid Oxide Fuel Cell development for mobility use

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Keywords: SOFC, vehicle, power density, metal support cell, AFA

SOFC (Solid Oxide Fuel Cell) is generally considered for residential and industrial power supply, but in recent years the research and the development of SOFC powered application has been spreading to various applications such as portable device, datacenter, high temperature steam electrolysis and so on. Under these circumstances, Nissan has been researching SOFC-powered system for mobility use as well as stationary use (Figure 1). The requirement of SOFC-powered system for mobility use is different from that of stationary use because operating environment for automotive application is very unique. Among lots of technical challenges from system level to cell level, the increase in power density and the reduction of rapid start-up time are two main challnges to realize SOFC system (Figure 2). In order to install SOFC-powered system on a vehicle, the development of metal supported cell and stack is desirable to realize smaller volume and lower thermal mass which link to improving both power density and start-up time.

In this presentation, technical challenges of SOFC for mobility use are shown. Then, as one of detailed technical topics, the progress of reducing ohimc resistance with using metal supported stack is described. In particular, the technical challnge to use AFA, alumina forming alloy, in a SOFC stack is described. Finally future challenges to expand SOFC application are summarized.

Figures

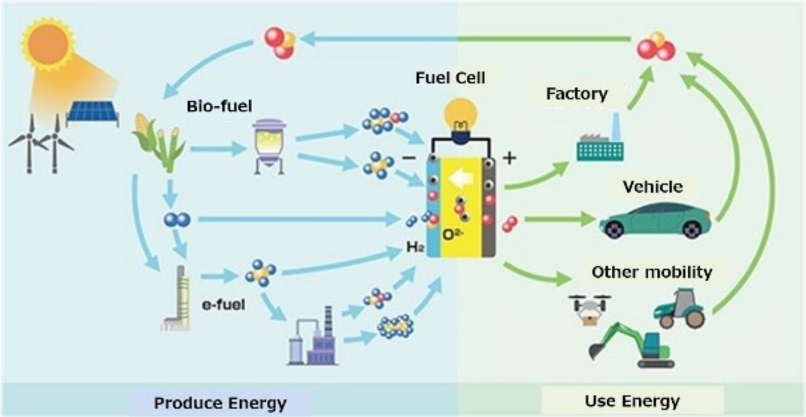

Figure 1. SOFC Research overview[1)] in Nissan

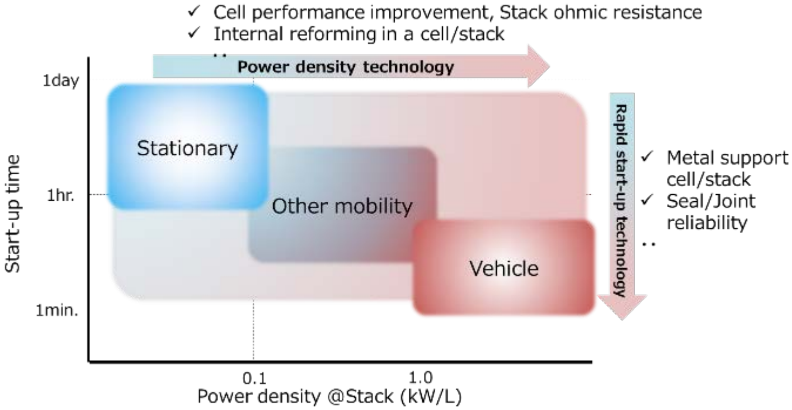

Figure 2. Challenges of SOFC for mobility use

Acknowledgments

Dr. Singh Prabhakar (University of Connecticut) is acknowledged for metal corrosion discussion.

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T1.2 CERAMICS-RELATED MATERIALS, DEVICES, AND PROCESSING FOR HEAT-TO-ELECTRICITY DIRECT CONVERSION AND THERMAL ENERGY HARNESSING

New directions in half-Heusler and metal phosphide thermoelectric materials

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Keywords: half-Heusler, metal phosphide, thermoelectric energy

Thermoelectric conversion can be used to generate power, scavenge ambient heat, is applied in thermal management, and is a potential carbon negative renewable technology. The past two decades have seen major advancements in materials design and greatly improved thermoelectric performance. However, large-scale application is held back by the high cost compared to grid-price electricity, and technical issues in translating materials performance to generators.

Scientifically, the challenge is to find materials that have both low thermal conductivity and outstanding electrical properties, whilst not losing sight of translation into a working technology. This is a difficult challenge but fortunately there is no fundamental limit on the thermoelectric performance.

We have focused on intermetallic half-Heusler materials, and more recently on metal phosphide thermoelectrics. Both are based on abundant elements and could provide a route towards sustainable thermoelectric energy conversion [1].

In the half-Heusler materials, we pioneered the use of interstitial Cu in the leading XNiSn n-type compositions [2]. This enables synergistic reductions of lattice thermal conductivity and improvements in the electronic quality of the materials. Competitive figures of merit, $zT = 1$ at 793 K are found for compositions with high X = Ti content.

Recently, we have used aliovalent alloying as a route to achieve unusually low lattice thermal conductivities, far below expected based on mass and strain disorder [3]. We postulate that this is driven by bond disorder, which unfortunately also reduces the electronic quality of the materials. This limits the maximum achievable performance, requiring a careful trade-off between thermal and electronic parameters.

Metal phosphides are underexplored but offer great structural diversity, often achieving low thermal conductivities, despite low gravimetric densities. The final part of this presentation will give an overview of our recent work on several ternary metal phosphides [4], including high-mobility CaCuP.

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Mixed-anion oxides for eco-friendly high-performance thermoelectric materials

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Keywords: material design, electronic transport, phonon scattering

High energy-conversion efficiency (*ZT*) of thermoelectric materials has been achieved in heavy metal chalcogenides, but the use of toxic Pb or Te is an obstacle for wide applications of thermoelectricity. Development of high-efficiency and eco-friendly thermoelectric materials has been a challenging issue. In this talk, I like to introduce our recent works on the development of eco-friendly high-performance thermoelectric materials using concept of mixed anions. Here, we introduce new design routes for strong phonon scattering and *ZT* enhancement of transition metal oxide, $SrTiO_3$ by hydride anion (H^-) substitution [1] and also recent discovery of high *ZT* ~2.1 in inverse perovskite Ba_3SiO without using toxic elements [2].

Usually, heavy (toxic) elements are widely used to reduce lattice thermal conductivity (κ_{lat}). On the other hand, we found that the light element H^- substitution largely reduces κ_{lat} from 8 W/(mK) of $SrTiO_3$ to 3.6 W/(mK) for $SrTiO_{3-x}H_x$ with $x = 0.216$. The mass difference effect on phonon scattering is small in the $SrTiO_{3-x}H_x$, while substituting a portion of the O^{2-} with H^- results in a mixture comprising a strong Ti–O bond and a weak Ti–H bond. These randomly distributed Ti–(O,H) bonds strongly enhance phonon scattering, in turn, largely decrease κ_{lat}. As a consequence, $SrTiO_{3-x}H_x$ bulk exhibits maximum $ZT = 0.11$ at room temperature and the *ZT* value increases continuously up to 0.22 at $T = 657$ K. The H^- substitution idea offers a new approach for *ZT* enhancement in thermoelectric oxides without utilizing heavy elements.

In addition, we recently discovered high *ZT* in toxic-element free Ba_3SiO with inverse-perovskite structure. Unlike normal perovskites, such as $SrTiO_3$, the positions of cation and anion sites are inverted in inverse-perovskites Ba_3SiO. So, they contain a large amount of the heavy element, Ba, and their crystal structure is formed by a soft flamework made up of weak O–Ba bonds. These characteristics realize the low $\kappa_{lat} = 1.0–0.4$ W/mK in Ba_3SiO bulk polycrystal at $T = 300–600$ K. In addition, the negatively charged Si anion contributes to hole transport with long carrier life time, and their highly dispersive bands with multiple valley degeneracy realize both high p-type electronic conductivity and high Seebeck coefficient, resulting in high power factor (PF). As a consequence of high PF and low κ_{lat}, Ba_3SiO bulk exhibits rather high $ZT = 0.16–0.84$ at $T = 300–623$ K. Finally, based on first-principles carrier and phonon transport calculations, maximum *ZT* is predicted to be 2.14 for Ba_3SiO at $T = 600$ K by optimizing hole concentration. Present results propose that inverse-perovskites would be a new platform of environmentally-benign high *ZT* thermoelectric materials.

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T1.4 Material Science and Technologies for Advanced Nuclear Fission and Fusion Energy

Ceramic composite R&D for fusion energy – U.S. Roadmap

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Keywords: SiC/SiC composites, refractory composites, structural composites, fusion energy

Refractory composites stand as pivotal materials for critical component and advanced subsystem concepts in the exploration of future fusion power. Over recent decades, the use of silicon carbide (SiC) ceramics and composites, most frequently in a form of continuous SiC fiber-reinforced SiC matrix (SiC/SiC) composites, has been assumed in various conceptual design studies. These studies were primarily intended to resolve the design challenges around liquid metal and/or helium cooled blanket, a fusion reactor subsystem that converts kinetic energy of fusion reaction products to heat and facilitates the tritium fuel breeding. Furthermore, there is a recognized imperative for damage- tolerant composites to replace conventional bulk refractory metals or alloys to enable robust plasma-facing components (PFCs) such as the divertor plates and the first wall armor. Moreover, the recent developments of refractory composite technologies have introduced expectations for extra-refractory composites, particularly those featuring ultra-high temperature ceramics, as potential high performance PFC materials. Although promising strides have been made in some material classes, it is crucial to acknowledge that these composite materials necessitate substantial additional research and development (R&D) efforts before robust components can be designed with technical confidence. In 2023, the U.S. fusion materials science and technology community initiated the development of
experts started the development of R&D roadmaps for fusion materials, encompassing the structural and PFC materials. The publication of the initial document is anticipated in 2024. This presentation gives an overview of the preliminary U.S. fusion materials R&D roadmap, with a primary focus on the refractory composite materials.

Acknowledgments

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T1.6 Advanced Batteries and Supercapacitors for Energy Storage Applications

Digital twins of battery manufacturing processes

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Keywords: rechargeable batteries, manufacturing, optimization, digital twins

In this lecture I discuss the concept of digital twin and how it can be used to optimize battery electrodes design and their wet manufacturing process, from powder to power. Different types of pioneering digital twins developed in my research group, coupling numerical simulations with Artificial Intelligence, are presented, with illustrative application examples arising from my past and ongoing research projects, such as the ERC-funded ARTISTIC (https://www.erc-artistic.eu/). Methodologies to ensure the proper experimental calibration and validation of these digital twins are also discussed. Demonstrations of inverse design of lithium ion, sodium ion and solid state battery electrodes are shared, together with the demonstration of the concept transferability to dry electrode processing methods. I also present our Virtual and Mixed Reality tools designed to support the training of students, researchers and operators in the battery manufacturing field. Finally, I will briefly introduce a startup, originating from our work, which gives the promise to be a game changer for battery manufacturing process optimization.

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Materials development for all-solid-state batteries – LGPS-type lithium superionic conductors

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Keywords: solid-state battery, lithium ion conductor

Solid-state batteries are attracting attention. There are advantages when batteries are solid-state. These include improved reliability and safety, increased energy density and power output, shorter charging times and an increased operating temperature range. However, there are still challenges in the development of solid-state batteries

We have been involved in the development of solid-state batteries. We investigated (1) the solid electrolytes to improve the performance of solid-state batteries, and (2) the battery reactions using model-type solid-state batteries.

(1) We have explored new solid electrolytes and found a material $Li_{10}GeP_2S_{12}$(LGPS) with conductivity comparable to or higher than the ionic conductivity of Li-based organic solvent electrolytes. It was also found that the power density of batteries can be dramatically increased by utilizing the advantages of superior ionic conductivity. In the present study, the electrolyte development is reviewed, including recent development of LGPS materials group and future challenges to improve their chemical and electrochemical stabilities and conductivities. Based the LGPS material developments, the intrinsic advantages of the solid-state battery, fast ion diffusion mechanism in the LGPS solids, and the technological development issues necessary for the fabrication of practical batteries will be described.

(2) We have developed model batteries based on the idea that battery reactions can be observed more in detail when batteries are solid-state. Battery reactions proceed at the electrode/electrolyte interface. It is not well understood how the electrochemical reactions at the interface and the changes in the electronic structure of the electrode proceed during charging and discharging. In liquid batteries, the electronic structure is difficult to determine due to restrictions in observation techniques. In solid-state batteries, the electrode-electrolyte interface can be considered as a heterojunction interface in semiconductors. Spectroscopic methods can reveal the electronic structure of the battery. The following topics will be reported: Construction of a thin-film battery to investigate battery reactions, the band structure of the battery, and changes in the band structure during charge-discharge reactions.

As solid-state batteries become practical devices, the battery science and technology will also progress. We expect a new battery science to appear with the new devices.

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Enhanced cathode-solid electrolyte interface for cycle-stable all-solid-state Li-ion batteries

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Keywords: all-solid-state Li-ion battery, NCM cathode, halide solid electrolytes, interface debonding

All-solid-state lithium-ion batteries (ASSLIBs) have been considered suitable alternatives to commercial lithium-ion batteries (LIBs) in the aspect of safety issues that come from using inflammable solid electrolytes to replace organic flammable electrolytes. Nevertheless, much room remains for a better understanding of their properties and behaviors to upgrade their performance to reach the practical application level. Ni-rich layered oxides, $LiNi_{1-x-y}Co_xMn_yO_2$ (NCM), are promising cathodes for high-energy ASSLIBs because of their high capacities and redox potentials, and low material cost when compared with conventional $LiCoO_2$. However, certain challenges associated with their use in ASSLIBs must be addressed for their effective use and industrialization. In particular, the structural integrity of the all-solid-state NCM composite electrodes suffers from not only intragranular cracks but also debonding at the cathode-solid electrolyte (SE) interface. The latter constitutes the major cause of fast capacity fade. To overcome this problem, it is a common practice to apply very high stacking pressure, typically higher than several tens MPa, on the ASSLIBs during operation. Lowering the battery operation stacking pressure, for example, to the level of the liquid-electrolyte batteries will certainly facilitate the wider applications of ASSLIBs. Using the composite cathode consisting of a $LiNi_{0.83}Co_{0.12}Mn_{0.05}O_2$ (NCM811) cathode and brittle Li_3InCl_6 (LIC) solid electrolyte (SE), this study demonstrates that forming a chemically reinforced cathode-solid electrolyte interface via limited interfacial reactions may serve as an effective means to mitigate interface debonding so as to enable ASSLIBs to maintain long-term operation under reduced stacking pressures.

Acknowledgments

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Novel 3D thermal energy storage materials based on molten salts fully encapsulated into patterned printed clay supports

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Keywords: thermal energy storage, molten salt, 3D printing, clays

The thermal energy is one of the most appealing energy sources to reduce the greenhouse gas emissions and the dependence on fossil energy resources. In this way, molten salts stand out as excellent thermal energy storage (TES) materials for medium-high temperature applications, including renewable energies like concentrated solar power (CSP) plants, which are able to dispatch power even during the night time, in contrast to the most well-known photovoltaic technology. However, these molten salts commonly exhibit energy efficiencies below expectations, are highly corrosive to the containers, and can present liquid leakage in their molten state, compromising their storage capabilities. To overcome this problem, a novel approach is presented, which is based on the development of three-dimensional (3D) engineered TES structures (3DTES) able to efficiently storage and release thermal energy to be potentially employed in CSP plants.

Highly macro-porous (~93%) 3D expanded clay supports have been printed by direct ink writing using a strategy that combines optimized patterned architectures with the addition of up to 20 wt.% of pore formers to the printable clay inks. Expanded vermiculite (EV) has been selected as clay material because its low cost, large specific surface area, and high chemical compatibility and thermal stability. 3D printed EV scaffolds have subsequently been infiltrated with molten sodium nitrate due to its high thermal capability and low supercooling, leading to promising 3DTES materials for medium temperature applications (melting temperature ~ 307 ºC), such as CSP systems.

A maximum encapsulation capacity of the molten salt into the scaffold of 87% has been attained, which comes from the full infiltration of the salt into the vertical and horizontal macrochannels of the supports, as well as from the penetration of the molten salt into the macroporous clay struts. The channels configuration and partial infiltration of the struts contribute to avoid liquid leakage of the molten salt inside the 3D structure. In addition, a good chemical compatibility between the supporting material and the salt has been observed. 3DTES exhibit an outstanding thermal energy storage efficiency of ~90% that is maintained after thermal cycling. Besides, they present low supercooling degree (2.7 ºC), good thermal conductivity (1.0 $W \cdot m^{-1} \cdot K^{-1}$), and high corrosion and mechanical resistance (compressive strength of ~46 MPa) despite their lightness (~1.6 $g \cdot cm^{-3}$). These findings encourage the use of 3DTES in medium-high temperature applications, among others, in renewable energies and waste heat recovery.

T2 Ceramics for Energy Conservation and Efficiency

T2.1 Advanced Fiber Reinforced Composites for Turbine Engines

SiC-based Ceramic Matrix Composite behavior enhancement for Gaz Turbines Hot Sections

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Keywords: SiC/SiC CMC, EBC, matrix cracking strength, thermomechanical behavior

Silicon carbide fibers reinforced silicon carbide based-matrix composites and Oxide fibers reinforced Oxide based-matrix composites, are probably becoming a major leading alternative for the design and manufacturing of the next gas turbine engines components as airfoils, shrouds, combustion chambers and exhaust. These materials offer higher temperature capability than the current state-of-the-art metallic superalloys. The growing interest in CMC technologies is directly linked to the new short-term engine design constraints for dual military and commercial aircraft, namely an increase of functioning temperature and an increase of mass saving, a drastic decrease of community noise and air polluting emissions and a specific fuel consumption decrease. During the last fifteen years, substantial research efforts have been devoted to evaluating a wide range of CMC and manufacturing routes. Available experiences, in term of sub-element rig tests and engine ground and flight tests, confirmed the expected gains and provided significant lessons in field service. Furthermore, design tools and tests methods have been optimized for fine understanding of behaviour, damage tolerance, design criteria and certification approach {1, 2]. The aim of this paper, after a brief description of the CMC interests for the next aero-engine generation, is to illustrate these different aspects, through different examples of Safran experiences, including different types of CMC associated to different type of component. These results come from several years of studies of Safran Ceramics. A focus will be done on specific tests methodologies development, for a better analyse of damage mechanism and some engine CMCs components tests will be presented.

Acknowledgments

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Technology trends and market status of fiber-reinforced ceramic composites materials in Korea

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Keywords: ceramic matrix composites, CMC, gas turbine

Ceramic matrix composites (CMC) are mainly applied in high temperatures and extreme environmental conditions. This can have a positive impact on the global environment by increasing efficiency in the aerospace, power generation, defense, and nuclear industries, contributing to solving the global warming problem in various ways.

In particular, SiC/SiC composite materials are currently a game-changer in the aviation engine field and are gradually expanding their application range. South Korea also has the technology to successfully manufacture and deploy its own supersonic fighter through the KF-21 program, and is considering applying CMC to fighters with improved performance in the future. Additionally, two engine manufacturers are also actively reviewing the application of CMC components and participating in various CMC development programs to maximize efficiency and secure international competitiveness. Accordingly, a value chain of universities and research institutes researching and developing CMC, material companies to commercialize it, and end users to utilize it began to form in Korea.

Starting with the SiC/SiC material component development project that began in 2007, we are currently preparing to mass produce 3rd generation SiC fibers (Tensile strength 2.5GPa, Elastic Modulus 300GPa, Oxygen content 1wt%). In addition, over the past 16 years, we have secured the basic technology for manufacturing material parts using LSI, PIP, and CVI processes. In particular, when applying the LSI-based process, we are currently producing and selling various aviation parts, and recently, we are developing a dipping-type infiltration process for mass production (Korea Institute of Energy Research, DACC Carbon, etc.). In addition, in the case of PIP, we are focusing on developing technology to minimize the number of impregnation-heat treatment processes and expand the application temperature range to 2000oC (Korea Institute of Materials Research). CVI process technology has conducted research on matrix strengthening using assisted whisker growth, and is currently conducting research on uniform matrix formation for parts with complex shapes (Korea Atomic Energy Research Institute).

Korea's CMC industry is not limited to gas turbine parts, but is currently expanding its scope of application to the entire industrial range, including small launch vehicles and defense fields, and an explanation of this will be included in the presentation material.

Additionally, the current Korean government has begun strategic investments to become a leading country in the aerospace industry, and is also making efforts to secure a larger market share in the defense industry. Above all, the government has recently placed great importance on research cooperation between countries, and the demand for research is greatly increasing. The CMC field is a very suitable topic for such international joint research, and our Korean research institutes are prepared to conduct co-research at any time, so we have high expectations for it.

Fiber-matrix interphases for damage tolerant and hot gas stable SiC/SiC composites

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Keywords: SiC/SiC composites, fiber coating, damage tolerance, hot gas stability

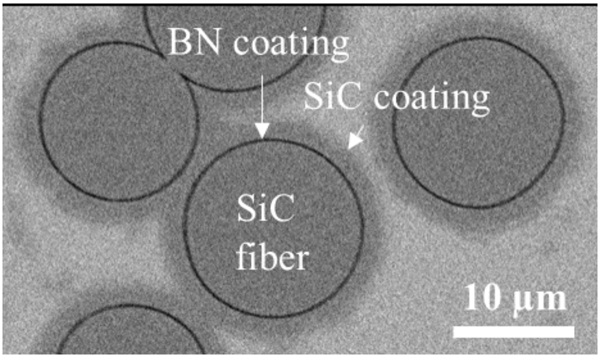
Non-oxide ceramic matrix composites (CMC) provide a damage tolerant failure behavior, a high proportional limit, a high stability at high temperatures and aggressive atmospheres, and a low weight. A prominent example is SiC fiber reinforced SiC (SiC/SiC), which is used for the application in aeroengines. The properties of a SiC/SiC-CMC crucially depend on the properties of the interface region between fiber and matrix, the so-called interphase. The interphase defines the adhesion between the fibers and the matrix. A low fiber-matrix bonding results in a quasi-ductile failure behavior and a high damage tolerance of the CMC. In addition, the interphase protects the fibers during CMC processing and under the conditions of use, e.g., under hot gas corrosive atmosphere.

To ensure full functionality of the CMC under application conditions, a specifc design of the interphase is crucial. Interphase modification in SiC/SiC can be realized by coating of the SiC fibers using chemical vapor deposition. Coating systems based on layers of BN and SiC can fulfill the requirements. Gentle processing routes are necessary to minimize damage to the coating system during SiC/SiC manufacturing by reactive melt infiltration.

To optimize the properties of the interphase in SiC/SiC-CMC, it is necessary to have a fundamental understanding of the interactions between SiC fibers, coating system, and SiC matrix during CMC processing and under the conditions of use. The reactions and damage mechanisms occuring on the nano- and microscale affect the macroscopic fracture behavior of the CMC. These correlations are investigated by extensive high-resolution material analysis, including transmission electron microscopy and single fiber push-out tests. A comprehensive picture of the failure behavior of the SiC/SiC material under hot gas atmosphere results. Based on the various experimental results material models for simulation of crack propagation in SiC/SiC-CMC are developed. The aim is a digital material development, which can predict the ideal interphase design and processing conditions and supports real SiC/SiC material development.

To summarize, the design of fiber-matrix interphases in SiC/SiC improves the failure behavior and the hot gas stability, supporting an implementation of CMCs in industrial applications such as turbines.

Figures



Cross section of SiC/SiC-CMC containing coated SiC fibers.

Acknowledgments

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T2.2 ADVANCED CERAMIC COATINGS FOR POWER SYSTEMS

PVD-based environmental barrier coatings for SiC-SiC CMC components: Current status, challenges and future directions

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Keywords: environmental barrier coating, PVD, CMC

Ceramic matrix composites (CMCs) are promising materials for components in the hot section of gas turbines and are already applied in the latest generation of aero-engines. They can withstand higher service temperatures than the currently used Ni-based superalloys. However, SiC-SiC CMCs possess an insufficient oxidation resistance under the presence of rapidly flowing water vapor as it is present in combustion atmospheres. They suffer from both volatilization of silicon hydroxide, which leads to severe surface recession, and steam enhanced oxidation. Therefore, environmental barrier coatings (EBCs) are mandatory that protect the underlying CMC. In this presentation, multilayer EBCs manufactured by PVD (physical vapor deposition) methods are introduced. Both SiC-based CMCs and model SiC-alloys were coated by magnetron sputtering and by high rate EB-PVD processes. A first layer consisted of a silicon-based bond coat. Oxidation of those Si-based bond coats at high temperatures and the corresponding SiO_2 oxide scale growth rate is a life limiting factor for the EBCs. In this work, two different coating deposition methods were used, namely magnetron sputtering and electron beam physical vapor deposition (EB-PVD) to deposit Si-based bond coats on SiC-SiC substrates. The upper layers consisted of an intermediate rare-earth di-silicate, and a mono-silicate layer for protection against water vapor recession on top. The coating architecture was designed to minimize chemical interactions between different layers and to have a strain tolerant microstructure. Samples were tested up to 1250°C in air in a furnace cycle test and under flowing water vapor at isothermal conditions. The EBC system showed no spallation after up to 1000hrs of cyclic testing and retains stable interfaces between the layers. The oxide scale growth rates for both sputtered and EB-PVD Si-bond coats were measured and its influence on the life time of EBC system will be presented. Special emphasis is put on the phase formation during a mandatory heat treatment of the initially amorphous EBC top layers and the consequences of surface roughness for PVD layers. While the uncoated CMC suffered from severe degradation under flowing water vapor and showed rapid loss of the matrix material after only 1h of testing, the EBC systems considerably lowered the mass loss and provide a good protection of the CMC in this test. Finally, the perfect coverage and good adhesion of PVD-based EBCs on sharp edges and on a real CMC vane structure is addressed. In addition, as $CaO-MgO-Al_2O_3$- SiO_2 (CMAS) is a well-known threat to the EBC functionality, an additional CMAS resistant top layer is necessary which adds more complexity to the multi-layer system. A multi-phase CMAS resistant coating containing Y-Fe-Si oxides has been developed and its applicability on a state-of-the art EBC system will be demonstrated and the CMAS infiltration results at high temperature will be presented.

Manufacture and characterization of advanced termal/environmental barrier coatings

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Keywords: atmospheric plasma spraying, ytterbium disilicate, water vapor recession

Environmental barrier coatings (EBCs) protect fiber-reinforced ceramics (such as SiC/SiC composites) from water vapor recession, which is a major concern in modern gas turbines. In addition to the EBCs, also thermal barrier coatings (TBCs) are needed on top for the thermal protection of the ceramic matrix composites. Both coatings are often made by thermal spray deposition methods; a standard coating material system for EBCs is an ytterbium disilicate (YbDS) topcoat with a silicon bond coat, standard thermal barrier coatings are produced from yttria partially stabilized zirconia (YSZ).

The paper will describe recent results on the APS deposition and characterization of advanced EBCs and also T/EBCs based on YbDS and YSZ.

Results of thermogravimetric measurements of SiC samples coated with silicon bond coat and dense ytterbium disilicate topcoat will give insight in the protection of the silicon bond coat from oxidation by the top layer. The comparison with samples only coated with a silicon bond coat showed a reduced oxidation rate of the sample revealing the low permeation rate of the top coat. In addition, the effect of the heat treatment of the topcoat on the oxidation rate of the bond coat will be shown.

Furthermore, results on the development and performance of combined environmental and thermal barrier coatings using yttria-stabilized zirconia (YSZ) as thermal barrier coating will be presented. Here recent findings on the influence of the degree of crystallization of the ytterbium disilicate before YSZ deposition on the lifetime of the systems in cyclic oxidations test will be discussed.

Finally, advanced characterization tools for investigating water vapor recession will be shown. In addition to furnace tests performed under slow flowing water vapor, the gas burner test rigs already allow testing with higher gas velocities (above 10m/s). The highest gas velocities are available with our high velocity oxygen fuel (HVOF) torch. The impact of the different test conditions on the recession rates will be discussed.

T2.3 ENGINEERING CERAMICS: ADVANCED PROCESSING, PROPERTIES, AND APPLICATIONS

Microstructure and properties of diamond reinforced ceramic materials

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Keywords: diamond, silicon carbide, microstructure, properties

Wear-resistant materials are becoming increasingly important for industry in order to produce sustainable products that conserve resources. One material with excellent tribological and wear properties are diamond reinforced ceramics, especially SiC bonded diamond materials, which can be produced without high-pressure processes. The lecture will present an overview concerning the preparation of such materials, the possibilities of microstructure design and the resulting thermal, mechanical and tribological properties.

Particular attention will be paid to the integration of the hard phase into the ceramic matrix. Diamond is metastable. Under sintering conditions, graphite can form at the interfaces. In the case of SiC-bonded diamond materials, which are produced by silicon infiltration of diamond preforms, the formation of the graphite layer at the interface can be avoided, which leads to a strong bonding of the diamond into the SiC matrix. Results on materials specifically produced with graphitic interface layers show that graphite at the interface does not fundamentally change the interface strength and properties. For example, the wear behavior in the sandblasting test is no worse than that of materials without a graphite interface. The wear rate under these conditions is more than a factor of 10 lower than for SSiC materials. Also, the strength of the interface measured in microcantilever tests is also comparable to the graphite-free interface.

During sliding experiments SiC bonded diamond materials show a low friction coefficient and nearly no wear. The analysis of the worn surface showed that after some initial wear of the SiC network, the wear is determined by the wear of the diamond particles. Similar behavior has been observed with other diamond-reinforced ceramics in which the diamonds are strongly bonded into the matrix.

The materials not only exhibit excellent wear behavior but also very good thermal conductivity of up to 650 W/mK.

The material is therefore interesting for a wide range of applications including nozzles, bearings other wear components and components for thermal management.

Acknowledgments

The presentation is based on data obtained in various projects. We would like to thank the sponsoring institutions (Fraunhofer-Gesellschaft Under Grant No. MAVO 831336; PREPARE 840066, US-Army Research Office under Cooperative Agreement Number W911NF-20-2-0115, BMWK Contract number SubseaSlide 03SX508F).

T2.5 ADVANCED POLYMER DERIVED CERAMICS (PDCS) AND RELATED MATERIALS FOR ENERGY APPLICATIONS

Preparation of highly efficient electrocatalysts from iron-doped polymeric precursors *via* pyrolysis or electrochemical oxidation

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Keywords: electrocatalyst, polymer precursor, pyrolysis, oxidation

Developing sustainable and environmentally friendly energy sources is a huge demand to solve the urgent problem of global scarcity of fossil fuels. Electrochemical water splitting, which involves splitting water into O_2 and H_2 without any byproduct formation, has been developed as one of the most efficient technologies for producing renewable energy.[1] To make use of this advanced technology for large-scale energy production, the development of highly efficient electrocatalysts is required. Since electrochemical water splitting is a surface-dependent reaction involving the adsorption of reactants, interfacial charge transfer, and desorption of intermediates/products, the compositions, morphology, and electronic structures of electrocatalysts should be optimized to obtain remarkable electrocatalysts for electrochemical water splitting. We have developed iron-doped Co-Mo sulfide (Fe-CoMoS) heterostructures with highly efficient water-splitting catalytic abilities from polymeric precursors obtained from cobalt (II) nitrate hexahydrate, iron (III) nitrate hexahydrate, phosphomolybdic acid hydrate and dithiooxamide, which can form a polymeric complex with Co^{2+} ions. Pyrolysis under nitrogen atmosphere gave the electrocatalysts. When diblock polymer with polystyrene and poly(acrylic acid) chains were added during the precursor synthesis without the use of the iron source, the mesoporous Co-Mo sulfide composite (CoMoS), which exhibited bifunctional activities for both the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER).[2] Intrinsic electronic structure optimization achieved by doping of iron into CoMoS (Fe-CoMoS) improved its catalytic activity and stability. Electrochemical measurements revealed that this structural optimization promoted enhanced electrical conductivity and increased the number of electrochemical active sites on the Fe-CoMoS, leading to its remarkable electrocatalytic performance as a bifunctional catalyst for both HER and OER in alkaline media. When a triblock polymer (polystyrene-*b*-poly(acrylic acid)-*b*-poly(ethylene glycol)) was added instead of deblock polymer during the precursor synthesis (without the iron source), a hollow CoMoS electrocatalyst was obtained, and the iron-doping further improved the catalytic activity for both HER and OER.[3] The iron-doped precursor itself, moreover, also exhibited electrocatalytic activity for OER.[4] After electrochemical activation of the iron-doped precursor under OER conditions, evolution of crystalline metal (oxyhydr)oxides with morphological reconstruction proceeded and catalytic activity was further improved.

Acknowledgments

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T2.6 SUSTAINABLE MATERIALS AND SYSTEMS FOR ENERGY EFFICIENT BUILDING AND STRUCTURES

Frequency and temperature dependent dielectric response of electrochromic tungsten oxide thin films

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Keywords: tungsten oxide, electrochromism, dielectric properties, smart windows

Electrochromic devices that exhibit reversible color changes under applied low voltage have promising applications for energy efficiency in buildings. In particular, electrochromic windows represent an emerging technology to control indoor lighting and improve building energy usage by modulating sunlight transmission. Among electrochromic materials, tungsten oxide has generated substantial interest due to its superior electrochromic performance as an active layer. This study aims to elucidate the underlying electrochromic mechanisms in tungsten oxide thin films through detailed investigations of dielectric properties. The real and imaginary dielectric behavior of tungsten oxide films were measured using broadband dielectric spectroscopy from 183-373 K temperatures across 10^{-1} to 10^{7} Hz frequencies. Analysis of the frequency and temperature dependence of the complex dielectric response provides insights into the nature of charge transport. The results indicate that the electrochromic switching process involves hopping of charged particles between localized states, in the tungsten oxide films. By establishing these fundamental conduction mechanisms, this work advances the rational design of efficient electrochromic devices with improved switching speeds for next-generation smart window applications for buildings.

T3 Ceramics for Environmental Systems

T3.2 Ceramics for Carbon Capture and Storage Technologies

Designing ionic liquid mixtures for direct air capture membranes with ceramic layers

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Keywords: direct air capture, ionic liquid, CO_2 absorption, separation membrane

In the pursuit of the 1.5°C scenario outlined in the Paris Agreement, achieving carbon neutrality by 2050 and implementing negative emissions thereafter is crucial. Besides electricity decarbonization, energy conservation, and fuel switching, integrating carbon capture, utilization, and storage (CCUS) from point emission sources into society is essential. Furthermore, to realize negative emission post-2050, the deployment of negative emission technologies (NETs), which directly capture and sequester CO_2 from the atmosphere, is imperative. NETs include afforestation, blue carbon, accelerated weathering, and direct air capture with carbon storage (DACCS), offering significant CO_2 reduction potential. While DACCS is presently expensive, technological advancements may render it cost-competitive with other NETs. Current DAC technologies employ chemical absorption or adsorption, requiring substantial thermal energy for CO_2 recovery. Several research groups, including ours, are investigating membrane-based DAC (m-DAC) technologies. As membrane separation, in principle, does not rely on thermal energy, m-DAC systems may operate solely on renewable energy sources.

The concentration of CO_2 in the atmosphere is 0.04%. To capture CO_2 at such low concentrations, facilitated transport membranes (FTMs) offer significant advantages in separation performance. Ionic liquids (ILs), non-volatile and non-flammable solvents, show promise as materials for FTMs because of their superior CO_2 permeability compared to conventional amine polymers. Our research group recently achieved a breakthrough in m-DAC by designing IL mixtures. Through molecular structure optimization and mixing ratio adjustment, we demonstrated CO_2 permeability and CO_2/N_2 selectivity of 25893 Barrer and 10059, respectively. As illustrated in Fig. 1(a), the CO_2 selectivity of the mixed IL membrane (red circle) exceeds conventional polymer membranes by 500 times with comparable CO_2 permeability (solid line). Theoretically, a single-stage mixed IL membrane can concentrate 0.04% CO_2 to 80%. ILs offer the advantage of facile membrane production. Fig. 1 (b) is a photograph of the prepared IL membrane. A layer of ceramic particles is coated on top of a porous hydrocarbon membrane, and the IL supported by the ceramic particles acts as the CO_2 separation layer. We successfully fabricated a prototype IL membrane using Roll to Roll technology with the gravure coating method, as shown in Figure 1(c). In the presentation, we will delve into the detailed characteristics of the mixed IL membrane.

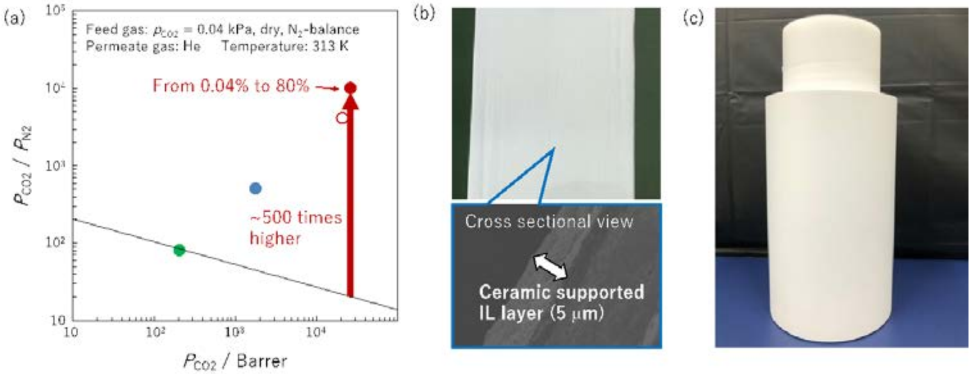

Fig. 1 CO_2 permeability and CO_2/N_2 selectivity of IL membranes with an upper boundary (Energy Environ. Sci., 12, 2733 (2019)), and photographs of ceramic supported IL membrane (b) and a prototype IL membrane (c).

T3.5 Advanced Sensors for Energy, Environment and Health Applications

Surface modifications for thin films gas sensors applications

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Keywords: surface modifications, thin films, gas sensing

Metal oxides have been identified as emerging candidate in sensing of several gases due to their unique properties including feasibility to doping, low cost in fabrication, higher stability, and non-toxicity. Metal oxides can be prepared in many formats such as nanotubes, nanowires, nanorods, and thin films. The later format especially those prepared by physical vapour deposition offers the advantages of easy scalability, excellent reproducibility, producing high purity materials, and high compatibility of the sensing materials with substrates. However, thin films have not been extensively used as compared to other nanostructured materials because of their slow response, low sensitivity, and long recovery time.

In our previous works, three efficient strategies were developed to enhance the gas sensing performance of thin films-based sensors synthesized by physical vapour deposition techniques. The first strategy including develop a facile experimental setup to prepare high surface area metal oxide thin films using thermal oxidation of as-deposited metal oxide at low values of oxygen partial pressure via a buffer gas mixture of H_2O and H_2 at different temperatures.

In the second approach, the as-prepared thin films such as ZnO and SnO_2 were modified by incorporating highly uniform and controlled size noble metals, such as, Ag, and Au in a series of three consecutive steps. First, metal oxide thin films were prepared by DC sputtering. Then, an ultra-thin layer of the noble metal was deposited on the metal oxide surface [2-4]. Finally, metal/metal oxide films were annealed at different temperatures to obtain nanostructured morphology of M on the metal oxide thin films.

In the latest method, we developed a new method to fabricated metal A/metal oxide/metal B systems with different contents of metal oxide, metal A, and metal B through sequential DC sputtering and subsequent post-heat treatment. This approch open the door for engineering the depletion layer of metal oxide thin films through decoration with a controlled amount of metals weights in addition to the variation of metal oxide layer thickness [5-6].

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Low level nitrogen oxide detection: Relevance for disease diagnosis, climate change and air pollution

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Keywords: electrochemcial, optical, agriculture, diesel emissions, asthma

N_2O (nitrous oxide), NO (nitric oxide) and NO_2 (nitrogen dioxide) are the three stable oxides of nitrogen and $NO+NO_2$ is referred to as NO_x. These oxides of nitrogen play an important role in some of the most important issues facing humanity today: climate change, atmospheric pollution, agriculture and biomarkers of inflammatory disease. Nitrogen chemicals in soil, including from fertilizers are converted into nitrous oxide (N_2O) and NO_x ($NO+NO_2$) by soil microorganisms. NO_x contributes to air pollution via formation of fine particulate matter and ozone, and N2O is a key greenhouse, 300 times more potent than CO2. NO_x emissions from diesel-based combustion caused 38,000 premature human deaths globally in 2015 and loss of global crop (soy, wheat, maize) production by 3-10%. Asthma-related illness continues to climb worldwide, some 334 million people suffer from asthma and these numbers are expected to increase. Measurement of exhaled NO is recommended by the American Thoracic Society as a quantitative, noninvasive and safe method for asthma diagnosis and subsequent treatment. To make an impact in these diverse areas, a unified challenge is to develop nitrogen oxide sensors that have high sensitivity (ppb-ppm level), and yet can discriminate against hundreds of other potential interfering molecules.

In this talk, we will discuss designing solid state electrochemical NO_x sensors that can alleviate the emissions from diesel engines, addressing an unmet need for NO_x sensors in the 1-20 ppm range for diesel emission control, since current commercial sensors do not function well in this range. Fertilizers, based on ammonium compounds and nitrates are essential for growing crops that feed humanity, but their use leads to the formation and release of N_2O and NO_x. Inexpensive N_2O and NO_x sensors that can be deployed for both soil subsurface and ambient gas measurements will allow farmers to use fertilizers judiciously. Our agriculture-focused sensors for N_2O utilize near-infrared spectroscopy, and sensors for NO_x are based on solid-state electrochemical sensors. These technologies have been demonstrated for making ppm and ppb measurements of ambient N_2O and NO_x, respectively. We will also present data on analysis of exhaled nitric oxide in breath at ppb levels using solid-state electrochemical sensors as a method for asthma diagnosis.

Selective sensors for non-invasive diagnostics and wearables

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Keywords: selectivity, sensors, non-invasive diagnostics, wearables

The next generation of semiconductor materials and processes will target personalized medicine and ubiquitous environmental, infrastructure, and health diagnostics while affording rapid computations. How this will be achieved is the big unknown; however, there are several research avenues currently been explored. We present here novel and convergent approaches for the accelerated maturation and manufacturing of the semiconducting materials of the future, with emphasis on scalability, sustainability, and affordability, targeting sensing systems and devices. We have pioneered the crystallo-chemical approach for selective chemo-sensing; and have advanced nanomanufacturing by producing novel, scalable tools for nanofibrous (woven and non-woven) (bio-)sensing materials. We have engineered advanced, one-of-a-kind type materials of diverse functionality, from electrospun single crystal metal oxide nanowires for use in sensing and photocatalysis to chemo-actuating semi-conducting polymer composites for wearable sensors. One example is our “Smart Connected Health” related project currently funded by the National Science Foundation that we lead. There is a team of experts including sensor materials, mechanobiology, wireless communications, nutrition, computer science and machine learning, assembled to produce novel, non-invasive, non-intrusive, widely accessible wearable sensors and health monitoring tools.

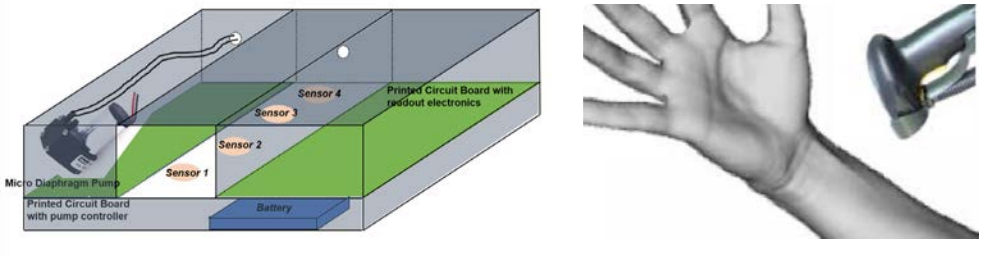

Figure 1: Schematic of one of the skin-gas devices developed in our lab for non-invasive and non-intrusive health diagnostics

Acknowledgments

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MEMS and solid state sensors for developing platform gas sensing technologies

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Keywords: hydrogen, gas sensors, semiconductor

MEMS and solid state sensing methodology offers new opportunities for developing platform gas sensing technologies based upon a number of scientific principles for widespread applications in safety, environmental protection, health and wellness applications, process control and enabling support for green technologies[1-4]. With anticipated growth in hydrogen production, storage, use as an important energy vector in fuel cells and other applications, hydrogen monitoring and control will assume a great importance to minimise losses and increase safe use of hydrogen. This paper will review the current methods available for sensing hydrogen in environment and in gaseous mixtures. MEMS and solid state sensors that have been developed in University of Cambridge are commercialized for hydrogen sensing and extended to many other gases. New research has led to development of miniaturized sensor on a semiconductor chip using the intrinsic property of the gas itself and results will be presented.

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T4 Cross-Cutting Materials Technologies

T4.1 COMPUTATIONAL DESIGN AND MODELING

Prediction of thermomechanical properties of model refractory ceramics using an innovative multiscale discrete element modelling approach

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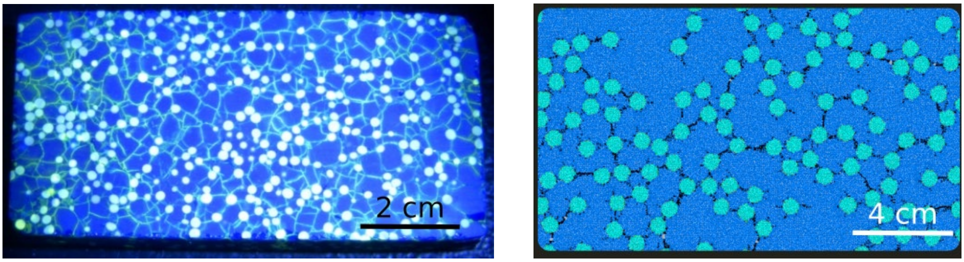
Keywords: discrete element method, refractory, ceramics, thermomechanical, microstructure

A large class of ceramics are, at microscopic scale, non-homogeneous materials. Among these, refractory materials used in very high temperature industrial processes are highly heterogeneous. Such refractories have multi-phase compositions and contain different sizes of aggregates, different bonding systems and additives. This complex design results from their operating conditions. Widely used as structural ceramics, refractories are also exposed to severe environments, often combining mechanical and thermal loads, corrosion and abrasion. In particular, refractories are subject to thermal shock, thermal cycling and severe thermal gradients. A key property for sustaining these conditions is the so-called thermal shock resistance, which depends on many macroscopic thermo-mechanical properties such as stiffness, fracture toughness, Poisson's ratio, thermal expansion coefficient and thermal conduction. These macroscopic properties are strongly influenced by the presence of microcracks, which can be voluntarily introduced into the initial microstructure to promote energy consumption during fracture processes. Mechanical or thermo-mechanical modelling of such complex microstructures, taking into account their micro-cracks, is largely based on continuum mechanical models: finite element method associated with cohesive zone model, extended finite element method, continuum damage mechanics or phase field methods. However, such methods have fundamental difficulties in dealing with multi-fracture problems such as crack initiation, crack extension, crack branching, multi-cracking or crack closure. The Discrete Element Method (DEM) is a promising alternative to continuum based approaches because DEM naturally can deal with discontinuities and has been successfully used to simulate the damaged microstructure of quite similar materials such as rocks and concretes. However, very few studies in the literature consider thermal effects at the microstructure scale that lead to microcracking and internal stresses. A first study was carried out in 2017 [1] for very simplified bi-phase systems (see Figure 1). In this study DEM was able to predict crack networks resulting from thermal effects and the induced changes in macroscopic properties in a very simplified multi-scale approach.



a) Real bi-phase alumina/glass material

b) DEM model of a bi-phase alumina/glass

Figure 1. Crack generated by thermal expansion mismatch in a model bi-phase material [1]

However, quantitative simulations are very difficult to achieve because DEM uses local force-displacement laws instead of the stress-strain relationships commonly used in mechanical engineering. In 2019, a new numerical approach called iDLSM [2] was proposed, which allows for continuum mechanics formulations within the DEM framework. The proposed study focuses on recent advances using this method applied to refractory materials.

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T4.2 ADDITIVE MANUFACTURING & 3D PRINTING TECHNOLOGIES

Ceramic processing with light

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Keywords: additive manufacturing, advanced ceramics, transparent, two photon polymerization

In order to be able to manipulate ceramic powder compacts and ceramic suspensions (slurries) in their volume with light, a minimum transparency of the materials is required. Compared to polymers and metals, ceramic materials are characterized by the fact that they have a wide electronic band gap and therefore a wide optical window of transparency. The optical window generally ranges from less than 0.3 µm to up to 5 µm wavelength. Light scattering properties of the ceramic particles can be tailored by their size. In this study, we present the physical background and material development strategies for the application of two-photon polymerization (2PP) [1,2], Xolography [3] and selective volumetric sintering [4] for the additive manufacturing of structures in the volume of ceramic slips and green compacts.

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Additive manufacturing of carbon and carbide materials for energy applications

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Keywords: carbide, toplogy optimization, additive manufacturing, stereolithography, binder jetting, selective laser sintering, thermal treatments

Ceramic additive manufacturing (AM) has been successfully employed to produce components with mid-high dimensional ranges. Some applications in electronics, biotech, microreactors demand for complex structures with higher precision. We present the state of the art on the three most promising ceramic AM techniques for carbon and carbide materials:

- binder jetting and
- selective laser sintering (SLS) of polymers.

These AM techniques form an intermediate product which must be further processed through a thermal treatment. It can be sintering for oxides, polymer infiltration and pyrolysis (PIP) or reactive metal infiltration (RMI). The last two for carbon and carbides.

Binder jetting and SLS techniques to date have a lower resolution, but they are better suited to produce carbon and carbide complex structures. These technologies have several advantages, i.e., high maturity, low cost and, thanks to new machines available on the market, a better resolution.

TPMS structures during their manufacturing process

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T4.3 NOVEL, GREEN, AND STRATEGIC PROCESSING AND MANUFACTURING TECHNOLOGIES

Additive manufacturing of ceramics from preceramic polymers

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Keywords: additive manufacturing, preceramic polymers, porous ceramics

Additive manufacturing of ceramics is somewhat limited by their high melting temperatures and the processing issues related to handling of feedstocks containing a large volume of particles. Processing slurry-based feedstocks, in fact, poses several challenges: a high amount of powder is required to promote densification and results in high viscosity, scattering and sedimentation phenomena in vat photopolymerization processes, as well as clogging problems at the nozzle for extrusion-based processes.

Some of these issues can be solved or mitigated when using all liquid feedstocks. Our research activities have therefore focused on additive manufacturing of ceramics from liquid feedstocks. In particular, we investigated the use of preceramic polymers as well as sol-gel solutions. Despite the many advantages related to their liquid nature, there are also some challenges related to the reactivity of sol-gel systems and to the high amount of solvent usually present.

Here, our strategies for producing high quality ceramic components using a variety of liquid feedstocks and different additive manufacturing techniques, from direct ink writing, digital light processing and two photon polymerization to robotic arm manufacturing and volumetric additive manufacturing will be presented.

Energy-efficient sintering of ceramics by rapid local heating

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Keywords: flash sintering, UHS, YSZ, alumina

Conventional sintering is a slow and energy intensive process, involving the heating of both the components to be sintered and the furnace to high temperatures for many hours or even days. Recently however, very rapid sintering, in only a few seconds, has been demonstrated using processes that apply the final heating locally, mainly to the component itself. There is thus the potential for tremendous energy savings in terms of both the time spent at high temperature and the mass of material heated.

Several methods of heating ceramic green bodies rapidly in this way have been demonstrated, including internal heating by passage of an electric current through the sample (flash sintering, FS) and local external heating by low thermal mass heating elements (Ultra-fast High-temperature Sintering, UHS). The first part of this presentation considers the mechanisms involved and whether there is a real acceleration of sintering or whether the apparently rapid sintering is mainly the elimination of the slow heating stages normally employed. The mechanisms considered include electrochemical reduction, plasma formation and microstructural refinement as well as the diffusion of matter that is ultimately responsible for sintering. It is shown that plasma formation can lead to secondary improvements in the sintering of boron carbide by cleaning the powders in the green body and that microstructural refinement in rapid heating of YSZ leads to a considerable acceleration of sintering in this system. However, experiments on alumina that effectively exclude everything except the sintering itself show, by the analysis of sintering kinetics and the use of tracer diffusion, that there is a further contribution to the genuine acceleration of sintering from grain boundary diffusion. The possible reasons for this are discussed, focusing on the possibility of non-equilibrium grain boundary structures.

The presentation concludes with a brief consideration of the factors that need to be overcome for rapid sintering technologies to be taken up commercially, including the non-uniformity of sintering, the level of energy and cost savings and the complexity of the process. Potential solutions are demonstrated.

T4.4 POWDER PROCESSING TECHNOLOGY FOR ADVANCED CERAMICS

Carbon nanotube thin films for energy applications via the floating catalyst chemical vapor deposition (FC-CVD) method

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Keywords: carbon nanotube, thin film, transparent conductor, solar cell

FC-CVD is a highly promising technique for the continuous, scalable synthesis of single-walled carbon nanotubes (SWNTs), especially for the direct deposition of highly conducting, transparent, flexible as well as stretchable SWNT thin films for electronics[1] and energy[2] applications. Our single walled carbon nanotubes have been used as core material to develop the new material of one-dimensional van der Waals heterostructures[3]. We have been developing FC-CVD systems with several carbon precursor molecules, including CO, C_2H_4, CH_4, ethanol, methanol, isopropanol, and toluene, using mainly iron catalyst nanoparticles. We have determined the SWNT atomic structure i.e. (n,m) distributions directly via the electron diffraction of individual tubes supported by the optical absorption spectroscopy studies. Using ferrocene as the catalyst precursor, CO as the carbon source and CO_2 as the growth promoter, we show that the SWNT (n,m) distribution and the related thin film color[4] can be directly tuned by adjusting the CO_2 concentration. Also, the fraction of metallic tubes can be tuned via adding carbon dioxide. We will present results on the synthesis of mainly semiconducting tubes from ethanol via adding methanol, and also from isopropanol as the carbon source when using nitrogen carrier gas with minor fraction of hydrogen as the carrier gas. The chiral angle distributions from both CO and ethanol are biased towards the armchair side, while those from hydrocarbons are rather flat. We will present nanotube thin film applications as capacitive touch sensor and as transparent electrodes in organic as well as perovskite solar cells[5] with flexible form factor.

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Formulation of micron-scale, nano-structured hetero-aggregates in opposed jet fluidized beds

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Keywords: nanoparticles. aggregation, fluidization, hetero contact, mixing

Micron-scale hetero-aggregates, i.e. aggregates made up of nanoscale primary particles of different materials, show superior performance compared to homo-aggregates in various applications, e.g. in (photo-)catalysis by formation of hetero-junctions between semiconductor nanoparticles. Thus, the catalytic activity of a hetero-aggregate system will be linked to the structure of the hetero-aggregate, i.e. the mixing of the components and the contact between the primary particles. In the context of photo-catalysis, especially systems based on titania and another semiconductor are widely employed for applications such as water splitting, the degradation of organic contaminants or solar cell applications (cf. particle-based variants of dye sensitized solar cells).

Within this contribution, the feasibility of opposed jet fluidized beds for formulation of titania-zirconia hetero-aggregates will be demonstrated and the effect of process parameters (feed composition, process time, jet velocity) on the intra- and inter-aggregate mixing will be discussed.

Hetero-aggregation in this setup is induced by the two consecutive mechanism: homo-aggregates are broken and de-aggregated in zones of high stressing and subsequently re-agglomeration of primary particles and fragmented aggregates to hetero-aggregates occurs in the top section of the jet fluidized bed.

The obtained hetero-aggregates are investigated by scanning electron microscopy (SEM). For characterization of the mixing of the TiO_2-ZrO_2 hetero-aggregates, energy-dispersive X-ray spectroscopy (EDX) within the SEM has been employed and the compositional variance within a single hetero-aggregates, respectively, the ensemble compositional variance is employed as a descriptor for intra- and inter-aggregate mixing. Prospects and limitations of SEM-EDX for mixing characterization of (porous) hetero-aggregates consisting of submicron primary particles are outlined.

The formation of hetero-aggregates is also addressed numerically by an Euler-Euler approach. The mixing behaviour of the solid phases in combination with the impact of the fluid phase, various solid factions and initial fluid velocities have been taken into consideration. By varying the solids load, the solids distribution during the process is shifting more towards high dense regions at the walls and the top section and dilute regions within the focus region of the Laval jets. Regions of interest for the formation of hetero-aggregates have been identified by considering the granular temperature between the two solid phases. Aggregate breakage is supposed to occur within the focus region of the Laval jets, whereas agglomeration is triggered in the top region of the jet fluidized bed. The regions of breakage and aggregation are more pronounced for higher initial air velocities and solids loads, as the collision probability increases.

Fabrication of transparent ceramics by slip casting in magnetic field and SPS

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Keywords: lanthanum silicate, YVO_4, grain size, orientation

Transparent ceramics can maintain their transparency and structural integrity at elevated temperatures, making them valuable for high-temperature environments and applications. Transparent phosphor ceramics can be expected to be high brightness in order to apply for lighting, displays, sensors, and optical communications, etc. Aother application for transparent ceramics is Laser. Extremely low porositeis are indispensable for taransparency in polycrystalline ceramics. Colloidal processing is a very effective technique for controlling the pore size distribution in green compacts before densification by sintering. The green compacts having small residual pores is expected to enhance the densification. Furthermore, spark plasma sintering (SPS) is also effective way for densification in low sintering temperature. In ceramics with anisotropic crystal structure, in-line transmittance deteriorates due to birefringence due to the difference in refractive index at grain boundaries. Crystallographic orientation is effective for improving the in-line transmittance when it is necessary to suppress birefringence at grain boundaries. Orientation can be controlled by a magnetic field even in a diamagnetic and paramagnetic ceramics.

In this study, the processing was applied to fabrication of transparent YVO_4 and lanthanum silicate. Single phase $La_{9.5}(SiO_4)_6O_{2.25}$ (LSO) powder was synthesized by solid state reaction at 1400 °C for 6 h. The slurry dispersed the milled LSO powder was consolidated by slip casting in a magnetic field (0 – 12 T). The green bodies were sintered at 1200-1550 °C in vacuum at pressure of 100 MPa.The c-axis orientation LSO was aligned parallel to the magnetic field and then transparency was achieved by densification using SPS. In the case of LSO with random orientation, the transmittance increased with the decreasing of grain size (Fig. 1) and with the increasing the degree of orientation.

In the case of YVO_4, the c-axis was aligned parallel to the magnetic filed. Sintereing additives enhances the density. However, excess amount of addtives deteriorated the degree of orientation. YVO_4 was densified by SPS at 1300 °C and 100 MPa.

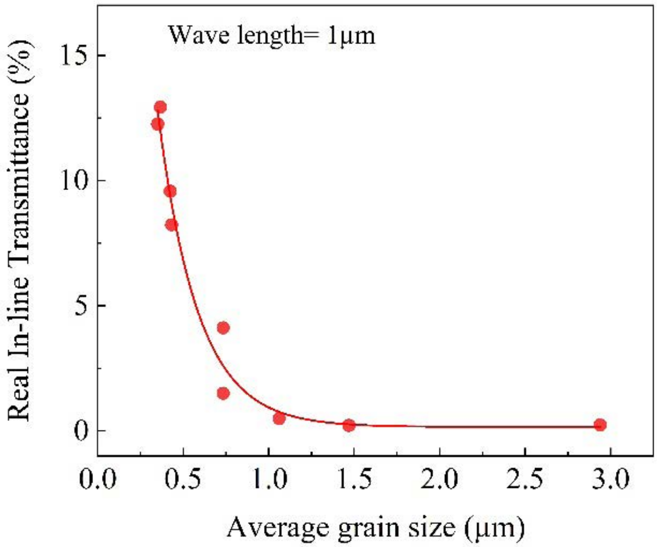

Fig. 1 In-line transmittance as a function of average grain size in random LSO

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T4.5 Advanced Materials, Technologies, and Devices for Electrooptical and Biomedical Applications

High peak power fiber lasers and their applications for ceramic cutting and drilling

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Keywords: fiber lasers, rare-earth doped fibers, ceramic cutting, ceramic drilling

Because of the outstanding stability compared to other types of lasers fiber lasers have been widely employed for industrial application. The relatively low peak power is one of the major limiting factors for fiber lasers due to the small core diameter and long length of the fiber. We have developed innovative rare-earth doped gain fibers with an extremely large core diameter single mode fiber. High peak power and high pulse energy fiber lasers have been developed.

Laser processing machines have been developed by using our picosecond and nanosecond high peak power and high repetition rate fiber lasers. A drilling speed of more than 60mm/s was achieved for 0.5mm thickness glass, which is more than 3 times faster than solid state lasers. Ceramic substrates of aluminum oxide, aluminum nitride, silicon nitride were cut and drilled by lasers.

With the rapid development of consumer electronics, there is an increasing demand for precision processing of crystals, glass and ceramic materials. Laser processing has outstanding advantages in the precision manufacturing of inorganic non-metallic materials with high quality, high precision, high efficiency, and environmentally friendly manufacturing. This presentation will describe the interaction of our nanosecond and picosecond fiber lasers with inorganic non-metallic materials.

T4.6 Multifunctional Coatings for Energy and Environmental Applications Applications

Novel applications of the powder aerosol deposition method in the field of energy conversion and energy storage

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Keywords: owder Aerosol Deposition Method, room temperature impact consolidation, all-solid-state batteries, perovskite solar cells, oxide and proton conductors, flexible thermoelectric converters

Lithium ion conducting electrolytes[1] and cathode active materials for all-solid-state batteries[2], sodium ion conducting membranes for post-lithium batteries[3], solar cells of organo-halide perovskites[4], materials for flexible thermoelectric generators[5] or others – such exciting applications can be manufactured at room temperature with the Powder Aerosol Deposition Method (PAD), besides of simple passivation films of alumina or zirconia. PAD is a novel spray technique to manufacture dense ceramic or ceramic-like coatings from a wide range of materials[6,7]. The deposition occurs fully at room temperature, directly from the dry powder. Film thicknesses range from ca. 1 µm to over 200 µm. A high-temperature step is not required; however, sometimes mild annealing improves the electrical properties.

At the beginning, this contribution introduces the audience into the field of PAD and overviews recent applications in the field of energy conversion and energy storage, as already introduced above. It gives also hints for future industrial commercialization.

In the second part, some scientific problems are discussed, like the influence of aerosol generation, the influence of particle and crystallite sizes as well as the question of plastic deformation of the nanosized crystallites that form during film formation.

Suggestions and opportunities for future research approaches conclude the presentation.

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T4.7 Materials for Extreme Environments: Ultrahigh Temperature Ceramics (UHTCs) and Nano-laminated Ternary Carbides and Nitrides (MAX Phases) Applications

Ti_3SiC_2 MAX phase based ceramic matrix composites

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Keywords: MAX phase, CMC, Ti_3SiC_2, creep

Alternative materials for high temperature applications might offer a solution to higher efficiency and low fuel consumption for jet engines. A possible candidate for such material is Ti_3SiC_2 which is a ceramic material with unique combination of mechanical properties at high temperature. Ceramics are brittle in nature and have a typically low Weibull modulus as compared to metals.

Ceramic matrix composites (CMCs) with bulk ceramic material as the matrix and a ceramic fiber as the reinforcement offers the possibility to have high strength at high temperature but present some limitations like high costs and very few applications despite the huge economical efforts in the last decade. The complex processing routes followed for the fabrication of CMC have limited the applications. The present work is about the fabrication of a CMC with Ti_3SiC_2 as the matrix and short SiC fiber as the reinforcement material.

A novel molten salt-based process was developed to synthesize high purity Ti_3SiC_2 at a large scale (1kg/batch) in air. The method involved mixing of elemental precursor with KBr salt and high temperature treatment at 1250 °C to obtain the desired Ti_3SiC_2 phase. Al was added to the reaction mixture to enhance the purity of Ti_3SiC_2. The effect of different levels of Al addition on the evolution of the Ti3SiC2 phase was studied. Apart from Ti_3SiC_2, a wide range of non-oxide ceramics like TiC, Ti_2AlC, Ti_3AlC_2, Cr_2AlC, Ti_2AlN, MoAlB and many more were synthesized for the proof of concept. Metals like titanium were also sintered in dense and porous forms using the same process in air. The method was referred to as Molten Salt Shielded Synthesis/Sintering (MS^3).[1,2] MS^3 process resulted in a reduction of the synthesis temperature of Ti_3SiC_2 along with other non-oxide ceramics. MS^3 process can be carried out in air without the need of expensive atmosphere-controlled furnaces. The dissolution of salt after MS^3 process results in micro-metric agglomerated powder which does not need to be milled unlike conventional solid-state reactions. The synthesized Ti_3SiC_2 powder was sintered in spark plasma sintering (SPS) furnace at 1250 °C with a uniaxial pressure of 80 MPa. Similarly, CMCs were also sintered in SPS by following a powder metallurgical process to mix the reinforcement with the synthesized Ti_3SiC_2 powder. The reinforcement of Ti_3SiC_2 was done in macroscale and microscale. The macroscale reinforcement was done by adding 10 and 20 vol.% chopped polycrystalline SiC fibers (1 mm) whereas the microscale reinforcement was done by adding 10 and 20 vol.% of single crystalline SiC whiskers. Compressive creep in the temperature and stress range of 1000-1300 °C and 20-120 MPa were performed on the fabricated CMCs.[3,4]

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What else can UHTCs do? Exploring UHTC microstructural complexity for new heat management strategies and applications

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Keywords: UHTC, processing, microstuctural design

Ultra-high temperature ceramics (UHTCs) have become almost a synonym of hypersonic applications and extreme environments. Thermal protective systems for hypersonic vehicles needs to survive large heat fluxes, extreme temperatures, extensive thermal gradients, stagnation pressures and oxidative environments. They also need to show minimal material ablation and overall weight, with complex shapes. Although outstanding development has been achieved over the past 20 years for UHTCs, the state-of-art manufacturing and design still revolves around solid microstructures as heat sinks for leading edges. Recent advances in manufacturing paved the way for exploring different UHTC microstructures that could lead to other heat management strategies and other applications, beyond passive cooling components in hypersonics. In this talk, innovative colloidal processing approaches will be discussed to introduce controlled porosity, textured microstructures and high aspect ratio building blocks for UHTCs, to tailor thermomechanical response in different directions within the same component, and enable innovative active and passive cooling strategies. This also opens the door to different type of applications beyond hypersonics for these materials.

T4.8 DESIGN, PROCESSING, AND APPLICATIONS OF NANOLAMINATED TERNARY TRANSITION METAL CARBIDES/NITRIDES/BORIDES AND MXENES AND MBENES

Origin and consequence of alumina scale buckling during high temperature oxidation of Cr_2AlC MAX phase

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Keywords: Cr_2AlC, buckling, oxidation

Single-crystal and fine-grained polycrystalline samples of Cr_2AlC were oxidized under dry air flow at temperature in the 1000-1400°C range during 100 h[1,2]. A continuous alumina layer forms on top of the Cr_2AlC surface whereas a Cr_7C_3 sublayer also appears (cf figure). In-lab characterization of oxidized Cr_2AlC samples shows strong damaging at the free surface, resulting from the buckling of the alumina scale[3]. In-situ X-ray diffraction measurements under synchrotron radiations were performed to measure the lattice strain during the first hours of oxidation process and further calculate the internal stress in the Al_2O_3 layers. Alumina layers undergo tensile stress during isothermal oxidation, showing that the buckling of the alumina scale does not result from the oxide growth. Such a tensile stress likely results from the Cr_2AlC to Cr_7C_3 phase transformation. During cooling, the tensile stress decreases down to compressive values, due to the thermal expansion coefficient mismatch between the film and the substrate, leading to buckling of the alumina layer. It is demonstrated that the dimensions of the buckles cannot be explained either by gas pressure or by the magnitude of the internal compressive stress in the alumina scale after cooling. The discrepancy between the experimental maximum deflection and the one predicted by the elastic theory results from a significant plastic deformation occurring in the alumina scale.

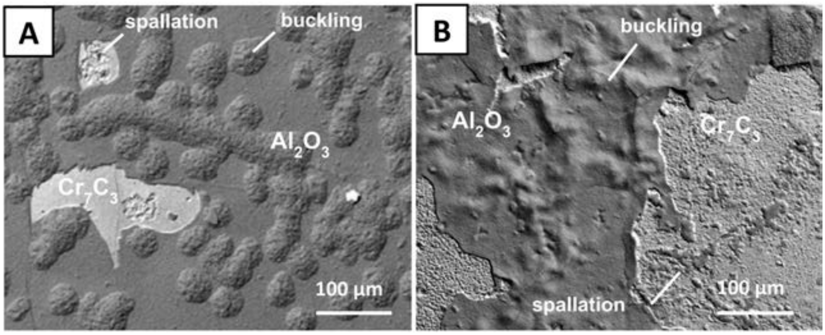

Figure: SEM surface micrographs, in back-scattered mode, of A) single crystal and B) fine-grained polycrystalline samples oxidized during 100 hours at 1400 °C and 1100 °C respectively.

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A review of manufacturing practices for MAB and MAB phases

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MAX and MAB phases have attracted a lot of attention due to their exceptional properties like machinability, triboactive behavior, and high temperature oxidation resistance. In order to commercialize these materials, it is vital to come up with novel practices for manufacturing these materials. In this presentation, I will present some of the recent development in optimizing the manufacturing of these phases. Detailed microstructural and phase analysis will be presented during the presentation.

T4.10 Environmental Friendly and Energy Efficient Manufacturing Routes for the Production Root Technology Applications

The effect of the TiC nanoparticle pushing-engulfment phenomenon on the mechanical properties of in-situ Al-based cast composites

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Keywords: AMMC, casting, in situ, TiC, pushing-engulfment phenomenon, tensile strength

In response to escalating environmental concerns, the automotive industry is increasingly focused on reducing vehicle weight to enhance fuel efficiency while maintaining safety and performance standards. Lightweight Aluminum-based Metal Matrix Composites (AMMCs) have emerged as a critical solution in this pursuit, offering significant potential for optimizing vehicle efficiency. Despite extensive research and discussions about their applications, commercial adoption remains limited, primarily due to challenges in the manufacturing process and the complex interactions between composite components.

This keynote address will explore the impact of the chemical composition of Aluminum-based alloys on the behavior and interaction of Titanium Carbide (TiC) particles within the composite matrix. We will discuss findings from research on three specific AMMCs: pure Aluminum (Al 1000), Aluminum with 7 wt.% Silicon (Al-7%Si), and commercial A356 alloy. The synthesis of these composites was carried out using the *in situ* method with a TiC powder mixture. The mixture was pressed and introduced as reactive compacts into a furnace during the metallurgical process.

Key insights from our research include: the distinct distribution patterns of TiC particles in different alloy matrices are influenced by pushing-engulfment phenomena at the solid-liquid interface, the formation of additional phases, indicating complex reactions within the Al-Si/TiC system, and variations in particle size and distribution, which affect the mechanical properties of the composites.

We will highlight the significant increase in tensile strength observed in the Al 1000/TiC composite compared to the Al-7Si/TiC and A356/TiC composites. These findings shed light on new factors influencing the performance of Al-based and Al-Si-based AMMCs and underscore the importance of material composition in developing high-performance, lightweight automotive components.

This lecture aims to provide a comprehensive overview of the current state of *in situ* AMMC research, address key challenges in their manufacturing, and discuss the future potential of these advanced materials in the automotive industry.

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T4.12 GRAPHENE AND 2D MATERIALS

Synthesis of a new 2D compounds: AlN

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Keywords: 2D, AlN, synthesis, new materials

2D-AlN is a thermodynamically stable compound that has been predicted by density functional theory (DFT) calculations. It has attracted considerable attention due to its ultrawide band gap (> 2.8 eV) and its strong adsorption of CO_2 (0.91 eV) molecules on its surface. This represents a breakthrough for CO_2 capture technologies because the adsorption of gases directly on the 2D-AlN nanosheets is a simple and sustainable alternative for replacing the current strategy of decorating carbon nanostructure with metal nanoparticles for gas storage and CO_2 capture. In addition, the high adsorption CO_2 selectivity in comparison with other gases such as CO, H_2, N_2, O_2, and NO (<0.5 eV) opens other potential applications like gas separation membranes and gas sensors, among others. The DFT calculations have put 2D-AlN in the spotlight, but so far, the synthesis of free-standing 2D-AlN layers have not yet been achieved.

In this work I will present a new strategy to synthesize 2D-AlN nanoflakes for the first time. First, I will introduce the precursor materials including their characterization and properties. Then, I will continue with the different approaches for the synthesis of the 2D nanoflakes and their main characteristics. Afterwards, I will present the preliminary characterization of these new 2D materials as well as their main applications.

T5 Technology, Society and Sustainability

T5.1 GLOBAL INNOVATIONS IN BIOMATERIALS, BIOMANUFACTURING, AND BIOTECHNOLOGIES

Drug delivery systems to the lungs with enhanced bioavailability, targetability and stimulus triggered release

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Keywords: drug delivery ststems, inhalable formulations, solid-lipid microparticles, polymer microparticles, lung cancer, chronic obstructive pulmunary disease, paclitaxel, antibiotics, quorum sensing inhibitors

Lung diseases, such as lung cancer, acute infections, chronic obstructive pulmunary disease (COPD), SARS-Cov2, are one of the most frequent causes of death worldwide, as they can significantly compromise gas exchange in the alveoli. Such diseases are usually treated with systemic therapy, although the lungs can be directly targeted through the airways. Thus, by using inhalable formulations, it is possible to obtain a higher concentration of active pharmaceutical ingredient (API) directly at its action site and reduce its amount distributed systemically. The two main benefits of inhalable drug delivery systems are: (1) reduced side effects due to lower doses administered than via typical enteral or other parenteral routes and, (2) in the case of antibiotics, lower chance to build up antibiotic resistance. To achieve the most effective therapy, powders for inhalation must have appropriate size (1-5 µm in diameter), uniform size distribution, aerodynamic properties to be deposited in the bronchiole/alveoli region, sufficient drug loading and required release kinetics [1].

In our group, we are working on lipid and polymer microparticles to be used as inhalable dry powder formulations. So far we have developed innovative, inhalable stimuli-sensitive drug carriers that are intended to improve the efficacy of lung cancer therapy through guided accumulation directly at the tumour site and controlled drug release triggered by an alternating magnetic field resulting in a local increase in temperature [2]. Such drug delivery carriers are in the form of solid lipid microparticles composed of fatty acids loaded with superparamagnetic iron oxide nanoparticles (SPIONs) and paclitaxel. The microparticles meet various criteria including: suitable aerodynamic properties, high drug loading efficiency, sufficient mobility in the magnetic field, melting temperature at hyperthermia conditions, and enhanced *in vitro* efficacy as studied in contact with healthy and cancerous lung epithelial cells under hyperthermia conditions [3].

Recently, we have been working on polymer drug delivery systems of antibiotics and quorum sensing inhibitors for the treatment of bacterial infections in patients with exacerbations of COPD [4]. Such systems are based on fast-degrading polyanhydride microparticles loaded with antibiotics (e.g., azithromycin, tobramycin, gentamycin) and quorum-sensing inhibitors (e.g., curcumin, linolenic acid). The microparticles are designed to ensure an appropriate size for inhalation, degrade within a few days, and release drug cargo, which is capable of killing bacteria causing COPD exacerbations and preventing biofilm formation. The system is cytocompatible with lung epithelial cells, as shown by *in vitro* and *ex vivo* tests.

Acknowledgments

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Recent advances in nanomedicine: sensors, implants, artificial intelligence, saving the environment, human results, and more

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Keywords: nanomedicine, orthopedics, infection, sensors, artificial intelligence, humans

Nanomedicine includes the use of nanomaterials to improve disease prevention, detection, and treatment which has resulted in hundreds of FDA approved medical products. While nanomedicine has been around for several decades, new technological advances are pushing its boundaries. For example, this presentation will present an over 25 year journey of commercializing nano orthopedic implants now in over 30,000 patients to date showing no signs of failure (over the past 5 years). Current orthopedic implants face a failure rate of 5 – 10% and sometimes as high as 60% for bone cancer patients. Further, Artificial Intelligence (AI) has revolutionized numerous industries to date. However, its use in nanomedicine has remained few and far between. One area that AI has significantly improved nanomedicine is through implantable sensors. This talk will present research in which implantable sensors, using AI, can learn from patient's response to implants and predict future outcomes. Such implantable sensors not only incorporate AI, but also communicate to a handheld device, and can reverse AI predicted adverse events. Examples will be given in which AI implantable sensors have been used in orthopedics to inhibit implant infection and promote prolonged bone growth. In vitro and in vivo experiments will be provided that demonstrate how AI can be used towards our advantage in nanomedicine, especially implantable sensors. Lastly, this talk will summarize recent advances in nanomedicine to both help human health and save the environment.

T5.2 GLOBAL YOUNG INVESTIGATOR FORUM

Advances of cold sintering in ceramic processing

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Keywords: cold sintering process, transparent ceramics, high-temperature metastable materials, thermoelectric materials

Cold sintering process is a green sintering technology developed in recent years, which can exponentially reduce the densification temperature of ceramics through the transient liquid phase and pressure introduced in the sintering process. Based on low-temperature sintering technology, it can not only greatly reduce the energy consumption required in the ceramic preparation process, but also greatly expand the design of ceramic composites, creating new opportunities for the performance optimization and improvement of ceramic materials. We will illustrate the advances of cold sintering process through the preparation and application of transparent ceramic materials[1, 2], high-temperature metastable materials[3, 4], and thermoelectric materials[5, 6].

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INVITED

T1 Ceramics for Energy Conversion, Storage, and Distribution Systems

T1.1 HIGH-TEMPERATURE FUEL CELLS AND ELECTROLYSIS

Structural and thermodynamic analysis of triple conducting electrode materials for protonic ceramic fuel cells

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Keywords: ionic conductivity, cathode, protonic fuel cells, electrolysis

Triple ionic-electronic conductors (TIEC) such BaCo0.4Fe0.4Zr0.1Y0.1O3-δ (BCFZY) have received much attention as high performance electrode materials for protonic ceramic fuel cells (PCFC)[1]. The conduction of all three species makes TIECs excellent candidates as cathodes in PCFCs due to their high activity, good stability, and facile synthesis routes. The properties of these materials, including their enthalpy of formation from oxides, can be significantly affected by oxygen vacancies and structural changes. Understanding these effects is crucial for the design and optimization of new materials with improved properties.The bulk characteristics of oxygen and proton diffusion along with surface exchange characteristics were recently determined for the triple-conducting BaCo0.4Fe0.4Zr0.2−XYXO3−δ suite of samples with varying Y composition[2,3]. Y substitution increased the overall size of the lattice due to dopant ionic radius and the concomitant formation of oxygen vacancies. A combination of DC four-point conductivity for electronic carriers and gas permeation (oxygen and proton transport) for ionic carriers has recently been utilized to fully compare transport across varying material compositions and atmospheric conditions.

In this study, we investigate the trends in the enthalpy of formation from oxides as a function of oxygen vacancy and structure affects. We also correlate these results with previously measured proton and oxygen kinetics in these systems. To achieve these goals, we used a combination of high temperature solution calorimetry, X-ray diffraction, neutron powder diffraction, and thermogravimetry.

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Exsolution mechanisms, phase stability, and redox-behavior of substituted strontium titanate perovskites

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Keywords: oxides, exsolution, metal nanoparticles, space charges, stability

Exsolution is defined as the phase separation of a solid solution due to a miscibility gap under specific conditions. In the context of catalysis, exsolution refers to the reduction of metal cations to the metallic state, forming nanosized particles on the surface. This process is initiated by exposing the material to reducing conditions, resulting in the release of oxygen from the host lattice and thus providing the driving force to exsolve certain cations for charge compensation. At surfaces and interfaces, however, strong electrostatic gradients and space charges typically control the properties of oxides. Here we reveal that the nature of the surface-dopant interaction is the main determining factor for the exsolution kinetics of nickel in $SrTi_{0.9}Nb_{0.05}Ni_{0.05}O_{3-\delta}$. The electrostatic interaction of dopants with surface space charge regions results in strong surface passivation, which manifests in a retarded exsolution response. We furthermore demonstrate the controllability of the exsolution response via engineering of the perovskite surface chemistry.

Ni-exsolution from perovskites has gained significant attention in the area of electrode materials for fuel and electrolysis cells due to potential high catalytic activity, tolerance to degradation, improved redox-cycling stability, and regeneration of the nanoparticles. In this context, the properties of the oxide host lattice after exsolution are insufficiently investigated. Since the exsolved nanoparticles are not percolated, their function is very different from that of a percolated Ni network and the electrode performance will strongly depend on the properties of the oxide backbone. The phase stability of the oxide during the exsolution process and its influence on mechanical stability of the perovskite backbone is not well investigated. It is therefore important to understand how the loss of a significant amount of B-site cations influences the physical properties of the oxide. We thus investigated the exsolution behavior and phase stability of bulk $Sr_{1-x}(Ti_{0.3}Fe_{0.7-y}Ni_y)O_{3-\delta}$ ceramics at various temperatures and atmospheres. Above a given temperature, $Sr_{1-x}(Ti_{0.3}Fe_{0.7-y}Ni_y)O_{3-\delta}$ partially transforms to a Ruddlesden-Popper phase, while reverting back to the perovskite phase during reoxidation. This phase transition resulted in material expansion and the formation of cracks.

Acknowledgments

The authors are grateful for the collaborative research funding from Forschungszentrum Jülich and the DFG (Deutsche Forschungsgemeinschaft) project SynSOFC II (275388933).

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Development of tuned SOEC electrode by spray coating

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Keywords: SOEC, spray coating, microstructure, oxygen electrode

Solid Oxide Electrolysis Cell (SOEC) is a key technology for the ongoing energy transition towards a low carbon future. It is the most viable route for the efficient utilization of renewable electricity to produce green hydrogen and fuels [1]. Although SOEC do not make use of expensive Pt, it still consists of rare earth elements (REE). To overcome the environmental and criticality challenges of REE, alternative materials are needed or REE should be recycled. Therefore, the European NOUVEAU project aims to make Solid Oxide Electrolysis Cell (SOEC) technology more sustainable and re-usable by developing novel electrode coatings and interconnect. Besides the material choice, the microstructure of the electrode coatings is important as well to obtain an optimal use of critical materials and to achieve an efficient working SOEC for green hydrogen production. The electrode microstructure will be tuned in (La-free) composition along the thickness of the electrode to have an improved thermal expansion match between the different layers. Such a structure can be achieved by spray coating as it allows to vary the composition along the thickness of the electrode and to create uniform electrode coatings [2].

In this work, a symmetric cell is fabricated by applying the electrode layers on gadolinium doped ceria (GDC) planar substrates, which serve as the electrolyte layer. As electrode material, a La-free oxide is selected by Centrale Lille to have a reduced amount of REE and produced by Marion Technologies. This material is mixed with Gd doped Ce oxide to obtain a tuned composition. This mixture was continuously varied so that the layer consists of 100 % of Gd doped Ce oxide near the interlayer and 25/75 % Gd doped Ce oxide/La-free oxide at the surface (see Fig. 1). The coating parameters such as atomization pressure, coating speed and suspension flow were optimized to obtain uniform coatings and to control the microstructure and thickness. The suspension formulation was adjusted to improve the adhesion and the quality of the coating. Microscopy was used to determine the coating thickness and porosity of the structure. Furthermore, electrochemical impedance spectroscopy was carried out.

Figures

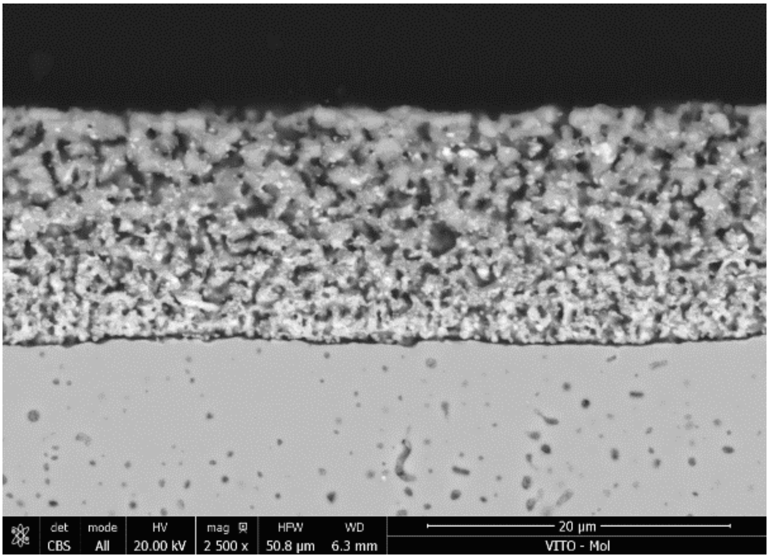

Fig. 1. An illustration of tuned porosity of electrodes obtained by spray coating.

Acknowledgments

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Identification and analysis of gas conversion losses in impedance spectra of solid oxide cells

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Keywords: solid oxide cell, gas conversion impedance, MEA, distribution of relaxation times

The electrochemical performance of solid oxide cells strongly depends on its area specific resistance (ASR). Experimentally observed ASR value obtained from I-V characteristics or rated power measurements contains contributions from electrode polarization resistance, ohmic losses resulting from ionic conductivity of electrolyte and gas conversion losses connected with the change of gas composition under current load conditions. The contributions to ASR resulting from electrode and electrolyte resistance are the matter of continuous improvement and should be separated from gas conversion losses to be able to perform in-depth analysis of contributions of different electrochemical processes in electrodes to total cell resistance.

In our previous work [1] it was shown that the contribution of gas conversion losses to ASR of cell and stack can be calculated from cell operating conditions and used as correction of ASR value obtained from I-V characteristics resulting in constant cell area specific resistance, which stays independent for various H_2-H_2O-N_2 gas mixtures. Up to date the correlation of calculated gas conversion losses to the responses observed in impedance spectra of single cells and stacks has not been analyzed in detail. Mathematical analysis of electrochemical impedance spectrum (EIS) resulting from of gas diffusion in pores and gas conversion in the gas channel over electrode performed by Jacobsen et al. [2] was simplified and applied to experimentally used flow field for gas supply to the cell electrodes. The results of this analysis have shown that gas diffusion losses for thin electrodes can be neglected and only gas conversion losses provide notable contribution to EIS resulting in semicircle with characteristic relaxation frequency in the range of 1-10 Hz. Moreover, the channel geometry has considerable influence on the relaxation frequency. The relaxation frequency values as well as magnitude of the impedance calculated and observed in EIS showed excellent agreement. The impedance spectra analysis by distribution of relaxation times method has been used to identify the shift of gas conversion impedance frequency in dependence on operation conditions. The dependence of the relaxation frequency on gas flow rate, gas composition and temperature has been investigated and excellent agreement with expected behavior found. It has been shown that the relaxation frequency of gas conversion semicircle strongly depends on gas flow rate only and that the changes in temperature and gas composition have nearly no effect on its position. The performed analysis allows to predict and to identify the position and magnitude of gas conversion impedance in EIS.

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Study on steel composition design for metal-supported solid oxide fuel cells and performance evaluation of assembled cells/stacks

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Keywords: solid oxide fuel cells, Amic-21/23, stainless steel, Crofer 22, pre-oxidation, stability

In this study, we proposed a novel design for ferritic stainless steel materials intended for use in metal-supported solid oxide fuel cells (MS-SOFC), incorporating elements like Fe, Cr, Mn, and Ti. Building upon this design, we developed Amic-21 and Amic-23 stainless steels and conducted comparative analyses against Crofer 22 and ZMG232G10, with a primary focus on their long-term oxidation behavior under cathodic and anodic atmospheres. The findings revealed that the optimized SOFC steel could develop dense oxide films primarily comprised of Cr, Fe, and Mn under reducing atmospheres on the anode side, displaying oxidation kinetics similar to Crofer 22.

To enhance the oxidation resistance of this stainless steel material, we proposed a pre-oxidation protective process. Following pre-oxidation treatment at 800°C for 20 hours, a dense chromium oxide layer formed on the stainless steel's surface, effectively bolstering its oxidation resistance. Furthermore, we discussed the impact of pre-oxidation processes utilizing (Mn,Co)3O4 spinel (referred to as MCO) coatings on the oxidation behavior and conductivity of the interconnect under cathodic atmospheres. For the Amic series stainless steels designed in this study, pre-oxidation treatment effectively mitigated Cr diffusion, substantially reducing oxidation and facilitating the generation of the cubic MnCo2O4 phase, thereby decreasing surface-specific resistance and enhancing the conductivity of the MCO coating.

Leveraging the Amic series steel developed in this study, we employed a low-pressure plasma spraying method to fabricate MS-SOFCs with a 10cm×10cm area, achieving low heat input to the metal support. At 500°C, the open-circuit voltage (OCV) remained stable within the range of 1.05-1.09 V, and the power density increased with operating temperature, reaching 0.4 W/cm^2 under equilibrium gas pressure conditions at 650°C. Furthermore, we assembled a solid oxide fuel cell stack, which underwent 6 thermal cycles in a 500-hour long-term stability test, demonstrating robust stability in terms of open-circuit voltage and maximum power density.

Advanced manufacturing of ionic conductors for solid oxide cells

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Keywords: 3D printing, additive manufacturing, fuel cells, reversible solid oxide cells

Nowadays conventional Solid Oxide Cells (SOC) are mainly based on multilayered functional ceramic materials produced by expensive and long manufacturing processes. Furthermore, conventional manufacturing techniques limit SOC geometries to typical planar or tubular ones.

Here we present the recent breakthroughs obtained by innovative additive manufacturing technology of functional ceramic for SOC. The use of stereolitography (SLA) of Yttria Stabilized Zirconia (YSZ) electrolytes was explored at IREC in order to produce complex shaped SOC, impossible to obtain with conventional methods. New designs are considered in order to increase the active area of the devices leading to an increase of the performance per projected area. 3D printed electrolytes geometries are also tailored with special geometrical features (with 25µm of resolution) that allows not only an increase on the volumetric power density but also other key advantages such as better mechanical properties or complex shaped sealing features. The implementation of SLA for YSZ manufacturing at the same time can lead to advantages at stack level: i.e. reduction of the overall volume of the stack, use of flat thin interconnects, high pressure resistance without the use of vessels.

In addition, hybridized (SLA + robocasting) multimaterial is presented together with co-sintering, characterization and preliminary electrochemical performance of the full printed device.

Figures

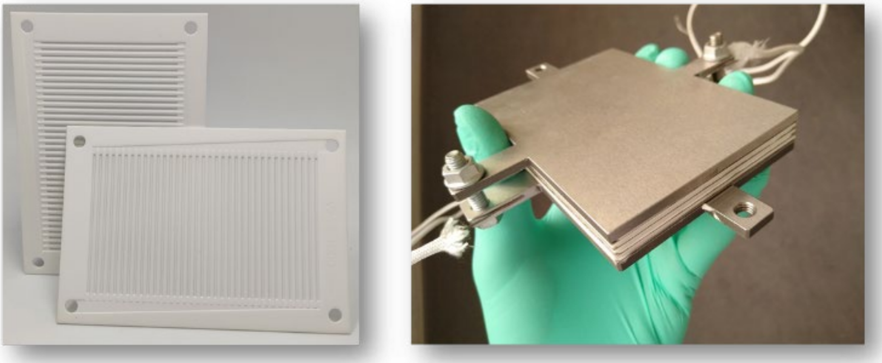

Figure: 3D printed YSZ electrolytes at IREC (on the left) and a sub-stack (3 cells) built and tested at IREC based on these cells

Acknowledgments

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Electrochemical systems for hydrogen and net-zero energy infrastructure

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Climate change remains a motivation and driving force for research, development, and implementation of clean, efficient, and cost-effective energy technologies for global deployment. In this presentation, we will examine the status of existing and emerging electricity generation trends with a focus on technology attributes. We will present the potential of various technologies for cost effective and commercial readiness to accelerate the transition to and adoption of net-zero and zero carbon emissions processes. Potential scenarios for utilizing carbon neutral fuels, carbon capture and utilization, and hydrogen generation for the enhancement of energy efficiency will be examined. In-depth review of the electrochemistry and electrochemical processes will be presented and technology gaps along with research needs will be discussed. Long term materials challenges, degradation processes and degradation mitigation approaches will be discussed.

NiCoP fibers as a novel catalyst for hydrogen production: preparation and efficiency

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Keywords: NiCoP catalysits, fibres, hydrogen evolution reaction, water splitting

Amidst the current global energy crisis fueled by soaring energy prices, environmental disregard, and relentless use of fossil fuels, extensive research and innovation are underway to explore clean, sustainable, and renewable energy alternatives. It is abundantly evident today that green hydrogen will predominantly serve as a pivotal element in the decarbonization of industrial processes and carbon-intensive sectors. Nevertheless, the production of green hydrogen remains noncompetitive, with around 60% of the overall cost attributed to the expense of renewable energy utilized for its production. Additionally, a significant contributor to the relatively high price of hydrogen is the expense associated with electrolyzer and fuel cell technology. The NiCoP transition metal phosphide has emerged as a highly promising candidate for replacing noble metals in the hydrogen evolution reaction. This study presents, for the first time, the straightforward synthesis of NiCoP electrocatalysts in the form of fibers, exhibiting a predominant one-dimensional structure achieved through needleless electrospinning technology and subsequent precise heat treatment. The research offers a precise methodology for fabricating NiCoP fibers, accompanied by experimental evidence showcasing their exceptional electrocatalytic performance in both alkaline and acidic environments. The fibrous NiCoP electrocatalyst were prepared at different sintering temperature from 700°C (F7) to 1100 °C (F10) in air followed by additional sintering at 700 °C in H_2, demonstrates a low hydrogen evolution reaction (HER) overpotential (η_{10}) of 141 mV in alkaline conditions and 146 mV in acidic conditions, alongside low Tafel slopes of 53 and 97.8 mV/dec, respectively (Figure). The electrocatalytic efficiency of the fibrous sample was compared with powder sample (P9) at the same conditions. In addition, the bimetallic phosphide exhibits exceptional activity in the oxygen evolution reaction (OER) within an alkaline medium (1M KOH), coupled with satisfactory durability during long-term stability assessments. The innovative fibrous structure of the material significantly contributes to the modulation of its electronic structure, thereby enhancing the density of electrochemically active sites and consequently improving its electrocatalytic performance in water splitting technology.

Figures

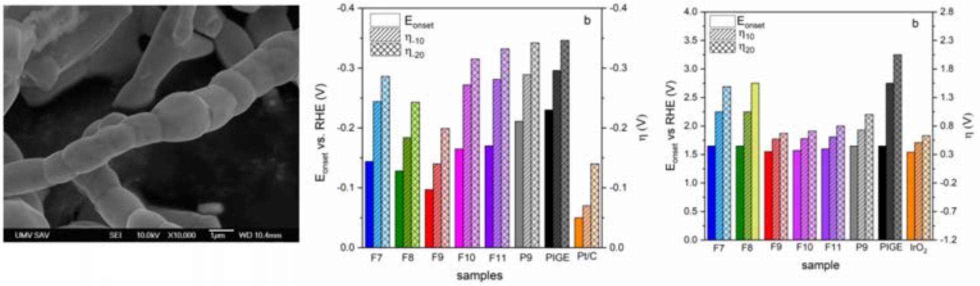

Figure. SEM image of NiCoP fibres with the LSV for HER and OER in 1M KOH.

Acknowledgments

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T1.2 CERAMICS-RELATED MATERIALS, DEVICES, AND PROCESSING FOR HEAT-TO-ELECTRICITY DIRECT CONVERSION AND THERMAL ENERGY HARNESSING

Enabling direct synthesis of quaternary thioantimonate $Ag_4MnSb_2S_6$ via novel approaches

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Samsonite ($Ag_4MnSb_2S_6$), a naturally occurring mineral found in hydrothermal veins, holds promise for thermoelectric applications due to its complex crystal structure – it crystallizes in the monoclinic crystal system (space group: $P2_1/n$ with a = 10.3861 Å, b = 8.1108 Å, c = 6.6637 Å, and β = 92.639°) – the presence of electron lone pairs on Sb^{3+} atoms, and the lack of extensive research on its synthesis under lab conditions.1 Indeed, authors have shown through the tetrahedrite phase ($Cu_{12}Sb_4S_{13}$), that the electron lone pair of Sb^{3+} may explain the ultralow thermal conductivity of $Cu_{12}Sb_4S_{13}$.2

The objective is to synthesize $Ag_4MnSb_2S_6$ through unconventional synthesis ways (hydrothermal synthesis and polyol synthesis process) to mimic the high pressure and temperature found in natural conditions. Then, subsequent structural, magnetic, and thermoelectric property evaluations will be conducted to assess the material's potential for thermoelectric applications.

This presentation delves into the exploration of two innovative synthesis methods, hydrothermal and polyol syntheses, for the synthesis of quaternary thioantimonate $Ag_4MnSb_2S_6$. By comparing their respective efficiencies and considering their inherent advantages and drawbacks, we aim to establish a comprehensive understanding of these techniques and their potential for producing high-quality $Ag_4MnSb_2S_6$.

Hydrothermal synthesis, while renowned for its ability to yield highly crystalline compounds using simple precursors and solvents, exhibits limitations in scalability due to its inherently slow reaction kinetics. Conversely, polyol synthesis, renowned for its rapid reaction rates and scalability potential, often produces compounds with relatively poor crystallinity, necessitating additional crystal growth processing as a follow-up step.

By critically evaluating these synthesis methods in light of their advantages and drawbacks, we strive to identify strategies for optimizing each technique and leveraging their synergistic strengths to achieve efficient and scalable synthesis of $Ag_4MnSb_2S_6$. This comparative analysis holds promise for unlocking the full potential of these methods and paving the way for the development of superior thermoelectric materials.

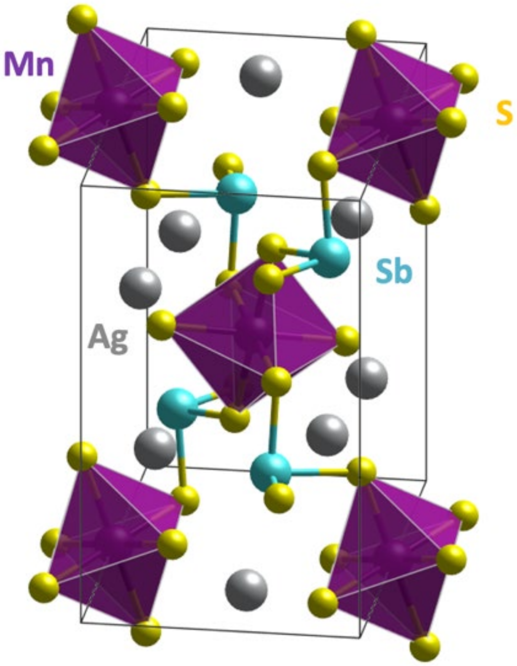

Figure 1: Schematic Illustration of the Samsonite Crystal Structure

Acknowledgments

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Nano-engineering of GeTe for high performance thermoelectric applications

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Keywords: GeSbTe, thermoelectric, W-doping

We study the structure, doping, and nano-engineering of GeTe for high figure-of-merit (ZT) in thermoelectric properties. DFT has been applied to elucidate the thermoelectric properties in the materials. With better vacancy control of pure GeTe, a ZT of 1.37 has been achieved. Additional Sb doping renders dramatic decrease in thermal conductivity, which is also confirmed by DFT calculation. A high power factor and low thermal conductivity, rendering a ZT of 2.35 has been achieved in GeSbTe. Further co-doping of W into the GST results in a ZT up to 2.93 @ 825 K, which is near 3.0, a milestone for thermoelectric figure-of-merit.

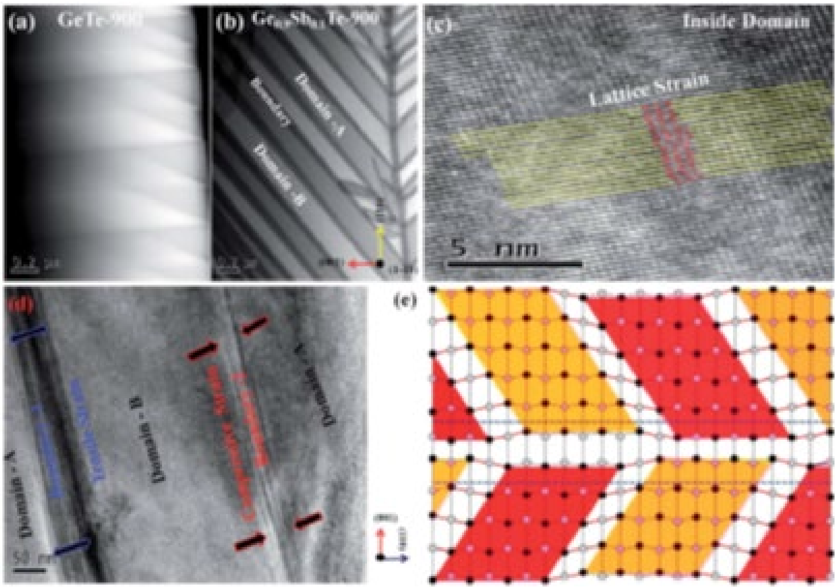

Fig. 1 (a) Microdomain structures of undoped GeTe-900, and (b) the herringbone domain structure of Ge0.9Sb0.1Te-900 with thickened domain boundaries. (c) The amplified view of Sb doping-centre introduced local strain within the herringbone domain of $Ge_{0.9}Sb_{0.1}Te$, as revealed by the gradual displacement that is used to relieve the local strain. (d) Herringbone domain structures for $Ge_{0.9}Sb_{0.1}Te$-900 with alternating tensile/compressive domain boundaries. (e) Schematic representation of the herringbone domain with alternating tensile/compressive strains, replotted following the atomistic model proposed by Lee et al.

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Texture control to achieve high in-plane thermoelectric performance in polycrystalline tin monosulfide co-doped with silver and sodium

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Keywords: sintering, texture, electrical properties, thermal properties, thermoelectrics

Tin monosulfide (SnS), an affordable IV-VI semiconductor compound, has emerged as a promising material due to its low toxicity, abundance, and potential for future applications in semiconductor devices. The strong lattice anharmonicity of SnS results in exceptionally low thermal conductivity at moderate temperatures, making it suitable for thermoelectric applications[1]. Despite its thermoelectric potential, the performance of polycrystalline SnS is observed to be lower compared to its single-crystal counterpart. Furthermore, the anisotropic performance between directions perpendicular (⊥P) and parallel (∥P) to the sintering pressure, respectively, complicates the preparation of the polycrystal. In this study, we successfully enhanced the in-plane (⊥P) performance of polycrystalline SnS through hot-pressing consolidation. The enhanced in-plane conductivity is crucial for utilizing the high carrier mobility of the lateral crystal structure, resulting in a higher figure of merit (zT) along this direction. Additionally, the incorporation of a small percentage of silver in sodium-doped SnS improved carrier mobility, leading to enhanced electrical conductivity without affecting thermal conductivity. With these improvements, our co-doped SnS exhibits a relatively high peak zT (⊥P) of 0.27 at 573 K, making it promising for low-temperature applications involving sulfur-based polycrystalline thermoelectric materials.

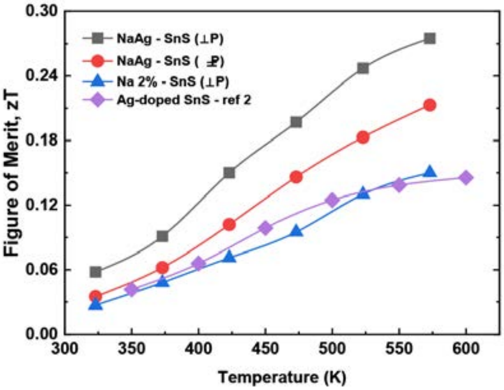

Figure 1 Temperature dependence of the dimensionless figure of merit (zT): zT=(S^2 σT)/k, where S is the Seebeck coefficient, σ is the electrical conductivity, T is the absolute temperature and k is the thermal conductivity.

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Texturing ceramics via electrospun nanoribbons: A route to high-performance $Ca_3Co_{4-x}O_{9-\delta}$ thermoelectrics

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Keywords: calcium cobaltite, electrospinning, microstructure, nanofibers, nanoribbons, thermoelectric properties, texturing

Calcium cobaltite $Ca_3Co_{4-x}O_{9+\delta}$ is a promising *p*-type thermoelectric material with good functional properties for high-temperature applications in air. The material exhibits strong anisotropic properties, so texturing and nanostructuring are mostly favored to improve the thermoelectric performance. Electrospinning is a suitable and cost-effective method to meet these requirements. In this work, flat-shaped $Ca_3Co_{4-x}O_{9+\delta}$ nanofibers, called nanoribbons, were electrospun and the resulting nanoribbons mats were further processed into a textured $Ca_3Co_{4-x}O_{9+\delta}$ ceramic. In previous work, we have shown that mats composed of a mixture of nanoribbons and cylindrical nanofibers exhibit good thermoelectric properties [1]. However, it is expected that the thermoelectric properties of the compacted sample can be further improved by using mats composed of flat nanoribbons only. Primarily because nanoribbons are expected to provide more efficient packing due to their flatness compared to cylindrical nanofibers, allowing for higher densification in the green body and ceramic, but also because of their potential contribution to sample texturing since the primary particles in the nanoribbons are expected to be flatly oriented. Therefore, we investigated the influence of electrospinning conditions and precursor composition on the microstructure of the electrospun material to obtain pure nanoribbons mats [2]. We found a strong dependence of nanoribbon formation on the polymer concentration in the electrospinning precursor and discuss the possible formation mechanisms. We also point out an important step in the calcination process of the nanoribbons to achieve texturization of the primary particles. Finally, we have fabricated green bodies and ceramics from nanoribbons mats and investigated their texturing using X-ray diffraction with measurement of pole figures of the (0020) lattice planes, with respect to the 4-dimensional space group symmetry, and scanning electron microscopy cross-sectional images. Good grain orientation and high crystallinity were also confirmed using selected area electron diffraction and high-resolution transmission electron microscopy. In addition, we measured the Seebeck coefficient and electrical conductivity of the nanoribbon-based samples to evaluate their thermoelectric abilities.

Acknowledgments

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Development of low work function two-dimensional electride materials for advanced thermionic energy generation

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Keywords: thermionic, density functional theory

Thermionic devices produce current by the application of a thermal gradient whereby the temperature at one electrode provides enough thermal energy to eject electrons from the metal surface. A computational -based material approach was used to determine the suitability of various materials as a practical thermionic converter. Comparisons are made between predicted and experimental measurements of Seebeck coefficients, thermionic emissions current and work function. The calculations were carried out using a projector augmented wave (PAW) method using a commercial code (Materials Design Inc.) MedeA incorporating the Vienna Ab-initio Simulation Package (VASP) as the computational engine. The calculation was based on density functional theory using the GGA-PBE-Sol exchange-correlation functional using and optimized mesh. This study makes predictions and comparison between experimental and theoretical data of electrical, structural, and crystallographic properties.

Lattice vibration and structure dimensionality in thermoelectric sulfides

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Keywords: thermoelectric, sulfide, structure, vibration, dimensionality

Thermoelectricity offers a promising solution to address energy scarcity by enabling the efficient conversion of waste heat into useful electricity. Continued research and development in this field can lead to the development of more efficient and cost-effective thermoelectric materials, which can play a significant role in addressing the global energy challenge. In this context, numerous studies have demonstrated the potential of sulfide materials for thermoelectric applications over the temperature range 300 – 700 K. Although most materials have high thermal conductivities, recent works demonstrated that extremely low thermal conductivities could be achieved in sulfides through order/disorder phenomena, rattling dynamics, and lattice anharmonicity.

During this presentation, recent advances in synthetic minerals and new sulphide compounds will be shown. Some peculiar structural features in connection with chemical bonds, atomic and nanoscale order/disorder phenomena, lattice vibration and structure dimensionality, were carefully examined to establish rules and correlations between the crystal structures, nano-microstructures, electronic structures, vibrational and thermoelectric properties. [1-7]

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Lattice defect engineering for high-performance Mg_2Sn and Mg_2Ge thermoelectric single crystals

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Keywords: thermoelectric performance, Mg_2X, single crystal, vacancy defect, dislocation

Mg_2X (X = Si, Ge, and Sn), belonging to an antifluorite-type cubic crystal structure, has attracted attention as one of the efficient thermoelectric (TE) materials. Most research has been dedicated to enhancing its dimensionless figure-of-merit zT by preparing Mg_2(Si, Ge, Sn) polycrystals (PCs) to attain low thermal conductivity.

In this study, we focused on Mg_2X single crystals (SCs), which generally have higher carrier mobility than PCs. An issue to be addressed is to reduce thermal conductivity. For this purpose, we prepared nondoped and elementary-doped Mg_2Sn SCs by a melting method under an Ar atmosphere [1–5]. All SCs contained lattice defects such as Mg vacancies (V_{Mg}), dislocation cores (DCs), and Sn-rich nanoprecipitates. V_{Mg} formed nanoparticle-like V_{Mg} regions. Owing to these lattice defects, the thermal conductivity of the SCs was lower than that of the PCs. In contrast, the electrical conductivity of the SCs was higher than that of the PCs, indicating that the lattice defects less affected electronic transport. The maximum zT values reached 0.83 at 650 K for an n-type Sb+B-codoped Mg_2Sn SC and 0.44 at 700 K for a p-type Li+B-codoped Mg_2Sn SC.

To further improve p-type TE performance, we prepared nondoped and Li-doped Mg_2Ge SCs, because a Li-doped Mg_2Ge PC showed the highest $zT = 0.45$ at 700 K among p-type Mg_2X PCs [6]. Similar to the Mg_2Sn SCs, the melting method was used. The nondoped and Li-doped Mg_2Ge SCs contained V_{Mg} and DCs. V_{Mg} regions were also found in both SCs. The Li-doping changed the conduction type of Mg_2Ge from n-type to p-type. Compared with the Li-doped Mg_2Ge PC [6], a lower thermal conductivity and a higher electrical conductivity were realized.

These results demonstrate the potential of Mg_2Sn and Mg_2Ge SCs with engineered lattice defects for TE applications.

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Revealing key chemical insights in solution-based thermoelectric material synthesis

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Thermoelectric materials allow for the reversible conversion between heat and electricity and have many potential applications. However, the current fabrication methods that have demonstrated superior performances to date are prohibitively expensive, rendering them impractical for large-scale applications. An alternative and promising approach, known as solution-processing, has gained significant traction. This method involves a series of steps, including nanoparticle synthesis, purification (leaching and annealing), and densification into a pelletized material.[1] A notable lack of attention has been given to the process, despite the crucial chemical changes occurring in each step, especially beyond particle synthesis. Even more alarming is the fact that many published works, even those that have been breakthroughs in the field, lack detailed reporting of these steps, hindering reproducibility across different laboratories.

Herein, we shed light on the importance of these steps, focusing primarily on the one most overlooked: the purification of the particles. Our investigation centers on a water-based, surfactant-free solution synthesis, as it is potentially one of the cheapest methods to produce thermoelectric powders. The material of choice for this study is SnSe, a highly relevant thermoelectric material. We demonstrate and rationalize the impact of the number of leaching steps, purification solvent, annealing, and annealing atmosphere on the material's thermoelectric performance. Our study reveals the origin of the observed differences, stemming from changes in composition, such as Sn:Se ratio, and impurity content in the powder which is dependent upon the steps prior to the consolidation. Even minor compositional changes, mostly undetectable by conventional analytical techniques, lead to distinct consolidated materials with different compositions but also different types and concentrations of defects. Additionally, the profound effect on charge carrier and phonon transport in the material is demonstrated and explained.

Our primary objective with this work is to emphasize the paramount importance of understanding the chemistry and identifying key chemical species throughout the process to optimize material performance. Furthermore, we advocate for detailed reporting of all steps, including purification, as it is imperative for material reproducibility.

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Toward a true continuous healthcare system

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Continuous monitoring of vital signs and timely treatment are the future trends for wearable and implantable healthcare systems, which inevitably require ceaseless power supply. Discharged batteries could be detrimental to the health of people, such as those with type 1 diabetes, whose glucose levels should be monitored and controlled through timely insulin injections. Here, we demonstrate a feasible true continuous healthcare system for type 1 diabetes by combining a low-energy micropump, self-powered glucose sensor, and ceaseless power supply. By converting body heat into electricity to charge a battery for 790.1 s, we acquired 136.8 mJ (100%) of energy, which was used to operate the micropump and sensor for 74.6 mJ (54.5%) and 25.3 mJ (18.5%), respectively; the surplus 36.9 mJ (27.0%) was stored in the battery. In addition, we are going to present our recent efforts to build a compact vital band which contains wearable sensors, unintermittent power supply, and flexible circuits located at a single location (i.e., the forearm). The vital band is specially designed for the continuous monitoring of the core body temperature (CBT) with novel CBT sensors and pulse rate sensor operated by intermittent power. These findings can help realize a true continuous healthcare system in the future.

Quantum materials for thermoelectrics

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Keywords: quantum materials, topological insulators, Dirac and Wey semimetals, thermoelectrics

Topological quantum materials, such as topological insulators and Dirac/Weyl semimetals, have a linear energy-momentum dispersion that leads to the electrons near the Fermi energy behaving like ultra-relativistic Dirac fermions.[1] Many of the topological quantum materials of current interests originate from the thermoelectric compounds well known in 1950s and 1960s. In this talk, I will present our studies on topological quantum materials, with an emphasis on topological thermoelectrics research in the past, present and future. Dirac linear dispersion can give rise to large Seebeck effect and Nernst effect in a magnetic field.[2,3] Combined with an ultrahigh carrier mobility, topological thermoelectric materials open a new avenue for the solid-state heat and electricity conversion, and quantum information science and technologies in a wide range of temperature.

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Utilizing magnetism to enhance thermoelectric materials

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Keywords: thermoelectric, Seebeck enhancement, magnetism, magnon drag

Development of thermoelectric (TE) materials is important, for energy saving via waste heat power generation [1], and IoT power sources [2]. For high TE performance, traditional trade-offs must be overcome, between Seebeck coefficient *S* and electrical conductivity s, and between electrical and thermal conductivity k [3].

For overcoming the first tradeoff, we have found that magnetism can be utilized to enhance the Seebeck coefficient and overall power factor (PF). Coupling of the electrical carriers with magnetic moments, can lead to magnon drag which was known from long ago in Fe, etc. to lead to increase in *S* at low temperatures. However, the recent advancement is the demonstration that magnon drag can actually lead to high performance, i.e. high power factors at higher temperatures, namely for $CuFeS_2$ chalcopyrite [4]. Recently, magnon drag was also proposed as the origin [5] of the huge power factor in metastable Fe_2VAl-based thin films [6].

We have also discovered TE enhancement in paramagnetic systems, namely we show that in cases with strong coupling of the electrical carriers with the magnetic moments, this interaction “drags” the carriers, leading to an increase in the effective mass which enhances the Seebeck coefficient. This will be detrimental to the mobility but overall, enhancements to the power factor have been able to be realised in high performance TE systems, the first example demonstrated being $CuGaTe_2$ [7]. Later this interaction was named as paramagnon drag. Magnetic ion doping enhancement has also been demonstrated for Bi_2Te_3 [8], skutterudite [9] for example.

Spin fluctuation was found to enhance the Seebeck coefficient in the Heusler alloy Fe_2VAl [10]. Spin entropy is also known to enhance *S* [11].

I will discuss the recent developments in magnetic enhanced thermoelectrics, including further experimental studies on spin fluctuation enhancement and improved understanding of the first antiferromagnetic magnon drag analysis in its role to enhance power factor.

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MgSb-based materials for tellurium-free thermoelectric devices

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Keywords: thermoelectric generator, atomic layer deposition, magnesium-based thermoelectric materials, tellurium-free, Zintl phase materials

Commercial thermoelectric modules have relied on Bi_2Te_3-based compounds because of their unparalleled thermoelectric properties at temperatures associated with low-grade heat (<550 K). However, the scarcity of elemental Te greatly limits the applicability of such modules. Here we report the performance of thermoelectric modules assembled from Bi_2Te_3-substitute compounds, including p-type MgAgSb and n-type $Mg_3(Sb,Bi)_2$,[1] by using a simple, versatile, and thus scalable processing routine. For a temperature difference of ~250 K, whereas a single-stage module displayed a conversion efficiency of ~8.5%,[2,3], a module using segmented n-type legs displayed a record efficiency of ~8.2% that is comparable to the state-of-the-art Bi_2Te_3-based thermoelectric modules. Our work demonstrates the feasibility and scalability of high-performance thermoelectric modules based on sustainable elements for recovering low-grade heat and and thermoelectric cooling (dT_{max}=72 K).

Fig. 1: Multi-segmented thermoelectric module based on $Mg_3(Sb/Bi)_2$ and MgAgSb.

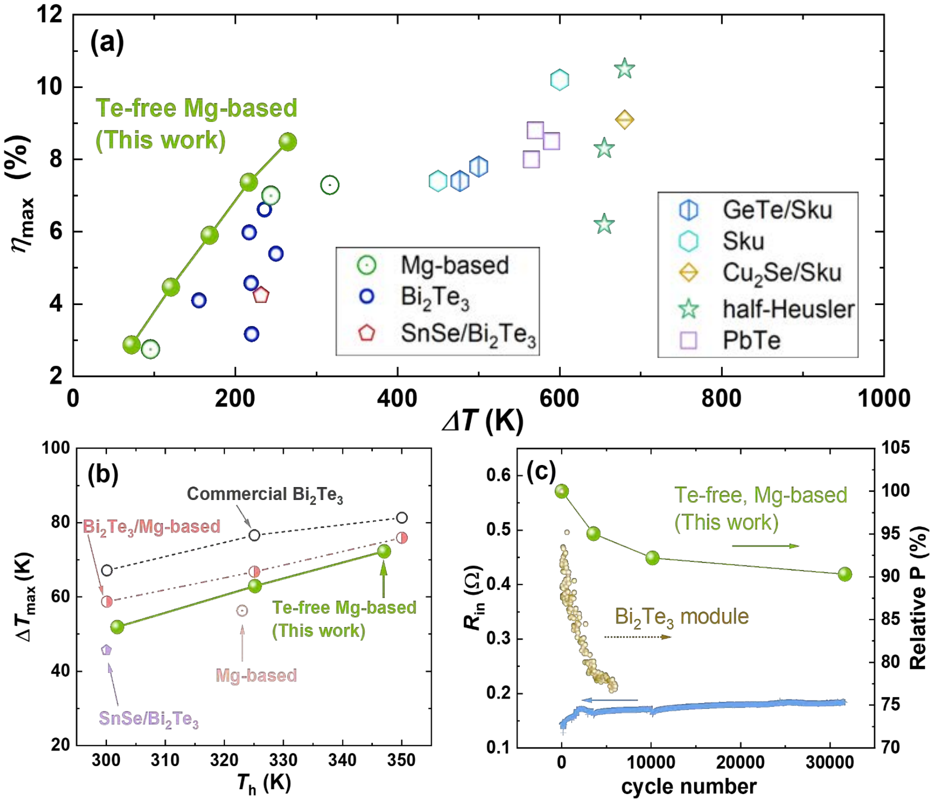

Fig. 2: Conversion efficiency of thermoelectric modules

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Thermoelectrics for the effective utilization of synthetic fuels in automotive

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Keywords: thermoelectrics, synthetic fuel, waste heat recovery, automotive

Synthetic fuels (e–fuels) will definitely have an important role to play in combating climate change. The efficiency for e–fuel utilization needs to imorove for automotive use. The purpose of this project is to improve the thermal efficiency by ~50% through the waste heat recovery including thermoelectrics, thermal insulation coating, heat exchanger, organic Rankine cycle and so on. This talk discusses our efforts to develop advanced thermoelectrics for effective utilization of synthetic fuel in automotive.

In this work, we developed robust and cost–effective $Mg_3(Sb,Bi)_2$–based thermoelectrics for automotive. The thermoelectric performance (avereage figure of merit zT) of $Mg_3(Sb,Bi)_2$ was successfully enhanced in the exhaust temperature range by tuning the Sb/Bi ratio. The electrodes were developed to provide good electrical contact for $Mg_3(Sb,Bi)_2$–based thermoelectric elements. Maximum conversion efficiency of ~3.5% was demonstrated in the prototype module composed of n–type $Mg_3(Sb,Bi)_2$ and p–type Bi_2Te_3 when the hot–side and cold–side temperatures were maintained at 473 K and 298 K, respectively. The improvement of thermal efficiency in the automobile through the developed thermoelectrics was simulated by GT–SUITE software.

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Synthesis of $SrTiO_3$/TiN Core/Shell-type nanoparticles and thermoelectric properties of their nanocomposites consolidated by Spark Plasma Sintering

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Keywords: strontium titanate, titanium nitride, heterostructure, diffusion barrier

Nanostructure engineering is nowadays the most important and promising pathway to higher *ZT* values. However, in principle, the complex nanostructures are thermodynamically non-equilibrial and hence thermally unstable, tending to transform toward energetically favourable coarser and simpler structures through thermal diffusion and grain growth. In this paper, we have employed titanium nitride (TiN) as heat-resistant diffusion barriers in oxide matrix.

Strontium titanate $SrTiO_3$ (STO), known as one of the most promising oxide candidates for TE applications, was used as the oxide matrix with large thermopower due to its heavy electron effective mass as large as $m^* = 6–7\ m_0$. Titanium nitride TiN was employed as thermally durable conductive layers to be inserted to grain boundaries of the STO matrix. In order to facilitate a good coverage of the grain boundaries with TiN, we first synthesized STO/TiO_2 core/shell nanoparticles via sol-gel prosess by using hydrolysis of titanium alkoxide. The TiO_2 shell was subsequently converted to TiN by nitrization at 1300 °C under flowing NH_3.The STO/TiN core/shell nanoparticles thus obtained were consolidated by using spark plasma sintering (SPS) to densify the oxide/nitride composites. The sintered samples were examined by powder XRD and SEM/EDS. The TE properties of the samples, the electrical conductivity σ, the Seebeck coefficient *S*, and the thermal conductivity κ, were measured from room temperature to 800 °C for the sample pieces cut from the sintered bodies.

The σ values of the samples increased with increasing TiN content, reflecting the metallic characters of the nitride. Accordingly, the absolute values of the negative Seebeck coefficient, $|S|$, decreased with increasing TiN content. The κ values of the samples were always higher for the samples containing TiN than that of neat STO, showing larger electron thermal conductivity for the samples with TiN as expected. However, most interestingly, the lattice thermal conductivity was lowest for the sample containing the largest proportion of TiN; this result can be attributed to enhanced phonon scattering at oxide/nitride heterointerfaces at a large quantity in the sample. As a result, a highest *ZT* value among the samples was obtained for the sample containing 20 wt% (nominal) TiN as $ZT = 0.14$ at 800 °C, being 8 times higher than that of the STO sample without TiN.

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Thermoelectric applications: from materials optimization to devices

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Keywords: thermoelectric materials optimization, weighted mobility, thermoelectric devices

Thermoelectric devices display the unique ability to directly convert heat into usable electricity, and vice-versa, without moving parts or the circulation of fluids, typically featuring a modular geometry. This gives them a great versatility and the potential to be employed in a wide range of applications, contributing for the mitigation of the global energy crisis. However, the toxicity of commercially available thermoelectric devices, the scarcity of some constituting elements and the low efficiencies (~5%) are issues that still need to be addressed in order to increase their practical use.

Recent advances in preparation techniques, simulation capabilities and materials science have led to the development of new thermoelectric materials that are not only more efficient, but also more economical and environmentally sustainable. Nevertheless, the thermoelectric properties of such materials depend on a variety of factors, like composition, presence of impurities, porosity or grain size, with their optimization generally being strongly dependent on the type of material and preparation/shaping conditins. Furthermore, despite the recent advances, the inclusion of the new materials into usable bulk thermoelectric devices is dependent on issues such as reactivity at working temperatures, the need for diffusion barriers or the quality of contacts.

This communication presents an example of the path from the optimization of materials to the development of thermoelectric devices. The thermoelectric materials used in this work are p-type semiconductors based on tetrahedrite (Cu12Sb4S13, a naturally abundant sulfosalt mineral), which are cheaper and less toxic than current commercial materials, making them a good alternatives for applications. The strategy for optimizing their thermoelectric properties and the use of weighted mobility are described. The challenges of manufacturing thermoelectric modules for applications close to room temperature using materials based on tetrahedrite (p-type) and magnesium silicide (n-type) are discussed, and several examples are presented on the thermal stability, diffusion barriers, device assembly, and computer simulations applying these emerging materials.

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Diamond-type copper chalcogenides for thermoelectric applications

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Keywords: chalcogenides, neutron diffraction, magnetism, electrical transport, thermal conductivity

Binary copper chalcogenides, $Cu_{2-\delta}Q$, (Q= S, Se), exhibit remarkable thermoelectric performance at elevated temperatures. Key to this high performance is the high mobility of copper cations within the chalcogenide matrix. However, this mobility also leads to degradation of the materials under operating conditions of a thermoelectric devices. At high temperatures, $Cu_{2-\delta}Q$ phases adopt structures related to that of antifluorite, in which copper cations are predominantly tetrahedrally coordinated by sulphur. This has motivated us to investigate a variety of complex copper chalcogenides, containing the same CuQ_4 structural unit that is present in $Cu_{2-\delta}Q$ at high-temperatures, as candidate thermoelectric materials.

These investigations have included the preparation and characterization of materials related to kesterite and stannite. Quaternary chalcogenides, Cu_2BCQ_4 (B = Zn, Fe, Mn, Co, C = Ge, Sn) of the kesterite and stannite family adopt tetragonal, diamond-like crystal structures. These may be considered as ordered derivatives of zinc blende, in which all cations are tetrahedrally coordinated. The two structures differ in the distribution of copper cations over the tetrahedral sites. Investigation of materials in the series $Cu_{2+x}BGe_{1-x}Se_4$ (B = Zn, Fe; $0.0 \leq x \leq 0.15$) demonstrates that at the same level of substitution, x, the presence of the magnetic Fe^{2+} cation enhances the figure of merit by *ca*. 67 % compared to that of the material containing non-magnetic Zn^{2+}. Electron doping through the introduction of selenium vacancies, leads to a further substantial increase in the maximum figure of merit of materials $Cu_2FeGeSe_{4-\delta}$, which reaches a value of $ZT = 0.47$ at d = 0.10.

In an effort to exploit further the beneficial impact of a magnetic cation on thermoelectric performance, investigations have extended to materials Cu_2MGeSe_4 containing the magnetic ions, M = Mn^{2+}, Co^{2+}. Powder neutron diffraction reveals differences in the detailed structure of the quaternary Fe-, Mn- and Co-containing phases, each of which crystallizes in a different space group. Neutron diffraction data also demonstrate that only the Mn-containing material undergoes a transition to a long-range magnetically ordered structure at low temperature. The quaternary selenides serve as parent materials for the investigation of the impact on structural and transport properties of chemical substitution. In particular, isovalent substitution in materials of general formula $Cu_2Fe_{1-x}M_xGeSe_4$ (M = Mn, Co) increases the average figure of merit over the temperature range $400 \leq T/K \leq 875$, Synchrotron powder X-ray diffraction data suggest this is associated with suppression of a phase transition that occurs in the parent (x = 0) phase. Further improvements in the maximum figure of merit are achieved through partial substitution of iron by cobalt, leading to $ZT = 0.53$ at 800 K at x = 0.075. This arises from simultaneous improvements in the electrical conductivity and Seebeck coefficient.

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Spin depedenent thermoelectric and magnetocaloric effects in perovskite oxides

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Keywords: longitudinal and transverse thermopowers, magnetocaloric effect, magnetic refrigeration, perovskits oxides

Following the discovery of spin Seebeck effect in magnetic metals and oxides, there is a growing increasing interest in spin based thermoelectricty in vatious materials from the perspectives of fundamental physics and potential applications. In particular, anomalous Nernst effect- the generation of electrical voltage transverse to the applied magnetic field and the temperature gradient in a sample is gaining much attention besides the spin Seebeck effect. The former effect does not need additional non-magnetic layer unlike the later. However, availabe studies on the anomalous Nernst effect in oxides are very few. In the first part of the talk, we give an overview of longitudial and transverse magnetothemolectricty, namely magnetothermpower and anomalous Nernst effect in Mn, Co and Ru based perovskite oxides and discuss their connecctions to magnetization and magnetic entropy. In the second part of the talk, I will focus on the potential of these oxides for magnetic refrigeration which exploits magnetic or spin entropy change. Correlations between the magnetic entropy change and magneothermpower in selected compounds will be discussed.

Acknowledgments

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From Heusler compounds to thermoelectric applications: Challenges and opportunities

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Keywords: thermoelectrics, Heusler, modules

Thermoelectric systems are solid-state devices used to convert heat into electricity or heat pumping using Seebeck and Peltier effect, respectively. While having competitive advantages such as ultra-long lifetime and virtually no maintenance costs, this technology has always been limited to niche applications such as space probe power or special electronic cooling. This limitation can be attributed to (i) the scarcity of the constitutive elements (Te, Ge,...) and the (ii) the performances of usual thermoelectric materials. While recent developments in the field mainly focussed on tackling these challenges, the time-to-market of new generations of thermoelectrics is still too long to have a significant impact in our path to a sustainable world. Indeed, going from new thermoelectric materials to modules involves to overcome many challenges in terms of joining, contact resistances, thermal stability while keeping the lowest processing costs as possible.

Fe_2VAl Heusler compound is a good candidate because of the large availability of its constitutive elements and its appealing thermoelectric performances at room temperature [1]. In this talk, we will present the main results obtained in our quest to large-scale thermoelectric applications: starting from Fe_2VAl synthesis and characterization [2,3] to its integration in conventional thermoelectric modules [4] and even further by looking at alternative modules configurations [5] and innovative processes such as additive manufacturing [6].

The developed modules have been integrated in several proof-of-concept set-ups for several applications in several fields such as industrial waste heat recovery and autonomous sensors for the internet of things. Finally, this technology have been recently licensed to a start-up called Thermo Power aiming at significanlty reducing waste heat and promote sustainability through the use of thermoelectricity.

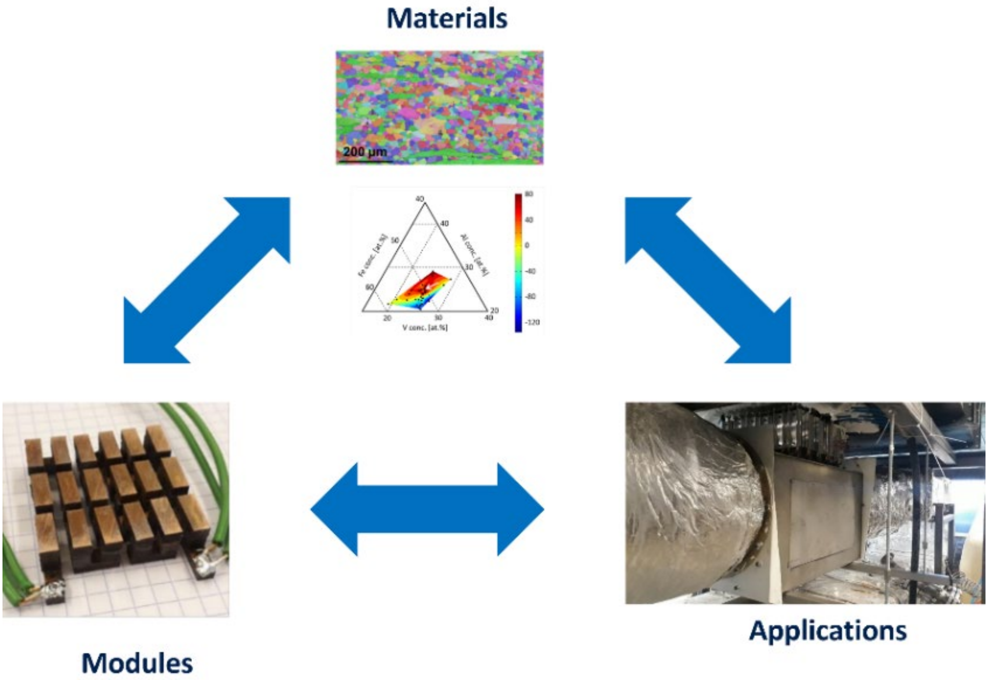

Figure1. Designs of thermoelectric materials, modules and applications are interrelated and should be considered as a whole to kickstart widespreading of thermoelectric solutions.

Acknowledgments

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Ductile thermoelectric materials

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Keywords: type your, keywords here, separated, by commas

Flexible thermoelectrics is a synergy of flexible electronics and thermoelectric energy conversion. To date, state-of-the-art thermoelectrics is based on inorganic semiconductors that afford high electron mobility but lack in mechanical flexibility. By contrast, organic materials are amply flexible but low in electrical mobility and power output; the inorganic-organic hybrid design is a viable material-level option but has critical device-level issues for practical application. In this talk, we report the recently discovered ductile inorganic thermoelectric materials such as Ag_2S and its alloys. They are typical semiconductors with tunable thermoelectric performance. At the same time, they are highly flexible and plastic, which are similar with the mechanical properties of metals. Furthermore, Upon compositional optimization, these silver chalcogenides reached a delicate balance between high carrier mobility, power factor, a figure of merit and good mechanical flexibility. The good thermoelectric figures of merit in flexible inorganic materials are achieved, opening a new avenue of flexible thermoelectrics. High electrical mobility yielded a normalized maximum power densitynear room temperature, orders of magnitude higher than organic devices and organic-inorganic hybrid devices. These results promised an emerging paradigm and market of wearable thermoelectrics.

Low apparent thermal conductivity of a single nanopillar mediated by surface phonon polaritons

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Keywords: nanoscale heat transfer, nanoribbon, low thermal conductivity, surface phonon polaritons

Independent control of thermoelectric (TE) properties, determined by intrinsic electronic and lattice structures as well as their coupled properties, has been a key to enhance the figure of merit (ZT) of TE materials. Introducing nanostructures has been able to significantly suppress the thermal conductivity while maintaining electrical properties, correspondingly achieving higher ZT. It origins from the distinct length scales of mean free paths of phonons and electrons, and as such, the range to selectively tune the thermoelectric properties is limited. I introduce a new approach to manipulate heat transport leveraging surface modes, unlike traditional methods that often involve intricate adjustments to lattice parameters within solids. The surface modes are mediated by so-called surface phonon polariton (SPhP), which is a new quantum of energy coupled by optical phonons and photons. It contributes to high radiative heat loss from the surfaces, resulting in less heat conduction through the volume. It obviates the need to tailor material properties through doping, defect engineering or nanocomposites, and it mitigates the risk of degrading electrical parameters. We designed nanopillars to fully leverage the surface modes and to reduce the apparent thermal conductivity. In this talk, I will also introduce our novel experimental platform to quantify the contribution of SPhPs as well as to measure the apparent thermal conductivity in an individual nanopillar.

The impact of incipient ionic conductivity in the low thermal conductivity of tetrahedrite

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Keywords: lattice thermal conductivity, neutron scattering, sulfides

The thermoelectric performance of tetrahedrites, which are minerals composed predominantly of environmentally-friendly and abundant copper and sulfur, is currently attracting considerable interest. Tetrahedrites, which are *p*-type materials with low lattice thermal conductivities, crystallise in a collapsed sodalite structure in which corner-sharing CuS_4 tetrahedra form cages. Each cage contains an octahedral cluster formed by six trigonal-planar copper cations. The origin of low thermal conductivity in tetrahedrite, $Cu_{12}Sb_4S_{13}$ has been previously attributed to the rattling vibrations of the trigonal-planar copper ions and has also been linked to a phonon instability arising from a low-temperature phase transition. Analysis of neutron and synchrotron X-ray diffraction data collected on tetrahedrite shows that copper rattling is a direct consequence of a tetragonal-to-cubic phase transition at 90 K, which results in a sharp increase, by approximately 200%, of the atomic displacement parameters of the trigonal-planar copper cations.[1] This phase transition occurs because of the orbital degeneracy of the highest occupied 3*d* cluster orbitals of the copper clusters found inside the sodalite cages. In the cubic phase, the trigonal-planar copper cations form regular octahedral Cu_6^{7+} clusters, which are electronically degenerate. Below 90 K, the octahedral Cu_6^{7+} clusters undergo a Jahn-Teller distortion, resulting in the formation of square-pyramidal Cu_5^{7+} clusters. The Jahn-Teller electronic instability which leads to the formation of the pentameric Cu_5^{7+} clusters, suppresses copper rattling vibrations due to the strengthening of direct copper-copper interactions.

At temperatures above 200 K, quasielastic neutron scattering (QENS) measurements on tetrahedrite, $Cu_{12}Sb_4S_{13}$, and copper-rich tetrahedrite, $Cu_{14}Sb_4S_{13}$, combined with molecular dynamics simulations, reveal that copper ion diffusion occurs.[2] However, although the copper ions are mobile between 200 and 400 K, they are largely trapped inside the sodalite cages. Analysis of inelastic neutron scattering (INS) data reveals the presence of a low-energy optical mode at 3-4 meV, which can be attributed to the intra-cage diffusion of the trigonal-planar copper ions, rather than to rattling. This low-energy optical mode, which softens on cooling revealing strong anharmonicity, is capable of strongly scattering the heat-carrying acoustic phonons, and hence lowers the lattice thermal conductivity.

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T1.3 EMERGING MATERIALS AND TECHNOLOGIES FOR SOLAR CELLS AND SOLAR FUEL TECHNOLOGIES

Emerging technologies for photocarrier mobility mapping in thin-film solar cells

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Keywords: solar cells, photocarrier mobility, inaging

As far as the utilization of semiconducting materials in solar cells is concerned, a parameter that is critically important is the drift mobility of photogenerated charge carriers, on which the solar cell photoconversion efficiency is highly dependent. However, information on the photocarrier drift mobility in solar cells has been so far relying only on single data-point measurements, even if cross-sectional photocarrier mobility mapping would be highly desirable. Here, we present a review of time-domain photocarrier mobility measurement techniques that will include time of flight (TOF) methods and charge extraction by linearly increasing voltage (CELIV).[1,2] We will then focus on the efforts from our team [3] concerning the integration of TOF and CELIV with confocal optical microscopy (COM) and scanning near-field optical microscopy (SNOM) for direct photocarrier mobility mapping, at the nanoscale in conjunction with atomic force microscopy (AFM) topography scans. Our methodology is based on the use of near-field effects and multimolecular electron-hole recombination to achieve local sensitivity to the photocarrier mobility.[3] As monomolecular recombination of excess carriers is the most frequent radiative pathway for electrons and holes in solar cells at low power density of illumination, while multimolecular recombination dominates at high power, enhanced multimolecular recombination occurs at the confocal plane or in the near field. Thus, the CELIV signal achieved under specific conditions in COMs and SNOMs provides enhanced information on the mobility of all of the cross-sectional layers except for the focal plane or the local point illumination in the near field. For example, by scanning the focal plane along the z axis, the mobility profile can be derived. To demonstrate our technique, we use it to investigate the carrier mobility in several different types of hydrogenated amorphous silicon (a-Si:H) solar cells.[3] The mobility maps obtained by our "confocal CELIV" techniques correlate well with well-known depletion layer effects and the hydrogen content profile in a-Si:H when this is measured independently. Our findings are in excellent agreement with models suggesting a critical role of Si–H bonding in lovcally determining the carrier mobility in a-Si:H solar cells.

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Frontiers in 2D materials for water splitting derived green energy: A focus on current challenges and future horizon

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Water oxidation using efficient catalyst, which is the anodic half-reaction of water splitting, plays a critical role in generating clean and abundant H2 fuel. 2D materials have emerged as promising candidates for water oxidation due to their unique properties such as their high surface-to-volume ratio, tunable electronic band structures, and large active surface areas.[1, 2] Yet, the key challenges of the field are (1) the activity, stability, and scalability of 2D nanostructures materials. Surface reconstruction and heterointerface engineering techniques have been employed to enhance properties such as electrical conductivity, stability, facile charge transfer, as well as to activate intrinsically active edge sites. These properties significantly influence the water oxidation performance of 2D nanostructures materials. (2) Another challenge is related to surface engineering, as the surface properties of 2D nanostructures materials greatly impact their performance in water oxidation. Optimizing the surface chemistry and morphology of 2D nanostructures materials is crucial for achieving high catalytic activity and stability. (3) Electrochemical performance is also a critical factor in the efficiency of water oxidation using 2D nanostructures materials. (4) Integration of catalysts is another challenge in the field. Strategies such as anchoring catalysts onto the surface of 2D nanostructures materials[3, 4] or surface confinement[5] have been investigated to achieve efficient water oxidation performance. Furthermore, the synthesis and characterization of 2D nanostructures materials for water oxidation require careful consideration. We will summarize the latest developments in the field, including results from our lab, highlighting the critical role of 2D composites to boost functionality toward efficient water oxidation.

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Strategies for catalyst development and performance enhancement in water splitting catalysis

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Keywords: 2D materials, interface properties, electro-catalysis, photo-catalysis, water splitting

The generation of clean energy from water electrolysis is a feasible solution to overcome the problems of energy crisis. However, this viable route depends on the utilization of Pt, which is scarce and expensive. Designing catalysts entirely based on Earth abundant materials is, therefore, the way forward. In this regard, 2D materials (layered or non- layered), and transition metal phosphides have got copious attention. [1,2] Here,we present strategies to enhance the catalytic (electrocatalysis, photocatalysis) performance of these materials giving a particular emphasis for transition metal chalcogenides (WS2, CuS, etc), transition metal phosphorus trichalcogenides (MPX3; X=S,Se), non-layered Cr2S3 and nickel phosphides. We discuss the advantages of these materials for catalysis and the different routes available to tune their electronic states and active sites. Experimental results show that doping and hybrid material formation play a significant role in optimizing the free energy of hydrogen adsorption and desorption on the vertically oriented nanosheets of WS_2. Another compelling issue in this research area is about solving the sluggish kinetics of the other half reaction (i.e OER) in water splitting catalysis. It has remained a bottleneck in realizing efficient performance. In this regard, nickel phosphide has an excellent track of performance.[3,4] We also discuss the mechanism behind the very good performance of Ni5P4 and CrOx-CuS toward electrocatalysis of OER. The metal phosphides or sulfides are not the true catalysts, rather in-situ generated metal oxides at the vicinity of phosphides/sulfides are. Moreover, We highlight the emerging layered MPX3 (M= Mn, Ni, Fe, Cu/In)[5] nanosheets as promising materials in sacrificial agent-free photocatalytic water splitting under simulated Sun light (AM 1.5G) illumination.

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T1.4 MATERIAL SCIENCE AND TECHNOLOGIES FOR ADVANCED NUCLEAR FISSION AND FUSION ENERGY

He ions irradiation effect of zirconium carbide solid solution ceramics

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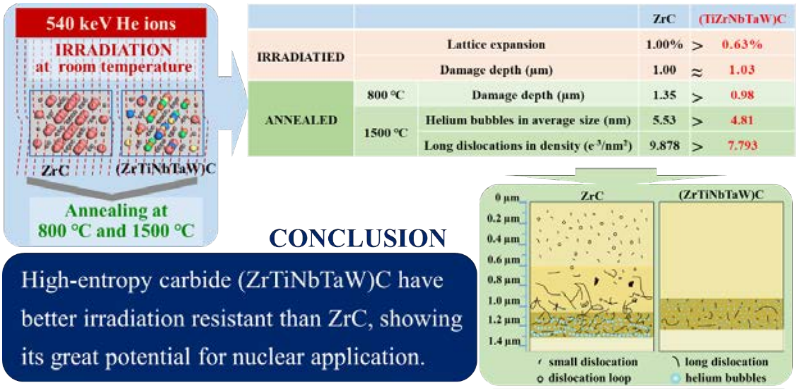
Keywords: entropy increase, solid solution, irradiation effect

The high-entropy concept provides an opportunity for the design of irradiation resistance materials from nano and atomic scales. Damage accumulation, swelling, segregation, He bubbles, and void formation are found to be considerably suppressed in Ni-based single-phase concentrated solid solution alloys. Different from the metallic bond-based HEAs, high-entropy ceramics (HECs) usually possess a mixture of covalent, ionic, and metallic bonds. Up to the present, there are very few related studies on the irradiation behavior of the HECs, particularly high-entropy carbide ceramics. In this work, the 540 keV He ion irradiation with a dose of 1×10^{17} cm^{-2} was performed at room temperature on (TiZrNbTaW)C high-entropy carbide ceramics. Irradiation-induced structural evolution and He retention behaviors after annealing at different temperatures were examined in depth by grazing incident X-ray diffraction (GIXRD) and transmission electron microscopy (TEM). The results show that the high-entropy design can improve the irradiation resistance of carbide ceramics. Compared with ZrC, the high entropy (TiZrNbTaW)C in the meantime brings about smaller lattice expansion and the favorable structural evolution phenomena including smaller He bubbles that are evenly distributed without abnormal coarsening or aggregation, segregation, and shorter and sparser dislocation. The ZrC-based solid solution ceramics in low and medium entropy have been also prepared and irradiatied by He ions. The results show that it is not the case that the larger the entropy is, the better the irradiation resistance will be.



			ZrC		(TiZrNbTaW)C
IRRADIATIED		Lattice expansion	1.00%	>	0.63%
		Damage depth (μm)	1.00	≈	1.03
ANNEALED	800 °C	Damage depth (μm)	1.35	>	0.98
	1500 °C	Helium bubbles in average size (nm)	5.53	>	4.81
		Long dislocations in density (e^{-3}/nm^{3})	9.878	>	7.793

High-entropy carbide (ZrTiNbTaW)C have better irradiation resistant than ZrC, showing its great potential for nuclear application.

Figure. Reduced He ions radiation damage in a ZrC-based high-entropy ceramic

Evolution of structural material selection and design for operation in fusion reactor environments

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Keywords: structural, metallics, steel, composites, creep

Commercial fusion energy continues to advance rapidly, with programmes such as the UK Atomic Energy Authority (UKAEA) Spherical Tokamak for Energy Production (STEP), the European DEMOnstration (DEMO) reactor, United States Fusion Neuron Science Facility (FNSF) and many efforts in the private sector already well underway. One key theme throughout the development of commercial plant concepts is the requirement for greater thermodynamic efficiencies to maximise net energy output, thereby increasing the economic viability of such designs. Therefore, high-temperature coolant concepts are being explored which often exceed outlet temperatures of 550°C.

Increased outlet temperatures therefore add to the list of challenges fusion plant structural materials must endure. These high temperature effects are often synergistic, coupling with high levels of radiation damage, corrosion effects and mechanical loads, to name but a few. Conventional structural materials, such as reduced activation ferritic martensitic (RAFM) steels have well-established limitations above operating temperatures of 550°C, driven by a severely reduced creep lifetime [1]. Advanced (A)RAFM steel variants are being developed to address this, using dispersions of carbides, nitrides and in some cases oxides, to enhance the strength and operating lifetime of structural steel. The UKAEA has established a substantial programme in this area called NEURONE (NEUtron iRradiatiOn of advaNced stEels) to develop a high temperature, radiation resilient, castable steel, capable of being produced at tonnage scale by 2028. These steels are targeting operating temperatures up to 650°C. Oxide dispersion strengthened (ODS) steels offer an alternative route to widen operating temperatures further, up to 700°C. However, efforts to utilise these steels at scale have been hampered by a limited supply chain, constrained manufacturing routes and difficult joining processes.

Beyond the realms of metallics, ceramic matrix composites (CMCs) such as silicon carbide composites (SiC_f/SiC) offer the capability to enable plant structural operation up to 1000°C. However, many challenges remain, particularly to address manufacture at scale, part quality, joinability and costs. The UKAEA HASTE-F (Hybrid Approach to Silicon carbide Technologies and Engineering in Fusion) project is exploring alternative approaches to SiC_f/SiC manufacture, using a flexible pre-impregnation system to develop parts of greater complexity with reduced residual porosity levels compared to conventional manufacture approaches.

This talk will explore these ongoing research programmes at UKAEA and outline the common unifying themes driving our research. This includes bridging the gap between metallics and ceramics and how hybrid component design may be able to utilise the strengths of both materials and unlock the potential to exploit novel engineering approaches towards commercial fusion plant design.

Acknowledgments

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Investigating mechanical and damage behaviour of ceramic matrix composites with X-ray computed tomography and micromechanical modelling

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Keywords: in-situ observation, microcracking, image-based simulation, FFT method, phase-field fracture model

CMCs have ceramic fibre architectures embedded in a ceramic matrix, which can be customised for different applications via the composite weave and the chemistry or structure of the fibre-matrix interface. Their macroscopic properties are highly controllable depending on material composition and manufacturing process. Reliable lifetime prediction and improved design of CMCs in nuclear applications require coupling of advanced experimental and simulation tools. For this purpose, full-field measurements are usually preferred or even mandatory. Although characterisation methods are becoming more and more powerful at all length scales, it is impossible to assess all the microstructural features of a complex material using one single experimental method. Also, experimental characterisation is usually costly and time-consuming. Numerical modelling can alleviate this issue. However, because of the complexity of their microstructure at multiple length scales, high-fidelity modelling framework is to be developed for predicting the thermomechanical behaviours and damage growth in CMCs. This talk will highlight some developments in experimental and numerical methods for understanding the structure-property relationship, It will give a brief overview of our previous collaborative efforts in this area and illustrate the potential of bridging the experimental and numerical techniques by image-based simulations.

Microcracking and heterogeneous deformation within CMCs are obsreved from in-situ X-ray computed tomography experiments [1]. Digital volume correlation is used to measure the 3D strain field and correlate it with the fibre architecture [2]. Some dedicated image processing alorithms are developed to analyse the XCT images in a quantiative fashion [3]. For the numerical analysis, we employ a solver based on the Fast Fourier Transform (FFT) technique, as an alternative to the classical Finite Element method. We demonstrate the capacility of the FFT solver in large-scale simulations with billions of elements [4]. This capability is important for the use of real microstructures extracted from XCT images, which enhances the fidelity of numerical simulations and allowing direct comparison against the experimental observations. At the microscale, a phase-field damage model is implemented, combining a frictional cohesive zone model, to describe various failure mechanisms, namely matrix cracking, interfacial degradation and fibre failure. The method is applied to investigating the effect of irradiaiton swelling of SiC/SiC composites. Although primarily focused on SiC/SiC materials for nuclear applicaiton, the methodology is applicable to other grades of CMCs, such as C/C-SiC [5].

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Andra's R&D program on ceramic materials as alternative and innovative solutions for the geological disposal of high-level radioactive waste

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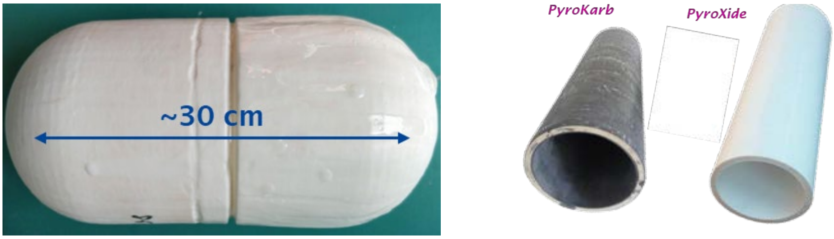
Keywords: alumina-based materials, mechnaical load, watertightness, sizing, corrosion

Andra is in charge of the project called Cigeo, an Industrial Centre for Geological Disposal of radioactive waste, where the high-level waste (HLW) will be disposed of underground, at ~500 m, inside horizontal tunnels (cells) dug in a claystone whose properties allow protecting the environment against the radioactivity for a very long timescale. For a shorter period (a few centuries), an additional (artificial) barrier, namely a container holding the waste primary package, will also be used. Currently, in Cigeo, low-carbon steel has been identified as the reference material for the HLW containers; another low-carbon steel is also selected for the cell liner.

These steels will be subjected to severe challenges, the corrosion under anoxic conditions, already considered *via* strict safety criteria, being one issue to consider owing to the associated $H_{2(g)}$ production. To ensure an even safer disposal, bulk, or coating materials much less prone to corrosion are also investigated. In this framework, R&D activities are conducted by Andra and his partners to select, size, qualify and fabricate ceramic-based components instead of steel ones. Here, we present the work carried out on alumina-based, very thick monolithic or ceramic-coated containers. Ceramic matrix composites for the cell liner are also shown to be promising candidates.



(a) (b)

Figure 1: (a) Small-scale prototype of a HLW ceramic container, and (b) prototypes of HLW ceramic cell liners (these liners use CMCs provided by the Pyromeral company).

Development of silicon carbide composite components for nuclear application

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Keywords: silicon carbide composites, tube, liquid phase sintering, joining

Silicon carbide (SiC) composites are promising materials for nuclear fission and fusion reactor systems due to engineered toughness by fiber reinforcement and intrinsic features of SiC, including low activation, chemical and environmental inertness, exceptional irradiation stability, and very high temperature mechanical performance. The key issues are to fabricate large scale production with uniform structure and complicated shaping for the component development. The objective is to develop fabrication technique for SiC composite components.

Flexible prepreg sheets were prepared. The prepreg sheet contains satin weave Hi-Nicalon type-S SiC fibers without coatings and SiC, BN and Al_2O_3 powders as matrix materials. The BN particle dispersion SiC composites were fabricated by liquid phase sintering with the stacked prepreg sheets. Various SiC composite components were fabricated. Braiding technique was also applied for a small diameter tube with 8mm inner diameter. The mechanical properties and microstructure were characterized for reference materials.

The BN particle dispersion SiC composites were fabricated successfully with uniform microstructure through thickness. The porosity was less than 5% even for the composites with curvature. The fiber/matrix interphase like C or BN is the weakest link in conventional SiC composites with fiber coating. The coatings are broken at the curvature if the coated fibers are bent during processing. No significant degradation of strength was observed at 1400C in air for the BN particle dispersion SiC composites. Oxidation of the composites was limited to near surface, because the composites didn't have fiber/matrix interphase. The composites didn't break following over 100 thousand cycles fatigue applying 190 MPa at 1400C in air. The 100 mm long box was fabricated and joined with the SiC composite tubes.

Mechanical testing of SiC_f/SiC cladding tubes for gas-cooled fast reactors

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Keywords: cladding of nuclear fuel, SiC, mandrel test

Silicon-carbide is considered as perspective structural material in nuclear reactor. It has low neutron capture cross section and excellent material properties at high temperatures. It is planned that SiC components will be used in gas-cooled fast reactors in the so called refractory core operated at very high temperature.

In the framework of the EU SafeG project, SiC_f/SiC composite claddings were fabricated by the liquid phase sintering using Al_2O_3 sintering additive at the Kyoto University. Hi-Nicalon type-S fibers were used without fiber coating. Matrix included BN particles. The tube samples were produced using prepreg sheets. Two series of samples were supplied for testing. In the second series higher tension was applied during wrapping of the prepreg sheets.

The Centre for Energy Research carried out the following experiments and examinations with SiC_f/SiC cladding tubes.

- high temperature treatment in He atmosphere (1000 °C, 7 h),
- high temperature oxidation in steam (1000 °C for 1 h, 1200 °C for 30 min).
- ring compression tests of as-received and heat treated samples,
- mandrel tests of as-received and heat treated samples,
- pressurization of 30 mm long tubes,
- scanning electron microscopy of as-received and tested samples.

The first results with testing SiC_f/SiC composite tubes are promising and this is the primary candidate cladding material for the refractory fuel of gas-cooled fast reactors. However, the currently used fabrication procedure needs further improvement to overcome the observed weaknesses.

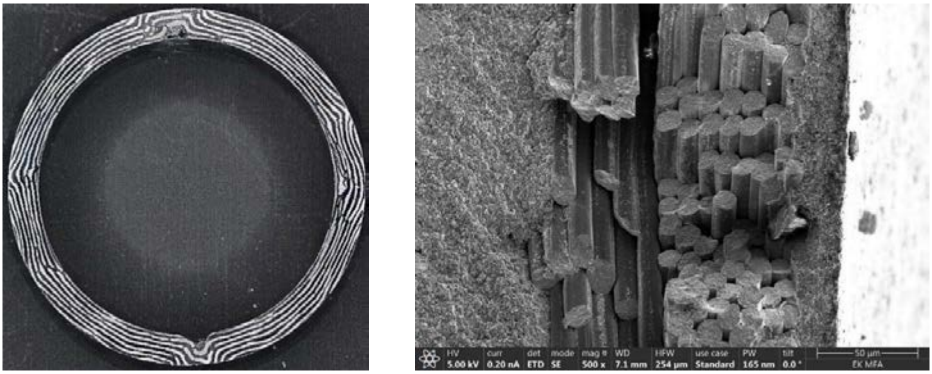

Figure 1. Cross section (left) and fracture surface (right) of the SiC_f/SiC cladding tubes

Acknowledgments

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Characterization of nuclear ceramics with spallation neutron probes

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Keywords: radiation effects, disordering, defects, ion irradiation, neutron total scattering

The development of durable nuclear ceramics has been central to efforts for advanced fission and fusion energy systems. There still exist, however, large gaps in the understanding of fundamental modes of structural degradation under harsh environmnets, including self-irradiation. We have shown that neutron total scattering measurements with pair distribution function (PDF) analysis can be utilized to uniquely characterize defects and disorder in a wide range of nuclear ceramics (e.g.,. pyrochlore, spinel, and actinide oxides). Key to this approach are swift heavy ions with a penetration depth of ~100 µm, which is high enough to produce sufficient quantities of irradiated material for characterization using bulk techniques [1]. Irradiation experiments are performed at the UNILAC accelerator at the GSI Helmholtz Center (Darmstadt, Germany) using typically Au ions of about 2 GeV kinetic energy. Irradiated samples were investigated at the Nanoscale Ordered Materials Diffractometer (NOMAD) beamline at the Spallation Neutron Source (Oak Ridge National Laboratory, USA). These measurements enable detailed analysis of both cation and anion defect behavior, and short-range order, which is particularly important for the investigation of amorphous materials. Recent results for several ceramics demonstrate that structural changes are more complex than previously thought with distinct processes occurring over different length scales [2]. For example, disordered pyrochlore and spinel oxides [3] are composed of local structural units that maintain atomic order and exist in configurations that are different than the expected average structure determined using traditional techniques (e.g., X-ray diffraction). Here, we will highlight the importance of short- and medium-range analysis for a comprehensive description of nuclear ceramics [4].

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Real time X-ray tomography imaging of cracks initiation and propagation in CMC-based nuclear fuel claddings at 1200°C

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Keywords: accident tolerant fuel, SiC CMC, X-ray tomography, deformation and fracture

Coated SiCf/SiC-based composites is a potential accident tolerant fuel (ATF) cladding of great interest to nuclear community. It is necessary to study their mechanical behaviour at elevated temperatures similar to accident conditions. In this work, a range of CMC cladding materials have been studied with varied braiding designs and coating thicknesses. The cladding tube was cut into a C-ring geometry and loaded under uniaxial compression combined with sychrotron X-ray micro-tomography for real-time imaging of the deformation, crack initiation and propagation processes. The tests were carried out over a range of temperature up to 1200°C and the impact of temperature on the mechanical behaviour of the different types of cladding designs will be reported. The data were analysed using image segmentation as well as digital volume correlation for 3D strain distribution. It was found that the inherent porosity of the composite part of the cladding tube varies with braiding/weave patterns and this affected the crack propagation from the outer SiC coating. For claddings with very thick outer coating, the strength is dominated by the coating strength and resulted in more brittle failure. A balance has to be reached between the thickness of the outer coating and underlying composites to enable gradual progressive failure. It is emphasized that the toughening mechanisms in the coating/composite systems vary with temperature, materials designs and the applied stress state. The conventional failure process in unidirectional mini-composite under uniaxial tension does not apply to such cladding composite materials under C-ring compression loading.

Metal-functionalized silica aerogels for capturing and sequestration of iodine

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Keywords: iodine, capture, sorbent, functionalization, metal, sequestration

The reprocessing of spent nuclear fuel is being used to recover fission products, such as uranium-235 and plutonium-239, for recycling. During this process, various gaseous fission products from the fuel are released into the off-gas system, with radioiodine ($^{129}I_2$) being of particular concern because of its long half-life (1.6×10^7 years) and the potential for its accumulation in the environment. There are a number of solid sorbents that have been developed and are under investigation for capturing radioactive iodine. They differ in iodine capacity as well as ease and cost of preparation. Owing to strong chemisorption for iodine, the leading approach to capturing radioactive iodine is silver-containing sorbents. However, silver is expensive and listed by the Enviromental Protection Agency as a hazardous waste due to its level of toxicity.

An intriguing option is to develop sorbents with a hierarchical structure or architecture at multiple length scales. They would consist of multiple levels of porosity and different metal chemistry than silver, e.g., Cu and Bi, and allow for increased surface area, improved mass transfer, and enhanced selectivity. This combination of pore sizes and chemical functionality would enable effective capture of iodine from complex off-gas streams.

The presentation will discuss the design, synthesis, and sorption performance of metal-functionalized silica aerogels and different strategies that have been developed to sequester iodine. This will include results from durability tests, a summary of highlights, and a prognosis for future research.

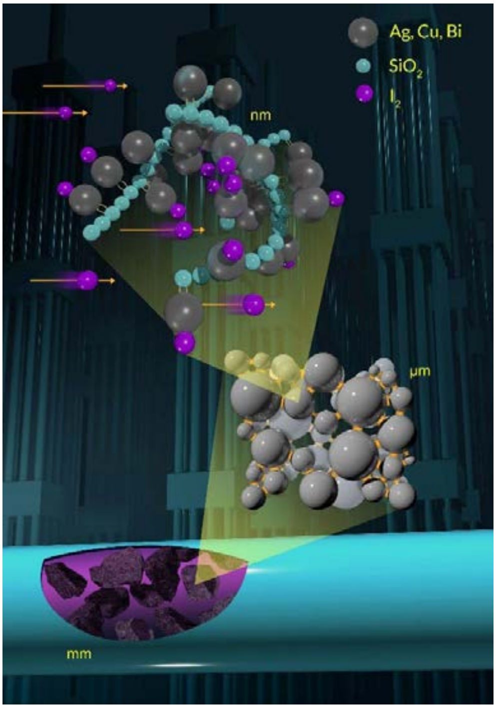

Figure 1. Hiearchical design of metal-functionalized silica aerogels for capturing iodine.

Wireless technology applications in advanced surveillance, diagnostics, and prognostics for nuclear facility

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Keywords: wireless technology, safety, nuclear power plants, surveillance, diagnostics, prognostics

KAERI is developing wireless technology that can be applied to nuclear power plants (NPPs) [1-3]. Currently, there exist limitations in applying wireless technology to NPPs [4]. For the safety considerations, NPPs categorize three different functions: category A - functions play a principal role in NPP safety, category B - a complementary role to the category A, and category C - an auxillary or indirect role, not category A and B. In NPPs, the use of wireless devices to systems supporting category A and B is excluded. Only the use of them to systems supporting category C is permitted. From the regulatory perspective, the wireless technology must meet NRC R.G. 1.180 and IEC TC SC45 standard. On the other hand, from the operation perspective, the power to wireless devices must last longer than, at least, the period scheduled for maintanence (*e.g.*, 18 months). To use wireless devices in NPPs, thus, the electromagnetic compatibility (EMC) and battery replacement issues must be resolved.

We have developed low-power wireless sensing technology to monitor micro-leaks on pipes in NPPs. This satisfies standard test method for leaks using ultrasonics, *i.e*., ASTM E 1002-05 Class II. Our low-power technology can provide a way to resolve the battery replacement issues. However, to use this in NPPs, wireless communication technology must comply with specific protocols under the NPPs environments. To address this, we are developing WiFi-Halow as well as WirelessHART communication modules to integrate the wireless sensing and communication. Some technical issues in developing WiFi-Halow are discussed. Our work will help building wirelss sensor networks (WSN) for NPPs' instruments.

Acknowledgments

We acknowledge the Korean government, Ministry of Science and ICT, for support (No. RS-2022-00144000 and KAERI tech-commercialization program).

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R&D status on Li-ceramics for fusion breeding blanket

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Keywords: tritium breeder, pebbles, Li-ceramics, breeding blanket, fusion energy

Tritium is one of the fuels for the fusion reactor, generated in a breeding blanket by nuclear reaction between neutron from fusion plasma and lithium in breeder material. Therefore, lithium-containing ceramics (Li-ceramics) is used as tritium breeder material in the breeding blanket of fusion reactor. In a solid-type breeding blanket for a fusion reactor, the tritium breeder material is usually used in a pebble bed form because of the efficiency and convenience of tritium extraction. In addition, it is able to increase the packing factor in limited space and to reduce the uncertainty of the interface thermal conductance. Therefore, the development of fabrication method for breeder pebbles and establishment of material property database of the pebbles and pebble bed are actively conducted for the realize of fusion energy.

Lithium metatitanate (Li_2TiO_3) is one of a candidate metarial for tritum breeder because of their high mechanical strength in high temperature, low activation property and chemical stability. Li_2TiO_3 pebbles have been fabricated by several methods such as rotating granulation method, extrusion-spheronisation-sintering method, sol-gel method, and direct/indirect wet method. These methods need relatively multiple and complicated fabrication steps. In addition, the dehydration reaction and substitution reaction were used for pebble shaping in the direct/indirect wet method. However, low process temperature was needed and some elements were remained as impurities in spite of high temperature removal process in the specific atmosphere. Therefore, the slurry droplet wetting method for the fabrication of breeder pebbles has been developed. This method has many advantages such as good process control, low cost, room temperature process and high yield for mass production. Recently, alternative methods, such as powder injection molding method and 3D printing method, are developing for the tritium breeder pebbles to secure the stability of microstructure and properties and to more increase the fabrication rate for mass production. In addition, the material properties is one of key design parameters for breeding blanket with high stability and performance. Therefore, physical and mechanical properties of breeder pebbles and pebble bed are being measured by using various techniques. In this presentation, manufacturing methods and material properties of Li_2TiO_3 pebbles and pebble bed for tritium breeder material in fusion reactor are addressed.

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Metal organic frameworks for off-gas management

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Keywords: advanced reactors, nuclear re-processing, advanced functional materials, MOFs, xenon, krypton, iodine

Several volatile radio-nucleides that include tritium, iodine, C-14 and noble gases (Xe and Kr) were released during the nuclear re-processing of the used nuclear fuel, advanced reactor operations and other souces. As per the Environmental Protection Agency (EPA) and Nuclear Regulatory Commision (NRC), these volatile radio-nucleides need to be captured and sequestered. Particularly, radioactive ^{85}Kr has a long half-life ($t_{1/2}$ = 10.8 years) and therefore must be captured and removed from the off-gas to prevent its uncontrolled release into the atmosphere[1]. Although Xe is generated as a fission product, by the time the fuel is reprocessed, all the radioactive isotopes have decayed to very low concentrations. In addition, high purity of Xe is used in many applications, including commercial lighting, propulsion, imaging, anesthesia, and insulation, therefore high purity of Xe recovered from these operations could provide additional revenue to offset operating costs of these nuclear plants and reduce waste (**Figure 1**).[2, 3] The current approach to separate Xe and Kr from other gases include the crogenic distillation which is projected to be very expensive, and laborious. Furthermore, accumulation of ozone due to the radiolysis of oxygen at cryogenic temperatures poses an explosion hazard during cryogenic distillation process. To address these issues, Pacific Northwest National Laboratory (PNNL) developing large number of materials and membranes to separate these gases at much higher temperatures than cryogenic distillation process. My presentation will provide detailed background, materials and membranes developed at PNNL to address the uncontrolled release of volatile gases and advantages of these materials in terms of other materials.

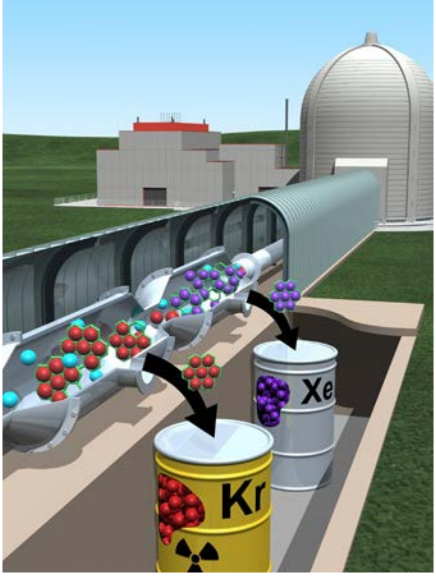

Figure 1. PNNL developed and patented adsorption-based technology to recover Xe and Kr from various nuclear processes using temperature swing adsorption at near room temperature.

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Radiation-resistant metal-organic framework enables efficient separation of krypton fission gas from spent nuclear fuel. *Nat Commun* **2020.**

Microstructure characterization in irradiated SiC ceramic composite matrix materials for light water reactor applications

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Keywords: SiC, CMC, LWR

Silicon Carbide (SiC) ceramic matrix composite (CMC) cladding is being pursued as one of the accident-tolerant fuel (ATF) cladding candidate materials for light water reactors (LWRs). It has excellent high-temperature oxidation properties, superior irradiation resistance, inherent low activation, and other superior physical/chemical properties. However, there are several technical challeges which the SiC CMC materials must overcome for use in LWRs. This paper summarizes those technical challeges and advancements made in recent years, and outlines the SiC based cladding material strategy. In specific, the hydrothermal corrosion behavior, the retention of hermeticity in normal operation and accident conditions, and the integrity of the end plug joint are among the key challeges to be discussed in this paper. Morphology of defects, including size and shape of voids, is one of the key factors which impact cladding performance and guarantees reactor safety. Therefore, understanding and quantification of the defects' size, location, distribution, and leak paths are critical to determining weakness in SiC cladding for its in-core performance and failure probabilities. Safety testing performed at the Transient Test Reactor (TREAT) and out of pile high temperature steam testing stage at ORNL provide additional insights on SiC behavior in accident conditions. 3D X-ray imaging generates critical microstructural defect information before and after the tests. Following the X-ray Computed Tomography (XCT) data analysis and visualization, advanced microstructure characterization using electron microscopy techniques such as Focused Ion Beam (FIB)/ Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) is conducted, which complements the findings from the XCT data, in particular quantification of nano-porosity and microcracks. The statistics of the defects and characteristics provide information regarding the mechanical responses of SiC cladding under reactor accident conditions and can be later correlated to manufacturing for processing and performance improvement, as well as modeling and simulations. A multi-scale modeling approach is currently under development for SiC CMC cladding to predict its thermal and mechanical properties and probability of failures under various operation and accident conditions.

Passivation film formation and composition effects in a titanium pyrochlore structure

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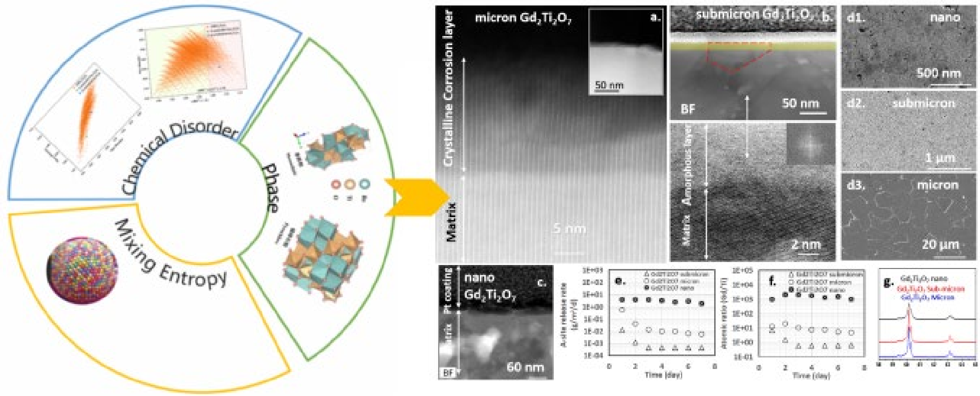
Keywords: nuclear wasteform, passivation film, corrosion, irradiation

Chemical durability of multi-component pyrochlore solid solutions (A2B2O7) with uranium incorporation under near-field environments is important for evaluating their application as potential nuclear waste forms/advanced fuel matrices. Here, compositional complex Ti pyrochlore solid solutions with/without uranium incorporation ranges from binary to high entropy were synthesized to investigate the chemical durability and corrosion induced surface alteration and passivation effect. Microstructure analysis reveals that an amorphous passivation film enriched in Ti is covered on the altered matrix which can be attributed to the dissoluton-reprecipitation mechanism with congruent release of A-site and Ti elements. Strong correlation is identified between chemical disorder, especially size disorder and leaching rate, while entropy shows negligible correlation with elemental release rate, suggesting important impacts of structural and sublattice characteristics in controlling chemical durability and elemental release of chemical complex Ti pyrochlore solid solutions.

Figures



Leaching behavior of controllable grain size $Gd_2Ti_2O_7$ pyrochlore after 14 days.

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Microstructural evolution of neutron shielding materials under radiation

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Keywords: ion irradiation, tungsten boride, hafnium hydride, neutron shielding

Spherical tokamaks offer many advantages compared to standard tokamak fusion reactors, such as enhanced plasma stability and higher cost-efficiency [1]. However, the narrow central hole in spherical tokamaks presents severe space constraints and engineering challenges. Advanced shielding materials are needed to efficiently attenuate the neutron and gamma radiation from the plasma and protect the high-temperature superconductors (HTS) from radiation damage [1,2]. Besides the excellent neutron and gamma attenuation properties, shielding materials must have a high resistance to swelling, and their microstructure should remain stable under high heat and radiation levels. The neutron irradiation-induced changes in fusion shielding materials can be reasonably simulated by performing ion irradiation experiments with particle accelerators [3].

This presentation will focus on recent progress in evaluating the microstructural evolution of candidate advanced shielding materials under radiation. Tungsten boride (WB and WB_2) and hafnium hydride (HfH_2) samples were irradiated with He and heavy ions at multiple temperatures (25-700 °C) and doses at the Dalton Cumbrian Facility in the UK. The irradiation-induced microstructural changes (defect formation, lattice swelling, phase change and amorphisation) were characterised using grazing incidence X-ray diffraction (GIXRD), electron backscatter diffraction (EBSD) and transmission electron microscopy (TEM). The hardness evolution was also examined using a microhardness mapping system in the unirradiated and irradiated tungsten boride samples. Coupled EBSD-hardness measurements revealed that the crystallographic orientation strongly affects the hardness values in WB_2. This study provides the first ion irradiation results on these materials and allows the relative stability of different tungsten boride phases to be compared for the first time. The radiation tolerance of WB, WB_2 and HfH_2 compared to other candidate shielding materials will also be discussed.

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The emerging high-entropy ceramics and their nuclear applications

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Keywords: high-entropy ceramics, inert-matrix fuel, immobilization matrix, high-level radioactive wasteform

In recent years, high-entropy ceramics (HECs) have attracted researchers' much attention. In recent years we synthesized a series of high-entropy ceramics including oxides, carbides and borides by different processes and their mechanical and thermal properties were mainly evaluated. The irradiation behavior and damage mechanism in high-entropy carbide ceramics as well as the immobilization ability of radioactive nuclear waste in high-entropy $A_2B_2O_7$-type oxide ceramics were also investigated. This presentation will report the preparation and characterization of a series of high-entropy $A_2B_2O_7$-type oxide ceramics $(Eu_{1-x}Gd_x)_2(Ti_{0.2}Zr_{0.2}Hf_{0.2}Nb_{0.2}Ce_{0.2})_2O_7$ (x=0, 0.5 and 1.0). The results demonstrate that the obtained high-entropy ceramics is potential candidate as immobilizing hosts for high-level radioactive waste. The static aqueous leaching test indicates that the normalized leaching rates for the simulated radionuclides Ce (LRCe) and Gd (LRGd) in as-prepared high-entropy ceramics are approximately 10^{-8}~10^{-6} $g·m^{-2}·d^{-1}$ after 42 days testing, much lower than those reported values in doped-$RE_2Zr_2O_7$ (10^{-6}~10^{-3} $g·m^{-2}·d^{-1}$). The excellent chemical durability is mainly due to the synergistic effects of the compositional complexity and severe lattice distortion. Compared to their ternary oxides, the low oxygen vacancy concentration slows down the migration and diffusion of cations. Moreover, the lattice distortion increases the lattice potential energy, also inhibiting the migration of cations. This study provides a strategy for the development and application of high-entropy ceramics as the wasteforms.

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T1.5 Nanostructured, and Hybrid Functional Materials for Energy and Sustainability

Exploring alternative electrodes beyond platinum for enhanced photovoltaic efficiency and stability

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Keywords: Pt-free electrodes, binary metal sulfides, co-polymer, solvothermal synthesis, electrodeposition

The increasing global demand for energy has intensified the search for sustainable and affordable alternatives to conventional energy sources. Dye-sensitized solar cells (DSSCs) offer a promising way to meet this demand due to their low cost, ease of manufacture and environmental compatibility. However, the dependence on platinum (Pt) as a counter electrode poses an economic and stability problem and hinders the widespread adoption of DSSCs. This presentation will address recent advances in Pt-free counter electrodes for DSSCs that aim to overcome these limitations. The focus will be on the synthesis, characterization, and performance evaluation of alternative materials. Various binary metal sulfides and composites such as $CuCo_2S_4$, $Zn_{0\cdot76}Co_{0\cdot24}S$, $FeCo_2S_4$, and $ZnCo_2S_4$@MWCNT as well as co-polymeric systems will be investigated. Remarkably, these materials show comparable or better performance than their Pt-based counterparts, representing a significant breakthrough in DSSC technology. The results highlight the feasibility of Pt-free counter electrodes for DSSCs that offer a blend of cost efficiency, environmental sustainability and equivalent or better performance compared to conventional alternatives. These advances promise a broad adoption of DSSCs as a sustainable renewable energy solution and pave the way for scalable and environmentally friendly energy solutions. By utilizing these innovations, the energy landscape will benefit from improved access to clean and renewable energy sources, paving the way to a more sustainable future.

Acknowledgments

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Fabrication of advanced materials for energy harvester and energy conversion devices

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Keywords: energy conversion, hybrid systems, MLD, MOCVD

Recent years have witnessed a pronounced increase of research activities on the synthesis of photoactive thin and ultra-thin layers with energy conversion properties in view of their applications to enhance the efficiency of photovoltaic (PV) devices. Up-conversion (UC), down-conversion (DC) and down-shifiting (DS) processes are the main luminescence mechanisms used for EC. Through this promising strategy it is possible to collect the radiation energy outside the absorption range of the material and thus to better exploit the solar spectrum radiation. Two different strategies have been applied: i) fluoride matrices, as CaF_2 and multicomponent $NaYF_4$ phases, have been applied as efficient hosts of lanthanides for up-conversion processes, and ii) metalorganic-inorganic hybrid systems consisting of an europium monolayer on NiO film as down-conversion layer.

In this presentation, an overview will be given on recent results on the fabrication of Ln-doped fluoride thin films through two different chemical routes: Metal-Organic Chemical Vapor Deposition (MOCVD) and sol-gel/spin-coating approaches. The synthesis and characterization of UC layers, of the type CaF_2: Yb/Er [1,2], CaF_2: Yb/Tm [1,2], β-$NaYF_4$: Yb / Er [2] and β-$NaYF_4$: Yb/Tm [2,3]. Both synthetic approaches use fluorinated metalorganic β-diketonate compounds, which act as single-sources, and have the advantage of being very reliable and reproducible methods for the fast production of films with high uniformity degree over large areas. Pros and cons of the two synthetic strategies will be discussed.

In addition, a full vapor phase approach based on the molecular layer deposition (MLD) to assemble the metalorganic monolayer component, of the type $Eu(\beta\text{-diket})_3L$, on the MOCVD grown inorganic component, NiO films, will be presented. This approach is based on the pre-activation of the NiO nanostructured film with water or ozone and the subsequent anchoring of the $Eu(\beta\text{-diket})_3L$ complex through a ligand-exchange reaction between one or two β-diketonate ligands and the terminal –OH groups of the NiO surface. X-ray photoelectron spectroscopy characterization confirmed the covalent anchoring of the luminescent europium(III) adduct onto nanostructured transparent NiO films. Downshifting properties of the Eu monolayer were evaluated through fluorescence spectroscopy. This system is of potential great interest for applications in tandem PV cells, since the NiO inorganic component is commonly applied as photocathode, while the Eu complex may further implement the use of the high energy side of the solar spectrum due to its downshifter properties.

Acknowledgments

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T1.6 ADVANCED BATTERIES AND SUPERCAPACITORS FOR ENERGY STORAGE APPLICATIONS

Exploring electrolyte and electrolyte-electrode interface for long-life cycling sodium-ion batteries

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Keywords: energy storage, sodium-ion batteries, electrolyte, surface science and engineering

The widespread integration of renewable energy sources necessitates the implementation of affordable, long-duration energy storage technologies. Lithium-ion batteries (LIBs) have been widely used in the electric grid sector due to their large-scale production, high roundtrip efficiency, and industry familiarity. However, they are impractical for long-duration storage of 10+ hours due to their high cost, safety concerns, and supply constraints. In contrast, sodium-based batteries (NaBs) offer a promising alternative, leveraging abundant and inexpensive materials such as sodium, manganese, and iron. However, NaBs must demonstrate exceptionally long cycle life (> 5000 cycles) to be viable for grid-based storage. This presentation discusses the crucial role of the electrolyte-electrode interface in electrochemical properties and cycling life, focusing on our efforts to develop novel electrolytes based on the sodium borate platform and explore fluorine-free alternatives. The findings from our materials discovery and characterization efforts offer valuable insights into the development of highly reversible sodium-ion batteries tailored for grid applications.

Mn-based oxide cathodes for secondary potassium-ion batteries

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Keywords: potassium-ion batteries, cathodes, layered oxides, ion exchange, capacity

Li-ion batteries have seen unprecedented success starting from consumer electronics to electric vehicles. The exponential usage of Li-resources has triggered concern and has catapulted the development of various monovalent and multivalent (post) Li-ion batteries particularly for stationary storage. One such battery candidate is potassium-ion batteries (KIBs), which can offer high energy density, reversibility, and operational safety along with materials economy owing to the natural abundance of potassium-based minerals.[1,2] Similar to Li-ion battery, graphite can be implemented as anode against energy dense K^+ insertion cathodes to fabricate full cell. To realize practical K-ion batteries, it is crucial to find economic and energy dense cathode materials. In this quest, the current presentation will focus on three novel Mn-based cathode insertion materials for KIBs.

First, P3-type $K_xNi_{1/3}Mn_{2/3}O_2$ layered oxide will be presented as a novel 3.2 V KIB cathode combining Ni redox activity at high voltage and Mn redox activity at low voltage.[3] Prepared by conventional solid-state synthesis, it exhibit highly reversible K^+ (de)insertion at ambient and elevated (40-50 ºC) temperatures. The $K_xNi_{1/3}Mn_{2/3}O_2$ layered oxide exhibits in-plane Mn–Ni ordering in the MO_2 sheets as a function of the K-content in the structure, leading to an interwoven and alternative row Ni–Mn ordering (for K = 0.5) and a $\sqrt{3}a \times \sqrt{3}a$ superlattice ordering (for K = 2/3). It involves solid solution K^+ (de)insertion mechanism. Ni addition can effectively tune the electronic, and structural properties leading to enhanced electrochemical performance. The second story will showcase the structure-electrochemical property relation in P3-type $K_yMn_{1-x}Co_xO_2$ binary layered oxide cathodes.[4] In this solid-solution family, Co substitution enhances the electronic conductivity and structural stability of P3 phases by minimizing the local lattice distortion. Co substitution leads to systematic shift of the Co^{4+}/Co^{3+} and Mn^{4+}/Mn^{3+} redox potentials along with improved cycling stability. The final section will elaborate soft chemistry derived layered P2-type $K_yCo_{1/3}Mn_{2/3}O_2$ cathode for KIBs. Prepared by ion exchange at ambient condition, it works as a stable 2.9 V cathode involving both Co and Mn redox activity. On a whole, these Mn-based cathodes will be demonstrated as low cost cathode candidates for potassium-ion batteries.

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Aqueous metal-ion rechargeable batteries

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Keywords: aqueous batteries, monovalent-multivalent ions, structure, ion transport, intercalation

This lecture will focus on aqueous metal-ion batteries,[1] an important alternative to the erstwhile non-aqueous Li-ion batteries. As water is the solvent, aqueous rechargeable batteries will not require a sophisticated and capital-intensive cell assembly line like non-aqueous batteries. Despite being economical, the hydrated metal ions pose several fundamental challenges leading to non-trivial energy storage. There is a lack of suitable electrodes and electrolytes, a major hurdle for the widespread production of rechargeable and reversible aqueous-ion batteries. In this lecture, I will discuss a few examples of aqueous batteries,[2-4] focusing on the diverse intricacies related to materials and the electrochemical energy storage characteristics of various monovalent/divalent aqueous battery systems. The energy storage mechanism will be discussed in the context of the findings from both experiment and theory.

Acknowledgments

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Structural and electrochemical properties of epitaxial thin-film electrodes grown by pulsed laser deposition

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Keywords: NMC, LTO, thin film electrodes, PLD, characterisation

In this presentation, the compositional, structural, and electrochemical properties of thin film electrodes prepáért by pulsed layer deposition (PLD) will be discussed. Thin film electrodes of the $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ (NMC 111) were prepared on (001) out-of-plane oriented $SrRuO_3$/Nb:$SrTiO_3$ substrates and thin film electrodes LTO thin films were grown by pulsed laser deposition on Nb:STO single crystal substrates with (100), (110) and (111) orientations. Structural properties of pristine NMC 111 and LTO thin films were characterized by high-resolution X-ray diffraction (HRXRD). Thin film electrodes were electrochemically characterized in the half-cell configuration using metallic lithium as a counter electrode and separator wetted with electrolyte as an ion conductive interphase. We will report the structural changes during the oxidation process (lithium removal) and the consequent reduction process (lithium insertion) for NMC111 thin film. Additionally, the electrochemical and compositional properties of LTO thin films with different orientations will be thoroughly discussed.

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Operando impedance spectroscopy study of Li metal stripping and plating

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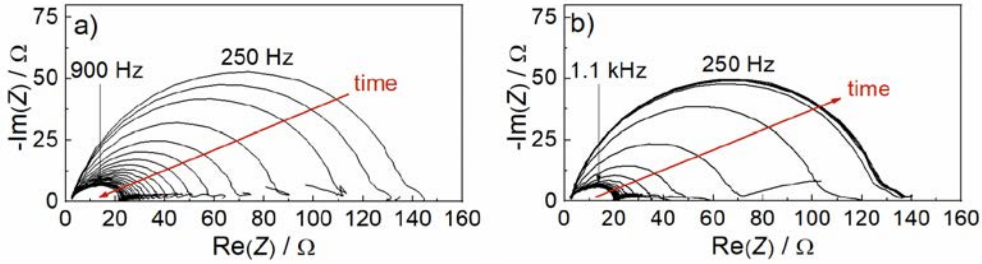
Keywords: impedance spectroscopy, Li metal anode, dendrites

Electrochemical impedance spectroscopy (EIS) is a valuable measurement tool, which is frequently applied to study and develop electrochemical systems. In the field of batteries, it is usually measured at open circuit voltage (OCV), when the cell is stable enough to ensure a reliable measurement. If we want to change the state of charge of the cell, the cell is usually first discharged/charged, the current stopped for a short period to stabilize cell's voltage and only then the EIS spectrum is measured. Although in this case the measurement is stable, it suffers from drawbacks. One is that the impedance of certain battery processes is different if under load or not, such as the charge transfer impedance. In practice, this means that the measured spectra, although smooth, will inevitably be different than those measured under load[1]. Furthermore, although paramount for ensuring a stable measurement, we should not disregard that the rest period can inflict change to the cell impedance.[2–4] An alternative is the so-called dynamic EIS, where a small amplitude excitation signal is superimposed on the direct current used for SOC change. In this case, the impedance is measured simultaneously as the cell's SOC is changed, *i.e. operando*, avoiding the issues previously described for OCV EIS measurements. We will present several applications of operando EIS. We have used it to study the formation of high surface area deposits and to detect the presence of dendrites growing through the separator in Li metal electrode cells.

Figures



Examples of dynamic impedance spectra measured on Li metal electrode during plating (a) and stripping (b)

Acknowledgments

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Oxygen-redox chemistry in high energy density battery cathodes

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Keywords: Li-ion batteries, Na-ion batteries, cathode materials, oxygen redox, disordered rocksalts

One of the biggest challenges facing lithium-ion batteries is how to increase their energy density. The cathode, typically a layered lithium transition metal oxide, represents a major limitation. One route to increase the energy density is to store charge at high voltage on the oxide ions in the cathode material. However, removing electrons from lattice oxide ions typically results in structural instability leading to voltage hysteresis and voltage fade over cycling. Understanding the mechanism behind oxygen redox is critical to overcoming these issues.

Our recent investigations into Li-rich cathodes have revealed that oxidized oxygen takes the form of O_2 molecules which are trapped in nanovoids in the structure. We have also shown that these trapped O_2 molecules can be reduced back to O^{2-} on discharge providing a viable charge storage mechanism to explain oxygen redox. In this talk, I will discuss the evidence[1-3] for the formation and reduction of trapped O_2 and explore the impacts this has on the performance of oxygen redox cathodes.[4] I will show how the formation of O_2 extends to 4d and 5d transition metal oxides[5], disordered rocksalt cathodes[6] and even to non-Li-rich cathodes[7]. Finally, I will show that it is possible to suppress this structural change and undergo reversible, high voltage O-redox without voltage hysteresis[8]. Altogether, this understanding helps to explain the unusual properties of oxygen redox cathodes and informs how they might be harnessed to boost the energy density of batteries.

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Multiscale modeling of layered oxide cathode materials

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Keywords: multiscale modeling, Li-ion and Na-ion batteries, cathode materials

By combining density functional theory (DFT) calculation, thermodynamics consideration, and finite element simulation, effect of doping and substitution on electro-chemo-mechanical properties of Li- and Na-based Layered Oxide (LO) cathodes is studied. It is shown that calculation of magnetic moment of elements using DFT with appropriate hybrid exchange-correlation functionals can be used to predict the redox mechanism of active materials during charge/discharge. Application of this approach to Ni- and Mn-rich LO materials for Li-ion and Na-ion batteries, repectively, is presented [1]. Moreover, correlation between transition metal composition, cationic and anionic redox, phase transition, and defect formation is discussed. Finally, a multiscale-modeling approach to model and predict properties of realistic microstructures is presented. Its application to model agglomerate and/or aggregate of LO primary particles and to simulate impact of doping and/or substitution on the initial stage of their cracking over cycling is discussed [2]. It is shown that some dopants tend to stay on the agglomerate surface forming surface oxides that can suppress crack formation as well as protect the cathode surface from electrolyte. This improves the cyclability of cathode materials in energy storages. However, some dopants can affect grain boundaries and thereby stability and rate performance [3].

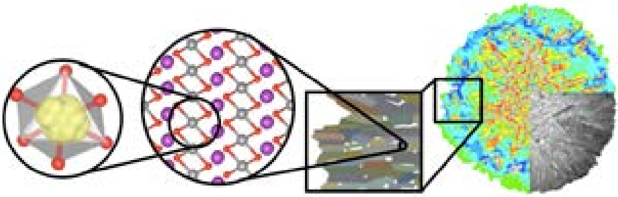

Fig. 1. Simulation of Cathode Materials for Li- and Na-ion Batteries: from Electronic- to Micro-scale.

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All oxide-based solid-state sodium battery fabricated by new sintering process

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Keywords: all solid-state battery, sodium battery, sintering agent, oxide-based solid electrolyte

All Oxide-based Solid-State Battery (AOSSB) is stable in air and keeps a high safety even in the event of a short circuit or other accident. To fabricate AOSSB, it is necessary to enrich the mechanical strength in the batteries and the ionic conduction between oxide based battery materials and prevent forming impurities due to side reactions between battery materials coinstantaneously by sintering them at high temperature due to hardness property of the materials. To avoid impurity formation, the sintering temperature must be lowered as much as possible. Sintering aids can be added or the oxide-based material itself can be softened to lower the sintering temperature [1].

In the former, it is good approach using a adequate sintering aid that can densify the material and keep ion conduction path at the lowest possible temperature. In the latter, the promising way to soften the oxide-based material is to select a carrier ion. Sodium-containing oxide based materials are often softer lithium, which is a typical carrier element for storage batteries [2]. Its characteristics of sodium element means advantageous for the fabrication of AOSSB.

I will talk a new sintering method and a new sintering agent for AOSSB in this session. It is required for sintering AOSSB to select both the electrode active materials and solid electrolyte with same sintering temperatures [3]. As one approach to solve the restriction, The new sintering method have been proposed to combine the multi-sintering-steps using the materials with different sintering temperatures [4]. Furthermore, borax has been found as a new sintering agent to enrich the mechanical and electrochemical properties in the battery. I will explain the charge-discharge performance of the batteries fabricated by the method and using the sintering agent.

Acknowledgments

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Supercritical CO2 assisted synthesis of sulfur/rGO composite cathodes for Li-S batteries

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To address the shuttle effect and improve electrical conductivity in Li-S battery cathodes, in the present study the distinctive properties of supercritical CO2 as solvent (SC-CO2) and the unique porous and layered microstructure of reduced graphene oxide (rGO) in crafting a high-performance rGO/sulfur composite cathode have been leveraged. The utilization of SC-CO2 technology enables efficient sulfur transfer and precise control of the microstructure of S/C composite cathodes for Li-S batteries. Notably, this process can be carried out at room temperature, distinguishing it from conventional techniques that necessitate higher processing temperatures. Additionally, the resulting product, i.e., C/S nanocomposite can be easily separated by depressurizing the SC-CO2. It was showed, that as-synthesized rGO/sulfur composite cathode exhibited outstanding performance (~1000 mAh g-1 at 0.1C) with an exceptionally low capacity decay rate of 0.03% per cycle even after 200 charge-discharge cycles. Moreover, the effect of the carbon surface chemistry on the electrochemical performance of the Li-S batteries has been investigated. As it was demonstrated the presence of the polar functional groups on the graphene sheets positively contributes to the chemical anchoring of the formed lithium-polysulfide species. This work suggests that the combined benefits of SC-CO2 technology and rGO as a sulfur host hold great promise for synthesizing efficient S/C composite cathodes with ultra-high cycling stability.

Design, construction and electrochemical performance regulation of high specific energy lithium sulfur batteries

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Keywords: lithium sulfur batteries, shuttle effect, host, functional seperator

Lithium sulfur batteries are one of the most promising energy storage devices due to their environmental friendliness, low cost, and high energy density. However, the sluggish electrochemical kinetics and severe shuttle effects of lithium sulfur batteries, as well as the significant volume changes in the sulfur cathode, and dendrite growth in the lithium anode seriously hinder their practical application. This report proposes various effective strategies from two aspects to adress the issues, that is, suppressing shuttle effect of lithium polysulfide on the cathode and accelerating the reaction kinetics of lithium sulfur batteries, and suppressing lithium dendrite growth on the anode. High performance lithium sulfur batteries have been successfully designed and constructed. For the shuttle effect, strategies such as constructing sulfur host (biomass-derived carbon, birds-nest like Co_3O_4 and CP@NiS/$NiCo_2O_4$)or directly using Li_2S cathode (free standing CC@Li_2S@C) are proposed. By optimizing the host materials, it can effectively anchor lithium polysulfides and alleviate the volume effect during its cycling process simultaneously; By designing and preparing multifunctional seperators (CNTs/Graphene hybrid, CNTs/g-C_3N_4, MgNCN-ND-g-C_3N_4, $LiVPO_4F$/CNT) and intermediate layers ($LiMoO_x$/super carbon/Nickl foam, Bi_2S_3/MoS_2), the physical confinement, chemical adsorption, and electrostatic repulsion can be used to limit the shuttle of polysulfides and enhance the catalytic conversion ability of lithium polysulfides through overpotential driving force, heterogeneous interfaces, and defect engierring, etc., thereby significantly improving the rate performance and cycling performance of lithium sulfur batteries. For the lithium dendrite, designing a lithium array with selective coverage of an artificial SEI composed of Li_2S_x using rolling method and low-temperature gas-solid reaction, constructing a lithium friendly three-dimensional current collector, or a current collector with gradient pore structure will effectively solve the problem of uneven deposition of lithium on the upper surface under high current density, thereby achieving a dendrite-free, high-efficiency, and long-life lithium anode. Based on the above strategies, lithium sulfur batteries with high performance have been successfully designed and constructed, which will ultimately provide more research basis for the practicality of lithium sulfur batteries.

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Mastering the sodium layered oxides and its reactivity with electrolyte for high performance Na-ion battery applications

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Keywords: layered oxides, interface reactions, electrolyte optimisation, Na-ion batteries

Energy storage devices are pivotal for realizing the full potential of renewable energy resources that are intermittent in nature. In this regard, lithium-ion batteries have found great applications, although we need complementary devices given the low availability of Li resources.Towards this purpose, Na-ion batteries (NIBs) find greater interest due to the greater abundance of sodium hence low cost, and similar chemistry and engineering as that of Li-ion batteries. However, there were many difficulties to reach the commercial applications of Na-ion technology, especially regarding electrode materials and electrode-electrolyte interphases. Our team, together with the start-up TIAMAT (France) has achieved commercializing Na-ion cells based on $Na_3V_2(PO_4)_2F_3$ (NVPF)- hard carbon (HC) chemistry by tuning the electrolyte composition.[1] As a step forward, we are in the verge of commercializing Na-ion cells with improved energy density by moving to sodium layered oxide cathodes. However, there are several difficulties associated with these materials in comparison to NVPF. First, the sodium layered oxides show poor structural stability upon cycling that in turn lead to particle cracking, transition metal dissolution, oxygen release and associated deteriorating reactivity with electrolyte on ageing.[2] Hence, it is essential to design a suitable layered oxide material with better structural stability, fine-tune the synthesis conditions to get the designed material in bulk quantities and finally to optimize an electrolyte formulation resulting in stable interphases with less resistance at low and high temperatures. Our experiences in designing layered oxide cathode materials will be discussed in detail, together with our attempts on electrolyte engineering. Finally, a comparison will be provided based on NVPF- HC and sodium layered oxide- HC explaining their possible applications in different energy storage sectors.

Acknowledgments

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‘Layered’ transition metal oxides as cathode materials for Na-ion batteries: Composition – structure – environmental stability – electrochemical behaviour/performance

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Keywords: layered transition metal oxide; structural aspects; air/water-stability; electrochemical behavior; Na-ion battery

‘Layered’ transition metal (T_M) oxides are a fascinating class of materials, whose properties can be suitably tuned in a variety of ways; such as, by selecting T_M-ions/dopants having preferred electronic configurations, engineering the crystallographic site occupancy by dopants, controlling/modifying the degree of covalence of T_M-O bonds, modifying lattice spacing(s), tuning phase assemblage etc. Such modifications done from the fundamental perspectives influence the performances of T_M-oxides for a variety of applications, including their widespread usage as cathode-active materials in alkali metal-ion batteries. In the context of the upcoming Na-ion battery system, O3-type ‘layered’ Na-T_M-oxides are promising as cathode-active materials due to their inherently high initial Na-content (as compared to the P2 counterparts); but suffer from instabilities caused due to multiple phase transformations during Na-removal/insertion and sensitivity to air/moisture. Against this backdrop, by tuning the overall covalency of the cation-oxygen bonds in the T_M-layer (which, in turn, influences the Na-O bond) and also with the help of a dopant having d^0 electronic configuration (*viz.*, no OSPE), we have been able to tune the composition and structural features to suppress the phase transitions upon Na-removal/insertion and improve the air/water-stability in significant terms; so much so that long-term cyclic stability has been achieved with health/environment-friendly ‘aqueous processed’ electrodes (sans, usage of toxic/expensive chemicals like NMP and PVDF) [*J. Mater. Chem. A* **8** (2020) 18064, *Adv. Energy Mater.* **13**[19] (2023) 2204407]. The changes in structural features, which have led to such outstanding water-stability, include differential contraction/dilation of the Na-‘inter-slab’/T_M-‘slab’ spacing and partial occupancy of the dopant at tetrahedral sites of the structure. The former aspect has also been invoked to enhance the Na-transport kinetics and, hence, the rate-capability of the, otherwise, inherently sluggish O3-structured NaT_MO_2-based cathode material [*ChemComm* **59** (2023) 4332]. Furthermore, in the context of the more ‘rate-capable’ P2-structured ‘layered’ Na-T_M-oxide based cathode materials, but lacking in terms of having a lower starting Na-content (typically, 0.67-0.7 Na-ions *p.f.u.*), a universal strategy towards designing and developing high Na-containing P2-structured ‘layered’ Na- transition metal oxides has been evolved. This is based on increasing the average ‘charge:size’ ratio of the cation-combination in the T_M-layer and concomitant T_M-O bond covalency, resulting in lower effective negative charge on O-ions; and, in turn, rendering the prismatic coordination of O-ions around Na-ions more favourable even at higher Na-content. Accordingly, by careful selection of the combination of non-T_M-/T_M-ions in the T_M-layer, a high Na-containing (*viz.*, ~0.84 p.f.u.) P2-type Na-T_M-oxide has been developed, which, as a cathode material for Na-ion batteries, exhibits a high desodiation capacity of ~178 mAh/g (@ C/5; within 2-4 V vs. Na/Na^+), exceptional cyclic stability pertaining to ~98% capacity retention after 500 galvanostatic desodiation/sodiation cycles @ 2.5C and also stability upon exposure to air/water [*Chem. Mater.* **34** (2022) 10470].

Migration of Mg in Na-O-Mg configuration for oxygen redox of sodium cathode

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Keywords: oxygen, redox, sodium, cathode, battery

Mn-based P2-$Na_x[Li_yTM_{1-y}]O_2$ cathode materials are available to reach high capacity through the combination of cationic and anionic redox in Na cells.[1–11] The Na–O–Li configuration induces the delivery of additional capacity assisted by the oxidation of oxygen when lone-pair electrons are formed in the O 2*p* orbital, provided that at least one of the following conditions is satisfied: 1) lattice oxygen evolution[1] or 2) migration of the Li element to Na layers although the corresponding charge transfer is kinetically sluggish.[2] The reaction is not limited to compounds that have alkali ions in the TM layer but is also available with divalent ions; namely, the presence of Mg in the TM layer, P2-$Na_x[Mg_yMn_{1-y}]O_2$ ($x = \sim 2/3$, $y = \sim 0.28$).

The effect of the 4*d* Ru element in P2-$Na_{0.6}[Mg_{0.2}Ru_{0.2}Mn_{0.6}]O_2$ is investigated. Ru-free $Na_{0.6}[Mg_{0.2}Mn_{0.8}]O_2$ is activated with the Mn^{3+}/Mn^{4+} redox, after which the charge is compensated by the sluggish oxidation of lattice oxygen (O^{2-}) to O_2^{n-} triggered by O_2 evolution from the oxide lattice. These effects are generally unfavorable and result in poor long-term cycle stability induced by the irreversible migration of Mg^{2+} from the transition metal (TM) to Na layers in the P2 structural framework. Benefiting from the covalent Ru bonded with O in the TM layers, the Mg migration reversibly progresses from the TM to sodium slabs without O_2 evolution in the structure. The associated reaction progresses via the active Mn^{4+}/Mn^{3+} and $O^{2-}/(O_2)^{n-}$ reaction in addition to the $Ru^{5+}/Ru^{4+}/Ru^{3+}$ redox pairs, endorsing the capacity increase (~210 mAh g^{-1}), with ~72.1% retention for 300 cycles.

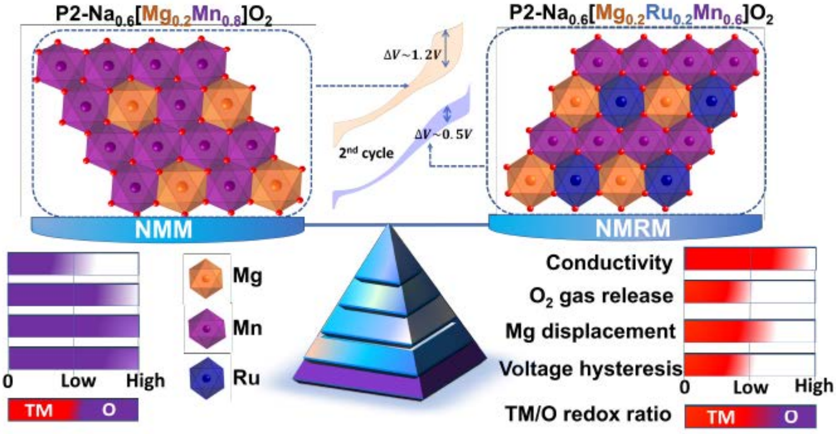

Figure 1. The presence of the higher-covalency Ru–O bond minimizes Mg migration from the TM to Na layers.

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Energetics of ionic transport on LiSiPON non-crystalline solid electrolytes

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Keywords: ionic conductivity, permittivity, ion transport energetics, local structure

Currently, LiPON with general composition $Li_wPO_yN_z$ is the most employed thin film electrolytes owing to its very low electronic conductivity ($< 10^{-12}$ S.cm^{-1}), the lack of grain boundaries and the ability to passivate Li metal. These properties result in outstanding cycling performances. Besides, LiPON thin films can be prepared by radio frequency (RF) magnetron sputtering. Nevertheless, their Li^+ conductivity remains moderate, ~ 10^{-6} S.cm^{-1} at 298 K. This moderate conductivity is a major limitation to increase the power density of microbatteries, but also for their use in all-solid-state batteries. As an attempt to further increase the ionic conductivity of LiPON thin films, several other derived systems were proposed based on the partial replacement of phosphorus by another network glass former, such as boron, germanium, silicon, and sulfur. This approach stems from the well-known phenomenon so-called mixed network former effect, firstly reported on glassy bulk systems, which can lead to decrease the activation energy and increase the ionic conductivity. Among all the reported systems, the replacement of P by Si seems to show the most important increment of ionic conductivity.

The activation energy (E_a) for ionic conductivity is actually constituted of two distinct contributions namely, migration (ΔH_m) and defect formation (ΔH_f) enthalpies, according to the following equation: $E_a=\Delta H_f/2+\Delta H_m$. These quantities are linked to structural features of the electrolyte that are strongly affected by chemical composition, and synthesis route. The debate regarding the $Li_wSi_xP_{1-x}O_yN_z$ system is centered on the resulting structure once nitrogen and silicon are incorporated and on its structural role regarding the ionic transport. Another exciting discussion is oriented towards the similarities and fundamental differences in terms of structure and ionic transport of these amorphous thin-film electrolytes and their glassy bulk counterparts. Therefore, the major goal of this talk is to shed some light on the interplay of chemical composition, local structure and ionic transport on $Li_wSi_xP_{1-x}O_yN_z$ amorphous thin films prepared by RF magnetron sputtering and glassy electrolytes prepared by the classical melt-quenching approach.

Herein, we apply a methodology based on impedance spectroscopy analyses to determine the partial contributions of defect formation and migration enthalpies to the overall activation energy for ionic conduction. The main results evidence that the well-known decrease in activation energy and enhancement of the ionic conductivity caused by the incorporation of nitrogen in amorphous LiPON is due to a drop in the migration enthalpy, while the defect formation enthalpy remains nearly the same. Moreover, when P is replaced by Si on $Li_wSi_xP_{1-x}O_yN_z$ amorphous thin films, a minimum in the dependence of the migration enthalpy on composition is spotted around a P/Si ratio close to unity. Finally, an astonishing difference arises when comparing the defect formation and migration enthalpies of $Li_wPO_yN_z$ amorphous thin films and $Li_wPO_yN_z$ glassy bulk electrolytes. While the activation energy on $Li_wPO_yN_z$ amorphous thin films is largely controlled by the migration enthalpy, on $Li_wPO_yN_z$ glassy bulk electrolytes the defect formation enthalpy is larger than the migration enthalpy. The variation of these quantities with the chemical composition and the synthesis route of these electrolytes is correlated with structural aspects unveiled by nuclear magnetic resonance spectroscopy or previously published experimental results and simulations.

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New halide-based Na-ion conductors: $NaNbCl_6$, $NaTaCl_6$, and some more

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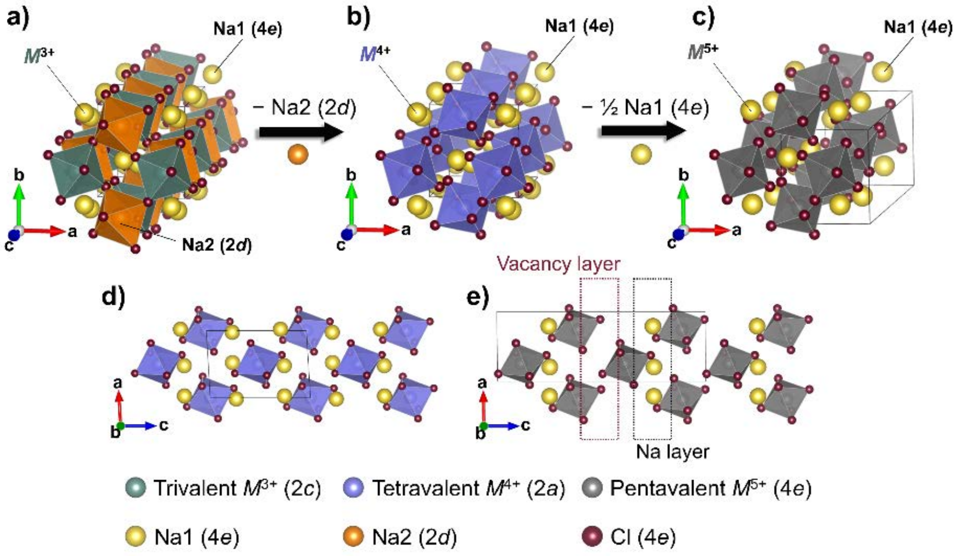
Keywords: solid electrolytes, solid state batteries, Na-ion batteries

All-solid-state sodium-ion (Na-ion) batteries are promising candidates for the post-lithium-ion (Li-ion) batteries owing to their improved safety and earth abundance, enabled by less- to non-flammable solid electrolytes (SEs). Ion-conducting halides are an emerging class of materials for solid electrolytes that may satisfy all requirements with their balanced ionic conductivity (> 1 mS cm^{-1} at room temperature), oxidation stability (~ 4 V), and room temperature processability. Ion-conducting halides first stepped into the spotlight in 2018 with the report of mechanochemically synthesized Li_3YX_6 (X = Cl, Br). Up to date, a wide variety of Li-ion conducting halides have been reported, e.g., $Li_3M^{3+}X_6$ (M^{3+} = In, Sc, Ti, Y, Ho, Er, Yb and X = Cl, Br, I), $Li_2M^{4+}X_6$ (M^{4+} = Zr, Hf and X = Cl, Br, I), $LiM^{5+}Cl_4O$ (M^{5+} = Nb, Ta) and $LaCl_3$-based Li-ion conductor. Many exhibits room-temperature ionic conductivity higher than 1 mS cm^{-1} and demonstrated stable cycling with the state-of-the-art cathode active materials operating > 4 V.

Despite the success in Li-ion conducting halides, only a few Na-ion conducting halides have been found to date, e.g., $Na_3M^{3+}Cl_6$ (M^{3+} = Y, Er, In), Na_2ZrCl_6 and $NaAlCl_4$, and their reported room-temperature ionic conductivity are mostly less than 0.1 mS cm^{-1}. With the less polarizing nature of Na ions, Na-ion conducting SEs tend to possess higher ionic conductivity than their Li-analogues, and indeed, higher ionic conductivity is generally reported in Na-ion conducting oxides and sulfides than those in Li-ion conducting counterparts. Inspired by the fact that the known Na-ion conducting halide-based SEs exhibit much inferior ionic conductivity to the Li-analogues, here we explore the new Na-ion conducting halides, $NaM^{5+}Cl_6$ (M^{5+} = Nb, Ta), achieving 0.1 mS cm^{-1} at 30 °C. This high ionic conductivity is attributed to the beneficial inductive effect and improved migration entropy and is one of the highest among the crystalline monoanionic Na-ion conducting halides.

Figures



Here the structural framework consists of MCl_{6x}^{-} is extended from tri- and tetravalent ions to the pentavalent ions, forming alternating Na-layers as with additional structural freedom on the metal sites.

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MXenes for all ‘strain-free’ solid-state batteries

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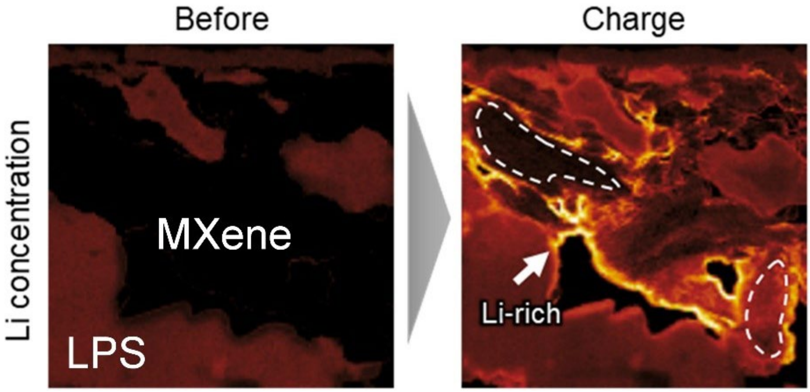
Keywords: all solid-state battery, zero strain, MXene

All-solid-state batteries with non-flammable inorganic solid electrolytes are a key technology to address the safety issues of lithium-ion batteries with flammable organic liquid electrolytes. However, conventional electrode materials suffer from substantial volume change during lithium-ion (de)intercalation, leading to the failure of the interface between the electrode materials and solid electrolytes and then severe performance degradation. In this work, we report strain-free charge storage via an interface between a transition-metal carbide nanosheet (MXene) and solid electrolytes, where MXene shows negligible structural change during lithium-ion (de)intercalation. Combined assessment including operando STEM-EELS elemental mapping clarified the strain-free nature of the MXene electrodes in the all solid-state batteries. In addition, the irreversible reactions at the MXene-electrolyte interface is visualized, explaining the inital irreversible capacities and relatively low rate capability of the MXene electrodes. A strain-free all-solid-state battery, which consists of $Ti_3C_2T_x$ anode and disordered rocksalt $Li_{8/7}Ti_{2/7}V_{4/7}O_2$ cathode, demonstrates a long-term operation owing to the strain-free nature of both electrode materials.



STEM-EELS mapping of MXene $Ti_3C_2T_x$ electrode in an all solid-state battery

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Impact of the anionic substitution and particles morphology on the energy storage performance of $Na_3V_2(PO_4)_2F_{3-y}O_y$

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Keywords: Na-ion batteries, positive electrode material, $Na_3V_2(PO_4)_2F_3$, structure-properties relationship

The polyanionic family of compounds, $Na_3V_2(PO_4)_2F_{3-y}O_y$ ($0 \leq y \leq 2$), has attracted significant interest as a positive electrode material for Na-ion batteries thanks to their high working potential combined with a specific capacity of approximately 128 mAh/g (for the reversible extraction of 2 Na^+ per formula unit) and outstanding stability during cycling. Capitalizing on these attributes, the French company Tiamat has successfully developed and recently commercialized the first Na-ion batteries based on carbon-coated $Na_3V_2(PO_4)_2F_3$ vs. hard carbon technology. [1]

Such impressive achievement is typically enabled by a thorough understanding of the structure-composition-morphology-properties relationship, facilitating further optimization of the active material's performance. For instance, a not optimized/controlled synthesis can lead to unexpected partial substitution of O^{2-} for F^- and the formation of vanadyl-type defects. [2] Our research group has demonstrated that the competition between the ionic V^{3+}–F bond and the covalent V^{4+}=O bond has a major effect on the structure of the pristine materials, and then on the phase diagram and redox mechanisms involved upon their cycling in batteries. [3]

In this presentation, the influence of the anionic substitution will be illustrated for series of phases $Na_3V_2(PO_4)_2F_{3-y}O_y$. combining mainly Synchrotron X-ray diffraction, electrochemistry, differential scanning calorimetry and spectroscopic studies. In addition to correlate the composition to the electrochemical behavior, the impact of this substitution on the thermal stability and thermal degradation mechanisms will also be discussed. [4] Besides, the comprehensive study that details the influence of the particle's size and morphology on the electrical conductivity and thus, on the energy storage performance will be presented. [5]

Acknowledgments

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Ceramic/polymer composite electrolytes for all solid-state sodium-ion batteries

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All-solid-state sodium-ion batteries (SSSIBs) are designed to address the safety concerns related to traditional liquid electrolyte batteries. By incorporating non-flammable solid electrolytes and electrodes, these batteries significantly reduce the risks of leakage and fire, making them a safer and more reliable energy storage solution. In this talk, we present a NASICON-type ceramic electrolyte $Na_3Zr_2Si_2PO_{12}$ (NZSP) with co-doping of Mg^{2+} and Sc^{3+} to achieve high ionic conductivity by means of alteration of crystal structure and microstructure. Mg^{2+} doping reduces the grain boundary resistance by forming a conducting $NaMgPO_4$ phase which may cause Na deficiency in the bulk. . Co-substitution of a trivalent Sc^{3+} along with Mg^{2+} at the Zr^{4+} site helps to increase Na content in the bulk. As a result, the Na ion mobility through grains and grain boundaries increases with this co-doping. The highest grain and grain boundary ionic conductivities ($\sigma_b \sim 1.78 \times 10^{-3}$ Scm^{-1} and $\sigma_{gb} \sim 0.4$ $mScm^{-1}$) and Na transference number (t_{Na+}~0.998) have been achieved for the optimized composition of $Na_{3.3}Zr_{1.8}Mg_{0.10}Sc_{0.10}Si_2PO_{12}$ (NZSP-0.1MS). This has led to the suppression of sodium dendrite growth and increased electrochemical stability of the ceramic electrolyte. The NZSP-0.1MS ceramic electrolyte is further employed in quasi-solid state cells; a decent discharge capacity of 91 mAh/g at 0.1C rate was obtained for "Zn doped (NVZP) (cathode)|| NZSP-0.1MS ||NVZP(Anode)" ceramic full cell.

NZSP-0.1MS ceramic electrolyte filler is further incorporated into the polymer-salt matrix to develop the PEO-NaTFSI/NZSP-0.1MS composite electrolyte. The all-solid-state cell comprised of composite electrode (NVZP/NZSP-0.1MS/PVDF-NaTFSI/C) and composite electrolyte PEO-NaTFSI/NZSP-0.1MS delivered a maximum discharge capacity of 105 mAh/g at 0.1C, at 60 °C with good rate performance and cyclic stability retaining 85% capacity over 80 cycles. At 1C a specific capacity of 78 $mAh.g^{-1}$ is reported for the Catholyte||PEO-NaTFSI/NZSP-0.1MS||Anolyte full cell. Interestingly, the capacity is restored to 97 mAh/g after returning to 0.1C, which suggests reversible electrochemical stability of the cell components. The all-solid-state sodium-ion cell design has achieved electrochemical performance comparable to conventional NVP-based liquid electrolyte cells. This advancement paves the way for the development of safer and next-generation sodium-ion battery technology.

Sacrificial salt versus presodiation in hard carbon-based Na-ion full cells

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Among the possible anodes for Na-ion batteries, there is wide consensus about hard carbons as one of the best options in terms of specific capacity, rate capability cost and sustainability, as these materials can be obtained from waste biomass, changing a residue into a material of technological value. In the last years, research about hard carbons applied as anodes in Na-ion batteries has developed high performing materials, but the further step towards a full Na-ion cell based on a hard carbon anode is only starting and there are not much published works regarding this issue. The main setback when balancing anode and cathode electrode mass to plan a full cell system is the great irreversibility of the hard carbons during their first cycle, that usually entails the need of a previous cycling of the hard carbon to precondition the negative electrode and form the SEI on it before matching up cathode and anode.

The use of a sacrificial salt as extra Na source in the cathode composition would avoid anode presodiation and reduce cell assembly time, with the only need of a first formation cycle to decompose the salt and generate the SEI.

In this work, hard carbon produced from sunflower seed shells by hydrothermal carbonization and further pyrolysis is used as anode material to explore different strategies to develop Na-ion full-systems in coin cell configuration: direct use of fresh anode, precycled anode (*vs.* Na^+/Na) and fresh anode with a sacrificial salt in the cathode formulation. These strategies are used in three different cathode chemistries: $Na_{2/3}Mn_{0.8}Fe_{0.1}Ti_{0.1}O_2$ layered oxide, and $Na_3V_2O_2(PO_4)_2F$ and $Na_3V_2(PO_4)_3$ polyanionic compounds. The material of choice as sacrificial salt is $Na_2C_3O_5$, as a not flammable compound that can be easily prepared by drying the commercial $Na_2C_3O_5 \cdot H_2O$ low cost reactant.

The effect of the different cycling/precycling protocols on the electrochemical performance is analyzed in terms of rate capability, cycling stability and battery energy density. The chemical species formed on the electrodes surface after the different assembly protocols and configurations during short-term and long-term cycling are studied by pre- and post-mortem characterization by Scanning Electron Microsocopy (SEM), X-ray diffraction (XRD) and X-ray Photoelectron Spectroscopy (XPS). Strong and weak points of the assembly and cycling strategies will be discussed based on experimental data.

Site-specific doping strategy for high-performance lithium-ion-battery cathode materials

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Keywords: cathode, structure-function relationship, neutron, synchrotron

Cathode is the well-known performance bottleneck of lithium-ion batteries (LIBs). All currently commercialised cathodes are crystalline and have a symmetrical structure forming a matrix of scaffold arrays, facilitating a specific route for the charge carriers to diffuse in and out, and offering the capability of storing and releasing lithium ions. Among promising cathode candidates for next-generation high-energy-density LIBs, disordered spinel $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO)[1] and lithium-rich layered oxide (LLO) $Li_{1+x}TMO_2$ (TM = Mn, Ni, etc.)[2] have garnered considerable attention due to their unique Fd-3m cubic space group and R-3m+c2/c intergrown structure, respectively, resulting in distinct 3D and 2D lithium-ion diffusion pathways and varied electrochemical performance, whereas their intrinsic issues hold back their wider applications. Our goal is to address the root causes of instability by targeting specific crystallographic sites through a fundamental structure/function relationship approach. The aid of neutron and X-ray scattering techniques enables us to achieve exceptional durability and phenomenal performance for intercalation-type electrodes. A noteworthy success in our research lies in the incorporation of Ru and Cr within the intergrown structure of LLOs through a site-specific doping strategy. By addressing the side effects of the oxygen redox reaction, the Ru-doped LLO demonstrates an extraordinarily stable voltage (decay rate <0.45 mV per cycle)[4], and a high capacity-retention rate, and the Cr-doped LLO achieves a remarkable battery performance, 99% of its initial discharge capacity after 200 cycles at 1C[5]. researchers. This presentation showcases the effectiveness of crystallographic-site-specific doping and sheds light on novel approaches for enhancing the electrochemical performance of LIBs. This work opens new horizons in the quest for advanced energy storage systems and paves the way for the design and development of even more efficient and long-lasting batteries.

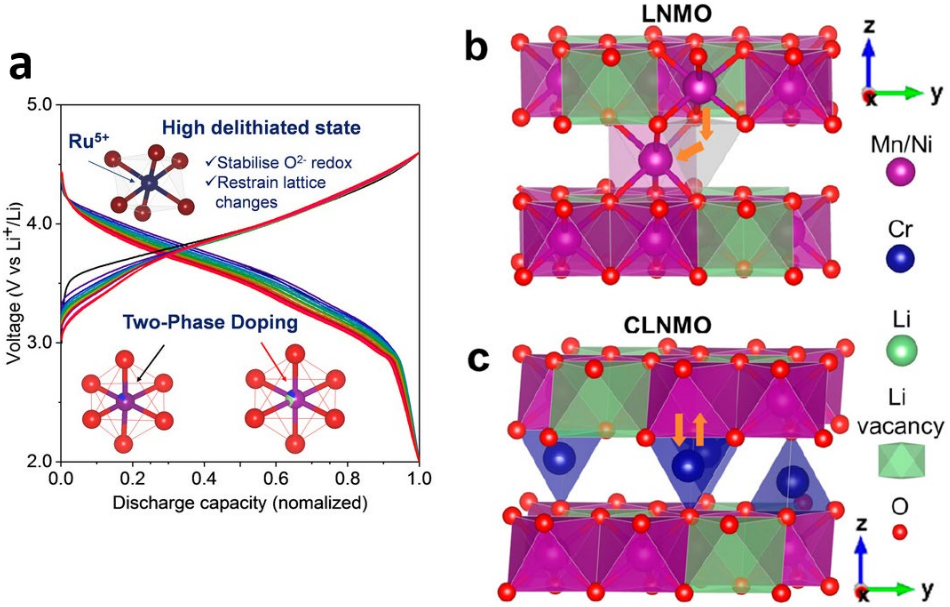

Figure 1. Schematic illustrations of (a) Ru two-phase doping effects on LLO and (b-c) how Cr doping mitigates the metal migration within LLO structure.

Acknowledgments

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Interplay of disorder, doping and conductivity in fast charging anode materials

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Keywords: batteries, disorder, fast charging, Na-ion

Despite the ubiquity of Li-ion batteries, there is a need for a significant increase in their energy density and fast charging capability. The currently employed graphitic anodes cannot be fast charged due to internal polarizations that result in Li plating, SEI breakage and further degradation resulting in cycling instability as well as safety related issues. Our group is interested in the a priori design of anode materials that can facilitate fast charging via an optimal combination of microstructure, porosity and electrical conductivity. By controlling the dopant density in titania-based nanomaterials, we were able to tune the degree of disorder in these materials. Intriguingly, the extent of disorder achieved in these materials via synthetic design, in turn, resulted in electrical conductivities spanning five orders of magnitude with a direct correlation to the extent of disorder. The differences in electrical conductivity and extent of disorder in these materials was found to influence Li^+ and Na^+ charge storage behavior at high rates as well as long term cycling stability.

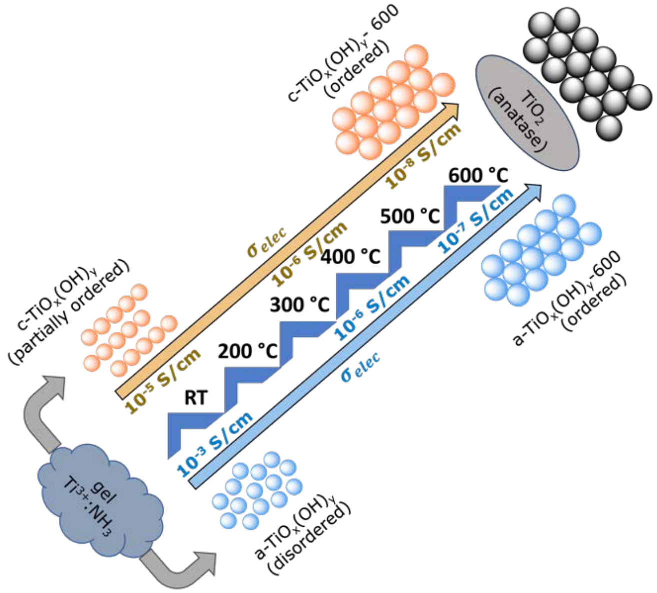

Figure. Tuning of Electrical and Ionic conductivities in disordered titanium oxyhydroxides

Acknowledgments

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Accelerating the development of new battery materials

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Keywords: Li-ion, Na-ion, cathodes, Materials Acceleration Platforms (MAP), self-driving labs

Battery innovation relies on developing new electroactive materials. To timely respond to the increasing demand for energy storage solutions, the European Battery 2030+ Initiative targets accelerating by 5-to-10 fold the current rate of battery materials discovery within the next 5-10 years [1]. Taking up this challenge requires disruptive approaches that allow rethinking the traditional experimentation process (based on researcher's chemical intuition and trial-error scheme), which is inherently slow and economically expensive. Indeed, the crystal-chemical space offered by the periodic table for the search for new battery materials is huge and still far from being exhaustively explored.

To accelerate the exploration of broad chemical spaces, our group is developing an autonomous Materials Development Platform, capable of making effective modelling-based predictions, self-driving inorganic synthesis and performing high-throughput characterization experiments. This requires a mind change in our approach to materials research, but also building new lab infrastructures and analytical tools, which include automated high-throughput synthesis modules, automated data analysis programs able to handle large amounts of data, as well as AI-aided experimental planners.

In this presentation, we will present several strategies explored at CIC energiGUNE to speed up the different stages of the development of new materials for Li-ion and Na-ion batteries. Such approaches include:

(i) the use of automated machine-learning-aided screenings of materials databases in search for new families of compounds that can be converted into electroactive materials [2, 3];

(ii) the development of solutions to automatize inorganic syntheses (e.g. co-precipitation, solvothermal, sol-gel; Figure 1) and characterization techniques (e.g. XRD, electrochemistry) [4];

(iii) the development of analysis tools for automated data treatment and analysis, including a Machine-Learning experimental planner, chemometrics approaches for data analysis of large XAS data sets, or the new FullProfAPP that enables automated Rietveld refinements of large series of data, in particular those generated from operando experiments [4, 5].

Acknowledgments

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Development of high-energy sulfur based nano-composite electrode materials in all-solid-state batteries

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Keywords: metal polysulfides, lithium-sulfur battery, all-solid-state-battery, high energy density

High energy battery is required for several applications such as vehicle use, and at the same time, all-solid-state batteries (ASSB) are thought to be favorable in safety issues when the energy density increased. Authors have developed a series of new positive electrode materials, nano-composite for ASSB, such as $LiVS_2$-Li_2S [1]. $LiVS_2 – 2Li_2S$ (Li_5VS_4) has high electric conductivity and high capacity. Electrodes of Li_5VS_4 works in ASSB without conductive additive and showed 600 mAh g^{-1} when 15 wt% of argyrodite-type solid electrolyte was added. In this study, we successfully increased the Li_2S content for capacity enhancement. $LiVS_2$-$3.5Li_2S$ ($Li_8VS_{5.5}$) also worked without or with slight amount of conductive additive (1 wt% is enough) to show more than 700 mAh g^{-1} (Fig. 1). Generally Li-S system is advantageous in gravimetric energy density, however, it has a drawback in volumetric energy density due to the lower density of materials used. We constructed the full cell using Si negative electrode and the volumetric energy density of the proto-type cell was estimated more than 800 Wh l^{-1}. This is higher than the volumetric energy density of commercial Li-ion battery of high energy type. The cell we developed showed better thermal stability than that using layered-oxide, NMC. Nano-composite materials seems promising for ASSB.

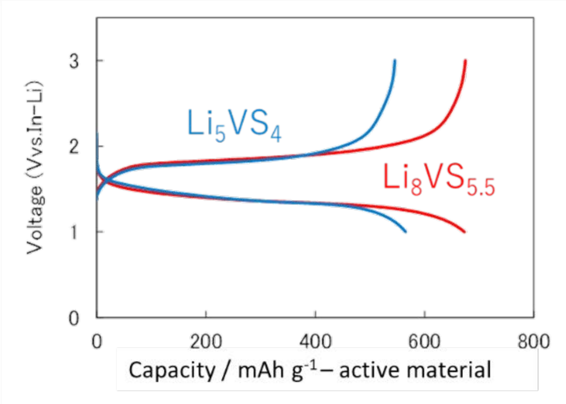

Fig. 1 First charge-discharge curves of In-Li / Li5VS_4 and In-Li / $Li_8VS_{5.5}$. Electrode is a pressed pellet (active material : solid electrolyte = 85 : 15 by wt.) , and total weight of electrode mixture is 10 mg. In-Li alloy was used as negative electrode. Test condition : 0.02 C 1.0-3.0 V vs. In-Li at 25°C

Acknowledgments

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Metal dicarboxylates as anode materials

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Keywords: metal acids, formulation chemistry, electrode preparation

Graphite is currently the anode of choice for the majority of lithium-ion batteries. Although widely used, it has a number of key limitations, including hazardous and expensive processing , the possibility of lithium plating especially in high-rate applications, and relatively low energy density or capacity. As such, there are significant opportunities to improve on the limitations imposed by graphite. This work explores transition-metal dicarboxylates as an alternative to graphite.

Our work started by exploring reported carboxylic acids, showing that during electrode processing the acids could react with the curent collector, e.g., Cu, producing the copper dicarboxylate.

From this point, we synthesized a range of metal dicarboxylates employing them as anode materials, determining their electrochemical performance and unravelling the lithium storage mechanism. In doing so, we have found that formulation chemistry, i.e., the way the electrode is prepared, has a significant impact on the performance of these materials. For example, water-based or n-methyl-2-pyrrolidone (NMP) formulation can dramatically change the capacity and cycling behaviour of a single species, as shown in Figure 1a. Hence, to fully understand and optimise the performance of these materials the effect of all relevant parameters, e.g., particle size, active material/conductive carbon distribution, formulation solvent, and transition metal oxidation state needs to be deconvoluted, as shown in Figure 1b.

Overall, this talk will provide an overview of the work we are undertaking with these compounds and how we are using processing methodology and mechanistic studies to understand function and optimise materials.

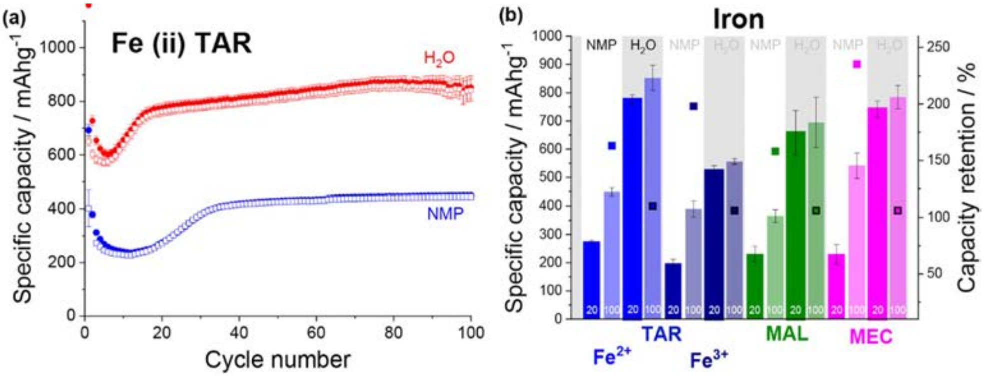

Figure 1. (a) Capacity versus cycle number for iron (ii) tartrate and (b) comparison of capacity at various cycle numbers for iron-based dicarboxylates.

Stable lithium metal anode: Regulated plating/stripping in 3D host

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Keywords: lithium metal battery, host materials, dendrite suppression, plating/stripping

The development of high-capacity and stable lithium metal anodes is pivotal for advancing the performance of next-generation lithium-ion batteries. However, several critical challenges, such as dendrite formation, capacity decay, and safety concerns, have hindered its practical application. All the strategies to prevent Li dendrites are based on the space-charge model for Li dendrite nucleation and growth which predicts that cationic and anionic concentrations exhibit unusual behaviour at Sand's time resulting in the development of excess positive charge and uneven electric fields at negative electrode which ultimately leads to dendrite nucleation and subsequent growth. Thus, Sand's time is the period of actual dendrite-free deposition after the onset of electrodeposition. Though the dendrite growth issue could be mitigated to a large extent, huge volume changes and poor coulombic efficiency (CE) persist at higher current density and high Li intake deposition in host less Li metal which can further deteriorate the overall battery performance. In this talk I will deliberate on the critical role of host materials in stabilizing lithium metal anodes by providing a protective environment that mitigates the formation of dendrites, a major cause of short circuits and safety concerns. The discussion will cover various aspects of host engineering, including material selection, design principles, and the influence of host structure on lithium metal deposition and stripping processes.

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Interfacial chemistry design for silicon-based anodes

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Keywords: silicon-based anode, interfacial chemistry, electrolyte, SEI, lithium-ion batteries

Our society is being electrified with lithium-ion (LIB) batteries whose application range is being expanded from electric vehicles and stationary energy storage systems to various e-mobilities, airplanes and submarines. Then, the demand for higher energy density and safe LIBs is continuously increasing for longer range use of LIBs and the safety of customers, respectively. Although an increase in the content of silicon (Si) of Si-graphite anodes toward Si-dominant anodes is of great interest for high energy density LIBs, swelling issue hinders the use of increased content of Si beyond the current level and brings the risk of safety hazard. One of the critical strategies for improved performance and safety simultaneously is to innovate electrolyte that enables the stabilization of interfacial chemistry, i.e., solid electrolyte interphase (SEI) layer, of Si-based anodes, which will suppress the swelling of Si, prevents Li-dendrites at graphite and stabilizes cathode interface. We will present our research results that electrolyte and interfacial chemistry designs yield performance improvement of Si-based anodes.

Acknowledgments

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Development of novel materials for Li-ion and redox flow batteries – applied research, modelling, and testing

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Keywords: Li-ion batteries, MOF, redox-flow batteries, applied research

Advanced rechargeable batteries are gaining high importance in the transition toward carbon neutrality, affordable, secure energy, sustainable and smart mobility, and circular economy. Their acceptability will highly rely on the improved quality, reliability, lifetime, and safety. The acceptance of these batteries' hinges on enhanced quality, reliability, lifespan, and safety standards. Moreover, a crucial aspect is their durability and the use of ethically sourced materials, minimizing negative environmental impact. The goal is to ensure that these batteries can be efficiently recycled, remanufactured, or repurposed at the end of their lifecycle, contributing to the return of valuable materials to the economy.

Until now, lithium-ion batteries (LIBs) are dominating the secondary battery market, finding widespread use in different areas, such as e-mobility, various portable electronic devices, and energy storage systems due to their high energy density, good stability, and track record. Nevertheless, the innovations of LIBs are highly anticipated from the electrode materials, electrolytes, separators, and cell structures. In addition to LIBs, redox flow batteries (RFB) are emerging as prime candidates for grid-scale stationary energy storage. Their capability to store large amounts of electrical energy for extended periods and release it quickly when needed, coupled with an extended lifespan and reasonable efficiency, make them attractive options. The redox couples and electrolytes play important roles in determining the energy density and cost of redox flow batteries.

In this study we are developing a novel battery component using modelling and real testing of different components with aim to build a hybrid battery energy storage system that simultaneously provides multiple services (mobile and/or stationary).

Figure 1 Redox flow battery testing rig and single cell for testing of battery components.

Acknowledgments

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Multi-faceted R&D innovations to understand battery chemistries and ceramic materials

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Keywords: oxide, phosphate, solid-state electrolyte, solid-state battery, *operando* microscope, additive manufacturing, performance, safety

The uses of ceramic materials in current and future energy storage battery technologies have penetrated or will soon penetrate the commercial space. However, as the complete understanding of their hazards is still lacking, it is necessary to investigate the potential risks of pre-commercialized battery chemistries through the whole design process.[1] The materials-level research and development (R&D) at the Electrochemical Safety Research Institute (ESRI) is studying early-technology readiness level (TRL),[2] new chemistry and novel engineering methods of energy storage and conversion through a safety lens.

This presentation focuses on several on-going collaborations to leverage combined learnings, including investigating the anatase-LMFP (lithium manganese iron phosphate) system, *operando* imaging of solid-state batteries (SSBs), and new additive manufacturing processes for cell fabrication.

The anatase-LMFP system can potentially be a chemistry pairing suited for fast charge conditions,[3, 4] and with Dr. Palani Balaya (National University of Singapore), the performance and safety of these materials for next generation lithium-ion batteries in the 18650 cylindrical cell format are investigated.

Operando optical microscopy often provides great visualization to identify interfacial reactions and resistances between battery layers during electrochemical cycling.[5] With Dr. Xiaonan Shan (University of Houston), this project aims to elucidate safety in SSBs through relating changes in light intensity and electrochemical signatures.

Finally, preliminary information regarding 3D-printing of anode-free all-solid-state batteries will also be shared from the collaboration with Dr. Fan Zheng (University of Houston). The Director of Research (Novel Materials & New Energy Forms), Dr. Wan Si TANG, will be presenting this talk for the Electrochemical Safety Research Institute (ESRI), under UL Research Institutes. At ESRI, we are interested in the energy storage safety from materials to cells and scaling up into commercially viable applications to advance the area of current lithium-ion batteries, future battery chemistries, and other green energy storage and conversion technologies.[6]

Acknowledgments

Collaborators: Dr. Palani Balaya (National University of Singapore), Dr. Xiaonan Shan (University of Houston), Dr. Fan Zheng (University of Houston)

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$Na_4Fe_3(PO_4)_2P_2O_7$ empowering: Synthesis guidelines for tailoring electrochemical performance

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Keywords: $Na_4Fe_3(PO_4)_2P_2O_7$, Na-ion batteries, sol-gel method, synthesis guidelines

Several developed cathode structures, such as $Na_aNi_{1-x-y-z}Mn_xMg_yTi_zO_2$, O3-$NaNi_{1/3}Fe_{1/6}Mn_{1/3}Mg_{1/12}Sn_{1/12}O_2$ layered oxides, polyanionic $Na_3V_2(PO_4)_2F_3$ and Prussian Blues Analogues (PBAs) have found their application in recently launched Na-ion battery prototypes. The cathode type dictates the potential application, since it is challenging to develop a cathode material that excels in longevity, economic feasibility, storage stability, scale-up viability, and energy density [1]. Usually, when selecting a cathode in terms of the highest energy and power density, there is a trade-off involving durability, economic considerations, and ecological impact.

By prioritizing ecological and economic matters, we focused our efforts on developing a novel, eco-friendly, and cost-effective polyanionic cathode for Na-ion batteries, with the composition of $Na_4Fe_3(PO_4)_2P_2O_7$ (NFPP). The literature survey of this NFPP polyanionic family [2], opened up unresolved issues: 1. Discrepancies regarding the use of phosphorous source (solely PO_4 or PO_4/P_2O_7 mixture) without elucidating the parameters governing NFPP stoichiometry and appearance of secondary phases; 2. Challenges associated with NFPP via a sol-gel synthesis, using both PO_4 and P_2O_7 units; 3. Problems with XRD and FTIR analyses when it comes to the formation of accompanying $Na_2FeP_2O_7$ (NFP) phase 4. Clarification regarding NFP presence and whether it boosts or deteriorates NFPP performance; 5. The challenge of attaining the theoretical capacity at elevated current rates.

These issues have been addressed in the course of this study through the synthesis of a series of samples, with different NFPP and NFP ratios, produced by varying amounts of citric acid and controlling pH [3]. Developed samples served as a platform to examine the formation mechanism of the polyanionic NFPP phase and its relationship with the secondary polyanion pyrophosphate phase. Our findings not only shed light on the synthesis process, by addressing the intricate interplay between iron species, citric acid, and oxalates but also suggested appropriate guidelines for the successful production of the NFPP phase. The mixed NFPP phase was found to have higher capacity when liberated from NFP, capable of reaching the theoretical value (129 mAh g^{-1} at 1 A g^{-1}) and displaying high-rate capability in Na-containing aqueous electrolyte. Lower, but more stable capacity over cycling, was measured with the organic type of electrolyte. The results can be helpful for the broad family of polyanionic compounds in light of their synthesis for tuning their sodium storage properties.

Acknowledgments

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High-energy nanostructured lithium insertion materials for advanced Li-ion batteries

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Keywords: lithium insertion material, phase transition, nanostructured material

The demand for electric vehicles equipped with Li-ion batteries is growing to develop low carbon society. Ni-enriched layered materials are used as electrode materials of Li-ion batteries for electric vehicle applications. Stoichiometric $LiNiO_2$ with cationic Ni^{3+}/Ni^{4+} redox is the ideal electrode material, but the gradual loss of capacity at the high voltage region, associated with Ni ion migration, hinders its use for practical applications.[1] Therefore, to improve electrode reversibility of $LiNiO_2$, less abundant Co ions and/or other electrochemically inactive ions, *e.g.*, Al^{3+} ions, are in part substituted for Ni ions. Nevertheless, the origin of improvement by metal substitution was a long-standing debate. Recently, the importance of non-stoichiometry and anti-site defects is discussed, and highly reversible pure Ni-based layered materials without metal substitution is successfully developed through defects engineering.[1]

Another important target is the development of a practical and high-energy Co-/Ni-free Mn-based positive electrode material, which is necessary for the economical electric vehicles. Now, for this purpose, $LiFePO_4$ is widely used, but its energy density is limited to ~500 Wh kg^{-1}, which is significantly low compared with Ni-rich layered materials (~800 Wh kg^{-1}) used for high-end electric vehicles. Moreover, the batteries with $LiFePO_4$ show lower volumetric energy density because of intrinsic disadvantages of phosphate materials with low packing density and inferior electronic conductivity. Recently, nano-structured Mn-based electrode materials are studied as emerging materials for this purpose.[2] However, these materials are generally synthesized by high-energy mechanical milling, which cannot be adopted for mass production. Recently, nanostructured $LiMnO_2$ with high-energy density (~800 Wh kg^{-1}) is successfully synthesized by using a conventional calcination reaction, which is potentially used for economical electric vehicle applications.[3]

To develop safe and high-energy advanced Li-ion batteries, the use of solid electrolyte is an important strategy. Nevertheless, inevitable volume changes of electrode materials on cycling lead to the difficulty to maintain the stable interface between electrode materials and electrolyte. Recently, non-layered electrode materials, *i.e.*, cation-disordered rocksalt oxides, are studied for high-energy advanced Li-ion batteries.[4] One of the important achievements is the development of high-capacity dimensionally invariable electrode materials, and this unique character originates from the isotropic volume change observed for non-layered materials. Indeed, the excellent reversibility for solid-state batteries is achieved for nanostructured cation-disordered rocksalt oxides with V ions.[5]

From these results, the importance of nano-structured lithium insertion materials for advanced and practical Li-ion battery applications is discussed in detail.

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T1.8 High Temperature Superconductors: Materials, Technologies and Systems

Crucial role of strange metal transport for high-temperature superconductivity in overdoped cuprates

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Keywords: high-temperature superconductivity, overdoped cuprates, strange metal phase, high-field magnetoresistance, Hall carrier density, superfluid density, non-quasiparticle-like carriers

High-temperature superconductivity in cuprates represents one of the largest mysteries in condensed matter physics, even after almost forty years of intensive research. Interestingly, it emerges from a normal (non-superconducting) metallic state, that is highly unconventional and therefore no less mysterious. Especially intriguing is the strange metal phase in the overdoped part of the phase diagram, where marked deviations from the standard Fermi liquid theory have been observed, which led to claims that the charge carriers there exhibit non-quasiparticle-like nature. Here we present our recent high-field magnetoresistance study on the two single-layer cuprates: (Pb/La)-doped $Bi_2Sr_2CuO_{6+\delta}$ and $Tl_2Ba_2CuO_{6+\delta}$, which clearly indicated that, besides these non-quasiparticle-like carriers, the strange metal phase contains also the standard quasiparticle-like carriers [1]. These findings elicit an inevitable question: which of these two types of carriers are responsible for superconductivity? Our detail analysis of the Hall carrier density and superfluid density from literature, for the two single-layer cuprates: $Tl_2Ba_2CuO_{6+\delta}$ and $La_{2-x}Sr_xCuO_4$, enabled us to postulate an empirical relation, which leads to a striking conclusion that, contrary to expectations from the conventional BCS theory, the superconductivity in the selected overdoped cuprates stems from the non-quasiparticle-like carriers [2]. If the proposed empirical relation is found in other members of the cuprate family and related materials, this will potentially shift the paradigm of the high-temperature superconductivity.

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$Nd_{1.85}Ce_{0.15}CuO_4$ and $La_{1.84}Sr_{0.16}CuO_4$ polycrystaline samples with improved critical current densities made by means of freeze-drying and spark plasma sintering

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Keywords: $Nd_{1.85}Ce_{0.15}CuO_4$, $La_{1.84}Sr_{0.16}CuO_4$, freeze-drying, spark plasma sintering, critical current density

With the aim of improving the critical current density of bulk cuprate superconductors characterised by high anisotropy, which is often limited by grain boundary weak links, we apply alternative synthesis techniques to increase the ceramic density and improve grain boundary quality.

Polycrystalline ceramic samples of the $Nd_{1.85}Ce_{0.15}CuO_4$ superconductor were made by means of freeze-drying followed by high temperature sintering and post annealing in vacuum. The ceramic density reached 90 % of the theoretical density. The onset critical temperature and the critical current density depends on the duration of the vacuum annealing treatment. For 2.5 h annealing, the critical temperature is 23.5 K, while the self-field critical current at 5 K reaches 4450 A/cm^2, a value that is significantly higher than previously reported for standard solid state preparation techniques.

On the other hand, $La_{1.84}Sr_{0.16}CuO_4$ ceramics made by consolidating pre-reacted powders by means of spark plasma sintering, can achieve near 100 % density when the treatment is conducted under vacuum. While as-treated samples show degraded superconducting characteristics, a post-annealing treatment results in significant grain growth and yield critical current densities of the order of 10^5 A/cm^2 at 5 K. For both types of compounds, the achieved values are higher than would be expected for non-textured polycrystalline ceramic pellets.

Acknowledgments

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T1.9 RECYCLING

Recycling of Solid-State Batteries – Challenge and opportunity for a circular economy?

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Keywords: solid state batteries, recycling, circular economy

All Solid State Batteries are currenctly developed at high pace. They have the potential to increase the energy by facilitiating the use of metallic lithium as the anode. Among other, strong efforts were made in developing suitable electrolytes, designing cells and increasing the compatibility between the different battery components.

In contrast, recycling of such battery systems is in the early steps, also related to the fact that end of life batteries are not available at large extent. In this contribution, potential recycling studies will be discussed for the different classes of solid electrolytes. Apart from the recovery of elemental ressources, we will explain how suitable recycling approaches could be designed to create energy efficient processes. Further, concepts on how to make batteries more recyclable by design will be elaborated.

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Scalable recycling strategies for end-of-life Solid Oxide Cell materials and their re-manufacturing

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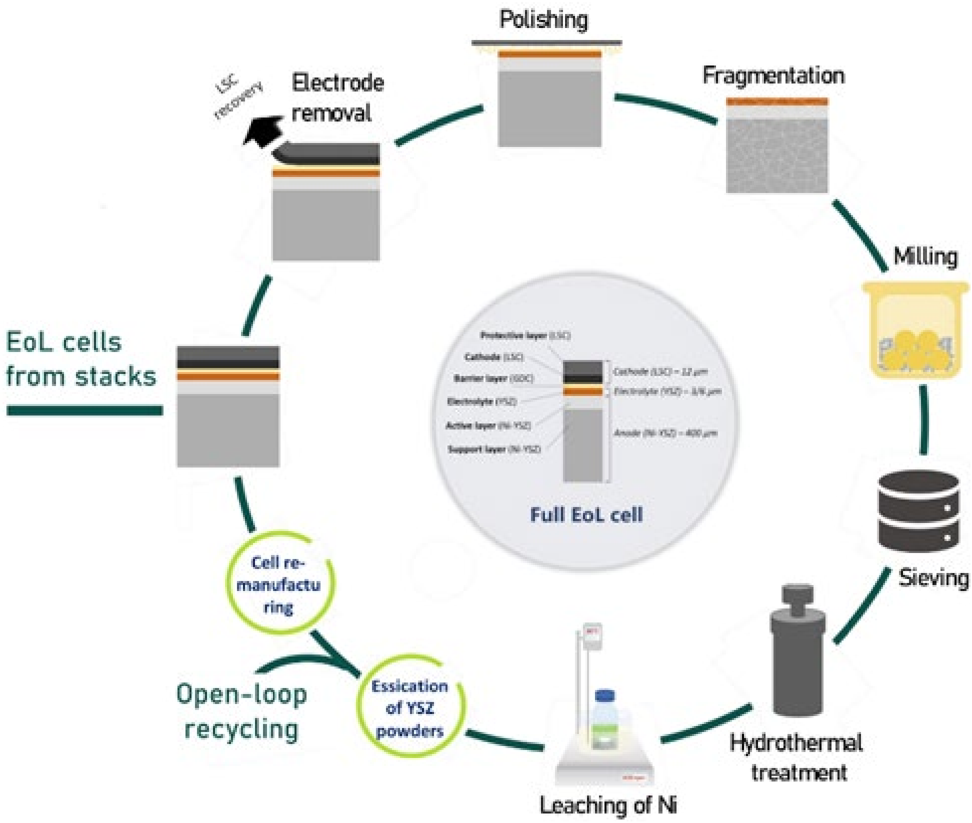
Keywords: recycling, ceramics, critical raw materials, solid oxide cells

Solid oxide cells (SOCs) provide a mature alternative to conventional power-generation sources to achieve the EU carbon-neutrality goal for 2050. However, the full deployment of SOCs is still hindered by the lack of efficient, scalable and cost-effective end-of-life (EoL) strategies that enable managing and valorizing waste products derived from cell operation and avoiding their disposal.

As the SOCs market is foreseen to remarkably increase shortly, the recovery and re-use of critical and high-cost materials is crucial to enable large-scale production and overall sustainability of SOC-based technologies. In this work, strategies for possible recycling routes of high-temperature SOC cell components (yttria, zirconia, Ni, La and Co materials) and cell re-manufacturing are presented and discussed.

A single-step recycling process optimized for the Ni-YSZ electrode components of EoL SOCs is described and upscaled from the lab scale to a pilot plant, enabling to target of the quantity required for the manufacturing of new SOCs containing 30 wt% of recycled material. The disaggregation of the Ni-YSZ composite and the selective extraction of Ni (recovered in the form of NiO) was achieved by treating the cell components inside a hydrothermal reactor in the presence of low-concentrated (0.6-1.0 M) HNO3 solutions, thus combining hydrothermal treatment and acid leaching. The processing parameters, including temperature, time, acid concentration, and solid/liquid ratio were optimized considering their mutual interactions to maximize the overall efficiency of the process, therefore minimizing waste flows, energy consumption and costs. Re-manufactured cells containing 30 wt% of recovered ceramic powders were electrochemically and mechanically characterized for comparison with standard virgin SOCs.



The overall strategy for recovery and reusing materials from EoL cells,
Ni-YSZ composite powder dismantled from EoL cells and recycled YSZ after hydrothermal and leaching treatment

Recycling and reusing the wastes generated in ceramic sanitaryware production

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Keywords: ceramic sanitaryware, waste, reusing, recycling, circular economy

Ceramic sanitary ware is a branch of the industrial ceramics industry and is the name given to vitrified products such as sinks, toilets, cisterns, bidets and urinals used in bathrooms, toilets and kitchens.

Ceramic sanitary ware production is a labor-intensive process, and therefore process waste is generated at every stage. The sludge is prepared in the production departments and taken into large stocks and delivered via pipelines to small bench stocks in the foundry benches where the shaping process will be carried out.After the shaping process, drilling, removal of excess, and retouching operations are applied. The product is dried by taking it into box type drying cabinets and then it is subjected to the glazing process after final checks. Glaze is prepared in the glaze production unit and delivered to the glazing units mostly with IBC tanks. Unfired process wastes are generated in all processes up to the firing stage. For example, mill and sieve washing water in the sludge production unit, wet pieces formed in the shaping unit, semi-products cracked from the drying cabinet and products broken during glazing are examples of unfired process waste. After glazing, the products are placed on wagons and subjected to the firing process in kiln. At the end of firing, some of the products are classified as poor quality "rejects" due to defects such as cracks, deformations and parts on the product.

The mentioned wastes can be used to produce some of the same types of products in the same campus where the waste was generated, contributing to the circular economy. In the relevant study, studies carried out with the aim of recycling waste into prescriptions are included.

T2 Ceramics for Energy Conservation and Efficiency

T2.1 ADVANCED FIBER REINFORCED COMPOSITES FOR TURBINE ENGINES

SiC_f/SiC Ceramic Matrix Composites' retained strength dependence on thermomechanical loading/environmental exposure history

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Silicon Carbide-based Ceramic Matrix Composites (CMCs) are attractive materials for use in high-temperature structural applications in the aerospace, power generation, and nuclear industries. Thermomechanical loading and environmental exposure can degrade CMCs' strength and life. The history of testing conditions influences the dominant damage mechanism(s). Consequently, chemical vapor infiltration (CVI) SiC_f/SiC ceramic matrix composites (CMC) incorporating Sylramic™-iBN or Hi-Nicalon™ S SiC fibers coated with boron nitride (BN) interphase and CVI-SiC matrix were exposed to a range of oxidative environments, mechanical loads, and elevated temperatures (2200 - 2700°F). Next, samples were evaluated via room temperature fast fracture tensile tests to determine residual properties, with the use of acoustic emission (AE) to assess stress dependent damage initiation and progression. Microscopy of regions within the gage section of the tested specimens was performed. Observed material degradation mechanisms are discussed.

SiC/SiC Ceramic Matrix Composite (CMC) development in the United States for commercial aircraft engine applications, with emphasis on events and programs that supported increasing TRL to 5

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Keywords: ceramic matrix composites (CMC), SiC/SiC, CMC hot section components

While ceramic matrix composite (CMC) research and development has been in progress in the United States (U.S.) for over 40 years, it was not until 2016 that CMCs began flying in the hot sections of commercial aircraft turbine engines as HPT (high pressure turbine) shrouds in the CFM International LEAP (Leading Edge Aviation Propulsion) engine. This presentation will review the evolutionary process that occurred in the U.S. which led to the emergence of melt infiltrated (MI) SiC/SiC composites as the high temperature, nonmetallic material of choice for replacing metallic hot section components. The significant impact of U.S. Government-led programs that were focused on the development and application of CMCs, such as the NASA (National Aeronautics and Space Administration) Enabling Propulsion Materials (EPM) and Ultra Efficient Engine Technology (UEET) Projects and the DOE (Department of Energy) CFCC (Continuous Fiber Ceramic Composite) and Advanced Turbine Systems (ATS) Programs, and the contributions made by a range of organizations including those from other countries which helped advance SiC/SiC technology are discussed. The content of the presentation was obtained from selected open literature from the past 40+ years and from researchers who have been involved in efforts to develop and apply SiC/SiC CMCs in aircraft engines. In addition, the presentation provides information about the GRC Hybrid SiC/SiC CMC system, as an example of a composite developed to address the need for 2700°F capable CMCs for further increasing turbine engine efficiency.

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A. Almansour, S. Arnold, R. T. Bhatt, and J. Haglage *NASA Glenn Research Center* (GRC); M. Verrilli, S. Viswanathan, and M. Manoharan *GE Aerospace (GEA);* R. Lowden (retired) *Oak Ridge National Laboratory (ONRL);* J. Holowczak and D. Jarmon (retired) *United Technologies Research Center (UTRC);* M. A. Alvin *National Energy Technology Laboratory (NETL);* M. Cinibulk *Air Force Research Laboratory (AFRL, Wright-Patterson AFB);* G. Morscher *University of Akron;* K. Luthra (retired*)* *GE Global Research;* R. Hobbs *Albany International Corporation*

How to consider sustainability in the development of ceramic matrix composites

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Keywords: SiC/SiC composites, sustainability, life cycle assessment

Ceramic matrix composites CMC are mainly developed for high temperature application in severe environments. One enthusiastic application has been identified in the field of aero-engines. By the use of SiC/SiC composites higher temperatures in the gas turbine can be achieved leading to higher efficiency. Additionally SiC/SiC come with a longer lifetime under critical conditions helping to make a gas turbine equipped with CMC even more attractive. With a consumption decrease of 10% with same performance the use of CMC in an aeroengine contributes already quite effectively on the reduction of the carbon footprint of airplanes.

Apart from the use phase it becomes also more and more interesting for the scientific community to evaluate the manufacturing of CMC parts along the whole processing chain considering environmental aspects. In our approach we develop a method to evaluate the environmental footprint of SiC/SiC manufacturing considering the liquid silicon infiltration (LSI) route. For this approach we establish first life cycle assessment (LCA) results on environmental impacts of the CMC production by correlating properties with environmental impacts during processing. The goal is to find a suitable tradeoff between individual properties and according manufacturing environmental impact. With this approach one can define the process of CMC as efficient as possible and correlate the process steps with the mechanical properties. With these so-called Pareto-efficient correlation one can deccide which process parameters lead to the best properties when environmental aspects are considered.

This work is leading to the design of – how we call it – “Sustainable Ceramic Matrix Composites” (SCMC) where the issues of LCA and circularity of the CMC are taken into consideration. The presentation will explain the overall approach and will show how data collected during manufacturing are correlated with mechanical properties and can furthermore be crosslinked with life cycle assessment approaches for more sustainable manufacturing.

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Oxidation of composites under an oxyacetylene torch environment inside a X-ray tomography equipment

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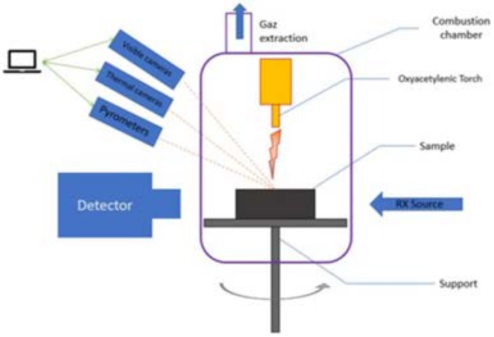
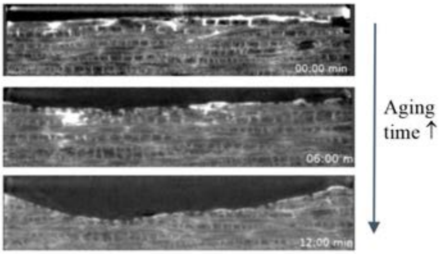
Keywords: UHTC, oxyacetylene torch

In space propulsion and atmospheric re-entry applications, the use of ceramic matrix composites requires improved oxidation resistance, such as UHTC matrices. Oxidation tests to simulate atmospheric reentry are mainly carried out with an oxyacetylene torch. However, only characterizations of the sample after oxidation or destruction tests are available in the literature. For the understanding of the aging mechanisms, the kinetic of generation of the oxide layer and the establishment of a degradation front, are difficult to extract. Indeed, these data are for one single aging time, after a quenching, resulting to a sudden cooling with stop of the thermal flux.

Thus, we propose to simulate an atmospheric re-entry by characterizing a composite in situ during an aging test, using X-ray tomography. To do this, an oxyacetylene torch is placed in a synchrotron X-ray beam to observe the change in the morphology and nature of material phases during the tests. The scientific advances will allow the understanding of oxidation mechanisms from a real time monitoring at ultra high temperature of the global behaviour and will constitute a reliable database for future modelling and numerical simulation activities on the behaviour of these materials.

Figures





C_f/C-ZrC-SiC composite: $ZrSi_2$ RMI
ESRF et SOLEIL (proposals MA5704 et ID 20221286)

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Thermal-mechanical limitations of oxide/oxide ceramic matrix composites and prospects for improvement

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Keywords: oxide CMC, thermal-mechanical aging

Lightweight, oxide/oxide ceramic matrix composites (OxCMC) are attractive materials for exhaust gas exposed turbine engine components. Despite many favorable physical-chemical properties, their limited high-temperature mechanical strength and creep resistance, but also limited knowledge on their aging behavior are frequently obstacles for their application in demanding environments and high-performance applications. Moreover, reproducible and scalable manufacturing processes are considered mandatory to exploit the full potential of OxCMC. Various studies on OxCMC consisting of different oxide fibers and matrices based on Al_2O_3 and mullite were performed to identify key degradation effects and possible mitigation strategies. Chemical modification of oxide matrices as well as the application of thick thermally sprayed protective coatings revealed the potential for increased application temperatures. In terms of OxCMC manufacturing technologies, DLR's recently introduced vacuum-assisted textile infusion processes IFOX offer promising time- and cost efficiency manufacturability as well as improved material properties with low scattering.

Development of SiC composite at KAERI for extreme environments

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Keywords: SiC_f/SiC composite; fabrication; property evaluation; nuclear application; gas turbine component

SiC ceramics are being considered as a material to be applied in high-temperature and high-radiation environments due to their excellent high temperature strength, chemical stability and radiation resistance. SiC_f/SiC composite reinforced with SiC fiber has the advantage of improving the catastrophic failure of monolithic SiC ceramics, thus expanding its application range to parts of various shapes for extreme environments. Researches on SiC_f/SiC composites and SiC coatings has been conducted at Korea Atomic Energy Research Institute (KAERI) over the past 20 years, focusing on components for high-radiation environments and high-temperature gas turbines, and is still ongoing. Major nuclear components to which SiC composites will be applied include nuclear fuel cladding tubes for advanced light water reactors, core components for next-generation nuvlear reactors, and TRISO coated nuclear fuel particles. Since high purity characteristics are very important specifications in nuclear applications, chemical vapor deposition (CVD) and chemical vapor infiltration (CVI) processes were mainly developed as manufacturing process. In addition to the nuclear application of SiC composites, KAERI expanded its research area by utilizing the developed CVD and CVI processes and applied them to the development of components for high-temperature gas turbines. In this presentation, the manufacturing characteristics, mechanical properties and performance evaluation results of SiC coated SiC and SiC_f/SiC composites manufactured based on CVD and CVI will be briefly introduced.

Characterisation of single-tow SiC/SiC minicomposites made by silicon Melt Infiltration (MI)

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Keywords: minicomposites, SiC/SiC, silicon melt infiltration, tensile strength

The consumption of fossil fuels and CO2 emissions must be further reduced to meet the Paris Agreement 2015 and goals of Flightpath 2050. In order to allow a higher temperature in the core part of jet engines, lightweight and high temperature resistant materials such as damage tolerant ceramic matrix composites (CMC) are under development. SiC/SiC based CMC with BN/SiC fiber coating and SiC matrix mostly produced by CVI process meet the material requirements in hot turbine sections. However, the disadvantage of CVI is the very long infiltration cycle and the remaining closed porosity in the matrix. To overcome these problems, MI with silicon in porous fiber preforms offers the possibility to generate a dense matrix and to reduce the high production costs of CVI processing. Since the silicon melt is very corrosive, the challenge is to protect the SiC fiber and its functional fiber coating from reaction with silicon and degradation during infiltration to achieve a high strength of the final CMC. For the study within the HotTurb project [1], we used single fiber tows based on Hi-Nicalon type-S instead of expensive textile preforms to investigate parameters during the MI process. Similar experiments investigating the strength of single SiC fiber tows, but only infiltrated with CVI SiC matrix, were performed in [2, 3]. In our experiments, we prepared ~60 mm long single rovings by matrix slurry infiltration, pyrolysis and final silicon MI. A water based low viscosity slurry containing SiC particles was used as the primary matrix [4]. For the infiltration experiments, several parameters such as coating thickness and furnace temperature were varied. Finally, a specific furnace setup and equipment were designed to perform uniform MI at low temperatures, preferably < 1420 °C. The fiber coating as well as the number of filaments of the tows which survived the process were examined by light microscopy. The tensile tests of the tows were performed using a Hegewald testing machine, and the fracture surface was examined by SEM. It could be shown that a certain coating thickness and other infiltration parameters must be adjusted accurately to avoid fiber and functional coating degradation during the silicon MI process. Moreover, for the in-situ characterization of the minicomposites, a specific high-temperature furnace is being developed enabling in-situ observation of the microstructure and crack formation under mechanical loading.

Acknowledgments
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Ablation behavior of C/SiC composites in plasma wind tunnel

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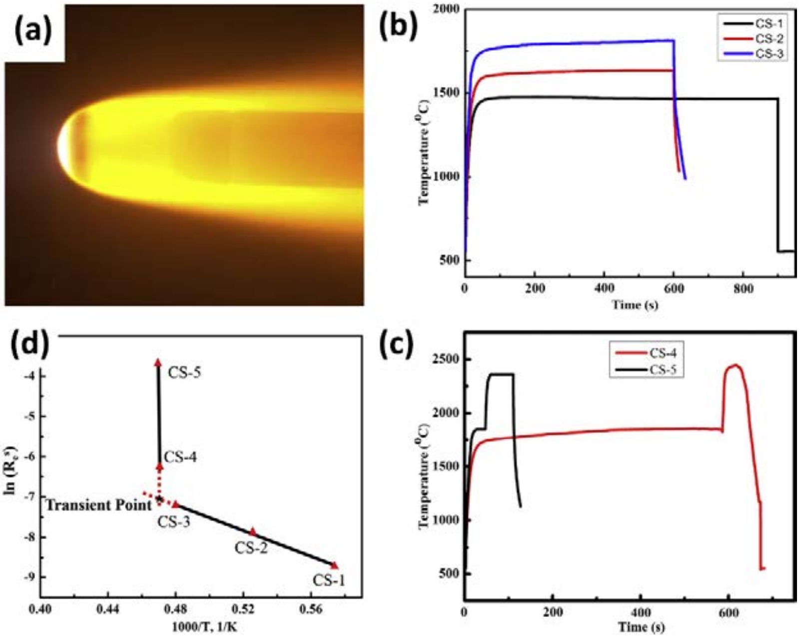
Keywords: CMC, C/SiC composites, ablation behavior

The ablation behavior is crucial to the application of carbon fiber reinforced silicon carbide (C/SiC) composites in thermal protection systems of spacecraft to enter the atmosphere or to cruise hypersonically in near space. Plasma wind tunnel is a suitable tool to simulate the service conditions of space vehicles. In this study, we systematically studied the ablation behaviors of C/SiC composites in plasma wind tunnel. The oxidation behavior of C/SiC composites in plasma is discussed. The results indicated that the oxidation under atomic oxygen condition dominated at low heat flux and stagnation pressure; however, rapid recession mechanism by sublimation and decomposition of SiC was observed at high heat flux and stagnation pressure. The temperature jump phenomenon during the ablation performed under high heat flux and stagnation pressure was attributed to the exposure of the carbon fibers to the plasma flow after consumption of the SiC coatings.



(a) Typical screenshot for the video recording of sample in plasma flow. (b)Temperature versus time curves obtained from plasma wind tunnel testing of the C/SiC samples, where surface temperature jump is not observed and (c) surface temperature jump is clearly observed, respectively. (d) Normalized erosion rate as a function of oxidation temperature in the logarithm form.

CMCs at GE Aerospace: Engines and beyond

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Keywords: GE CMC, SiC, Ox, industrializtion, manufacturing

For over 3 decades, GE Aerospace and GE Research have been heavily invested in the development and commercialization of CMCs for applications in turbine engines. While the best-known product is the melt infiltrated SiC/SiC in the CFM LEAP and GE9X engines, GE now commercially produces Ox/Ox, C/SiC, and SiC/SiC CMCs for a variety of applications. Challenges experienced in taking CMCs from laboratory development to full-scale industrial manufacturing will be discussed along with potential future opportunities for CMCs.

T2.2 ADVANCED CERAMIC COATINGS FOR POWER SYSTEMS

Material design of environmental barrier coatings to mitigate against CMAS attack

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Keywords:EBC, CMAS, design, thermodynamics

Environmental barrier coatings (EBCs) having excellent resistance to a Ca-Mg-Fe-Al-Si-O melt (CMAS) at temperatures above 1300 °C are required to promote practical applications of SiC fiber-reinforced ceramic matrix composite parts in next-generation engines. However, systematic design guidelines for mitigating against CMAS attack have not yet been proposed.

In this study, for nine kinds of model EBCs that have excellent water volatilization resistance at high temperatures, a thermodynamic descriptor Ψ that indicates the reactivity between an EBC and CMAS at 1400 °C was proposed. A model EBC disk with a CMAS pellet was placed in a furnace held at 1400 °C and then removed after 20 h to suppress crystallization and/or separation of the CMAS phase during heating, and crystallization from the residual CMAS melt during cooling.[1] The thickness of the corroded layer was then measured from SEM images of the cross section of the CMAS-YbAG disk pair, and the microstructure of the corroded layer was observed using energy-dispersive X-ray spectroscopy, electron backscatter diffraction, and transmission electron microscopy. Fig. 1 shows the relationship between Ψ and the corroded layer thickness for each EBC. The logarithmic thickness decreased linearly with increasing Ψ, demonstrating that Ψ is an extremely effective indicator for predicting the optimal structure of EBCs to achieve excellent CMAS resistance.

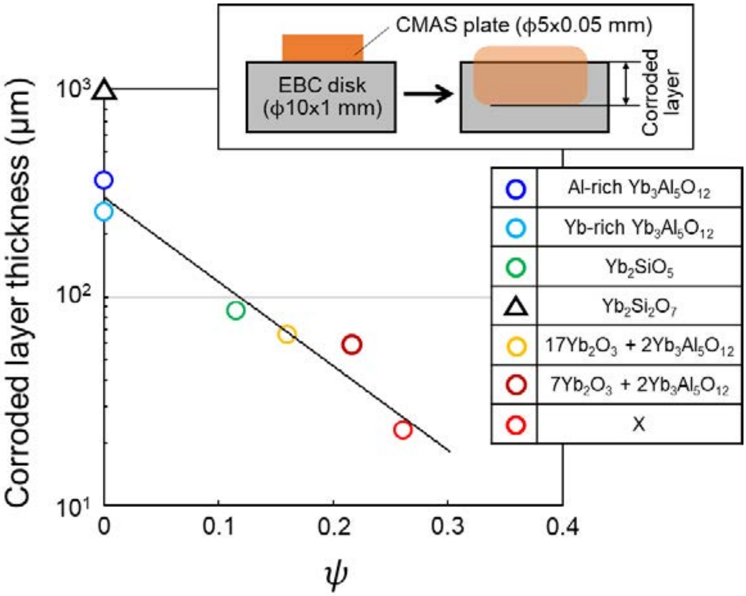

Figure 1. Corroded layer thickness for EBCs as function of ψ at 1400 °C for 20 h.

Acknowledgments

This work was supported by NEDO (New Energy and Industrial Technology Development Organization) and Development of New Innovative CompositeMaterials and Forming Technologies.

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Oxidation kinetics of slurry environmental barrier coatings for SiC/SiC Ceramic Matrix Composites

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Keywords: EBC, oxide bond coat, slurry process, oxidation rates

The upper use temperature of current environmental barrier coatings (EBCs) for ceramic matrix composites (CMCs) is limited by the low melting point of Si bond coat (1414C). The next generation CMCs, with up to 1482C (2700F) temperature capability, require a new EBC with a higher temperature bond coat. Oxide-based bond coats are a logical option to replace the current Si bond coat due to their high melting points. Plasma spraying is the most widely used EBC manufacturing process. A slurry process has been developed as an alternative process, whose benefits include non-line-of-sight process capability and low cost.[1] Another benefit of slurry process is the fast turnaround time that allows a rapid exploration of a vast spectrum of complex oxide chemistries. Oxidation is the most critical life-limiting degradation mode for EBCs. Oxidation-induced EBC failure is due to the stresses caused by the SiO_2 oxide scale. The reversible phase transformation of SiO_2 scale between □ and □ cristobalite at ~ 230C in thermal cycling and the mismatch in thermal expansion between SiO_2 scale and EBC are the main contributors to the stresses. Longer EBC life, therefore, requires slower oxidation rates. This paper will discuss the oxidation kinetics of slurry EBCs comprising an oxide bond coat and the key variables affecting the oxidation kinetics.

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High entropy zirconates for TBC applications – influence of cationic parameters on phase formation and properties

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Keywords: high entropy oxides, thermal barrier coatings, phase formation, thermophysical properties

High entropy oxides (HEOs) have attracted great interest in recent years because of their unique and tunable properties. They were first mentioned in 2015 by Rost et al. [1] proposing the composition (Mg,Ni,Co,Cu,Zn)O with the five cations in equiatomic proportions on the cationic site in the NaCl structure. Like high entropy alloys, HEOs consist of five or more cations in approximately equal amounts distributed (statistically) on one or more sublattice sites, resulting in a configurational entropy S_{config} larger than 1.5 R [1]. The high configurational entropy affects the materials characteristics due to the cocktail effect, sluggish diffusion, and lattice distortion.

In terms of application as TBC materials, HEOs are promising because the high configurational entropy results in improved phase stability at high temperatures. Due to the different cations, phonons are additionally scattered, which leads to a reduction of thermal conductivity. However, there is a lack of systematic studies regarding phase formation, stability, and properties.

In this work, high entropy zirconates with the general formular $A_2Zr_2O_7$ and up to nine different cations in equimolar amount on the A site were investigated [2]. The composition has been varied systematically to evaluate its influence on crystal structure and material properties. Phase formation, phase stability, thermophysical properties and corrosion resistance were investigated. The results support the idea that HEOs are promising TBC materials.

Figures

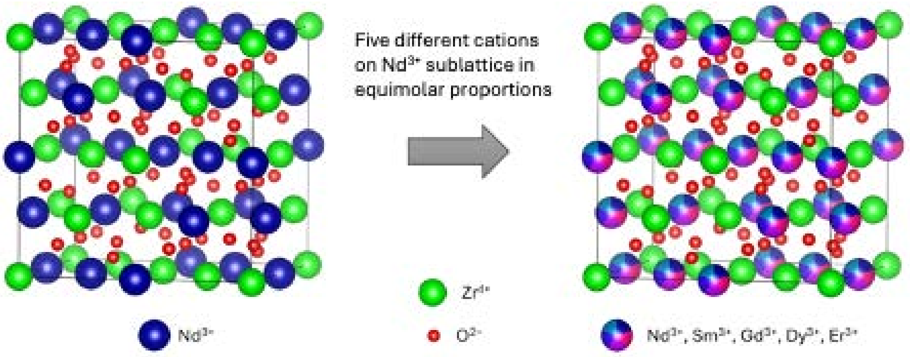

Illustration of the idea of replacing the cation on the A site of $A_2Zr_2O_7$ with five in equimolar composition.

Acknowledgments

The author acknowledges the experimental work conducted by the PhD students Patrick Hutterer (DECHEMA research institute, Frankfurt, Germany), Jonas J. Pflug, Manuel Schenker and Giulia Bianchi (all Justus Liebig University). The work was supported by the German Federal Ministry of Education and Research (BMBF, grant no. 03XP0301A) and the German Federal Ministry of Economic Affairs and Climate Action (BMWK, grant no. 20E2222A).

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Fundamental issues in plasma spraying of silicate environmental barrier coatings for ceramic composites

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Keywords: silicates, environmental barrier coatings, plasma spray, ceramic composites, gas turbine engines

Rare-earth silicate based Environmental Barrier Coatings are now used to protect SiC fiber reinforced SiC composites from environmental damage during high temperature operation in engines. Due to the large differences in vapor pressures between silica and the rare-earth oxide, the coating formed by plasma spray is invariably affected by stoichiometric changes induced by the plasma spray process. This in turn affects the thermo-structural properties of the system with concomitant implications on coating performance and durability. Furthermore, the as-sprayed materials preferentially form an amorphous phase due to the high glass transition temperature of silicates and sluggish viscosities. As such much of the coating is metastable require careful heat treatment of the substrate coating system to minimize thermal stress and associated cracking.

In this presentation, insights gained through fundamental research on process-stoichiometry-phase-structure-property linkages is critically analyzed for different EBC chemistries along with deliberate variations in process conditions to provide a framework for fundamental description of the deposition process and post-spray thermal treatments. Performance of coatings in controlled moisture testing and in select CMAS exposures will be presented.

Understanding materials degradation under ammonia atmosphere at elevated temperatures for pure ammonia combustion gas turbine system

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Keywords: NH_3, carbon neutral, bondcoat, alumina

Ammonia (NH_3) is expected to be an alternative fossil fuel for power generation. Ammonia has several advantages as a carbon free hydrogen carrier such that the weight ratio of hydrogen is 18%, which is higher than a conventional hydrogen absorbing metal and that it can be liquidized at -33 ˚C or at room temperature under 8.5 bar, which is convenient for transportation. Recently, a two-stage rich-lean combustion has been proven to suppress unburn NH_3 as well as NO_x below a practical level, which accelerates the combustion research to realize pure ammonia gas turbine for power generation[1-3)]. However, ammonia fuel-rich environment at the first stage combustor can create a reduced atmosphere at high temperatures, which may lead a deterioration of metallic and ceramic materials. In this presentation, we will overview our recent development of ammonia gas turbine power system. Then, our recent research to investigate such a degradation under ammonia reduced atmosphere will be mentioned. Several metallic substrates as well as CoNiCrAlY coating deposited by high-velocity oxy-fuel flame spraying were tested under 10-20%-NH_3 diluted by N_2 at elevated temperatures. The nitridation and subsequent degradation occurred, but they did not happen monotonically with temperature and time. The existence and role of alumina layer will be discussed together with the nitridation of metallic components, which will give some implications for thermal barrier coating system for ammonia combustion gas turbines.

Acknowledgments

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Phase regulation of rare earth silicate environmental barrier coating for SiC_f/SiC composite

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Keywords: environmental barrier coating, rare earth silicate, phase control

SiC_f/SiC composite engine components critically requested high-performance environmental barrier coating (EBC) that can withstand harsh thermal and chemical attacks against combustion environment. Typical EBCs provide reliable protections to SiC_f/SiC components up to the surface temperature of 1300°C. However, EBCs failed capability of corrosion resistances to hot steam and molten CaO-MgO-Al_2O_3-SiO_2 (CMAS) deposit at higher temperatures, as well as the phase instability and amorphization during atmospheric plasma spray fabrication. To address these critical challenges, we adopted effective multilevel design, including phase regulation and microstructure modification of rare-earth silicate EBC. The developed EBCs showed significantly enhanced reliability and support the advancement of SiC_f/SiC composite engine components.

Design principle of multi-entropy ceramics with desired characteristics: a case study of rare earth silicate with optimized thermal expansion behavior for thermal environmental barrier coatings

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Keywords: multi-entropy ceramics, thermal environmental barrier coatings, phase formation capability, thermal conductivity; thermal expansion

Multi-entropy ceramics, including high-entropy ceramics, present a vast and largely unexplored compositional space for materials innovation. The recent advent of entropy engineering in rare earth (RE) silicates has opened up expansive compositional avenues in the development of advanced thermal environmental barrier coating (TEBC) materials for SiC-based ceramic composite components within the hot sections of gas turbine engines. This approach provides the ability to finely tune thermal conductivity, resistance to CMAS (calcium-magnesium-aluminosilicate), and water vapor resistance at elevated temperatures.

Nevertheless, achieving targeted characteristics through entropy-driven compositional design within specific RE silicate structures, such as monosilicate RE_2SiO_5, apatite silicate $RE_{9.33}(SiO_4)_6O_2$, and disilicate $RE_2Si_2O_7$, poses a significant challenge due to variations in coefficient of thermal expansion (CTE) arising from different combinations of rare earth elements (monosilicate: 5.5-10.3 × $10^{\wedge-6}$ $K^{\wedge-1}$; apatite silicate: 8.7-10.8 × $10^{\wedge-6}$ $K^{\wedge-1}$; disilicate: 4.3-5.2 × $10^{\wedge-6}$ $K^{\wedge-1}$).

Here, we propose a universal design principle based on the ionic features of RE elements. Employing this principle, a series of novel medium-entropy RE silicates have been synthesized, encompassing monosilicate, apatite silicate, and disilicate structures. Systematic investigation of thermal conductivity and thermal expansion behavior across various lattice structures of these medium-entropy silicates has been conducted. The underlying thermodynamic mechanisms have been elucidated through advanced microscopy techniques including SEM-EDS, FIB, and TEM.

Ultimately, employing this design principle, a five-component equimolar monosilicate has been successfully synthesized, marking a significant advancement in tailoring RE silicates with desired characteristics for applications in thermal environmental barrier coatings.

Thermochemical equilibrium between rare-earth oxides and silicate melts, and new insight into EBC design

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Keywords: environmental barrier coating, CMAS, termochemical equilibrium

Environmental barrier coatings (EBCs) are needed to protect SiCf/SiC ceramics from degradation advanced modern gas turbines. The EBCs with thermomechanical robustness against calcium-magnesium-aluminum-silicate deposits are in high demand. The thermochemical equilibrium between rare-earth oxides and calcium-magnesium aluminum-silicate deposit was investigated at 1300oC. The primary goal was to understand the influence of rare earth constituents on crystallization behavior of reaction products. The variation of rare earth constituents results in the transformation of crystalline products from apatite/silicocarnotite to garnet/diopside, which accelerates the consumption of CMAS melt and facilitates corrosion mitigation. A pseudo-ternary phase diagram was established, which had a great potential to describe phase equilibrium in coating-deposit systems and could provide guidance for compositional design of corrosion-resistant coatings.

T2.3 ENGINEERING CERAMICS: ADVANCED PROCESSING, PROPERTIES, AND APPLICATIONS

Micro/nano mechanical testing of high - entropy ultra - high temperature ceramics.

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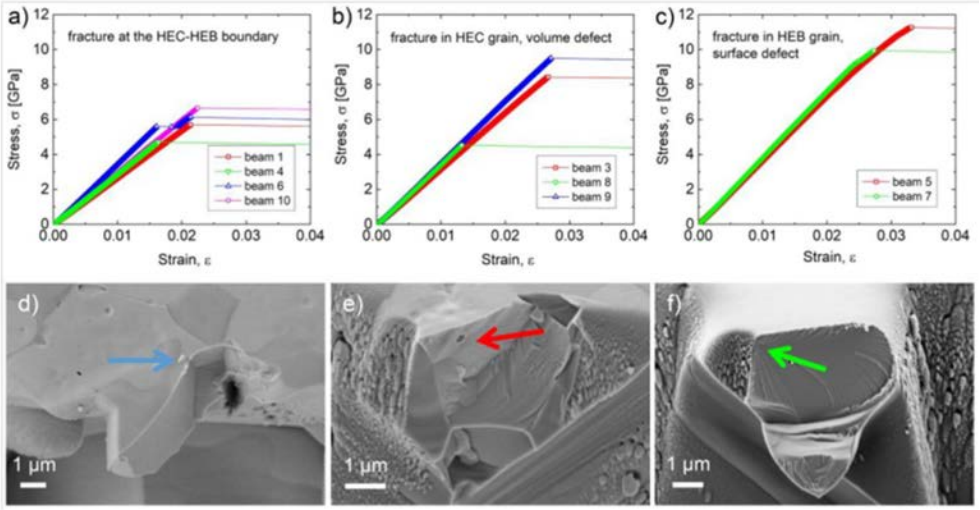
Keywords: high entropy ceramics, nanoindentation, micropillar/cantilever tests

The deformation and fracture characteristics of different ultra – high temperature high entropy ceramics – carbides, nitrides, carbonitrides, dual – phase systems, etc, were investigated connected with the processing routes and nano/micro mechanical testing of these systems. The microstructure and fracture characteristics were investigated using X-ray diffraction (XRD), scanning electron microscopy (SEM) in combination with electron back scattered diffraction (EBSD) and transmission electron microscopy (TEM). Atomic structure and local chemical disorder was determined by means of scanning transmission electron microscopy (STEM) in conjunction with energy dispersive X-ray spectroscopy (EDS. Depth-sensing nano-indentation of individual grains of bulk systems has been applied to study the nano/micro hardness and deformation characteristics. Micro-compression test of micropillars prepared by focused ion beam from oriented facets of grains were studied. During micro-cantilever tests in bending deformation and fracture characteristics of individual grains and grain boundaries have been investigated. The hardness values of differently orientated grains showed significant angle dependence. A strong influence of the grains orientation on compressive yield stress and rupture stress values was found during the micropillar test, too. The active slip systems for individual systems have been recognized. The bending strength of micro-cantilevers was strongly dependent on the character/size of the present fracture origins which were in all cases in nano-metric range. The fracture toughness of the individual grains and grain boundaries were investigated, too.



Some selected stress–effective strain curves of microcantilevers with the corresponding three main fracture origins as a,d) grain boundary, b,e) volume defects in highentropy carbide grains and c,f) surface defects of beams in high-entropy boride grains.

Dissimilar brazing of Al_2O_3 ceramic and copper using AgCu-(Sn, Ti, Zr) interlayer

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Keywords: active brazing, alumina, copper, AgCu

Ceramics find diverse applications in electric vehicles, aerospace industries, nuclear and chemical-powder plants. Despite their potential across various sectors, incorporating ceramics into intricate shapes presents lots of manufacturing and economic challenges. The concept of joining ceramics to metals emerged as a promising strategy to address these existing difficulties in the manufacturing process. The fusion of metals with ceramics imparts complementary properties that neither material possesses individually. However, achieving a robust joint interface between ceramics and metals poses numerous obstacles. The properties of ceramics and metals fundamentally differ in terms of bonding nature, as well as chemical and physical attributes. Metals exhibit a metallic bond with free electrons, while ceramics form covalent or ionic bonds with highly stable outer-shell electrons. Therefore, molten metal does not wet the ceramic surface, thus limiting the prerequisite condition for joining, i.e., establishing intimate contact between ceramic and metal surface. Furthermore, the substantial differences in physical properties, such as elastic modulus, strength, and Coefficient of Thermal Expansion (CTE) mismatch between ceramics and metals, lead to significant residual stress during cooling, impacting joint strength. Various methods for ceramic-to-metal joining exist, including adhesive bonding, active metal brazing (AMB), diffusion bonding, and transient liquid-phase bonding. AMB, owing to its simplicity and favorable joint properties, stands out as the widely adopted ceramic–metal joining technique. This process involves brazing ceramic–metal surfaces using an Active Braze Alloy (ABA) in a vacuum furnace.

In this study, we focused on evaluating the influence of Sn, Ti and Zr in a Ag-Cu filler metal for brazing a Cu/Al_2O_3 joint. Optimal wettability of alumina was achieved with a 5 wt% Sn content. The microstructure of the brazed joint revealed an Ag-rich matrix, a Cu-rich phase, and observed Cu-Ti intermetallic compounds along the bonded interface. Notably, intermetallic compound (IMC) formation in the filler increased as the Sn content approached 10 wt%. The shear strength of the brazed joint exhibited an increase with Sn content up to 5 wt%, peaking at approximately 15 MPa. However, strength diminished when the Sn content exceeded 5 wt%. The effect of Zr was also briefly examined, and the brazability of the Cu/Al_2O_3 was improved with the dual addition of Ti and Zr to the AgCuSn interlayer.

Effect of Y_2O_3-RE_2O_3(RE= Nd, Sm, Tb, Dy, Tm)-MgO additives on mechanical and thermal properties of silicon carbide ceramics

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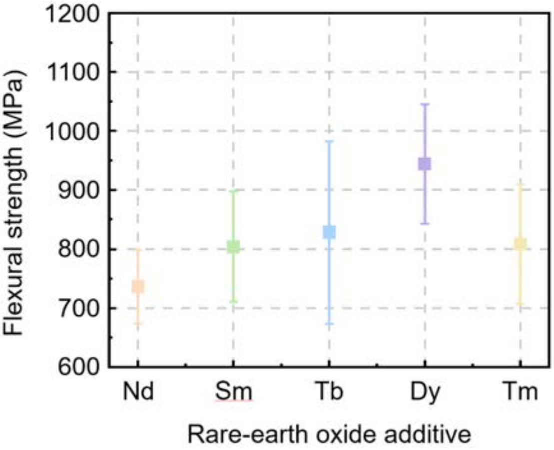
Keywords: SiC, flexural strength, thermal conductivity, rare-earth oxides

Newly developed SiC ceramics incorporating Y_2O_3-RE_2O_3 (RE = Nd, Sm, Tb, Dy, Tm)-MgO additives were hot-pressed at 1900 °C under 35 MPa for 3 hours in nitrogen, achieving relative densities ≥ 98.7%. Among these, the composition containing 0.747 wt% Y_2O_3, 1.233 wt% Dy_2O_3, and 0.551 wt% MgO exhibited the highest flexural strength of 943.8 ± 101.5 MPa at room temperature. Thermal conductivities ranged from 87.9 to 125.2 W/m·K, with the highest value observed in the composition containing 0.756 wt% Y_2O_3, 1.235 wt% Tb_2O_3, and 0.551 wt% MgO.

Figure



Flexural strength of SiC ceramics with Y_2O_3-RE_2O_3 (RE = Nd, Sm, Tb, Dy, Tm)-MgO additives

Densification and mechanical properties of boron carbide ceramics reinforced with silicon carbide fibers

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Keywords: B_4C-SiCf ceramic composite, SPS densification, microstructure, mechanical properties, ablation resistance

Boron carbide ceramics reinforced with silicon carbide fibers (B_4C-SiCf) were fabricated through spark plasma sintering, incorporating varying SiCf content ranging from 2.5 to 10 wt.%. The B_4C-SiCf mixtures underwent heat treatment using the Field Assisted Sintering Technique (FAST) for Spark Plasma Sintering (SPS) at temperatures of 1800°C and 2000 °C for 5 minutes, applying a pressure of 70 MPa in an argon atmosphere. Heating and cooling rates were set at 100°C/min and 50°C/min, respectively. The study investigated the influence of the initial powders ratio on the sintering behavior, relative density, microstructural development, and mechanical properties of the composites.

Results indicated that the sintered ceramic materials contained only the initial compounds, namely B4C and SiC phases. Scanning Electron Microscopy (SEM) micrographs illustrated that the sintered composites consisted of densely compacted B_4C and SiC grains, exhibiting a uniform distribution of both phases.

The highest relative density (> 99%) was achieved in the sample with 95% B_4C and 5% SiCf, sintered at 2000 °C. The composites demonstrated microhardness values ranging from 31 to 43 GPa, depending on the constituent content and densification temperature. The maximum microhardness was attained in the composite with 95% B_4C, sintered at 2000 °C.

To assess the composites' performance under extreme conditions, the ablation resistance was evaluated using a flowing oxyacetylene torch test. The material containing 5 wt.% SiCf exhibited superior ablation resistance compared to other compositions investigated. The study concluded that the SPS technique proves highly effective for densifying additive-free B_4C-SiCf ceramic composites, showcasing promising properties for applications in extreme radiation environments.

Effect of electric field/current on high-temperature behavior of 8YSZ polycrystal

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Keywords: flash event, crack healing, creep, diffusion, 8YSZ

Flash event[1)], which is a unique behavior occurring when an electric field larger than a critical value is applied to a ceramic green compact, can succeed to lower the sintering temperature of ceramic powder compacts. Currently, it is confirmed that the flash event effectively works also to high temperature behavior of bulk ceramics, such as deformation,[2,3)] joining[4)] and crack healing[5)]. Irrespective of the many research works, however, the effect of the electric field/current on the high temperature processing is still unclear. The present study, therefore, was carried out to make clear the effects of i) the DC/AC electric currents/fields[6)] and ii) grain size[7)] on the high temperature behavior under the flash event using polycrystalline zirconia ceramic (8Y-CSZ) as a reference material.

Although the high-temperature behavior was accelerated by the flash event significantly more under the AC field than under the DC field. For example, although the crack healing occurs even under the static annealing without the electric field, the healing rate was 4 times faster than that of the static annealing without electric current/field.[6)] Under the flash event, the high-temperature behavior is apparently accelerated in fine grained 8Y-CSZ than in coarse grained one, suggesting that the grain boundaries play an important role in the flash event.[7)] The enhanced processing cannot be explained only by the thermal effect caused by Joule heating, but non-thermal effects caused additionally by the flash event. Especially, the high-temperature behavior under the flash event would be accelerated through the field/current-enhanced diffusional processes, especially through the grain boundary diffusivity of the cations.

Acknowledgments
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Oxidation mechanisms of multicomponent carbide ceramics

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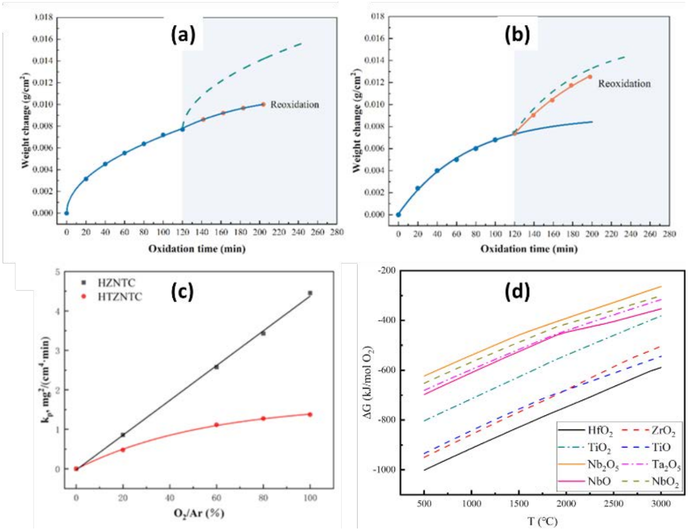
Keywords: UHTCs, multicomponent carbide ceramics, oxidation behavior, active oxidation

In this study, we take the $(Hf_{0.2}Ti_{0.2}Zr_{0.2}Ta_{0.2}Nb_{0.2})C$ (HTZTNC) and $(Hf_{0.25}Zr_{0.25}Ta_{0.25}Nb_{0.25})C$ (HZTNC) as typical samples to investigate their oxidation rate-controlling step and the factors to determine the oxide morphologies. The results indicate that the outward diffusion of metal-containing substances is the rate-controlling step for HTZTNC with the generation of high-pressure TiO during prolonged oxidation, while the inward diffusion of oxidant is the controlling-step for HZTNC, in which the vapor-pressure of corresponding metal-containing oxides are too low to diffuse out. The elements in the resultant oxide during oxidation shows gradient distribution, which is consistent to a preferential oxidation order driven by the oxidative free energy of each element. The vapor pressure of elemental oxidation can also have an important effect on the structure of the oxide layer. It is also noted that the rapid growth of oxide scale in HZTNC ceramics accumulates oxidative stress due to the lack of continuous outward diffusion of the element, leading to eventual fracture with prolonged oxidation. Herein, it is concluded that the rate-controlling step for oxidation of multicomponent carbide ceramics is determined by the vapor-pressure of the corresponding metal-containing oxides, and the oxide morphologies are determined by both the chemical potentials for oxidation and the vapor-pressure. This understanding could provide criteria to design the oxidation resistance of multicomponent carbide ceramics.



Mass per unit area of the samples at 1300°C as a function of oxidation time: (a) HTZTNC; (b) HZTNC. (c) The relationship between k_p and the different oxygen partial pressures. (d) Ellingham diagram for each composition of HTZTNC

T2.5 Advanced Polymer Derived Ceramics (PDCs) and Related Materials for Energy Applications

Polymer-derived ceramic coatings for stainless steel corrosion resistance

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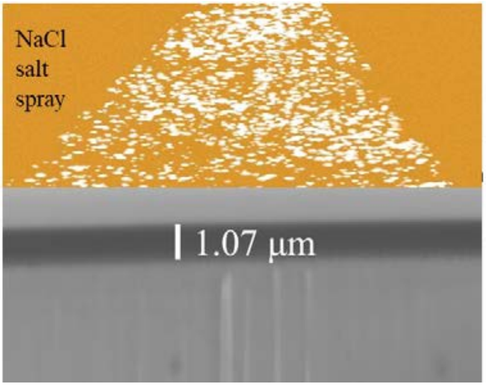
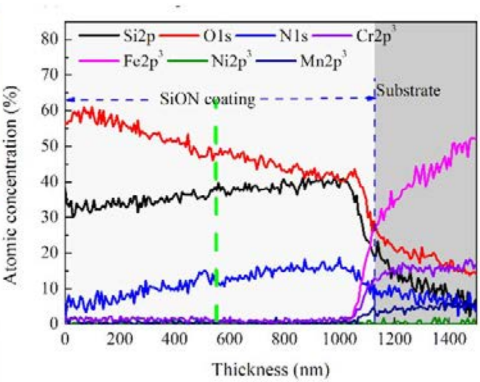
Keywords: polymer-derived ceramics, perhydropolysilazane (PHPS), coating, stainless steel, weld, chloride corrosion, interdiffusion, mechanical properties, failure resistance

Corrosion of spent nuclear fuel storage canisters is a serious concern due to the deposition of corrosive marine salts by inducing chloride-induced pitting corrosion. Ceramic coatings are desirable options thanks to their high resistance to corrosive environments and good mechanical properties. However, the interfacial compatibility with the steel substrate is a challenge.

In our work, SiON coatings were created using perhydropolysilazane (PHPS) on the weld region and the base stainless steel region with different microstructures and compositions. The influences of the weld and base steel compositions and microstructures on coating formation, composition, microstructure, mechanical properties, and corrosion resistance were investigated. The SiON coatings show a higher nitrogen content and a lower oxygen content on the base metal than on the weld metal. Salt spray tests show that the differences in mechanical properties and compositions on the weld and base steel substrates do not significantly affect the function of the corrosion-protective coatings. However, when the coating thickness is high, the corrosion resistance decreases. In addition, a SiOCN coating has been developed based on polysilazane and polysiloxane preceramic polymers. The multilayer coating system consists of a 600 nm thick SiON bond coat, a 66 nm thick SiOC buffer layer, a 604 nm thick SiONC main coat, and a 50 nm thick SiON/SiO_2 top coat. Coating compositions and structural evolution were analyzed. The SiOCN amorphous coating shows improved hardness and reduced modulus than the SiON layer only. The coating can also be repaired after damage. Our coating systems provide a new approach to extending the lifetime of nuclear waste containers in corrosive conditions and important guidance regarding the desirable coatings and thicknesses for best corrosion prevention.

Figures





Acknowledgments

This work was financially supported by the US Department of Energy (Grant Number DE-NE0008963).

T2.6 Sustainable Materials and Systems for Energy Efficient Building and Structures

3D printed lightweight advanced building material from waste glass-based geopolymer

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Keywords: 3D printing, hollow glass microspheres, waste glass, lightweight geopolymer

The production of Portland cement requires vast amounts of energy and raw materials. Unfortunately, it also generates a significant amount of CO_2, which contributes to global warming. By 2020, the global cement industry is expected to produce 5.9 billion tons of cement, producing over 4.8 billion tons of CO_2 emissions [1]. This is a concerning situation, and it is urgent that we find ways to reduce CO_2 emissions from cement manufacturing. Notably, the production of Portland cement alone contributes to 5-7% of all CO_2 emissions [2].

The solution to this problem requires the development of efficient building materials and building processes. Lightweight constructions are increasingly used in construction sectors because using low-density materials reduces the structural weight of products. Geopolymers, mainly aluminosilicate materials produced from industrial by-products, are alternative building materials with low CO_2 emission, excellent properties, and high durability compared to ordinary Portland cement. The geopolymer technology prvides a solution by using industrial byproducts (waste) containing aluminosilicate phases with little negative impact on the environment. Combining different source materials containing aluminosilicate and alkali solutions with optimization of curing temperature, alkali concentrations, additives, Na_2O/SiO_2 ratio, etc., gives geopolymer-like materials/cements good mechanical properties and a high durability. Due to their mechanical properties and environmental benefits, geopolymer-like materials appear as future prospective construction materials with applications in different areas.

3D printing of building materials offers several environmental and economic advantages by reducing construction errors, costs, time, and safety risks compared to conventional construction systems. 3D printing process of lightweight geopolymer-like materials would be a potential game-changer in the building industry. This study presents a method that utilizes waste glass powders with an alkali solution (3-5 M NaOH) to produce a geopolymer-like paste through direct ink writing 3D printing. A mixture of hollow and solid glass microspheres was incorporated as fillers to enhance printability and adjust density. Additionally, alumina-zirconia silica refractory (AZS) was included to investigate its impact on mechanical properties. After printing, the samples underwent curing at 40°C for 48 hours, followed by a 14-day ambient temperature treatment. Subsequently, the printed samples were fired at 800°C to evaluate their thermal behavior. The results demonstrated a favorable trade-off between compressive strength and density in the printed samples. The fired samples transformed into lightweight glass ceramic foams while keeping their printed structure.

Acknowledgments

This paper is a part of the dissemination activities of the project FunGlass. This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 739566. The authors also gratefully acknowledge the financial support from the Slovak Grant Agency of the Ministry of Education, Science, Research and Sport, VEGA 1/0456/20.

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T2.7 ENERGY EFFICIENCY AND GREEN TECHNOLOGIES IN CERAMIC MANUFACTURING INDUSTRIES

Development of ceramic components for energy efficient combustion technology for gas burner applications

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Keywords: energy, combuston, porous, radiant, burners

The conventional gas burners for domestic and commercial applications not only have low thermal efficiency but emit harmful emissions into environment due to high presence of carbon monoxide & nitrogen oxide in flame. Investigations were carried on the development of ceramic components for the replacement of metallic burner casing, metallic burner base, and burners by the combination of ceramic materials like Silicon Carbide & Cordierite. A development study on burners and their thermal efficiency was carried out on two types of porous radiant burners (PRB). Thermal efficiency of both burners was found to be around 56-65%.

The carbon monoxide emission from PRB was found to be 54-58 ppm in comparison of 355-545 ppm of conventional burner system. NOx emission was 2.10 – 5.00 ppm for PRB in comparison to 28-56 ppm of conventional burners. This work has been done as a mission of clean energy & sustainable solution for LPG Gas burners & stoves. These burners are not only energy efficient but also produces convection cum radiant heat & emits far infra-red rays, which belong to the positive spectrum of light operating at a frequency bandwidth of 300GHz to 430-THz.

In both the burner systems, ceramic materials with low thermal expansion, high thermal shock resistance and good thermal conductivity were used and assembly was developed. Complete burner component system with the use of ceramics is eco-friendly in manufacturing as well as in use.

T3 Ceramics for Environmental Systems

T3.1 PHOTOCATALYSTS FOR ENERGY AND ENVIRONMENTAL APPLICATIONS

Nanostructured iron-based absorber and catalyst materials for solar energy conversion

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Keywords: spinels, photocatalysis, electrocatalysis, water splitting

Efficient conversion and storage of solar energy are crucial steps in the establishment of a renewable and carbon neutral energy supply. Photocatalysis and photoelectrochemistry are considered promising to make use of the large amounts of sunlight that reach the surface of earth. They render the direct conversion of light into chemical energy possible, circumventing the problem of expensive energy storage using batteries that comes with the use of photovoltaics. In recent years, earth-abundant spinel ferrites have emerged as auspicious materials for applications in photo(electrochemistry) and photocatalysis. They have the inherent ability to absorb a large part of the visible light spectrum with band gaps around 2 eV, while being at the same time stable against photocorrosion. To overcome their charge carrier limitations, my group utilizes modern synthesis techniques to prepare nanostructured spinel ferrites.

In the last years, we have developed fast microwave-assisted sol-gel syntheses yielding phase-pure spinel ferrite nanoparticles of e.g. $MgFe_2O_4$, $CoFe_2O_4$, $NiFe_2O_4$, $MnFe_2O_4$ and $ZnFe_2O_4$ at temperatures as low as 170-200 °C.[1-4] The crystallite size can be tailored by post-synthetic heat treatment, however the materials are already (partly) crystalline as-prepared, with specific surface areas of around 200 m^2/g and good colloidal stability. Photocatalytic and electrocatalytic experiments will be presented, as well as the conversion of some spinel oxides into sulfides, e.g. pendladites.[5] A new direct microwave synthesis for nickel-iron sulphide nanosheets for electrocatalytic CO_2 reduction will also be presented,[6] as well as a novel microwave synthesis for macroporous $CaFe_2O_4$ foams for hydrogen generation.[7] Recent results on using nickel-iron sulphide nanosheets as co-catalysts in photocatalytic hydrogen production will also be presented,[8] as well as the synthesis of high-entropy spinel oxide nanoparticles at low temperature.[9]

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Photoelectrochemical water splitting using hematite-based photoanodes

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Keywords: water splitting, hematite, photoanode, co-catalyst, heterojunction

Hematite (α-Fe_2O_3) receives great attention as photoanode in water splitting devices due to its abundance in nature, environmental friendliness, high photochemical stability, and a narrow bandgap of 1.9–2.2 eV. Despite these favorable properties, α-Fe_2O_3 is handicapped by short excited-state lifetime, poor water oxidation kinetics, limited hole diffusion and subpar electrical conductivity, leading to predominant electron–hole recombination in the bulk, interfaces, and surfaces, thereby constraining PEC efficiency.

Several strategies exist to overcome the limitations of α-Fe_2O_3, including heterojunction construction, doping, morphology advancement, and co-catalyst loading. In my talk, I pay attention to these strategies and show examples on the possible outcomes of their combinations.

First, the nuanced impacts of a thin co-catalyst layer over morphologically controlled, doped or pristine α-Fe_2O_3 will be introduced, in connection to surface states denoted as S1 (higher energy) and S2 (lower energy). We prepared isomorphous hematite nanoarrays with a thin layer of amorphous copper oxide (CuOx), composed of a blend of Cu(I) and Cu(II) species. Remarkably, we discovered that in pristine α-Fe_2O_3, the S2 state played a pivotal role in activating the CuOx ad-layer for water oxidation. Notably, CuOx was activated indirectly through the equilibrium with the S2 state, despite available, high-energy holes of S1. As a result, in the case of Ti-doped α-Fe_2O_3 devoid of the S2 state, the presence of CuOx caused a loss of efficiency.

Second, we layered economically viable pyrolytic carbon nanotubes (p-CNTs) as solid-state mediators to accelerate the charge transfer between the α-Fe_2O_3 and the boron-doped graphitic carbon nitride (B-C_3N_4) component of a type II heterojunction. This synergistic combination resulted in a remarkable enhancement in photocurrent density compared to pristine α-Fe_2O_3. The highest donor density could be confirmed for α-Fe_2O_3/B-C_3N_4/p-CNT, compared to α-Fe_2O_3 or α-Fe_2O_3/B-C_3N_4. Superstructuring the B-C_3N_4 and p-CNT onto pristine α-Fe_2O_3 enhanced the charge separation and transfer efficiencies, moreover, mitigated recombination losses. DFT calculations suggested the type II charge transfer mechanism switched to enhanced Z-scheme type by simple deposition of p-CNT on α-Fe_2O_3/B-C_3N_4.

Achieving such cost-effective and efficient hematite-based photoanodes offers an opportunity to fabricate tandem PEC devices for low-cost solar fuel production.

Acknowledgments

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Magnetic photocatalytic nanocomposites based on carbon nitride and magnetite nanoflowers for the removal of dyes at neutral pH

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Keywords: carbon nitride, iron oxide, magnetic nanocomposites, nanoflowers, dye removal

Carbon nitride (g-C_3N_4) has demonstrated exceptional potential for environmental decontamination. As a metal-free photocatalyst responsive to visible light, g-C_3N_4 has exhibited high performance in various environmental applications. By synergistically combining the inherent properties of g-C_3N_4 with those of an integrated phase, this approach offers a greater array of reactive sites and heterojunctions, enhancing its ability to capture and degrade a wider range of compounds. Notably, decorating g-C_3N_4 with magnetic nanoparticles creates magneto-responsive adsorbent platforms that can be remotely controlled by external magnetic fields, facilitating easy recovery and reuse in remediation techniques. This study investigates the development of magnetic nanocomposites through the in-situ incorporation of magnetite (Fe_3O_4) nanoparticles (NPs) with spherical and nanoflower-like morphologies into graphitic carbon nitride sheets using two different synthetic methods. The nanomaterials were characterized using TEM, SEM, XRD, FTIR, BET, zeta potential analysis, vibrating sample magnetometry, and UV–vis absorption spectroscopy. The integration of magnetic NPs into the carbon nitride matrix improved the optical and textural properties of the composites. The effect of the NP morphology on the adsorptive and photocatalytic properties of the nanocomposites to remove methylene blue (MB) from aqueous solutions was evaluated under various pH conditions (acidic, neutral, and basic) through batch tests. Under extreme pH conditions, the nanocomposites displayed comparable or lower MB removal capacity compared to pure g-C_3N_4. However, in a neutral medium, the nanocomposite containing Fe_3O_4 nanoflowers demonstrated a significantly higher removal efficiency (>80%), attributed to its high adsorption capacity and excellent photocatalytic activity in this pH range. This nanocomposite presents a promising approach for removing cationic dyes from water through magnetic assistance, as it eliminates the need for pH adjustment of the polluted effluent, thereby reducing costs and environmental impact in the dyeing industry.

T3.2 CERAMICS FOR CARBON CAPTURE AND STORAGE TECHNOLOGIES

Microwave modulation of the redox properties of solid state materials for energy storage and CO_2 conversion

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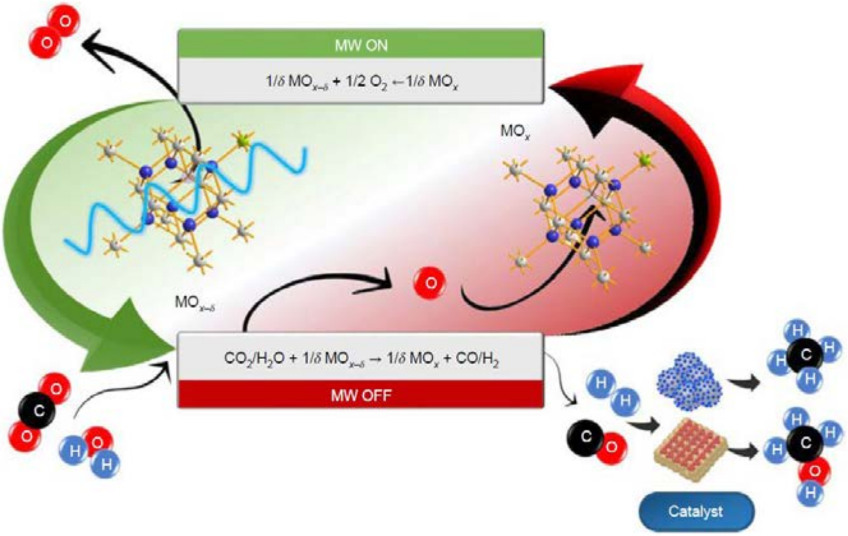
Keywords: microwaves, redox reactions, CO_2 conversion, low-carbon technology, electrification

Adapting industrial processes to low-carbon technologies and renewable electricity requires novel tools to electrify unitary steps as well as efficient energy storage, i.e. through catalytic synthesis of valuable chemical carriers. The recently discovered use of microwaves as a reducing agent for solid materials offers a novel framework in the enhancement of this chemical conversion route, as it promotes the formation of oxygen vacancies and surface oxygen exchange at low temperatures.

By this procedure, ceramic oxides, such as doped CeO_2 and ZrO_2, can be chemically reduced, leading to an instantaneous outstanding raise in electrical conductivity and resulting in a non-equilibrium high-energy state. The input of a suitable sweep gas on MW switching-off leads to the material reoxidation via gas deoxygenation and the formation of valuable molecular energy carriers, as H_2 from water or CO from CO_2, which further enabled CH_4 production when integrated with a Sabatier reactor (Figure 1).[1] Besides, we have demonstrated that the redox process is reproducible, reversible, and cyclable, and the extent of the O_2 yield depends on the material properties and microwave power.[2]

The ability of microwave radiation to evolve O_2 and transmute the redox catalytic behavior in oxides can be used in the electrification of several catalytic processes, such as the selective functionalization of alkanes, green H_2 production and conversion of CO_2.



Schematic illustration of the microwave-induced redox cycle.[1]

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Enabling the manufacturing of hierarchical and layered ceramics

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Keywords: manufacturing, sintering, shape control, laminates, membranes, hierachical ceramics

The production of ceramics for energy components has been a long-standing challenge. Multi-materials, layered structures and hierarchically porous components are required for performance of membranes, fuel cells, batteries, and more. Their processing, and particularly their sintering, is prone to be affected by anisotropy, distortions and even cracking, due to the non-uniform densification kinetics. The raising field of Additive Manufacturing (AM) is introducing previously unthinkable design freedom, but also additional new challenges in terms of shape retention and shrinkage anisotropy in the following sintering steps. By modeling the sintering process in a simple finite-element-based platform, strategies to minimize these issues are defined. The stresses developed at the interfaces turn out to be key, and process optimization guidelines are drawn based both on the interface geometry and on the sintering routine. Strategies to maximize process efficiency and uniformity with field-assisted sintering techniques are also outlined.

Concept and application of sustainable materials processing using ultrasound for carbon neutrality

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Keywords: sonochemistry, low cost, low emission, room temerature, nanomaterial

Now, a variety of high-value-added technologies as nanotechnology and the high value-added products as nano metal particle related materials using it can be requested various fields. Nanoparticles is one of the most important nanomaterials because nanoparticle manufacturing is an essential component of nanotechnology. Nanoparticles are fabricated by a variety of processes. In general, the traditional metal nanoparticles fabrication processes are basically either physical or chemical methods. Fig.1 shows relationship of cost and environmental impact for nanoparticle fabrication. Conventional processing is often problematic in terms of synthesis conditions, processes, cost, and waste emissions, which is a problem that must be solved when considering the SDGs, including carbon neutrality.In industry, well-balanced fabrication is needed in order to control the cost and protect the environment. However, it is difficult to manage both low cost and low environment impacts in these traditional methods. Therefore, it is required innovative fabrication design in order to break through these problems. Ultrasound processing is one of chemical process. In general, the properties of a specific energy source determine the course of the chemical reaction. The ultrasonic irradiation differs from traditional energy sources in duration, pressure, and energy per molecule. The chemical effects of ultrasound do not come from a direct interaction with molecular species. Instead, they are derived principally from acoustic cavitation, which can produce temperatures as high as those on the surface of the sun and pressures as great as those at the bottom of the ocean.[1] However, ultrasound generation uses a wide range of energy sources that can be used from cleaning to reducing applications. Ultrasonic cavitation generated hot spot in solution and slurry. Because this hot spot generated pulsingly innumerably with high temperature and high pressure in a short time, this has an influence on the chemical reaction locally. In solid-liquid system, supersaturation greatly changes in solid-liquid interface by cavitation.

We developed new low cost and low emission (carbon neutrality) various nanomaterials synthesis method that achieved by sonochemical solid-liquid processing in roome temperature. This new synthesis method is with the ultrasonic as non-equilibrium reactor and the metal oxide or metal and alcohol based solvent are used for the raw material. We have synthesized nano metal related materials by ultrasound in liquid-solid system and controlled morphology of products. The alcohol based solvent and the metal oxide or metal powder are put in the beaker and only irradiated by ultrasound. The metal oxide simply was reduced into metal and morphology of metal nanoparticles was changed by various conditions. In case of silver oxide and gold oxide mixture, silver-gold alloy can be synthesized at room temperature by ultrasound.[2] This fabrication method is extremely clean and safety processing, so it can also be applied for various nanometerial syntehsis. In presentasion, various low-emission, carbon-neutral nanomaterial synthesis processes and concepts will be presented. [3, 4]

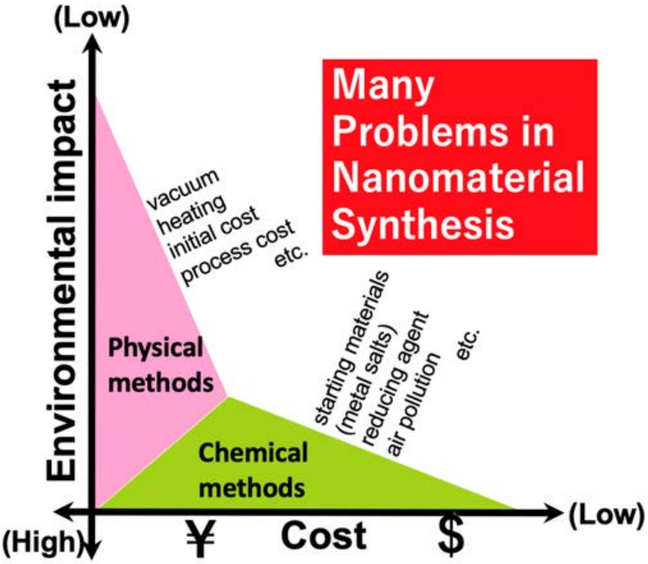

Fig.1 Relationships of cost and environmental impact for nano material fabrication.

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Production of methane from carbon dioxide using zirconium-tin oxide based catalysts

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Keywords: methanation, catalyst, carbon dioxide, zirconium-tin oxide

Methanation (conversion of CO_2 and H_2 into CH_4 and H_2O using a catalyst) has been paid attention due to the decrease of the CO_2 emission and the generation of CH_4 as a fuel. To date, various kinds of catalysts for metahanation have been studied, while high pressure and high concentration of hydrogen were generally required. From the viewpoint of the energy cost and the safety, the atmospheric pressure and low concentration of hydrogen are desired; however, such moderate conditions are thermodynamically unfavorable to proceed the methanation; e.g., 3wt%Ni/CeO_2 showed 36% of the CH_4 yield (CO_2 conversion: 51%) (atmospheric pressure, 1vol%CO_2-5vol%H_2-94vol%Ar, 450°C) [1].

In order to convert CO_2 into CH_4 effectively under moderate conditions, $ZrSnO_4$ [2] was focused as a mother solid. Since $ZrSnO_4$ with a distorted crystal structure has redox properties owing to the valence change of $Sn^{2+/4+}$, the CO_2 adsorption and the bond cleavage of CO_2 are expected to be facilitated. Furthremore, $Ce^{3+/4+}$ was introduced into $ZrSnO_4$ to improve redox properties with the synergistic effects of $Sn^{2+/4+}$ and $Ce^{3+/4+}$. In this study, therefore, we prepared 18wt%Ni/20wt%$ZrSn_{1-x}Ce_xO_{4-\delta}$/γ-$Al_2O_3$ (Ni/$ZrSn_{1-x}Ce_xO_{4-\delta}$/γ-$Al_2O_3$) catalysts, composed of Ni, $ZrSn_{1-x}Ce_xO_{4-\delta}$, and γ-$Al_2O_3$ having high surface area. The catalytic activity was investigated by using fixed-bed flow reactor, where the reactant gas of 1vol%CO_2-4vol%H_2-95vol%Ar was fed under atmospheric pressure (50 $mL\cdot min^{-1}$) over 0.1 g of the catalyst.

Figure 1 shows the temperature dependencies of CO_2 conversion and CH_4 yield of Ni/$ZrSn_{0.90}Ce_{0.10}O_{4-\delta}$/γ-$Al_2O_3$ and Ni/γ-Al_2O_3, where the Ce loading amount was optimized to be $x = 0.10$. The use of $ZrSn_{0.90}Ce_{0.10}O_{4-\delta}$ enhanced the catalytic actvity compared to that of Ni/γ-Al_2O_3, and the Ni/$ZrSn_{0.90}Ce_{0.10}O_{4-\delta}$/γ-$Al_2O_3$ catalyst showed the high CH_4 yield (61.0%) and the high CO_2 conversion (58.4%) even at 350°C.

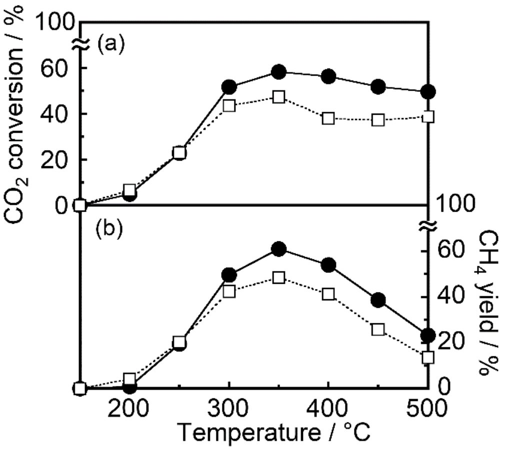

Figure 1. Temperature dependencies of (a) the CO_2 conversion and (b) the CH_4 yield for Ni/$ZrSn_{0.90}Ce_{0.10}O_{4-\delta}$/γ-$Al_2O_3$ (●) and Ni/γ-Al_2O_3 (□).

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Ceramic aerogel for carbon-sequestering insulation materials

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Keywords: ceramic aerogel, nanoporous, additive manufacturing, insulation, carbon sequestration

To exploit the high temperature superinsulation potential of anisotropic thermal management materials, the incorporation of ceramic aerogel into the aligned structural networks is indispensable. However, the long-standing obstacle to exploring ultralight superinsulation ceramic aerogels is the inaccessibility of its mechanical elasticity, stability and anisotropic thermal insulation. In this study, we report a recoverable, flexible ceramic fiber-aerogel composite with anisotropic lamellar structure, where the interfacial cross-linking between ceramic fiber and aerogel is important in its superinsulation performance. The resulting ultralight aerogel composite exhibits a density of 0.05 g/cm3, large strain recovery (over 50%), and low thermal conductivity (0.0224 W/mK), while its hydrophobicity is achieved by in-situ trichlorosilane coating with the water contact angle of 135°. The hygroscopic tests of such aerogel composites demonstrate a reversible thermal insulation. The mechanical elasticity and stability of the anisotropic composites, with its soundproof performance, shed light on the low-cost superelastic aerogel manufacturing with scalability for energy saving and carbon-sequestration building applications.

Subnanometer cluster and nanoparticle-based catalysts in CO_2 hydrogenation towards C1 and higher C products under low pressure: Control of performance by size, composition & support

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Keywords: subnanomeyter cluster, bimetallic, nanocluster, CO_2 conversion

The presention will focus on the thermocatalytic conversion of carbon dioxide by two families of copper-based catalysts: (1) atomically monodisperse mono- and bimetallic clusters made of handful atoms deposted in vacuum with mass selction from molecular beams, supported on technologically relevant oxide- and model carbon-based supports [1-2] and (2) by wet-chemical ways synthesized nanoclusters on various oxide supports with variable morphology [3-5].

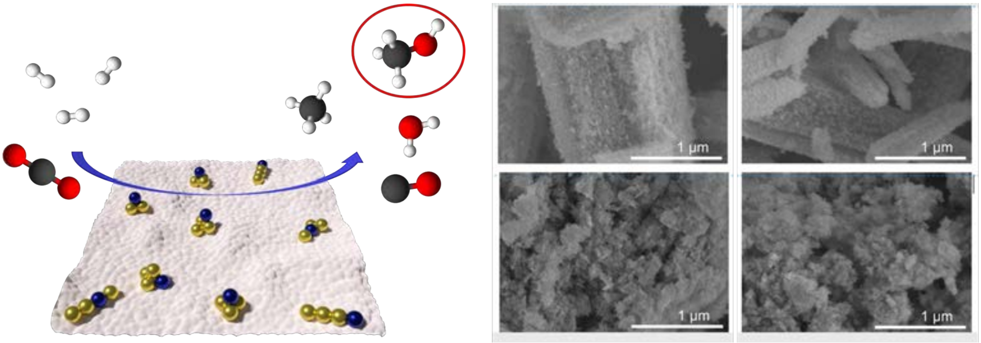

Figure 1. Left: Schematic of CO_2 convesrion on subnanometer clustes. Right: Iron-oxide supports with variable morphology – supports for nanopatrticulate catalysts.

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Partially substituted perovskite-type oxide catalyst prepared by thermal decomposition of heteronuclear metal cyano complex

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Keywords: perovskite-type oxide, cyano complex, A-site substitution, themal decomposion

Perovskite-type oxide (ABO_3) catalyst is attractive much attention in the field of environmental-friendly catalytic reactions: not only complete oxidation of hydrocarbon and CO, but also dry reforming reaction (CH_4+CO_2=2CO+2H_2) utilizing CO_2 captured [1]. We have reported that ABO_3 catalyst can be prepared by thermal decomposition of heteronuclear cyano metal complex precursor (CN method) [2]. This novel method provided high surface area- and high homogeneous-ABO_3 catalyst because of structural similarity between precursor and product (Fig. 1(A)). Such a high surface area is considered to come from the formation of pore during the thermal oxidation process in CN method (Fig. 1(B)). The ABO_3 catalysts prepared by CN method were applied to heterogeneous catalytic reactions of gas-solid, liquid-solid, and gas-solid-solid systems [3]. In the present study, we focused on the preparation of partially substituted ABO_3 catalyst ($A_{1-x}A'_xFeO_3$) by CN method for improving catalytic activity.

Heteronuclear metal cyano complex, AA'[Fe(CN)$_6$]nH_2O (A and A': lanthanide metal ion and/or alkaline earth metal ion), was prepared as a precursor of $A_{1-x}A'_xBO_3$ catalyst, followed by calcination at 500-1000 ^{o}C. The resulting oxide was characterized by XRD, BET, H_2-TPR, and XAFS methods.

$La_{1-x}Ca_x[Fe(CN)_6]nH_2O$ calcined at 700 ^{o}C showed XRD pattern assigned to perovskite-type phase in the wide range of $0 \leq x \leq 0.73$. XRD peaks due to perovskite-type structure were shifted to higher angle with increasing x. This suggests that La ion (0.136 nm) was substituted by Ca ion (0.134 nm) to yield $La_{1-x}Ca'_xBO_3$. A similar result was observed for $La_{1-x}Ce'_xFeO_3$ catalyst which was prepared from $La_{1-x}Ce_x[Fe(CN)_6]nH_2O$ precursor.

H_2-TPR measurements were conducted for $La_{1-x}Ce'_xFeO_3$ catalyst prepared by CN method. No reduction peak was observed for $LaFeO_3$ (x = 0). The large reduction peaks of $La_{1-x}Ce'_xFeO_3$ catalyst (x > 0) were observed at 200-500 ^{o}C. The intensity in the reduction peak increased with increasing x, indicating that the reduction was accelerated by Ce ion. The reduction peak of $La_{1-x}Ce'_xFeO_3$ catalyst was very similar to that $La_{0.67}Sr_{0.33}FeO_{3-\delta}$. This result supports our idea that $LaFeO_3$ catalyst partially substituted by cerium ion can be prepared by CN method.

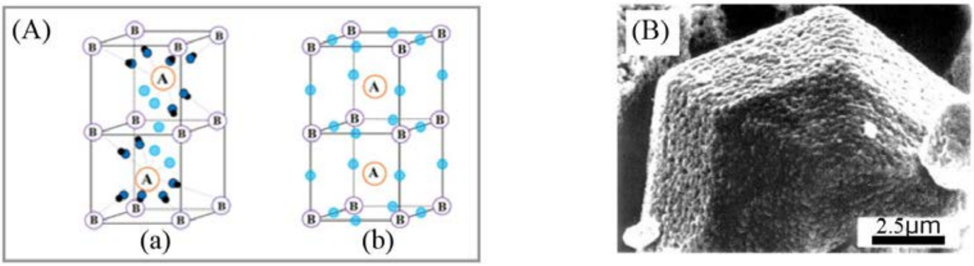

Figure 1. (A) Structures of (a) heteronuclear metal cyano complex and (b) perovskite-type oxide, (B) FE-SEM photograph of $LaFeO_3$ particle prepared by CN method.

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Manufacture, performance and stability of Ba(Zr,Ce,Y)$O_{3-\delta}$ proton-conducting materials

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Keywords: proton-conducting, manufacture, performance, stability

Proton-conducting membranes have great potential for applications in proton conducting membrane reactors for the production of commodity chemicals or synthetic fuels as well as for use in solid oxide fuel cells [1-3]. Ba(Zr,Ce,Y)$O_{3-\delta}$ perovskite oxides are of particular interest due to its proven high proton conductivity and good chemical stability [4]. In this work, fabrication of Ba(Zr,Ce,Y)$O_{3-\delta}$ samples, including thick pellet, thin tape-cast and multi-layered half-cell, were studied to prevent the typical challenges like warping, cracking and delaminating [5]. Materials with different stoichiometries were investigated, on their conductivity and chemical stability against NH_3 and H_2O, to select the most promised candidate for future compact membrane reactor. Mechanical behaviors including elastic modulus, hardness, fracture toughness and creep were investigated to warrant long-term structural stability [6-8]. Dual-phase material micro-pillar splitting behavior was for the first time reported and interpreted according to the post-test slice-by-slice FIB milling for in detail microstructure observation (Fig. 1). Thus, a systematic investigation on Ba(Zr,Ce,Y)$O_{3-\delta}$ materials was carried out to pave the road towards widespread application of proton-conducting membranes.

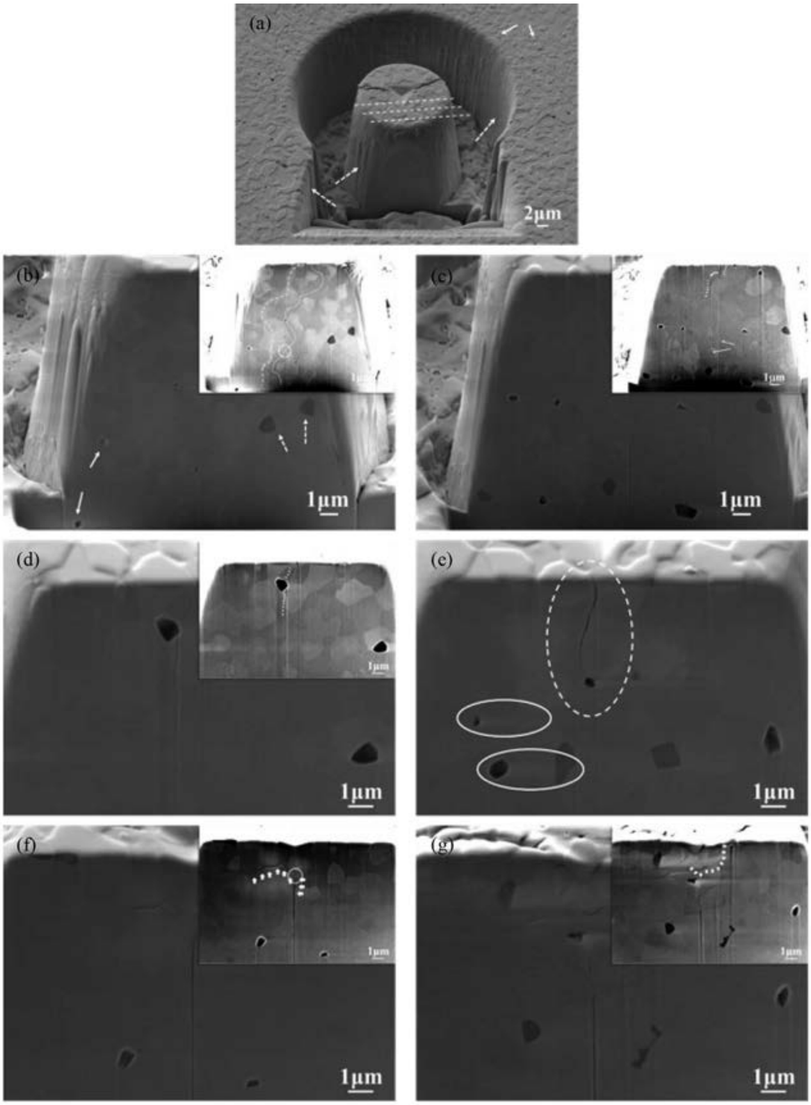

Fig. 1 Slice-by-slice FIB milling of pillar with one kink. (a) Firstly, a window was milled. The solid arrows mark blister-like morphologies. The curtain artifacts, straight down to the pillar bottom, is marked by dashed arrows. Further FIB milling was performed to follow the direction of the 3rd crack, as marked by dashed lines. (b) The solid arrows indicate pores, and the dashed arrows mark Ni exsolution. The dashed and the dotted line mark the individual phases' connections of GDC15 and BCZ20Y15, respectively. The circle marked region in the line demonstrates a path although narrow but indeed connected in spatial. (c) The long arrows mark the FIB curtaining artifact. The short arrows mark that crack propagation stops at GDC15, and then continues to propagate in BCZ20Y15, as marked by the curved arrow. (d) The crack propagates through BCZ20Y15 towards pores and deflects after encountering the pores (marked by the short arrows). (e) Crack deflection due to pores (dashed circle). Fuzzy bands, marked by the solid circles, due to charging and drift. (f) The median and radial cracks are marked by short arrows. The location of the initial crack nucleation was marked by a circle. (g) The plastic zone, marked by the short arrows.

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T3.3 Geopolymers, Inorganic Polymer Ceramics and Sustainable Composites

Additive manufacturing of geopolymer and geompolymer composites

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Keywords: geopolymer, bionic structure, additive manufacturing

Additive manufacturing of geopolymers with desirable patterns, compositions, and properties holds great promise for sustainable construction materials, porous adsorbent, and high-temperature ceramics. Current research mainly focuses on the rheological behavior of geopolymer slurry, 3D printing of geopolymer with high resolution, and hierarchical structures. In this paper, we reported a universal method to realize direct ink writing of geopolymer materials regardless of alkaline cation types. Then geopolymer of bionic structures were prepared and strengthening and toughening mechanisms were investigated. Current results proved that 3D printing together with bionic-structure designing provide a novel method for the composites of lightweight, high strength & toughness, and superior impact resistance, which would lead to a resurgence of interest in new lightweight and reliable structure design strategies.

Organic-based synthesis of geopolymers and conversion to ceramics

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Keywords: geopolymers, aluminosilicates, alternative forming methods, geopolymer-derived mullite, other geopolymer compositions

Alkali geopolymers are a facile forming route for alkali aluminosilicate ceramics because they are formed as fluids and crystallize upon heating to about 1000 °C. It is also possible to replace the alkali cations by an ion exchange process, expanding the number of ceramic compositions that can be made while taking advantage of the versatility in forming afforded by geopolymers. However, the ion exchange process is very slow for small bodies and entirely impractical for pieces thicker than a few millimeters. This thesis investigated the synthesis of geopolymers with organic bases rather than inorganic alkali hydroxides. This would avoid the use of alkali cations entirely and greatly widen the range of ceramics formable via geopolymers. The successful organic base tested was guanidine, for its ability to form geopolymers with $Al_2O_3SiO_2$ ratios of 1:2 and 1:4 as well as 3:2 to match the composition of mullite, a common ceramic. Guanidine was successful, causing reaction at room temperature and producing bodies with atomic structures and microstructures similar to the equivalent sodium geopolymer compositions.

Crystallization of the organic based geopolymer occured upon heating to 1600 °C. The Al_2O_3•2 SiO_2 and Al_2O_3•4 SiO_2 compositions produced mullite + glass and the $3Al_2O_3$•$2SiO_2$ compositions became almost pure mullite. The amount of porosity and crystal morphology varied with the organic base, overall composition, and choice of precursors used to reach the mullite composition. The use of organic base geopolymers for producing non-mullite ceramics was demonstrated by the synthesis of cordierite (2 MgO•$2Al_2O_3$•$5SiO_2$) from a guanidine, metakaolin-based geopolymer.

A CO_2 laser sintering method is extremely efficient in terms of processing time. While an oven may take hours to reach the desired temperature, a laser can achieve the same temperature in just a few seconds. After laser sintering, a notable contraction of the mullite precursor composition, geopolymer sample was observed, which can indicate a good densification and proved the effectiveness of the method used seen in Fig. 1.The microstructure of the grains was observed to take the form of needles which were evenly dispersed across the entire surface of the sample.

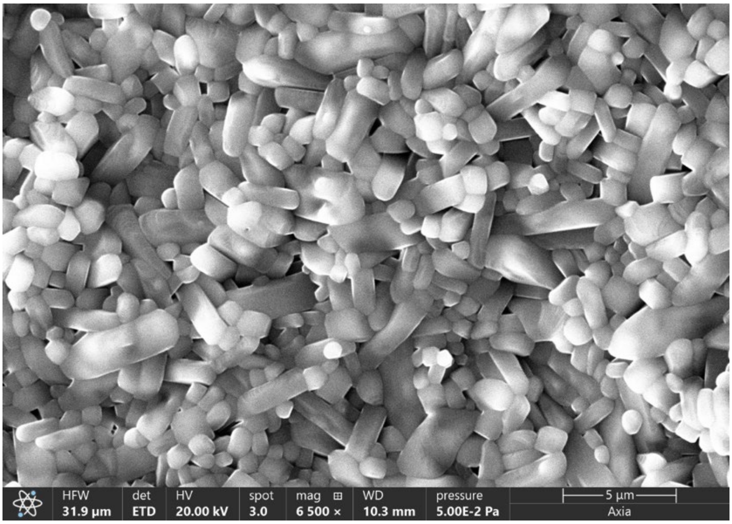

Fig. 1. SEM micrograph of laser-sintered, organic-based geopolymer converted into mullite needles.

Using one-part geopolymer to development rapid-setting repair materials and its application

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Keywords: geopolymer, repair materials, high early strength

Geopolymer materials have been developed for more than 35 years of development. In contrast to Ordinary Portland cement (OPC), geopolymer materials have numerous excellent properties, including high early strength, nice durability, and lower carbon dioxide emissions. Consequently, geopolymer materials hold significant promise as substitutes for OPC. In addition, geopolymers' high early strength characteristics are very suitable as repair materials.

The conventional method for producing geopolymers involves blending alkaline solutions with aluminosilicate materials. However, the handling, transportation, and storage of alkaline solutions pose considerable challenges for factories, thereby restricting the widespread adoption and market acceptance of geopolymer materials.

This study focuses on using solid-state alkaline activator to develop one-part geopolymer. This study will develop [Geopolymer paste - Repair materials], and [Geopolymer mortar - Repair material]. The experiment parameters will discuss the effect of solid-state alkaline activator dosage amount, solid activator fineness, and GGBF slag/Coal fly ash ratio on the mechanical and workability properties of geopolymer materials.

According to the experiment results, the compressive strength of [Geopolymer paste - Repair materials] can be reached over 30 MPa after curing for 4hr. The compressive and flexural strength of [Geopolymer mortar - Repair material] can reach over 30MPa and 4.5MPa, after curing for 4hr. The shrinkage rate of mortar can be controlled at lower than 0.1%.

This study also conducts repair performance test of [Geopolymer mortar - Repair material] [Geopolymer mortar - Repair material]. The repair test included two parts. First part, analysis of the compressive strength repair rate of the OPC specimens after adhesion [Geopolymer mortar - Repair material] with different slant angles. Second part, using [Geopolymer mortar - Repair material] as pavement repair material and test the repair properties on site. According to the experiment results, the repairing rate of [Geopolymer mortar - Repair material] can be higher than that of commercial products no matter what the slant angle(30^o, 45^o, 90^o) is in the repair test. About on-site repair test, it is easy to operate and requires less manpower when using [Geopolymer mortar - Repair material]. Through the falling weight deflection test, it was found that pavement after using [Geopolymer mortar - Repair material] to repair it, can meet the strength requirements after curing for 4 hrs. After curing for 1 day, its strength can be significantly higher than current pavement.

The research has successfully developed a new type of repair material by using one-part geopolymer technology. It is hoped that the practical application can be carried out after more testing in the future.

Novel applications of geopolymers and alkali-activated materials in water and wastewater treatment

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Keywords: alkali-activated materials, geopolymers, wastewater treatment, water treatment

The application of geopolymers and alkali-activated materials (AAMs) in water and wastewater treatment has attracted increasing interested in the last approximately 20 years. It revolves around the flexibility in their preparation; low-energy synthesis conditions; possibility to use several silicate, aluminosilicate, or alkaline wastes as raw materials; and promising technical performance. The properties of geopolymers and AAMs can be tailored by changing their raw materials, preparation method, or by applying post-synthesis physicochemical modifications.

Recent developments in the synthesis and modification methods of geopolymers and AAMs for water and wastewater treatment applications are discussed. Of synthesis methods, a combined granulation–alkali activation–direct foaming process is presented which enables to obtain highly porous alkali-activated granules in a simple set-up utilizing a granulator. This process can be also expanded to prepare porous granules so that the AAM phase acts as a binder to another powdered raw material. Of modification methods, the use of silane coupling agents are discussed.

Finally, novel applications of geopolymers and AAMs addressing timely water pollution issues are discussed. In these applications the porosity and modifiability of geopolymers and AAMs are exploited to obtain the required properties. For instance, in water disinfection, microplastics separation, and abatement of micropollutants, silver nanoparticles, superhydrophobic coating, or catalytically active metals are introduced to the materials. The performance results are highly promising indicating that geopolymers and AAMs have high potential in environmental engineering.

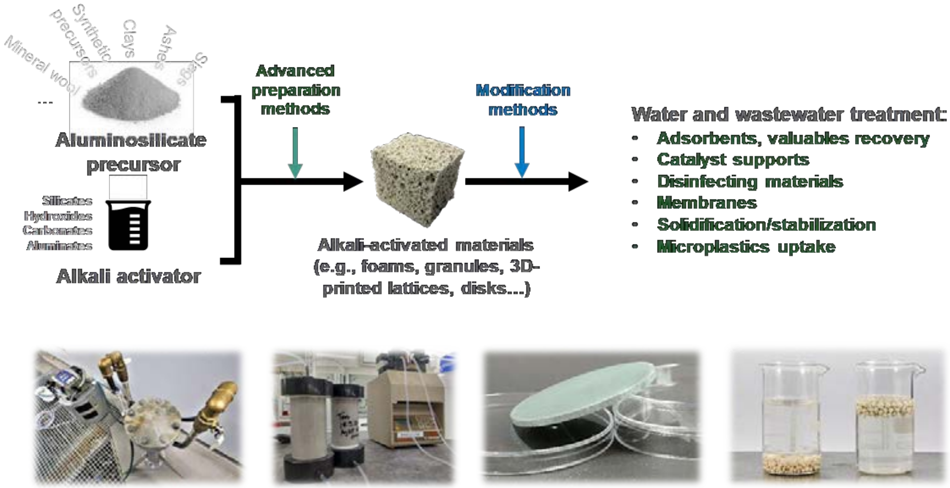

Fig. 1. Preparation, modification, and applications of geopolymers and AAMs in water treatment.

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Additive manufacturing of geopolymers

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Keywords: additive manufacturing, geopolymers, porous ceramics

Geopolymers possess a chemical composition similar to zeolites, intrinsic micro- and meso-porosity and have ion-exchange capabilities; these features make them highly interesting for environmental applications as sorbents and catalysts for multiple reactions. Moreover, the possibility of room to low temperature consolidation, low CO2 emissions and the fact that they can be obtained from waste make geopolymers attractive from the processing point of view.

Our group has been exploring Direct Ink Writing as an additive manufacturing route for hierarchically porous components comprising geopolymers as active material and/or as a matrix for active fillers such as zeolites and activated carbons. Lattices and other structures with designed macroporosity above 50%vol were fabricated and characterized in terms of microstructure, mechanical properties, specific surface area and permeability. Specific compositions and functionalization protocols were developed for selected applications, including biodiesel production catalysis, CO_2 adsorption, water purification from cationic and anionic pollutants as well as pharmaceuticals.

Large scale binder jetting of geopolymer-based components has also been carried out, for fire protection applications in tunnels, adding either metakaolin or a reactive slag to the powder bed and generating parts by selective jetting of an alkaline solution. In addition, temperature-resistant molds for the production of blown art glass parts have been successfully manufactured.

Geopolymers based adsorbents for the selective separation of CO_2 and eutrophication pollutants

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Keywords: geopolymer, adsorbents, separation, pollutants removal

Geopolymers are increasingly studied as alternative, economical and eco-sustainable solid adsorbents for the removal of pollutants from liquid or gaseous systems [1-3].

These materials are very versatile and through the optimization of the stoichiometry, phase composition (also in composites), and structural and textural properties (directly linked to micro-macrostructure) they can be customized for specific adsorption purposes.

In particular several geopolymers and composites have been produced and characterized, for separation and purification applications, exploiting adsorption mechanisms for the capture of CO_2 or nitrogen or phosphorous-based pollutants in wastewater, comparing them to benchmark adsorbents commonly used at large scale.

Particular attention was paid on the correlation between material formulation, properties and performances for the targeted application, in order to identify the most suitable geopolymer-based material.

The use of geopolymers offers several advantages as the possibility to customize eco-friendly materials (low energy production process) and to identify geopolymer matrices able to actively increase, in composites, the performances of other adsorbents such as zeolites, apatites, hydrotalcites.

Furthermore, from a technological point of view, the use of geopolymers allows to easily tailor the shape of the final solid adsorbent exploiting near-net shaping tecniques or through cold sintering processess.

Acknowledgments

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T3.4 Porous and Cellular Ceramics: Porosity Design and Engineering Applications

Highly porous scaffolds from direct ink writing of engineered silicone-based emulsions

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Keywords: polymer-derived ceramics, direct ink writing, bioglass, mullite, cordierite

Silicone polymers have been considered as feedstock for various silicate ceramics, when added with reactive fillers, in the form of metal oxide, hydroxide and carbonate powders [1]. A key feature is represented by the easy shaping of components by several polymer-shaping techniques, including modern additive manufacturing technologies, performed directly with polymer/filler blends, before the ceramic conversion in air. Nanosized fillers generally enable the synthesis of silicates at quite low temperature (compared with that required by conventional raw materials), in a high degree of phase purity, according to the quasi molecular mixing of the metal oxides and the silica residue left by the oxidative decomposition of silicones. However, complete homogeneity is hardly achieved and the viscosity of silicone/nanofiller pastes may be excessive. The lack of full homogeneity, in addition, generally prevents the obtainment of silicate glasses.

The present paper aims at overcoming the limitations of nanosized fillers and at offering new strategies for the synthesis of several silicate ceramics, coupled with shaping into highly porous scaffolds, by direct ink writing of silicone-based pastes. All developed scaffolds are actually ′hierarchically porous′, according to the definition of reticulated structures (from the overlapping of extruded filaments) with ′spongy′ struts (from controlled gas release). Such structure is intended to support applications in bone tissue engineering or in catalysis, depending on the adopted formulation.

In a first case study CaO precursors, such as hydrated calcium nitrate and acetate salts, are used for the sythesis of a glass (at only 700 °C) with composition resembling that of 70S30C (70 mol% SiO_2, 30 % CaO) bioglass [2]. The homogeneity required for glass synthesis is achieved according to the emulsification of aqueous solutions of the calcium salts in water-unsoluble blends of silicone polymers and organic additives. In a second case study, nearly stoichiometric mullite ($3Al_2O_3{\cdot}2SiO_2$) and cordierite ($2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$) are achieved by the thermal treatment (at 1300-1400 °C) of silicone resin embedding, in emulsion, droplets of aqueous suspensions of reactive alumina (γ-Al_2O_3), possibly added with magnesium nitrate. In all cases emulsions are supported by the use of surfactants and are directly usable as inks; the porosity of ceramics, after thermal treament, is almost linearly proportional to the water content of starting emulsions

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Porous ceramics – from processing to novel applications

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Keywords: porous ceramics, simulation, characterization, application

Cellular materials offer a wide spectrum of applications such as catalyst support structures, lightweight materials, energy adsorption or energy storage materials. Due to several ways of processing and different materials, a wide range of material properties e.g. thermal conductivity, mechanical strength or damping can be adjusted, measured and verified, with regard to the expected properties. Various techniques for processing porous ceramics and their corresponding composites independent of material are presented. Especially in heterogeneous and homogeneous porous structures and their composites, only global effective material properties can be determined and measured. For example, the knowledge on the predominating influence of the microstructure on the global properties is the key for designing materials with desired properties. To fill this gap and enable a "look-in" a microstructure model derived from µ-CT measurements (see highlights in Figure 1) carried out at certain processing steps can be used as model for FEM-calculations. Combining estimated material properties by experiment with microstructure models offers the possibility to carry out different simulations over different hierarchical levels in order to design the structures for future applications of porous ceramics.

Engineered porous ceramic structures for catalysis

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Keywords: precursor derived ceramics, engineered porosity, photocatalysis, electrocatalysis

Engineering porosities and controlled microstructures is vital in increasing the catalytic activity due to high surface area and surface volume. In this talk, I provide three examples of high engineered porosities significantly affect the catalytic properties. The first example is based on freeze casted ceria meant for catalytic applications. We fabricated porous ceria for high temperature catalytic applications that demand structural integrity accompanied by resistance to sintering and with improved gas permeability. By adopting freeze-casting technique, we demonstrated open porosities as high as 88% and catalytic activity obtained via temperature programmed reduction exemplified interesting potential of these class of engineered materials with hierarchical porosities. The second example is based on precursor derived TiO_2/SiOC based nanocomposites with highly stable anatase phase providing visible light photocatalytic activity and superior adsorption of organic dyes. The microporous and mesoporous ceramic nanocomposites with highly stable anatase phase, stable till 1200 °C exemplified interesting photocatalytic properties. With an average pore size of 6.8 nm and surface area of 129 m^2/g and pore volume of 0.22 cm^3/g, these mesoporous ceramic nanocomposites exemplified visible photocatalytic activity which was attributed to Ti-O-C/TiC bonds resulting in the reduction of band gap by 0.2 to 0.9 eV. Concomitantly, it was also found out that the heterojunctions formed amorphous SiOC and crystalline TiO_2 minimized recombination of electron-hole pairs. The third example is based on vanadium-based nanocomposites which were synthesized as oxygen reduction reaction (ORR) catalysts with the objective of elucidating the effect of microstructure changes on catalytic efficiency. High-temperature treatment of the pyrolyzed samples beyond 1300 °C induced the crystallization of β-SiC as well as VC. Furthermore, Raman spectroscopy confirmed the segregation of sp^2-hybridized, turbostratic free carbon. The samples exposed to 1300 °C revealed a specific surface area of 239 m^2/g. The electrocatalytic activity of the sample heat-treated at 1300 °C showed the best performance with respect to the ORR performance with onset potential (E_o) and half-wave potential ($E_{1/2}$) values of 0.81 and 0.72 V, respectively.

Figure

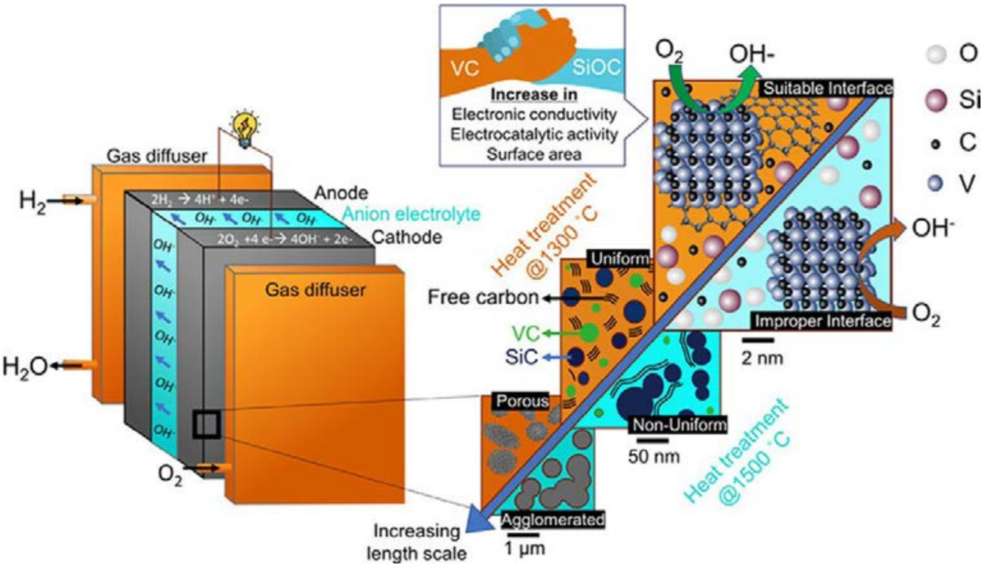

Figure-1: Electrochemical performance of SiVOC nanocomposites for the oxygen reduction reaction

Inner and outer strut surface area of reticulated foams – not just an interface to the surroundings

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Keywords: reticulated foams, hierarchical porosity, functionalization

Reticulated foams - made by impregnation of a polymer foam template - possess a unique hierarchical pore structure. Visible to the naked eye with a diameter of 1 mm to 5 mm, the foam cells constitute the actual foam structure. These cells are enclosed by the respective solid phase forming an irregular framework of struts and vertices. Due to the manufacturing process, the struts and vertices are hollow and contain a second class of porosity - the hollow strut cavities with a dimension of approximately 0.2 mm in diameter. The hollow strut cavities are typically connected to the cell pores by longitudinal cracks in the strut material. A third class of porosity is found inside the strut material itself: submicron pores, adjustable in size by the densification process of the solid phase during heat treatment.

These different pore classes give a unique opportunity for functionalization of reticulated foam structures. Examples are infiltration techniques for hollow-strut cavities filling for improvement of the mechanical strength, capillary force-driven impregnation processes of the submicron strut material porosity for additional functionality generation, e. g. electrical conductivity, or application of active-coating processes on the strut´s inner or outer surface. Nevertheless, for a successful functionalization of a porous structure the accessibility of the respective pore or surface area is mandatory. The techniques of functionalization, e. g. by infiltration, or crystallization coating, are established and well understood. However, the adaption and optimization of the porous structure, in order to provide accessibility of the pores and the surface areas, provide significant room for R&D.

Therefore, the talk will give examples of functionality addition to ceramic (and metal) foams, and it will focus on the tailoring of the structure of reticulated foams, for example for the improvement of the accessibility of the hollow strut cavities by generating aligned lamellar strut pores.

Near-net size fabrication of porous ceramics through controlling shrinkage during drying and sintering

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Keywords: porous ceramics, near-net size fabrication, porosity, shrinkage

In the preparation process of porous ceramics, especially in the drying and sintering stages, large volume shrinkage is often accompanied, which affects the high porosity and comprehensive properties of porous ceramics, and increases the subsequent processing costs. Therefore, it is very important to control and reduce the shrinkage in the preparation process and realize near net size preparation for high performance porous ceramics. This report focuses on some specific measures to control and reduce the shrinkage in the preparation process of porous ceramics, so as to realize the near net size preparation of porous ceramics. First, by selecting the solvent with high saturated vapor pressure and low surface tension, the shrinkage of porous ceramic green body in molding and drying is reduced by using gelcasting process. Secondly, by adding shrinkage compensating agent, the shrinkage of porous ceramics can be reduced effectively, and even zero shrinkage can be achieved, so as to realize the near net size preparation of porous ceramics. Finally, in the process of reactive sintering of porous ceramics, low-density materials are formed to generate volume expansion, which counteracts the sintering shrinkage, thus realizing the preparation of near net size porous ceramics.

T3.5 Advanced Sensors for Energy, Environment and Health Applications

Influence of electrode, electrolyte and thickness of electrode on the sensitivity of mixed-potential sensor for NO2 and CO gas

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Keywords: gas sensor, mixed-potential, solid electrolyte, sensing electrode composition, sensitivity, NO_2, CO

In this paper, we will highlight the simplicity and versatility of the mixed-potential sensors for sensing environmentally harmful and toxic gases such as nitrogen dioxide (NO2) and carbon monoxide (CO). We have used different oxide ion conducting electrolyte compositions bearing different crystal structures, different compositions and structure of sensing electrode and their thickness for designing the solid-state gas sensors. The influence of various physical, structural and chemical parameters of the solid electrolyte and sensing electrode on the performance of sensing ability of the gas sensor to various target gases and potentially interfering gases prevailing in the combustion process emissions have been investigated. The results of sensor response has been studied over a range of temperature and concentration of target gases in order to demonstrate the efficacy of each of the mixed-potential sensor. The sensors investigated in the series of our investigation primarily carried out by the researchers demonstrated that the sensors exhibited high selectivity, high sensitivity, low response time and a reproducible response to target gases. We will demonstrate that the composition of the electrode and thickness does play an important role in dictating the response characteristics of the mixed-potential gas sensors. A typical figure showing the sensing response of the mixed potential sensor to NO2 gas and potential interfering gases is shown in the adjacent diagram.

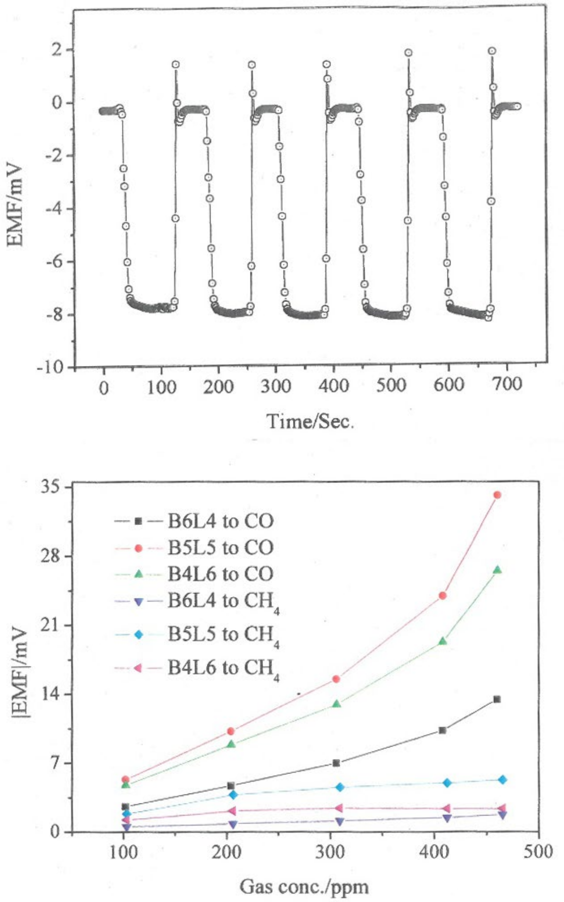

Figure 1: Response of CO sensor at 615 C (Top) and Response of three different electrolyte compositions to CO and CH4 gases at same temperature (Bottom).

Acknowledgments

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T3.6 ADVANCED MATERIALS AND MEMBRANE TECHNOLOGIES FOR SUSTAINABLE WATER PURIFICATION AND DESALINATION SYSTEMS

Preparations and characterizations of low-cost porous ceramics for water purification

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Keywords: microfiltration, porous ceramic membranes, low-cost

Recently porous ceramic membranes have become a subject of special interest due to their outstanding thermal and chemical stability. Porous ceramic membranes and reticulated porous ceramics can be applied to wastewater remediation and air cleaning, respectively. To alleviate the manufacturing cost issues of porous ceramics, recent research is focused on the utilization of low-cost raw materials. In this study, the authors introduced porous ceramic membranes and reticulated porous ceramics prepared from low cost raw materials such as diatomite, kaolin, pyrophyllite, and silicon carbide. And the authors report the results of our efforts to determine whether the authors could prepare a low-cost ceramic membrane that could control the average pore size, the largest pore size, the flexural strength and the air/water permeability effectively. The pore characteristics of the specimens were studied by scanning electron micrography, mercury porosimetry, capillary flow porosimetry, and a dead-end microfiltration system with particle counters.

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Repeated stacking of Ti_3C_2 nanosheets on ceramic membranes for improving organic solvent retention in semiconductor wastewater

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Keywords: ceramic membrane, MXene, nanomaterial, semiconductor wastewater

Ceramic membranes, known for their exceptional chemical stability, have found practical applications in the treatment of semiconductor wastewater. In this study, we have developed an innovative ceramic nanofiltration membrane featuring a nanochannel network created by two-dimensional (2D) nanomaterials, enabling high-performance separation and permeation. This accomplishment is realized through precise control of the size and thickness of MXene nanomaterials, which can be tailored using various coating conditions. The repeated stacking of MXene nanosheets onto the ceramic membrane substrate resulted in the formation of additional nanochannels and surface chemistry modifications, leading to significant enhancements in pollutant removal. These MXene-coated ceramic nanofiltration (NF) membranes significantly improved the removal efficiency of representative organic contaminants in semiconductor wastewater when compared to the pristine ceramic membrane. It enhanced the removal efficiencies by 4.2 times for dissolved silica, 3.7 times for dimethyl sulfoxide (DMSO), and 2.5 times for isopropyl alcohol (IPA). Furthermore, the MXene ceramic NF membrane exhibited exceptional fluoride removal capability, achieving approximately 99.1% removal, in addition to organic solvents. These findings not only help meet regulatory standards for wastewater discharge but also provide valuable insights into the transport behaviors of contaminants and their separation mechanisms. This innovative approach brings us one step closer to efficient and sustainable solutions for semiconductor wastewater treatment.

Acknowledgments

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Integration of electrospinning and additive processing for energy harvesting and atmospheric water using nature-inspired shapes

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Keywords: harvesting, energy, water, future, transdisciplinarity, exponential technologies, biomimicry, 3D printing, electrospinning, sustainability

Strategic integration of synthesis methods has been used to develop new and unique devices and is reported in this presentation. One of the strategies is employing digitally controlled fabrication by combinatorial synthesis viz. electrospinning and 3D printing/additive processing. Using the integration of configurations, elaborate shapes, and patterns are printed with mesostructured stimuli-responsive electrospun membranes, allowing for in-plane modulations, and compensations due to internal interlayer stresses induced by swelling/shrinkage or mismatch, thus guiding shape morphing behaviors of electrospun membranes to adapt to environmental changes. Recent progress in combinatorial processing includes materials and scaffold constructs that are used for tactile and wearable sensors, filtration structures, sensors for structural health monitoring, biomedical scaffolds, tissue engineering, and optical patterning, among many other applications to support the vision of synthetically prepared smart material designs that mimic the structural aspects with digital precision. A recent method called 3D jet writing was recently reported that propels electrospinning to adaptive technologies for manufacturing scaffolds according to user-defined specifications of the shape and size of both the pores and the overall geometric footprint. This presentation focuses on two specific applications: energy and atmospheric water harvesting. Recent advances in next-generation triboelectric nanogenerators (TENG), the integration of finite-state machines (FSM), and built-in edge computing in onboard IoT devices have reduced the energy requirement, thus shifting the energy storage requirements to built-in power generation and ambient sources. The first part of the presentation describes the synergetic integration of exponential technologies in several examples that minimize energy storage and reduce energy consumption. Some other applications that include IoTs, IoB, and onboard energy harvesting devices are tactile sensing for biomedical applications, smart agriculture, and transportation logistics. A brief discussion of the concerns elaborating on privacy with IoT and IoB will be presented. The second part of the presentation articulates the future of water from a holistic and futuristic standpoint including the use of exponential technologies and transdisciplinary research by using the nature-inspired solution while mitigating the micro/nano plastics footprint in the environment. By mimicking nature and using a strategic combination of electrospinning and 3D printing, unique shapes and configurations to capture atmospheric water are presented.

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T4 Cross-Cutting Materials Technologies

T4.1 Computational Design and Modeling

Transition from computation to data-driven materials design

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Keywords: Gd doped Ceria, oxygen ion transport, multiscale calculation, standard vocabulary and schema for materials research data

For a long time, materials science has relied on experimental and computational studies for materials processing, structural characterization, and property analysis. However, as research data accumulates and the digital working environment, including machine learning technology, becomes more accessible, a significant shift is occurring in materials research: from causality-based to correlation-based knowledge creation. My research interest extended recently from computational study of materials phenomena to the structure of materials research data.

In the first part of this presentation, I will discuss recent computational research on oxygen ion transport in doped ceria. Trivalent dopants within the CeO_2 lattice generate oxygen vacancies crucial for oxygen diffusion. However, these dopants also have two adverse effects on oxygen vacancy migration: they trap oxygen vacancies to the dopant and block vacancy migration by increasing the energy barrier for vacancy transport. We conducted a study on the oxygen diffusion in Gd-doped CeO_2 with La or Y co-dopants using molecular dynamics (MD) simulations. This allowed us to compare the behavior of vacancy trapping and blocking caused by the dopants. The trapping was characterized through statistical analysis of the coordination number (CN) of cations on a large scale. To investigate the blocking effects caused by the dopants, we utilized first-principle nudged elastic band analysis. Our findings indicate that the oxygen diffusion, as measured by the mean square displacement of oxygen in doped CeO_2, is enhanced when the trapping of oxygen vacancies is reduced through co-doping. However, the changes in the energy barrier against oxygen migration in the co-doped lattice do not consistently align with the diffusion behavior. This result clearly demonstrates that oxygen ion transport is primarily governed by the trapping of oxygen vacancies[1].

In the second part of this presentation, I will discuss recent efforts in Korea towards standardizing materials research data. Standardizing data keywords, types, and numerical units poses a significant challenge for efficient data retrieval from various sources. Additionally, connecting data on material composition, structure, process peculiarities, and performance across different application fields is crucial for materials design using machine learning methods. Machine learning models will be developed by studying the relationships among these characteristics, necessitating their implementation in the database's data structure. The Committee for Materials Research Data in Korea has proposed a materials data structure capable of consistently managing various materials research data. They have introduced the concept of a "materials system" as a standard scheme for materials research data that can handle data from a wide range of applications. Based on this data schema, the Committee has published a dictionary of standard materials vocabulary, available on the GitHub platform[2].

Acknowledgments

Committee for Materials Research Data is supported by the National Research Foundation through the National Center for Materials Research Data in Korea.

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Hierarchical thermal transport in complex-structure ceramics

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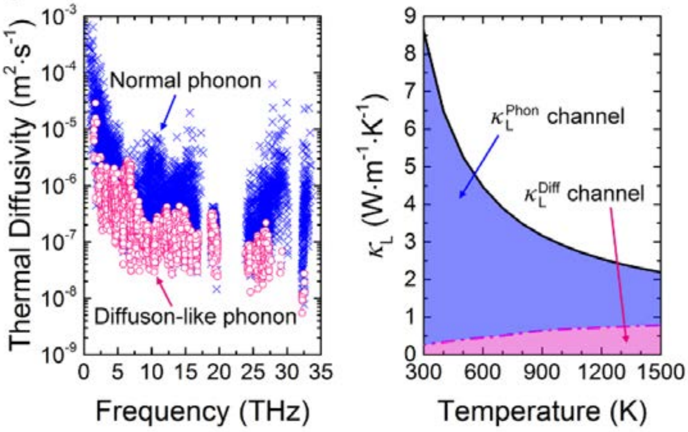
Keywords: thermal transport, phonon, density functional theory

The mechanism of thermal transport for complex-structure ceramics is a long-standing challenge in the community of thermal management. Many complex-structure materials show glass-like temperature (*T*) dependence of lattice thermal conductivity (κ_L), particularly at high-temperature ranges, which contradicts the $\kappa_L \sim T$ dependency of crystallines predicted from the traditional Peierls-Boltzmann transport theory (PBE). This intriguing puzzle calls for theoretical and computational advances beyond the PBE framework. In this study, the mechanisms of thermal transport for some prototype complex-structure ceramics, such as rare-earth silicates, pyrochlores, etc., are comprehensively studied. It is found that there coexist well-defined phonon modes, which transport heat in the propagative way; together with large amounts of strongly perturbated modes whose mean free path is smaller than or comparable to the interatomic spacing, which could be defined as "diffuson-like phonons" and transfer heat in the diffusive way. Then, a dual-phonon thermal-transport theory is proposed to account for combined contributions from both propagation and diffusion thermal-transport channels, and a computational workflow for the calculation of κ_L is established. The results are expected to advance the theoretical understanding and computational paradigm for the κ_L of complex-structure ceramics, and cast light on the thermal management in many fields such as thermoelectrics, high-temperature protective coatings, etc.

Figures



Hierarchical thermal transport from different channels in $Yb_2Si_2O_7$.

Additive kernel based methods for stable machine learning from sparse data: From materials informatics to orbital-free DFT

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Keywords: machine learning, Gaussian process regression, materials informatics, large-scale ab initio modeling

Machine learning (ML) has become increasigly popular as a means to predict materials properties from descrioptors of chemical composition and structure ('features'). ML is also actively used to improve modeling methods, in particular for the construction of force fields and recently also for DFT functionals including kinetic energy functionals (KEF) that hold the promise of routine large-scale ab initio modeling with orbital-free DFT.

In all these applications, the ML problems are typically of regression type (or can be cast as such), and kernel regressions and neural networks (NN) are most widely used types of methods for them. These methods have high expressive power but, being general, require more data than physically motivated approaches and suffer from lack of insight. In many practically important settings, data are sparse; in particular, as the dimensionality of the feature space *D* increases, sampling is bound to be sparse, and this cannot be solved by adding more data (the 'curse of dimensionality'). Specifically NNs also suffer from a large and growing with *D* number of nonlinear paramaters, which causes high CPU cost and overfitting. Kernel methods, being effectively linear regressions with nonlinear basis functions, appear then particularly appealing as combining high expressive power and stability.[1]

We will demonstrate how in high *D* and with sparse data, kernel regressions lose their superior expressive power and become equivalent to low-order polynimial fits,[2] and the property of locality of commonly used Matern type kernels (which are used for this property) is lost.[3] Finding optimal hyperparameters in this regime also becomes difficult.[4]

We will show that these problems can be effectively addressed by using orders of coupling expansions achieved by using additive kernels.[5–8] This approach also help generate insight while preserving the generality of the methods. Additive kernels also allow obtaining an NN type representation without nonlinear optimization and with optimal neuron activation functions.[9,10]

We wills show examples from materials informatics (machine learning bandgpaps of double perovskites with a better accuracy than heretofore)[11] and from machine learning of KEFs.[7,12]

Acknowledgments

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Modeling heat transfer in porous and composite ceramics with applications to CMC processing and thermal protection systems

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Keywords: heat transfer modeling, image-based modeling, porous ceramics, ceramic composites

The research on porous and composite ceramics developed to withstand high thermal fluxes at high temperatures involves important questions on thermal transfer modeling. Indeed, it is of crucial importance to obtain a correct assessment of the thermal gradients and heat fluxes in these materials, not only during their use as thermal protection systems or heat converters but also during their manufacturing by methods involving thermal gradients.

This talk will address some of the underlying challenges of heat transfer modeling related to this context:

(i) how to obtain an effective, homogenized thermal conductivity from a composite material's structural description by micrographs *without using the classical periodic homogenization techniques*? We will describe a novel and efficient technique to address this question in the frame of Finite Element computations.

(ii) how to efficiently simulate mixed conductive/convective heat transfer in large, complex, 3D images? A solution based on a hybrid Monte-Carlo/Random Walk method [1] will be described and discussed.

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Modeling defect-enhanced ion track formation in perovskites

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Keywords: perovskite, ion track, thermal spike, ion irradiation, modeling

Oxide perovskites exhibit fascinating properties that identify them as key materials for the next generation of multifunctional devices, and ion-beam modification can be used to tune functionality. While it is well-established that atomic-level defects are created by elastic energy transfer from ions to atomic nuclei, S_n, the effects of inelastic energy loss to electrons, S_e, is more complicated. Pre-existing defects stimulate amorphous track formation at 300 K in $SrTiO_3$ and $KTaO_3$ irradiated with high-energy ions with S_e values above a threshold [1-5]. The nanotrack cross-sections increase with S_e and level of pre-existing disorder, and the threshold in inelastic energy loss, S_{et}, decreases with increasing disorder. In the case of pristine $KTaO_3$, temperatures greatly exceeding the melt temperature (i.e., larger melt radii) are required to form observable amorphous tracks in order to offset the significant rate of radial recrystallization during quenching [6]. Insights from the application of the analytical thermal spike model [6] to ions in the low velocity regime suggests that increasing the concentration of pre-existing defects causes a decrease in effective melt temperature (decrease in energy for melting) and an increase in efficiency of track formation. Molecular dynamics simulations combined with the inelastic thermal spike model confirm that the formation of these amorphous tracks is due to melt-quenching along the ion trajectory [8-10]. Furthermore, the increase in stored energy with increasing level of pre-existing disorder effectively decreases the energy required to melt along the ion trajectory.

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Physical properties and irradiation-energy transport in metal diborides for extreme environments

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Keywords: radiation effects, transition-metal diborides, high-entropy materials, irradiation-energy transport

Today's technologies rely on an increasingly complex palette of materials, with individual materials made from increasingly complex mixtures of chemical elements. Extreme conditions, such as high temperature, high current, high pressure, and high radiation environments, can push materials from thermal equilibrium to far-from-equilibrium and pose unique challenges to predict their performance. Knowledge on how chemical disorder resulting from multi-principal elements, such as in high-entropy materials (HEMs), can be utilized to tailor physical properties, to enhance or control energy transport, and to improve irradiation tolerance. Such modifications or element substitution can lead to the design of complex materials with specific functionality and improved performance, thus offering opportunities for materials discovery.

In this presentation, physical properties and irradiation response in a high-entropy transition-metal (TM) diboride $Hf_{0.2}Nb_{0.2}Ta_{0.2}Ti_{0.2}Zr_{0.2}B_2$ and its subsets have been investigated and are discussed in terms of valence electrons and lattice distortion. Surprisingly, instead of generally expected ceramic behavior, the predominant mechanism for energy conduction in these TM-diborides is through electrons, with transport properties similar to some high-entropy alloys. The irradiation response of these TM-diborides is characterized using grazing incidence X-ray diffraction and electron energy loss spectroscopy coupled with scanning transmission electron microscopy. Black dot dislocation loops are visible at low doses, whereas dislocation networks are observed with increasing fluence. While up to ~4% volume expansion is determined in these diborides, the crystalline structure remains stable under room temperature irradiation, preserving the hexagonal AlB_2 phase.

Composition complexity in HEMs gives rise to local chemical disorder and a diverse range of tunable bonding environments that are not typically possible in conventional materials. Substitution disorder is expected to modify defect dynamics and energy dissipation processes. Despite the potential of these materials, there is a lack of systematic studies on the relationship of composition-structure-property. Chemical disorder in HEMs and the associated physical properties (e.g., electrical resistivity, thermal conductivity and thermal expansion) have yet to be understood. To reveal the atomic or electronic structure responsible for differences in material properties, a detailed characterization of elemental distribution, the accompanying electronic structures and lattice distortion, as well as the corresponding scattering mechanisms and energy transfer, are crucial in determining the impact of various species. The evolving comprehension of complex materials at the atomic and electronic levels provides a compelling pathway to investigate their chemical and physical properties. This, in turn, opens numerous exciting research opportunities in materials science.

T4.2 ADDITIVE MANUFACTURING & 3D PRINTING TECHNOLOGIES

Tailoring microstructure and architecture of 3D-printed advanced ceramics: challenges and opportunities

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Keywords: 3D-printing, alumina, texture, damage tolerance

The combination of ceramics with other materials has enabled the fabrication of hybrid systems with exceptional structural and functional properties. However, a critical issue affecting the functionality and reliability of these systems is the initiation and uncontrolled propagation of cracks in the brittle ceramic parts. Bio-inspired design concepts in current ceramics engineering have proved successful in obtaining highly reliable ceramic materials with enhanced fracture resistance. For instance, tuning the location of "protective" layers within a ceramic multilayer architecture can significantly increase its fracture resistance, while retaining high strength. The use of tailored residual stresses in embedded layers can act as an effective barrier to the propagation of cracks from surface flaws, providing "damage tolerance". Moreover, by orienting (texturing) the grain structure, similar to the organized microstructure found in natural systems such as nacre, crack propagation can be controlled within the textured ceramic layers. In this contribution, the potential of employing lithography-based ceramic manufacturing (LCM) process to design multi-phase layered architectures is presented, which can contribute to the fabrication of future 3D ceramic components with enhanced damage tolerance. Several examples are presented: (i) A multi-material approach to combine alumina-zirconia layers sandwiched between pure alumina layers, yielding a characteristic strength higher than 1 GPa on the multi-material system, compared to ~650 MPa in monolithic alumina. (ii) 3D-printed highly textured alumina fabricated combining the LCM technology and Templated Grain Growth (TGG) during sintering to provide higher toughness while retaining strength, and (iii) 3D-printed components with outstanding thermal shock resistance owed to the embedded compressive layers. These studies open new possibilities in the fabrication of complex 3D ceramic-based multi-material geometries with tailored microstructures, which could be a new pathway for designing complex parts with outstanding mechanical strength and reliability.

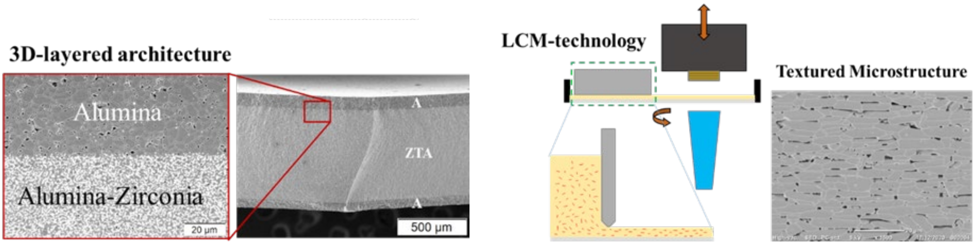

Figure 1: Examples of 3D printed multi-material architectures with tailored microstructures.

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Ceramic AM: Is there still room for academic research?

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Keywords: additive manufacturing, ceramics, multi-material

With their ability to produce functional parts directly from CAD data, additive manufacturing (AM) technologies have an enormous potential for industry. The ultimate advantage of AM over traditional manufacturing methods is the freedom of design which makes it possible to introduce new features in the design of parts without the limitations of conventional forming techniques.

Vat photopolymerization (VPP)-based processes are the most widespread AM technologies for high-performance ceramics, due to the high precision and good materials properties, which are achieved through the high green density because of the use of highly filled slurries but this technology cannot be used for all applications. Lithography-based Ceramic Manufacturing, a process from the family of VPP techniques, has already been established for fabricating ceramic materials and is already pushing strongly into the ceramic industry. This presentation will give an overview of the status quo and describe some innovative industrial applications, which already use ceramic AM. Industry reports are already forecasting that the market for ceramic 3D printing will grow multiple times over the next few years and the implementation of ceramic AM will move forward in new applications and domains.

This contribution will present exemplary use cases where AM was able to combine these material properties with the profit-oriented requirements of scaled-up industrial mass production. These use cases, including a successful manufacturer whose annual output now reaches 4 million parts, will show how companies have already integrated 3D printing into their workflow and have entered into serial production. An assessment of the potential of ceramic 3D printing will demonstrate how far serial production in ceramic additive manufacturing has already come, while also highlighting current limitations and giving an outlook into the future.

It seems that ceramic additive manufacturing has already reached its peak and no further academic research is necessary to push the frontiers of this technology. However, there are still new applications to be developed, and academic research will be crucial to successful; The list is long and ranges from simulations, modeling and design to material and process development, advanced post-processing methods and in-depth characterization to perform root cause analysis. The recently rapidly growing field of 3D multi-material printing with ceramics also requires a high level of support from science and research if it is to develop successfully and find its way into industrial applications.

Tuning the rheological properties of feedstocks for droplet deposition with thermoplastic 3D printing

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Keywords: additive manufacturing, material jetting, colloidal processing, zirconia, rheology

Droplet deposition with material jetting based additive manufacturing methods, such as thermoplastic 3D printing (T3DP), depends greatly on the rheological properties of the feedstocks. Feedstocks should exhibit shear thinning behavior in the suitable dynamic shear stress-rate range. However, there are other important parameters, such as yield stress and storage/loss moduli defining rheological properties of thermoplastic-based feedstocks and are crucial during deposition.

This study investigated the effect of particle interactions and the degree of weak flocculation on the shear thinning behaviour, yield stress and storage/loss moduli of paraffin wax-based feedstocks containing 40 vol.% of zirconia (3Y-TZP) micron-sized powder. Steric stabilization of the feedstocks was provided by varying ratios of surfactants with different chain lengths; stearic acid (2.4 nm) and Solsperse 3000® (10 nm). The surfactant chain length and composition mixture dictated the magnitude of continuous, weakly flocculated attractive particle network in feedstocks, affecting their viscosity, (non)monotonous shear thinning behaviour, yield stress magnitude and loss/storage moduli, which were all crucial in the droplet formation dynamics and the quality of the printed layers during the T3DP forming process. The results of the present study extend the guidelines for the processing of printable, non-Newtonian, thermoplastic ceramic feedstocks for the T3DP additive manufacturing technology.

Transparent feedstocks for photon-based additive manufacturing technologies for powder processing of ceramics

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Keywords: transparent, photon-based, vat photopolymerization, zirconia

Photon-based additive manufacturing technologies such as SLA, DLP, LCM, moreover volumetric two-photon-polymerization, Xolography and holographic technologies promise the highest accuracy and dimensional freedom. But to transfer the light through the feedstock it needs sufficient transparency at the used light wavelength. Ceramic particles used for powder processing routes act as scattering sites and therefore hinder the light transmission, unless…

The particle size and particle size distribution are chosen small and narrow enough. Particles which are smaller than roughly 1/10th of the light wavelength, mostly nanoparticles around 5nm size, decrease scattering vastly. This turns resins even with homogeneously distributed ceramic weight fraction of up to 80% transparent again. Feedstocks could be prepared for the highly accurate two-photon-polymerization gaining the smallest yttria stabilized zirconia structures with a resolution of 500nm and unique mechanical properties. The same feedstocks could be applied to DLP and LCM as layer-by-layer AM-technologies for bigger parts. Hybridizing both technologies lead to ceramic parts with microscopic accuracy at macroscopic dimensions. The feedstock was even applied to the volumetric Xolography with the highest transparency requirement so far and to versatile and flexible holographic AM.

Highly filled nano-particle containing transparent ceramic feedstocks open the way for technical ceramics in high precision manufacturing where the performance and durability and accessibility are increased and created by the unique ceramic properties such as mechanical strength, chemical and thermal resistance and biocompatibility

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Additive manufacturing of ceramic components – why not yet established in industrial series production?

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Keywords: additive manufacturing, ceramics, series production, challenges

Ceramics are used where other materials fail. Their main advantages are their excellent thermal, chemical and mechanical properties. However, ceramics are not yet widely used because, in addition to their low ductility, complex mechanical processing using conventional methods (e.g. milling and turning) poses a major challenge. In addition, the integration of various functions into one component is only possible to a limited extent.

Additive manufacturing (AM) technologies act as a "game changer" here. Geometrically highly complex ceramic components with previously unattainable functionality can now be produced.

So far so good. But why don't we see additively manufactured ceramic components everywhere?

In this presentation, I will discuss the technical, economic and regulatory challenges that still exist along the entire process chain for ceramic AM components.

What still needs to be done and where, and what approaches are there?

Innovative horizons: 3D printing unleashes the potential of technical ceramics for prototyping and industrial scale production

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Keywords: ceramic 3D-printing, material extrusion, stereolithography, prototyping, industrialization

In today's rapidly evolving manufacturing landscape, 3D printing or additive manufacturing (AM) has emerged as a game-changer, offering unparalleled flexibility and efficiency not only for the prototyping world but also in various industries. One particularly exciting realm where 3D printing is making significant strides is in the domain of technical ceramics, where innovative technologies are enabling both prototyping and industrial-scale production with unprecedented precision and reliability. Over the years, many AM companies have emerged with cutting-edge processing technologies capable of producing ceramic parts with highly intricate geometries for nearly every imaginable application. One such pioneer is 3D Ceram Sinto Tiwari GmbH, which stands at the forefront of this revolution, offering two state-of-the-art 3D printing technologies: Material Extrusion with its Multi-additive Technology (MAT) system and Stereolithography (SLA).

The revolutionary MAT process empowers users to 3D print complex ceramic parts with remarkable speed and accuracy. By precisely extruding ceramics from a feedstock in the form of pellets, filaments, and water-based suspensions through a nozzle, and then directly milling the deposited layers, MAT enables the creation of intricate prototypes with exceptional surface finish, tight tolerances, and desirable mechanical properties post-sintering. Furthermore, MAT's versatility extends to a wide range of ceramic materials, opening up endless possibilities for many industries. Designers and engineers can rapidly iterate their designs, test new concepts and feedstock options, and refine products with ease, making MAT ideal for prototyping and manufacturing a small number of parts.

For scale-up applications and the mass production of parts with the highest and consistent precision, SLA stands as another groundbreaking technology provided by 3DCeram with over 15 years of experience. By harnessing the power of photopolymerization, SLA facilitates the precise layer-by-layer curing of liquid resin with a UV-laser to create intricate and dense ceramic parts with unparalleled accuracy and detail. With SLA, manufacturers can achieve high volumes of ceramic components with minimal waste, revolutionizing traditional production methods and enhancing product performance in challenging environments. 3DCeram offers a wide machine portfolio suitable for every scale-up production line, capable of producing ceramic parts in a building volume ranging from 100x100x150 mm to 600x600x300 mm. This enables our customers to establish an industrial workflow with highly repeatable and flawless processing across a wide range of scales. Additionally, the efficiency of 3DCeram's SLA process translates to faster production cycles and shorter time-to-market for new products, providing manufacturers with a competitive edge in meeting customer demands and staying ahead of the competition. Moreover, the streamlined workflow and reduced material waste, facilitated by our innovative CERIA artificial intelligence platform and Photo-resin reusing system, further contribute to cost savings and sustainability goals.

Additive manufacturing of advanced ceramics for demanding applications

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Keywords: 3D printing, advanced ceramics, filters, batteries, armour, bioceramics

The processing of advanced ceramic powders and suspensions into useful engineering components has been investigated via a series of research projects each focusing on a different stage of the manufacturing route viz., (i) the ability to control the agglomerates present in the ceramic powder resulting in the production of a free-flowing and crushable powders, (ii) the formation of low viscosity but high solids content ceramic suspensions suitable for 3D additive layer manufacturing (3D printing) and (iii) the use of novel field assisted sintering techniques (FAST). This holistic approach helped to transfer the developments achieved in each stage of the manufacturing process to the next and resulted in the ability to form fully dense, complex advanced ceramic components whilst restricting the grain growth to a minimum.

The methodology has been employed to develop various advanced functional ceramic components such as 3D printed $BaTiO_3$ based light-weight PTCR heaters for automotive and aerospace applications that surpasses existing commercial counterparts, ultra-low loss microwave dielectrics for beyond 5G communication devices, high temperature filters, 3D battery structures, conformal antennas, additively manufactured (AM) zirconia based biomedical components exhibiting vastly superior hydrothermal ageing resistance and mechanical performance suitable for use in biomedical implants (eg., hip/knee prosthesis, finger joints, dental and jaw repairs), as well as ceramic armours for ballistic applications. Significant sustainability advantages were noted with AM+FAST combination compared to conventional manufacturing methods in terms of reduction in material wastage and process energy efficiency. 3D printing of hydrothermally immune nanostructured dental implants was regarded as one of the six best modern technological developments in materials science by a recent BBC documentary (Materials of the Modern Age: The Secret Story of Stuff). These novel advancements are covered by a series of patents and papers and this talk will provide an overview of some of these developments.

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Additive manufacturing of optical ceramics

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Transparent ceramics have been fabricated by using nozzle extrusion 3D printing methods and lithography-based digital projection. The ceramic green bodies were printed into complex geometries by using different viscous aqueous slurries. Transparent alumina ceramics were fabricated using an extrusion-based 3D printer and post-processing steps including debinding, vacuum sintering, and polishing. Scalable, massive fabrication of complex three-dimensional (3D) structured highly transparent Nd: YAG (Y3Al5O12) ceramics was achieved by a lithography-based (photopolymerization) digital light processing or digital light projection (DLP) 3D printing method. The work demonstrated transparent ceramics can be prepared using a simplified process without the traditional mold and cold isostatic pressing procedure. It can serve as a potential method of making customized transparent ceramic components and it is also useful for fabricating ceramics structures with relatively full densification.

T4.3 NOVEL, GREEN, AND STRATEGIC PROCESSING AND MANUFACTURING TECHNOLOGIES

Organic-free direct ink writing and consolidation of glass and ceramic slurries

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Keywords: alkali activation, gelation, direct ink writing, waste glass, mullite, cordierite

A key requirement in additive manufacturing, by direct ink writing (also known as robocasting), is the pseudoplastic behaviour of pastes (also kwown as ’inks’). The transition from a low viscosity state (at high shear rates) to a high viscosity (at low shear rates), favours the ejection from nozzles and the preservation of shapes, respectively. This is generally achieved by mixing ceramic powders with organic additives, to be carefully removed upon thermal treatment, but there are important opportunities for the develoment of fully inorganic inks. A fundamental example is provided by geopolymer-yielding slurries, resulting from the suspension of metakaolin powders in concentrated aqueous solutions of alkali hydroxides and silicates. The pseodoplastic behaviour is determined by the progression of polymerization reactions, involving oligomers released in solution according to the alkaline attack of the same metakaolin [1].

The present paper aims at offering new strategies for fully organic-free processing, exploited in the upcycling of waste glass [2] as well as in the development of cordierite- and mullite-based components [3]. The novelties rely, compared to geopolymer-yielding pastes, on changes in the material undergoing alkaline attack and/or in the attacking compound. In the first case, we will show that fine glass powders (<70 µm, recovered from dismantled pharmaceutical containers or from fibre manufacturing) undergo a quite particular interaction with NaOH or KOH solutions: slurries show progressive hardening by condensation reactions involving hydrated layers, on the surface of glass powders, formed upon disruption of glass network operated by OH^- ions. These reactions imply the regeneration of Si-O-Si and Si-O-Al bonds, as strong and durable bridges between adjacent particles. Slurries in the early stages of reaction may be used as pseudoplastic pastes, for the manufacturing of reticulated constructs. These products are directly usable, as catalytic supports, just after drying. In the second case, we will show that the disruptive action of OH^- ions can be supported by ammonium hydroxides instead of alkali hydroxides. Polymerization reactions of activated metakaolin, added with talc and/or reactive alumina (γ-Al_2O_3), yield alkali-free composite gels, to be transformed into phase-pure cordierite or mullite ceramics. Again, activated suspensions may be printed in the form of reticulated constructs. Applied to bioglasses, this alkali-free ′basic′ activation allows for the printing of ′green′ scaffolds, later converted into glass scaffolds by viscous flow sintering, with no alteration of the chemical composition.

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New advances in high-precision ceramics technology

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Keywords: high-precision ceramics, alumina strengthened porcelain, pyroplastic deformation, near-zero liquid sintering shrinkage

Attaining precise control over the geometry of pottery ceramics presents a challenge due to undesirable pyroplastic deformation and sintering shrinkage, leading to significant production losses within the ceramic industry. Therefore, the development of high-precision ceramics technology becomes necessary, particularly in additive manufacture. In this presentation, we will show the latest advances in high precision ceramics production.

Firstly, achieving a balance between densification and pyroplastic deformation in porcelain, especially across a wide range of firing temperatures, is intricate due to inherent trade-off. We will outline our strategies for attaining this balance by precisely modulating high-temperature viscosity using IA and IIA oxides and high-temperature crystal precursors, respectively. Secondly, unpredictable shrinkage arising from liquid sintering, especially in pottery ceramics employing natural minerals as raw materials, remains a pressing issue. We will introduce a novel approach for effectively managing both shrinkage and pyroplastic deformation by promoting anorthite crystallization through the incorporation of wollastonite.

By addressing the issues of pyroplastic deformation and sintering shrinkage, high-precision ceramics can be developed. Our methodologies not only facilitate the production of high-precision ceramics but also contribute to resource and energy conservation, promoting sustainable development.

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Nanoimprint of Au-based thin film metallic glasses for plasmonic applications

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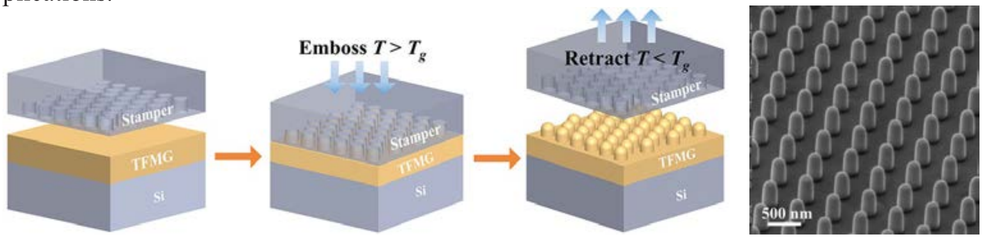
Keywords: thin film metallic glasses, sputtering, thermal imprint, plasmonics

Metallic glasses (MGs) could be obtained by quenching from the melt at a cooling rate high enough to suppress nucleation/growth of crystalline phases, and they have a glass-like amorphous structure. Because of the amorphous structure, MGs have no grain boundaries/ dislocations and hence possess very high strength (~2 GPa). Also, like glasses, MGs have polymer-like viscous flow behavior at temperatures above the glass transition temperature, T_g. MGs provide a challenge of engineering applications for their unique structure and properties. However, plasmonic applications have been rarely explored for MGs. In this work, we unveiled that certain compositions of Au-based MGs possessed negative dielectric constants and could be used as plasmonic materials. Furthermore, with a low glass transition temperature of Au-based thin film MGs (TFMGs), we were able to fabricate large dimensions of nanostructures using an inexpensive thermal imprint method in air instead of other costly lithography methods.

We fabricated fully amorphous AuCuSi TFMGs using magnetron sputtering, and performed nanoindentation creep tests in the temperature range of 50 ºC to 170 ºC to characterize the viscous flow behavior and to determine the T_g of the film. We fabricated nanostructures by thermal imprinting on the film at a temperature slightly above the T_g, and conducted both measurements and simulations to demonstrate that our fabricated nanostructures were suitable for surface-enhanced Raman scattering (SERS) applications. It is worth noting that in the absence of grain boundaries in amorphous TFMGs, damping due to increased scattering at grain boundaries does not occur and SERS could be improved. Also, compared to regular SERS substrates of textured Si with deposited Au films, imprinted Au-based TFMGs provided complete coverage of Si underneath and the vibrational signal of Si lattice would not show in Raman spectra to possibly overlap signals of analyte and decrease the accuracy of sensing. Our results suggested new avenues for applying a low-cost and high-throughput method on AuCuSi TFMGs to fabricate large dimensions of substrates for plasmonic applications.



(a) (b)

Fig. 1. (a) Schematics showing thermal imprint on Au-based TFMG to fabricate SERS substrate. (b)SEM image.

Acknowledgments

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Densification, microstructure and properties of advanced ceramics sintered under high/ultrahigh pressure

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Keywords: densification, microstructure and properties of advanced ceramics sintered under high/ultrahigh pressure

High/Ultrahigh pressure sintering technology is one of the most important research scopes for advanced ceramic materials. It could not only resolve the contradiction between high density and fine grain structure during ceramic sintering, but also lead to unique microstructure and fantastic properties. In traditional sintering method, atomic diffusion is considered as the dominate densification mechanism in pressure sintering. But in our study, it has been found that the plastic deformation and creep etc. caused by high pressure could dramatically improve the densification. The related unique microstructure could contribute to the high properties such as hardness and strength. Based on the new phenomenon, we investigated the densification behavior, microstructure evolution and properties of typical ceramics under different pressure scales. Combined with the modeling results, the dominate densification mechanism of ultrahigh pressure and high temperature sintering technology, and the relationship between dominate sintering mechanism and properties were studied.

Fast laser processing of silicon carbide ceramic materials

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Keywords: SiC, selective laser printing, densification, comprehensive properties

SiC-based Ceramic composites are promising for usages as various large-scale and complex-shaped components. However, the intrinsic brittle nature of SiC ceramics inhibited their wide application. Incorporation of chopped carbon fiber as a reinforcing phase could enhance its reliability. During recent years, efforts have been devoted to fast forming techniques to reduce excess carbon reduction. Additive manufacturing of SiC-based ceramics by adopting various techniques, including digital light processing, direct ink writing, selective laser printing, and et al were emerged.

In previous study, our group conducted investigation on direct ink writing of C/SiC ceramic composites. The critical point was the preparation of homogenous C/SiC green bodies. In recent study, we combined selective sintering and liquid silicon infiltration for a higher-efficiency and higher-performance-component fabrication. We prepared complex-structured composites therefrom. The relationship between microstructure tailoring and mechanical performance was investigated.

Acknowledgments

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Spray freeze granulation drying of aluminum nitride and silicon nitride powders

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Keywords: spray freeze granulation drying, silicon nitride, aluminum nitride

Dry pressing is one of the techniques to make a green body with simple shape and good productivity. However, it has been reported that the defects resulting from granules prepared by spray drying degrade the strength of ceramics. Spray freeze granulation drying (SFGD), which is one of the techniques to prepare granules from the ceramic slurry, provides softer granules to result in homogeneous green body and sintered body with high strength. In general, the slurry for SFGD is prepared using water as a dispersion media, which is not suitable for nonoxide ceramics, such as AlN and Si_3N_4, because of reaction with water during mixing to form oxides or hydrates to degrade the properties of ceramics. The ideas to be slove the problem is to improve the water proofness and to use nonaqueous solvent. In this study, SFGD of AlN and Si_3N_4 powders was carried out.

For AlN powder, graphene coating by mechanical treatment, which was carried out under a compression and shear field, was investigated in order to give water resistance to the particles for preparation of ceramics using aqueous slurry. The graphene-coated aluminum nitride particles showed excellent water resistance, since the pH value of the aqueous slurry did not change and aluminum hydroxide was not detected even after stirring for long time. The relative density of the AlN ceramics obtained with the composite particles was high, and their secondary phase was also found to be yttrium aluminate having less oxygen than those prepared without graphene coating, due to suppressed hydrolysis. Thermal conductivity of AlN ceramics prepared from graphen coated particles was 133 W/mK, which was higher than that from phosphate coating reported in the previous study.

For Si_3N_4 powder, SFGD was carried out using slurries prepared in a mixture of tertiary butyl alcohol and cyclohexane. The eutectic composition of the mixture resulted in the granules having a homogeneous internal structure, though the granules prepared from an excess amount of tertiary butyl alcohol and cyclohexane included larger pores. Si_3N_4 ceramics were fabricated using the freeze-dried granules prepared from the eutectic composition of tertiary butyl alcohol and cyclohexane. As a result, it was found that highly dense and homogeneous β-Si_3N_4 ceramics were obtained using granules prepared by SFGD, which showed higher strength than those from granules by conventional seiving technique.

Recovery and reuse of magnetic silica-coated iron oxide particles for green chemical mechanical planarization

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Keywords: chemical mechanical planarization, core-shell nanoparticles, magnetic separation, recycling

Chemical mechanical planarization (CMP) emerges as a crucial process in nano-scale semiconductor patterning. However, it raises environmental concerns due to increased waste generation, prompting questions about its long-term sustainability. We explore an innovative waste management and recycling approach that employs magnetic separation, utilizing magnetite (Fe_3O_4)@silica (SiO_2) core-shell nanoparticles as CMP abrasives. Due to the high magnetic properties of the magnetite core, the nanoparticles can be effectively separated and recovered from spent CMP slurry under the external magnetic field. Additionally, by regulating the thickness of the SiO_2 shell, we can control the surface charge and mechanical properties of the abrasive. Compared to conventional SiO_2 nanoparticles, Fe_3O_4@SiO_2 core-shell nanoparticles with optimized shell thickness demonstrate higher removal rates and improved surface smoothness in tungsten CMP. The recycling efficacy of these particles is confirmed through multiple CMP cycles, maintaining consistent removal rates and surface quality, thus highlighting the potential of magnetic separation for sustainable CMP.

Progress of silicon nitride ceramics

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Keywords: silicon nitride, microstructure, mechanical properties

Silicon nitride is one of the most widely used engineering ceramics for a variety of structural applications because of their excellent mechanical properties. During the last four decades, a great deal of research effort has been devoted for tailoring the microstructures through innovative sintering process and enhancing the properties, leading to tremendous progress of silicon nitride. Particularly, in recent years, a lot of attention has been collected to studies on small or thin parts of silicon nitride ceramics because of their expanding application field. This paper gives an overview on such recent progress of silicon nitride ceramics, focusing on the processing (or sintering)-structure-properties relationship, with some examples of how a unique processing route generates a novel microstructure, which brings enhanced properties in turn. Particular emphasis is placed on microstructural elements, including grains, pores, particles, and interfaces at different scale levels, as well as their effects on the mechanical and thermal properties.

$Y(Ta_{1-x}Nb_x)O_4$ single crystals for scintillator applications

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Keywords: single crystal, scintillator, X-ray imaging

Importance of X-ray imaging applications are now growing rapidly in many fields including security inspection, medical diagnostics, and non-destructive testing. Typical apparatus are X-ray baggage & Cargo scanners, X-ray CT, and X-ray inspection machines. One of the most widely used scintillator for these applications is $CdWO_4$ (CWO) single crystal. However, the alternative of CWO has been demanded since long time due to the existence of the toxic element, Cd. We have been looking for the environmentally friendly potential candidate, i.e. Cd-free, which can alternate CWO single crystal.

In this work, single crystals of $Y(Ta_{1-x}Nb_x)O_4$, where x ranges from 0 to 1, are introduced, as a potential Cd-free alternative of CWO. These single crystals were grown by the floating-zone method. The grown crystals have shown high light yield and low aftergrow comparable to CWO. The detail will be shown in the presentation.

Effects of TiC content on the microstructure and properties of B4C–TiB2–graphite composites by reactive hot pressing Sintering Processing

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Keywords: B4C–TiB2–graphite, agglomerates, mechanical properties, crack deflection

B_4C–TiB_2–graphite ceramic composites were fabricated via reactive hot pressing sintering using B_4C and TiC as the raw materials. With an increase in the TiC content, the grain size of B_4C decreased continuously because B_4C grain growth was inhibited by the TiB_2 and C reaction products. However, excessive TiC content caused an increase in TiB_2 and graphite grain size and the formation of TiB_2–graphite agglomerates. When the composition of the ceramic composite was 95.1 wt%B_4C–3.9 wt%TiB_2–1.0 wt%graphite, the Vickers hardness and bending strength was optimized at 34.9 GPa and 688 MPa, respectively. The results showed that crack deflection is the main toughening mechanism of B_4C–TiB_2–graphite ceramic composites, and the effect of TiB_2–graphite on crack propagation is particularly significant. When the composition of the ceramic composite was 75.6 wt%B_4C–19.4 wt%TiB_2–5.0 wt% graphite, the fracture toughness was optimized at 6.77 $MPa \cdot m^{1/2}$. These results provide guidelines on how to effectively control the combined properties of B_4C–TiB_2–graphite ceramic composites in future investigations.

T4.4 POWDER PROCESSING TECHNOLOGY FOR ADVANCED CERAMICS

Field-assisted sintering processes as innovative sustainable routes for high-temperature ceramics

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Keywords: flash sintering, ultrarapid high temperature sintering, high-temperature ceramics, tungsten carbide, zirconium diboride

The increasingly current environmental awareness linked to climate changes and the scarcity of energy resources is permeating also the industrial sector of the production of ceramic materials. Nowadays, the carbon footprint associated with the production of ceramics depends fundamentally on the use of energy to process them, where firing alone accounts for 55%–80%. For all this, numerous research activities are trying to identify processes with lower environmental impact and, above all, with limited energy consumption. Initiatives aimed at activating, inducing or sustaining sintering processes through the use of electric fields or currents can be placed in this framework, preferably without resorting to particularly expensive machinery. Among these, the very recently proposed techniques identified as flash sintering (FS) and ultrafast high-temperature sintering (UHS) appear extremely promising although their application at an industrial level still requires numerous investigative and validation activities.

An area where the above-mentioned issue is even more problematic is that of refractory or high-temperature ceramics, which typically can only be consolidated at very high temperatures under the action of significant pressures or through the addition of compounds that facilitate the diffusion mechanisms / sintering, typically in inert atmosphere.

In this presentation, the application of FS and UHS on tungsten carbide, zirconium diboride and their composites is reviewed. Such materials behave notoriously like metals from an electrical point of view and therefore do not show the well know thermal runaway phenomenon when subjected to the contemporaneous effect of temperature and electric field as observed in the flash sintering of most ceramics. In addition, their chemical nature makes them prone to oxidize at high temperature in non-protecting environment. The conditions are discussed here to achieve high density and no oxidation when FS and UHS techniques are used with the aim to identify possible evolution of the process to real applications and actual issues which need further investigations. The correlation between the processing condition and material structure and composition is also analysed in detail.

Acknowledgments
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Grain boundary engineering in high-entropy perovskite oxides to improve thermoelectric performance

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Keywords: high-entropy, thermoelectric, material engineering, figure of merit, grain size

Thermoelectric (TE) materials enable direct conversion between heat and electricity and offer a pathway for more sustainable and environment-friendly energy generation. The TE potential of a material is evaluated based on a dimensionless figure of merit $ZT = S^2\sigma T/(\kappa_e+\kappa_l)$. Accordingly, TE materials are effective when they combine a high power factor ($S^2\sigma$) with low electronic (κ_e) and lattice (κ_l) thermal conductivities [1]. According to Weideman-Franz law, however, there is a direct correlation between thermal and electric conductivities, restricting their decoupling or independent optimization. Hereon high entropy materials have shown promising potential in reducing the coupling between thermal and electrical conductivities due to strong lattice distortion in a highly symmetric crystalline structure [2, 3]. High entropy oxides (HEOs) are a subclass of high entropy materials [4], where the random and homogeneous mixing of nearly equimolar five or more cations (depending on the lattice/sub-lattice structure [5]) allows formation of stable crystalline single phase oxide structures.

Among several perovskite compounds, n-type perovskite titanates have revealed promising TE performance in recent years. However, these perovskites suffer from high thermal conductivity (>10 W/mK), resulting in poor ZT values compared to conventional TE materials (thermal conductivity ~1 W/mK) [3]. In order to overcome this limitation and increase the ZT, high entropy perovskite oxides have been developed with A and B-sites in a ABO_3 structure homogeneously populated with ≥5 cations to maximize the configurational entropy and form a stable single phase structure [6]. They can be sintered preserving a refined microstructure due to their lower grain boundary energies compared to their low entropy counterparts [7]. This in return increases the phonon scattering centers at grain boundaries, and the large differences between cationic mass and interatomic forces [8] furthermore reduce the lattice thermal conductivity.

In this study, A and B-site substituted $[(5M)_1(5N)_1O_3]$ single phase HEO powders using A = La, Bi, Sr, Ba, Na, and B = Zr, Hf, Ti, Nb, Ta, W, Fe/Mn have been synthesized via a solid-state reaction method. In order to further decrease the lattice thermal conductivity and increase the carrier concentration in single-phase HEOs, the powders were afterwards donor doped before spark plasma sintering (SPS). Furthermore, the addition of cellulose nanofibres prior to SPS sintering was evaluated for an in-situ formation of a graphene-like networks at the grain boundaries to enhance the electric transport (charge collection) and scatter mid-wavelength phonons (dominant carriers of thermal energy [9]). The resulting effect on thermal conductivity and overall ZT is reported.

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Investigation of easily degradable adhesive structures and adhesives assuming the electric pulse separation

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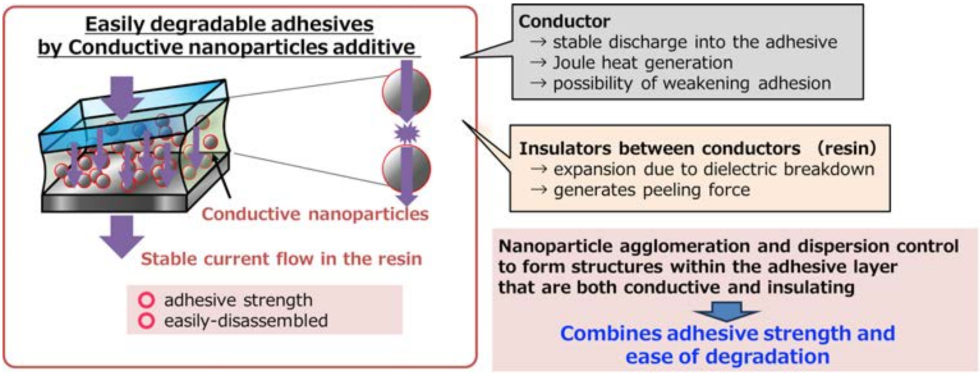
Keywords: multi-material, electrical pulsed discharge, separation, recycling, circular economy

Advanced dismantling technology is required to realize the Circular Economy. In recent years, multi-materials are often bonded and joined to reduce weight, but it is difficult to dismantle them precisely only by conventional mechanical grinding, while heating and solvent addition methods have a large environmental impact and cost for separation. Therefore, there is a need for a precise dismantling method with a small environmental impact and cost for the adhesion and bonding of multi-materials.

The authors have focused on the electrical pulsed discharge as such a dismantling method. This method uses Joule heat generation by electrical pulsed discharge and shock wave generation and expansion due to plasma generation to precisely separate on the discharge paths. So far, we have succeeded in separating lithium-ion battery current-collecting foil and adhesive particles [1], and in separating resin from silver and copper wires in solar panel cell sheets. However, common adhesive structures often do not provide a convenient electrical pulse discharge path. Therefore, we have attempted to separate the adhesive by introducing notches, metal spheres, and thin metal wires into the adhesive structure to dismantle them using the electric pulse method. However, these methods tend to reduce the bond strength. Recently, the authors have investigated a method of dismantling adhesion by dispersing conductive nanoparticles in the adhesive and discharging electric pulses into them to induce plasma. By controlling the dispersion structure of the nanoparticles in the adhesive layer, the authors hope to create an easy-to-disassemble design by assuming the electric pulse method during disassembly, without reducing the adhesive strength [2].

Figures



Concept of Nanoparticle Aggregation and Dispersion Control for Easily Degradable Adhesion

Acknowledgments

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Development of Si_3N_4 substrate from tape casting and gas pressure sintering

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Keywords: silicon nitride, tape casting, thermal conductivity

Si_3N_4 ceramics exhibited excellent mechanical properties and high theoretical thermal conductivity, is a prospective substrate candidate for power electronic devices. However, the development of high thermal conductivity Si_3N_4 is a challenge, because it is difficult to balance the high thermal conductivity and high strength. Usually, high temperature with long time holding are required for development of high thermal conductivity, while excessive grain growth and low bending strength will be resulted. Up to now, how to develop silicon nitride substrate with both high strength and high thermal conductivity is still a challenge.

In this paper, a strategy was proposed to avoid the long time holding through the introduction of Y_2O_3-MgO-C as the sintering additives and silicon powder as the starting material. High thermal conductivity Si_3N_4 ceramic was prepared through tape casting, nitridation and gas pressure sintering at 1900ºC, 0.9MPa with 2-6h holding. The influence of carbon addition on the sintering behavior, phase, microstructure, mechanical properties, and thermal conductivity of Si_3N_4 was studied. The grain boundary and the second phase character is studied. Si_3N_4 ceramics with relative density and thermal conductivity as 99% and 98 W/m·K respectively can be obtained. The mechanism for the microstructure development and the resulting thermal and mechanical properties were discussed.

T4.5 ADVANCED MATERIALS, TECHNOLOGIES, AND DEVICES FOR ELECTROOPTICAL AND BIOMEDICAL APPLICATIONS

Nanoparticles in optical fibers, new opportunity for biomedical sensors

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Keywords: optical fiber, nanoparticles, sensors, OBR, TRA, biosensors

Nanoparticles in optical fibers were first studied in 1998 to modify the local environment of luminescent ions [1]. The aim was to develop new lasers and amplifiers. In this context, light scattering induced by the presence of nanoparticles was considered harmful. However, in 2018, it was demonstrated that this light scattering could, on the contrary, be exploited to make sensors, particularly for the biomedical field [2]. Sensors are interrogated using two different methods. The first is based on the analysis of backscattered light using an OBR (Optical Backscatter Reflectometer), derived from OFDR (Optical Frequency Domain Reflectrometry) [3]. This approach enables the fiber to be probed along its entire length, with a spatial resolution of the order of 10 µm. The other approach is based on Transmission-Reflection Analysis, *i.e.* determining the ratio between transmitted and reflected intensity. This technique is well known for determining the location and intensity of a single event occurring on the fiber. However, the use of machine-learning has recently made it possible to extend this analysis to the detection of two or three events simultaneously [4].

In this presentation, we will review the various applications of these nanoparticle-containing optical fibers for the detection of temperature, stress, strain, biochemical environment, cancer cell detection, and more generally their use in e-health.

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Nonlinear crystals: a unique platform for optical frequency synthesis and new quantum states ol light generation

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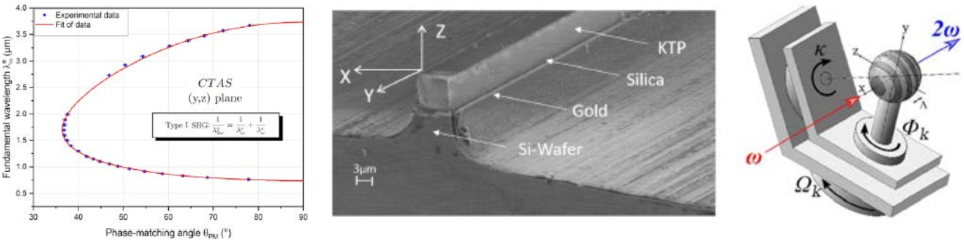
Keywords: crystals, nonlinear optics, frequency conversion, quantum optics

Nonlinear optics relies on the coupling between photons and electrons, the last ones allowing the first ones to merge or split. The efficiency of this "photonic alchemy" is high when the intensity of light is large and when electrons of matter are relatively weakly linked. All the matter states, *i.e.* plasmas, gas, liquids and solids, can exhibit nonlinear optical properties. But among all these media, the organized solids, *i.e.* the crystals, lead to the biggest diversity of nonlinear optical interactions and applications due to their rich symmetries and chemistry, and to their purity and hardness. Associated with lasers, the crystals with nonlinear optical properties allow intense beams to be generated over a huge spectral range of the electromagnetic waves, from ultra-violet to far infra-red, leading to numerous devices and applications. Parametric light has also a strong interest in quantum physics since it enables the generation and manipulation of new quantum states of light. Among the various nonlinear processes, twin-photon and triple photons generations, which corresponds respectively to the birth of two and three correlated photons from the splitting of a single photon, allow to manipulate the quantum properties of light. These generations are driven by an optical pump field: it can occur spontaneously, which is called spontaneous parametric down conversion, or it can be forced by a seed field oscillating at one or both of the generated photons frequencies; this is the optical parametric amplification, or optical parametric oscillation if the process is enhanced by a resonant cavity.

This invited talk gives a quick overview of the 3-photons and 4-photons coupling showing the ability of both of these nonlinear interactions to convert laser frequency or generate new quantum states of light using bulk crystals and crystal waveguides based on birefringence phase-matching or quasi-phase-matching.



(a) (b) (c)

Second Harmonic Generation birefringence phase-matching tuning curve of a CTAS bulk crystal (a) [1]; KTP crystal ridge optical waveguide for phase-matched Third Harmonic Generation and Triple Photons Generation (b) [2]; scheme of a PPRKTP sphere used for the study of the angular distribution of quasi-phase-matched Second Harmonic Generation (c) [3].

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RF-sputtering deposition technique for fabrication of glass based flexible 1D photonic crystals and active planar waveguides

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Keywords: flexible glasses, RF-sputtering, 1D photonic crystals, active planar waveguides.

We present the RF-sputtering fabrication of flexible 1D photonic crystals and active Er^{3+}-doped planar waveguides. These structures were deposited on ultrathin flexible glass and exhibited remarkable results in terms of both optical and mechanical properties. The use of RF-sputtering demonstrates promise as a scalable technique for creating flexible photonic devices[1,2].

Moreover, we delve into the design, fabrication and performance of flexible 1D photonic crystals produced through multi-layered deposition via RF-sputtering on a flexible thermosetting polymer. Notably, these results are comparable to those obtained from the film deposited on glass. We further conduct experimental spectroscopic analysis under various bending configurations, which aligns well with numerical simulations. This comprehensive study establishes the reliable operating conditions for photonic devices.

Acknowledgments

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Fabrication of RE-doped transparent hexagonal fluorapatite ceramics

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Keywords: transparent ceramics, laser, phosphor, fluorapatite, spark plasma sintering

Transparent ceramics have been widely studied for various applications, especially in high power solid-state lasers. However, the host materials are limited to cubic crystal structure due to grain boundary scattering by birefringence. The realization of non-cubic transparent ceramics is attractive in a wide range of photonics fields. It is known that the grain boundary scattering is porportional to the average grain size and the refractive index difference at the grain boundaries [1]. One way to reduce the scattering in non-cubic ceramics is to densify the ceramics with significantly small grains comparative to wavelength of light as shown in Fig. 1 [2].

In this study, high optical quality non-cubic fluorapatite ($Ca_{10}(PO_4)_6F_2$: FAP or $Sr_{10}(PO_4)_6F_2$: S-FAP) ceramics were fabricated through liquid phase nano-powder synthesis and densification by spark plasma sintering (SPS) technique. By using the low temperature SPS to suppress grain growth during the sintering process, full densification with fine microstructure could be achieved. The average grain size of the ceramics were evaluated to be approximately 100 nm, and the in-line transmittance were comparable to the theoretical values. Laser oscillation were demonstrated for Nd:FAP, Yb:FAP, and Nd:S-FAP ceramics though composing crystal grains are almost randomly oriented [2-4]. In the presentation, the details of fabrication process, sintering behavior, microstructure, optical and fluorescence properties for some RE-doped fluorapatite ceramics will be discussed.

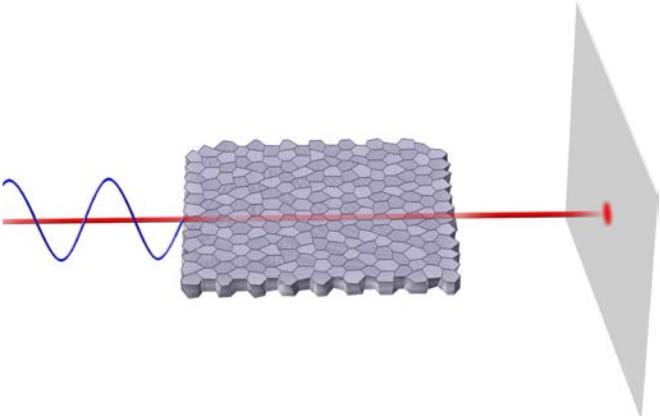

Fig. 1 Schematic of optical scattering in fine-grained non-cubic ceramics [2].

Fig .2 Sample photos of Er, Nd, and Yb-doped FAP ceramics.

Acknowledgments

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Phase diagram and single crystal growth of $Li(Nb,Ta)O_3$ solid solutions

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Keywords: crystal growth, solid solutions, segregation, curie temperature

Lithium niobate ($LiNbO_3$) and lithium tantalate ($LiTaO_3$) belong to the most widely used ferroelectric materials, with applications that range from novel electronic and micro-mechanical devices to nonlinear optics. Lithium niobate-tantalate ($LiTa_xNb_{1-x}O_3$, LNT) solid solution single crystals are expected to allow for implementation of unique material's properties such as tailored birefringence combined with large temperature stability.

Well-characterized single crystals of sufficient size and quality are an essential prerequisite for an in-depth analysis of the material's properties and the development of new functional components with superior properties. Elaboration of a reproducible crystal growth process, in turn, calls for profound knowledge of the phase diagram of the underlying material system. For the growth of LNT crystals the relevant system is the Li_2O—Nb_2O_5—Ta_2O_5 ternary system. However, there are good reasons to treat the junction of congruently melting $LiNbO_3$ and $LiTaO_3$ as a pseudo-binary system. This system was investigated in greater detail. Thermophysical data of the end-members and of grown solid solution samples were obtained from thermoanalytical measurements and first-principal studies, and were used to draw an improved version of the phase diagram that is now in good agreement with our crystal growth experiments.

LNT solid solution crystals were grown using the Czochralski technique. The crystals show distinct chemical inhomogeneities arising from cellular growth under constitutional supercooling conditions caused by strong component segregation during growth. Numerical model experiments were carried out to study transport of heat and mass in the involved phases. Due to large Prandtl and Schmidt numbers of the melt (for $LiNbO_3$ $Pr \approx 37$, $Sc \approx 104$, no data known for $LiTaO_3$) convective flow is the dominant transport mechanism in the liquid. The key to increasing interface stability is therefore the efficient removal of excess solute at the interface by the help of convection. As a result, solid solution crystals are obtained with larger regions that are nearly homogeneous in composition

Acknowledgments

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Fabrication of IR transparent ceramic composites using Spark-Plasma-Sintering (SPS) Processing

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Keywords: IR, transparent, composite, SPS

Infrared (IR) light is an important wavelength band for sensing technologies because it can provide us thermal and chemical information. For realizing the sensing technologies that enable to utilize the IR wavelength, it is essential to create window materials that possess high mechanical properties enough to protect infrared sensors in addition to IR transparency. However, since the mechanical properties of the well-known IR transparent ceramics are lower, high strength IR transparent ceramics are required. In order to achieve both optical and mechanical properties simultaneously, structural design such as fine and composite microstructures is essential. Among several sintering techniques, SPS processing is known as a useful technique that enables to attain fine-grained and dense materials. In this work, therefore, the SPS technique has been employed to achieve fine grained and dense composites having excellent mechanical and optical properties. In my talk, we will report several IR transparent composite materials[1,2)] fabricated by the SPS technique.

Acknowledgments

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Development of scintillators having nanostructure

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Keywords: scintillator, nanoparticle, in-vivo application

Scintillators are phposphors that emit optical photons (scintillation) upon irradiation of ionizing radiation. They are widely used for radiation detection in scintillation detectors. In addition to the application in radiation detection, scintillator particles are used in some in-vivo applications. Among them, Ce-doped GAGG ($Gd_3Al_{5-y}Ga_yO_{12}$) microparticles were used as the light source in a mouse to control the behavior of the mouse via external X-ray irradiation [1], where GAGG was used as because of its high scintillation yield and high stopping power of X-rays owing to its high density. To use in a less invasive manner, nanoparticles are desirable. In addition, to be combined with various photoreceptor molecules, it is desirable that the scintillation wavelength of the nanoparticles can be changed. We have developed GAGG nanoparticle scintillators to satisfy these demands.

We synthesized GAGG nanoparticles via sol–gel method using tartaric acid according to a procedure in a previous paper [2]. Aqueous solutions containing tartaric acid and metal nitrates in a stoichiometric ratio were stirred at room temperature for 24 h and subsequently at 80ºC for 2 h. After drying the solution for longer than a night, dry gel was obtained. The dry gel was calcined at different temperatures for 6 h to obtain nanoparticles.

In the case of Ce^{3+}-doped nanoparticles, the photoluminescence (PL) excitation and emission spectra revealed that the emission at around 550 nm is derived from 5d–4f transition of Ce^{3+} ions. The highest PL quantum yield (QY) of 91% was obtained with Ce^{3+} concentration of 0.1 mol% relative to Ce + Gd, (Gd+Ce):Al:Ga=3:3:2, and calcination temperature of 1300ºC. Based on the pulse height spectra, the scintillation light yield of as high as 13,800 photons/MeV was estimated. To achieve emission at longer wavelength, we synthesized Eu, Sm, or Pr-doped GAGG nanoparticles. Among them, in Eu-doped GAGG, luminescence bands owing to 4f–4f transition were observed, and the PL QY of 98% was achieved with Eu concentration of 5 mol% relative to Eu + Gd.

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Temperature stability of field-induced strain in PLZST antiferroelectric ceramics

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Keywords: temperature stability, antiferroelectric ceramic, field-induced phase transition, PLZST

(Pb,La)(Zr,Sn,Ti)O3 (abbreviated as PLZST) antiferroelectrics, with complex perovskite structure, could undergo various phase transitions once applied an external field, including electric field, temperature, stress, etc. The phase transitions usually involve generation/release of polarization, huge field-induced strain, as well as changes in dielectric, piezoelectric, electrocaloric and pyroelectric properties, which enable it to be promising candidates applied in high-tech energy storage capacitors, actuators, transducers and pyroelectric detectors designs. In order to understand the relationship among its composition, structure and property, effects of field-induced phase transition behaviors of PLZST AFE ceramics were systematic studied in this work.

Temperature stability of field-induced strain in AFE ceramics, with tetragonal structure, was belived as one of bottlenecks restricting its further applications. To investigate field-induced strain in PLZST, virgin and poled (Pb0.97La0.02)(Zr0.85Sn0.08Ti0.07)O3 AFE ceramics, were prepared and investigated systematically. A strain response of ~0.4 % within a temperature range (20 °C-190 °C) was achieved in as-poled (Pb0.97La0.02)(Zr0.85Sn0.08Ti0.07)O3 AFE ceramics, accompany by a fluctuation of field-induced strain within ± 5.5 %. Theoretical analysis indicated that huge strain response, as well as a higher temperature stability, was related to the preference-oriented antiferroelectric domains in as-prepared PLZST AFE ceramics.

Radio-photoluminescence characteristics of Eu-doped K*M*PO$_4$ (*M* = Mg, Ca, Sr, Ba) ceramics

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Keywords: phosphor, dosimeter, radio-photoluminescence, radiation-induced luminescence

Currently, phosphors are used for a variety of purposes, and one of the applications is radiation dosimetry. Scintillation, thermally-stimulated luminescence (TSL), optically-stimulated luminescence (OSL), and radio-photoluminescence (RPL) are well known luminescence phenomena induced by ionizing radiation in such applications. Among them, materials exhibiting RPL are not only used for radiation dosimetry, but are also being considered for optical storage devices and high-resolution radiation imaging. RPL dosimeters have some advantages over conventional TSL and OSL dosimeters: RPL dosimeters show almost no fading and can be read repeatedly. Although RPL materials have advantages over other dosimeter materials as described, the number of materials that exhibit RPL is still limited, and there is much room for material research. Eu:K*M*PO$_4$ (*M* = Mg, Ca, Sr, Ba) can contain doped Eu luminescent centers in both the divalent and trivalent states depending on the preparation conditions. The fact suggests that Eu:K*M*PO$_4$ can be an RPL material potentially. In this study, we report on our investigation and evaluation of changes in RPL properties upon varying the Eu concentration of Eu:K*M*PO$_4$ ceramics.

Figure 1 shows the appearance of the Eu:K*M*PO$_4$ ceramics under UV irradiation before and after X-ray irradiation. While the unirradiated samples showed red emission, the samples after X-ray irradiation show a change in luminescence color. This result indicates that the RPL phenomenon was detected in all samples. Figure 2 shows the PL spectra of the Eu:K*M*PO$_4$ ceramics before and after 10 Gy of X-ray irradiation. In the *M* = Mg and Ca samples, the Eu^{2+} and Eu^{3+} emissions overlap, but in the *M* = Sr and Ba samples they are completely separable. The complete separation of the emission spectra before and after X-ray irradiation is an important feature for applications. In my presentation, we will report on the other RPL properties of Eu:K*M*PO$_4$ ceramics in detail.

Figures

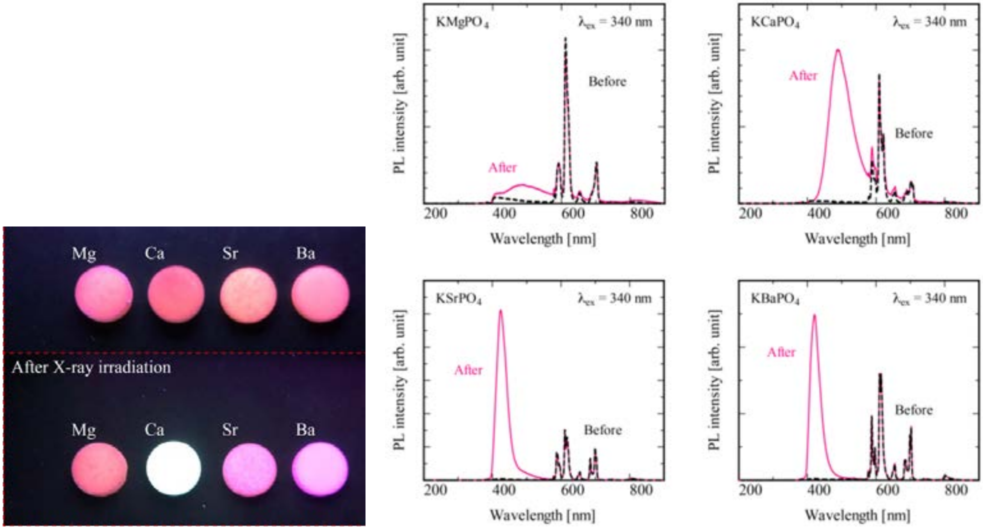

Figure 1 (Left) Photograph when irradiated with 253 nm ultraviolet light and (Right) PL spectra before and after 10 Gy of X-rays irradiation of Eu:K*M*PO_4 ceramics.

Innovative fibers for new light sources and original assemblies of materials

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Keywords: infrared glasses, tellurites, chalcogenides, non linear optical fibers, supercontinuum, hybrid fibers

Light sources in the mid-infrared (IR) between 2 and 20 µm, and even toward the far-infrared above 20µm, are of great interest for molecular sensing, medical, security and defense applications [1]. The availability of broadband, coherent and high-brightness fibered sources has many advantages compared to thermal IR sources or quantum cascade lasers, and the generation of supercontinuum (SC) in engineered optical fibers pumped by femtosecond lasers is one way to reach this goal [2,3]. In these waveguides indeed, an initial high peak power laser pulse, spectrally narrow, interacts with the nonlinear medium in such ways that its spectral width expands drastically during its propagation. Over the last decade, considerable efforts have been made to push forward the results obtained with SC fibered sources in the NIR to the mid-IR [4-7]. This implies to combine a material science trajectory related with glasses compositions, their infrared transparency and optical quality with the engineering of light matter interaction in dedicated waveguides, especially to enhance the optical nonlinear interaction between an initial propagating pulse and the optical fiber in which it is propagating. We propose to describe the field through tellurite glasses and chalcogenide glasses and through the engineering of optical fibers from standard step index to tapered profiles trough microstructured ones. Since the infrared glasses of interest for nonlinear optical applications are generally low Tg glasses, new paradigms have emerged in terms of materials combinations and design of new multimaterial optical fibers. Indeed, these glasses can be combined with each other and together with different materials such as polymers or metals to give rise to new optical fibers combining different functionalities, optical, electrical, mechanical for example. We propose to give here some new insights in the field.

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Smart growth, from combined crystal growth methods to artificial intelligence management: chemical composition control and enhancement of single crystal quality

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Keywords: single crystal growth, artificial intelligence, functional materials

At present time, standard and versatile techniques for growing single crystals from a high temperature liquid phase and using, for instance, the Czochralski, Bridgman or flux processes, are commonly available in worldwide laboratories and dedicated companies for obtaining a wide range of inorganic bulk crystals: oxides, halogenides and semi-conductors [1-3]. Two categories of materials are usually regarded: congruent-melting compounds, which are grown from a melt, and non-congruent-melting compounds, which are grown from a high temperature solution. However, due to intrinsic peculiarities of each technique: thermal distribution, heating medium, possible range of growth kinetics, as well as specific thermomechanical and chemical features of gaseous, liquid and solid phases, as-grown boules with the required quality can display a limited useful volume. Indeed, boules can exhibit local defects such as colour centres, dislocations, chemical vacancies, cracks, impurities or cluster inclusions, which decrease drastically the crystal performance.

On one hand, in order to improve the crystal size and quality with a low rate of defects, we present the combination of different conventional growth methods as a way to achieve the growth of targeted compounds and solid solutions with enhanced compositions, properties and quality [4-7].

On the other hand, we present a study that integrates machine learning with numerical modeling. The objective is to unravel the nonlinear relationship between crystal growth process parameters and furnace geometry on one side, and solid/liquid interface shape and v/G (growth rate over temperature gradients) on the other side. We exemplify this approach by focusing on defect-free YAG and Ge crystals [8].

Various examples of applications in the fields of optics, piezoelectricity, multiferroics and alkali-ion battery are presented [4-9].

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Latest advances in Li_2MoO_4 bulk crystal growth for heat-scintillation cryogenic bolometers

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Keywords: crystal growth, bulk crystal, oxide, heat-scintillation cryogenic bolometer

Because of their high resolution and low detection energy thresholds, crucial experiments aimed at understanding the origin of the neutrino mass and at detecting directly dark matter require the detection of extremely rare events, such as neutrinoless double beta decay (*2β0ν*), by double readout heat-scintillation cryogenic bolometers. In the latter case, these bolometers simultaneously generate a nuclear event and record it in the same crystal that constitutes their core. The most promising crystal to achieve this goal is lithium molybdate Li_2MoO_4. The central part of a Czochralski puller has been designed through numerical simulation in order to optimize the temperature field around the crystal [1]. Initial Li_2CO_3 and MoO_3 powders have been purified by hydrogenocarbonation and by ammoniac route in aqueous solution, respectively. We are now capable of producing routinely kg-mass Li_2MoO_4 single crystals with 50 to 62 mm in diameter, in different growth direction orientations, at a faster pulling rate than by the low temperature gradient Czochralski method. The crystallization mass yield reaches 81% and can still be improved. The crystals do not exhibit any twins, their dislocation densities are in the range $0.8–1.4 \times 10^4$ cm^{-2} for the crystals 50 mm in diameter and their radiopurities match with the expected bolometer operation specifications [2]. The dislocations in Li_2MoO_4 are oriented along the [11-20]-direction and contained in the (0001) plane, corresponding to the basal glide system. In this talk, we will show how crystals with varied diameters grown in different Czochralski configurations exhibit different bolometer operations. The role of fractures will be detailed, together with scintillation properties which result in one of the highest light yield (0.97 keV/MeV, ~1300 photons/MeV) amongst Li_2MoO_4 scintillating bolometers, on the γ-rays and muons detection bands. Mechanical properties measurements reveal that Li_2MoO_4 crystals have a low mechanical hardness which decreases when temperature increases. With new inputs from compressive tests at high temperatures, anisotropic stresses occurring during growth have been recalculated by finite element numerical simulation of heat transfer and thermo-elasticity, by means of the same modelling procedure as previously published but applied to the specific set-up configuration used for growing the crystals. The temperature, velocity and stress fields were calculated at three different solidification distances during the growth, and the calculated and measured interface deflection compared. The temperature gradient in the crystal reaches a maximum of 30 $K.cm^{-1}$, which is always located close to the triple phase line. In addition to interface deflection assessments by rapid extraction experiments of the growing crystal at several solidification distances, we measured temperature versus time profiles in selected points of our set-up during the growth of the crystals and also found a good agreement between measured and calculated temperatures. The velocity field in the liquid phase displays only one counterclockwise vortex, the center of which remains in the upper part of the liquid and moves towards the triple point line as solidification proceeds. The velocity decreases as solidification proceeds too, from typically u_{max}=0.015 to 0.011 m/s. All stresses in the xz section of the crystals are now below the minimum crack formation threshold (σ_{min}>3 MPa, σ_{max}<7.5 MPa at 650°C), as determined from uniaxial compressive tests, and they are the strongest at the periphery of the crystal when the shoulder is formed, and in the middle of the solidification interface at further growth stages. The fact that Li_2MoO_4 exhibits a fragile cracking behaviour without plastic response (either by dislocation multiplication or by twin formation) is a rather uncommon feature for an ionic crystal.

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Development of heavy single crystalline scintillators

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Keywords: scintillator, single crystal, radiation detector, luminescence

Scintillators are one of the luminescent materials, and have a function to convert a quantum of ionizing radiation to thousands of low energy photons immediately via interactions between the material and ionizing radiation [1,2]. When the target of detection is high energy photons such as X- and □-rays, heavy materials are preferable for scintillators since the detection efficiency against high energy photons depends on density and effective atomic number. Up to now, many types of materials have been examined for scintillators, such as single crystal, glass, and opaque and transparent ceramic [2]. Among them, bulk single crystal scintillators have been used owing to a superior optical quality including high transmittance and luminescence efficiency.

In the conference, some recent results of development of heavy scintillators mainly containing Lu, Hf, Ta and Tl are introduced. These materials were synthesized by some single crystal growth techniques such as the floating zone and bridgeman method. After the synthesis, they were examined on optical (photoluminescence excitation and emission spectra and decay curve) and scintillation (radioluminescence spectrum, decay curve, afterglow and pulse height) properties. In Lu-based crystals, rare earth doped Lu_2O_3 crystals are introduced, and especially, Tb-doped one shows a high scintillation light yield. In Hf-based ones, some results of rare earth doped $AEHfO_3$ (AE = alkali earth) crystals are presented, and Ce-doped $(Mg,Ca)HfO_3$ shows a high scintillation light yield [3]. Among Ta-based crystals, $Mg_4(Nb,Ta)_2O_9$ crystals have a high light yield due to charge transfer luminescence of Ta/Nb and O [4]. In Tl-based crystalline compounds, $TlMgCl_3$ shows a high light yield and energy resolution [5]. In the conference, these results will be introduced.

Acknowledgments

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Tb-doped fluoride visible laser with kW peak power operation

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Keywords: visible laesr, blue laser diode, high peak power laser, laser procesing

Utilizing Terbium (Tb)-doped materials as a laser amplification medium in the visible spectrum for high pulse energy achievements shows great promise. Nevertheless the initial demonstration of Tb lasers in 1967, there has been a notable scarcity of research in this area[1,2]. There has been reactivated by two key developments: Yamashita et al.'s 2007 demonstration of continuous-wave oscillation in a Tb-doped ZBLAN fiber laser[3], and, a decade later, the demonstration of a Tb-doped fluoride single-crystal by Kränkel's group[4]. Building on these findings, our team has now achieved the first Q-switched oscillation of a Tb laser[5]. Achieving this feat required nearly five decades, a testament to the progress made in Tb-doped laser gain media and the innovation of excitation light sources around 488 nm, like optically pumped semiconductor lasers or blue laser diodes[6].

Tb-doped YLF has a very long fluorescence lifetime of 4.9 ms and a high energy storage capacity. A semiconductor laser with a pumping wavelength of 488 nm can be used, and by using Tb-doped YLF, a green laser beam (544 nm) with high peak power can be generated without using nonlinear optical effects. This is very promising as a laser light source for metal processing such as copper. In this presentation, the historical background, the latest research status, and the direction of material development will be reported.

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Octahedral molybdenum cluster complex-graphene oxide nanosheet nanocomposite material for enhanced photoinactivation of bacteria

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Keywords: octahedral molybdenum cluster complex, graphene oxide, hybrid, photoinactivation

The effective photoinactivation of bacteria, *Staphylococcus aureus*, was achieved by using octahedral molybdenum cluster complex, $[Mo_6I_8(OCOC_4H_8PPh_3)_6]Br_4$ (Mo_6), synthesized from molybdenum, iodine, sodium methanolate, and (4-carboxybutyl)triphenylphosphonium bromide,[1] and graphene oxide (GO), which was prepared by the treatment of graphite with a mixture of sulfuric acid and sodium nitrate, and subsequently with a potassium permanganate solution.[2] The preparation of the GO/Mo_6 nanocomposite was achieved by simply mixing a dimethyl sulfoxide (DMSO) dispersion of Mo_6 and a DMSO solution of GO, subsequent stirring, and addition of aliquot of the mixture to deionized water.[3] High-angle annular dark field (HAADF) imaging of scanning transmission electron microscopy of the product showed that the GO nanosheets were decorated with Mo_6 nanoaggregates. Since the zeta potentials of the aqueous dispersion of GO and that of Mo_6 were −34 ±13 and 8 ±6 mV, respectively, it is reasonable to assume that electrostatic interaction between GO and Mo_6 was present in aqueous medium, leading to the decoration of GO nanosheet surface with Mo_6 nanoaggregates. The photoluminescent behavior of the aqueous solution of the GO/Mo_6 nanocomposite was different from that of pure Mo_6. The luminescence intensity of Mo_6 was decreased drastically after nanocomposite formation, indicating that the interaction between GO nanosheet surface and Mo_6 nanoaggregates led to the quenching of the luminescence. The quenching of the triplet state of Mo_6 by oxygen was suppressed after composite formation, suggesting that the electron transfer from Mo_6 to GO was likely to occur. The photoinactivation of *Staphylococcus aureus* was evaluated by irradiating the 460 nm light to the cultures of *Staphylococcus aureus* incubated as planktonic cells. While the culture with Mo_6 showed mild photoinactivation behavior, the addition of the GO/Mo_6 nanocomposite resulted in drastic photoinactivation behavior.

Acknowledgments

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T4.6 Multifunctional Coatings for Energy and Environmental Applications

Room-temperature ceramic coating: Current status of understanding RTIC phenomenon in AD method and future prospects for application development

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Keywords: aerosol deposition, ceramic coating, RTIC phenomenon, thick film, room temperature

Dense and highly adhesive lamination of functional ceramic materials is the key to the realization of electronic devices, energy, and environment-related devices. Aerosol Deposition (AD) method[1]-[4] is a unique approach for metal and ceramic coating, where solid state submicron metal and ceramics particles are accelerated by gas flow up to 100 - 500 m/s and then impacted onto a substrate. AIST found interesting consolidation phenomenon of ceramic particles in this method over 20 years ago. During collision of fine particles and interaction with substrate, these ceramic particles, not only for oxide materials but also for non-oxide materials, formed thick, dense and hard ceramic layers at room temperature. No additional heating for solidification of ceramic powder was required. The room-temperature impact consolidation phenomenon (RTIC) of ceramic particles (a phenomenon in which ceramic particles solidify at room temperature without sintering), which was clarified by research on the aerosol deposition method, is characterized not only by the fact that it is a room-temperature process, but also by the fact that it is denser than the conventional thermal spraying method. It has a very important meaning as a principle for obtaining a ceramic coating with high adhesion. Until now, the densification mechanism of ceramic coatings by the AD method has been explained by the fragmentation and the plastic deformation of colliding fine particles. However, there are many unclear points about the mechanism of plastic deformation and interparticle bonding of ceramic fine particles at room temperature.

In this lecture, we will discuss the current state of understanding of the principles of the AD method and the future prospects for its application, based on reports on the elucidation of the mechanism of the AD method which has recently begun to be studied in various fields.

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Thin-film ceramics for energy applications

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Keywords: thermoelectrics, nitrides, physical vapor deposition, thermal conductivity

Thermoelectric devices have the potential to contribute to energy harvesting in society by directly converting heat into electricity or vice versa. However, the conversion efficiency of thermoelectric devices of today is limited. In this lecture, I present an overview of our work on multicomponent CrN-, ScN-, and $Ca_3Co_4O_9$-based thin films. We have developed methodology for highly textured as well as nanoporous virtually phase-pure $Ca_3Co_4O_9$ thin films. These can further be deposited on flexible mica substrates, enabling flexible inorganic thermoelectric thin films that withstand repeated bending. They can also be made as free-standing films and as nanoporous materials for reduced thermal conductivity. ScN thin films exhibit an anomalously high power factor (S_2/ρ) for transition metal nitrides, but has high thermal conductivity, thus its ZT is low (~0.2). To reduce lattice thermal conductivity, potential strategies are nanostructuring, alloying or nanoinclusion formation. Pure CrN exhibits n-type conduction with a high power-factor enabled by a high electron concentration thermally activated from N vacancies, and alloys can be made of rocksalt-$Cr_{1-x}Sc_xN$. Multicomponent alloying of ScN and CrN in alloys such as CrMoVWN or combinations thereof offer further possibilities for tailoring the thermoelectric properties and growth conditions.

Cr-rich spinel phase formation in alumina dispersed 316L stainless steel processed by spark plasma sintering

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Keywords: Cr-rich spinel, spark plasma sintering, oxide dispersion strengthened steel, ceramics, alumina

Oxide dispersion strengthened (ODS) 316L stainless steel alloys with two different compositions of 0.33 wt% Al_2O_3 and 1wt% Al_2O_3 were prepared by attrition milling and spark plasma sintering (SPS) process [1]. SPS is an effective and ecomomic alternative of hot isostatic pressing providing benefits, like rapid heating, limitation of grain growth, and efficient densification kinetics. The mechanical properties of 0.33 wt% Al_2O_3 composite were better (e.g. higher bending strength) due to more uniform distribution of alumina at the grain boundaries. Formation of the spinel phase was observed by TEM. The spinel phase had dominantly Cr_2AlO_4 composition and was surrounded by an amorphous silica phase. The presence of silica implies the analogy with geological formation of spinels in mafic or ultramafic rocks with low oxygen fugacity and presence of silica phase [2]. The conditions that may occur during SPS can be similar to those of geological spinel formation, especially taking into account the possible formation of "melt pockets" between the steel grains, where the local temperature and pressure can be temporally higher than the nominal process temperature. Cr and Si, necessary for the phase transformation, may segregate from the stainless steel alloy at SPS conditions. The lattice parameter of the spinel phase is 8.36Å independent of the local composition variation. The lattice parameter of the spinel phase is close to the high end among chromite related spinels [3] which implies that octahedral sites of spinel structure are mainly occupied by Cr^{3+} or possibly Fe^{3+} cations.

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T4.7 Materials for Extreme Environments: Ultrahigh Temperature Ceramics (UHTCs) and Nano-laminated Ternary Carbides and Nitrides (MAX Phases) Applications

Effect of multiple cations on the microstructure, properties and ablation behavior of ultra-high-temperature ceramics

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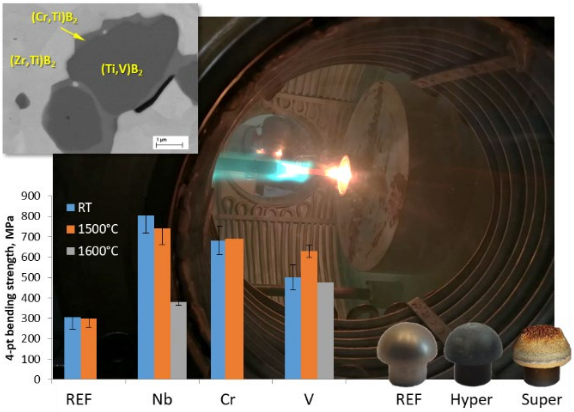
Keywords: type your, keywords here, separated, by commas

Multi-phase ceramics based on ZrB_2-SiC and doped with TiB_2 and either Cr, Nb or V are prepared by powder metallurgy and hot pressing to obtain a multi-scale microstructure comprising a boride matrix displaying the core–shell feature where nano-inclusions could precipitate from the super-saturated solid solution.

TiB_2 completely dissolved in ZrB_2 in presence of Nb forming a homogeneous multi-phase $(Zr,Ti,Nb)B_2$ solid solution, whereas it remained a discrete phase when combined to Cr or V resulting into a dual microstructure with core-shell morphology.

Microstructure details are then correlated to the mechanical properties at elevated temperatures up to 1600°C and to the ablation behavior upon exposure to subsequent supersonic-hypersonic flows that reached Mach number in the 3-5 range, achieving surface temperatures over 2300°C.



Microstructure of multi-phase solid solution based on $(Zr,Ti,Cr)B_2$, bending strength at various temperatures and aspect change of a model based $(Zr,Ti,V)B_2$ on upon ablation in Hypersonic and Supersonic regimes.

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T4.8 DESIGN, PROCESSING, AND APPLICATIONS OF NANOLAMINATED TERNARY TRANSITION METAL CARBIDES/NITRIDES/BORIDES AND MXENES AND MBENES

Replenishing the limited Al-reservoir of Cr_2AlC MAX phase coatings in oxidizing environments

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Keywords: MAX phases, oxidation, diffusion

Cr_2AlC MAX phases has often been at the center of several investigations because of it exhibits a very good oxidation resistance at high temperatures. However, long oxidation durations often lead to the failure of the MAX phase. The oxidation of Cr_2AlC is first characterized by the outward diffusion of Al species which react with the oxidizing environment and form an oxide scale at the surface of the MAX phase. As Al species continue to diffuse the MAX phase becomes depleted in Al, which results its decomposition into Cr-carbides. The presence of these carbides is then typically accompanied by pore formation and ultimately the failure of the MAX phase part. To avoid the failure of the component, suppressing, or at least, delaying the formation of Cr-carbides by forming a highly protective oxide scale is very important. However, the formation of the oxide scale will depend on many parameters including the roughness and texture of the MAX phase, but also the temperature and humidity levels of the oxidizing environments. Therefore, to avoid MAX phase decomposition, the concept of an Al-reservoir able to continuously supply a MAX phase coating with Al upon oxidation is suggested.

Fine and coarse-grained Cr_2AlC MAX phase reservoirs were designed and produced using spark plasma sintering (SPS). Coarse grained MAX phases were obtained by sintering pre-made Cr_2AlC powders, while fine microstructures were obtained by reactive sintering of elemental Cr, Al and submicron carbon black powders. The reservoirs were then used as substrates for Cr_2AlC coatings processed by high-power pulsed magnetron sputtering (HPPMS). The MAX/MAX assemblies were then oxidized in air at 1100 °C, in an open furnace. The oxide scale thickness of each assembly was measured along with the Al content left in the MAX phase coatings. Al replenishment was observed in the case of the fine-grained reservoir as the Al content present in the coating, after oxidation, was larger than that measured in the coating deposited on the coarse-grained substrate and on an Al-free substrate (MgO), for which no Al replenishement is expected. The mechanisms that come into play were related to the original microstructure of the reservoirs but also to the changes that they go through during oxidation. Finally, to showcase the element supply that occurs from the substrate to the coating, a different MAX phase substrate was used, Cr_2GeC, to track the possible replenishement with more ease.

Improving the ab-initio prediction accuracy for the elastic and mechnaical properties of MAB and MAX borides

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Keywords: MAB phases, elastic moduli, damage tolerance, thernal expansion, first principles

The MAB phases [1] and recently-discovered S-group elements containing MAX borides [2] have attracted much attention becasue of the unqiue combnation of ceramic- and metal-like proerties, and promissing structural and functional applications. After examining the intrinsic and thermodynamic stability, some practical approches are proposed in the present work to more accurately predict their elastic and mechanical properties.

By calculating the lattice constants and elastic moduli of MoAlB, Fe_2AlB_2 and Mn_2AlB_2 using typical exchange-correlation functionals, the observed positive correlation between the calculation errors of elastic moduli and those of cell volumes suggests a method to significantly improve the calculation accuracy for elastic moduli using the experimental cell volume to correct the input model (volume correction method), resulting in satisfactory results. Furthermore, a two-step strategy is proposed for the precise high-temperature elastic moduli with the help of quasi-harmonic approximation for the most accurate high-temperature cell volume using an exchange-correlation functional in the first step, and another one used in the volume correction method in the second step.

Using the “bond stiffness” model as well as the associated criterion for damage tolerance and fracture toughness, the strongest covalent bonding is formed between B and M/B atoms while the weakest bonding is formed between M/B and A atoms. For most Al-containing MAB phases except 512-type, the ratio of bond stiffness of weakest M-Al or Al-Al bonds to the strongest M-B bonds (k_{min}/k_{max}) falls into the range of 1/3-1/2, indicating their high damage tolerance. But this is not true for the Si-containing ones, with the k_{min}/k_{max} greater than 1/2 and strong M-Si bonds. Moreover, the ratio of bond stiffness of weakest M-S to the strongest M-X bonds (kmin/kmax) over 1/2 indicates the intrinsic brittleness of all S-containing MAX phases except Nb_4SC_3. Of much interest, the experimental fracture toughness of the MAX and MAB phases decreases with increasing the k_{min}/k_{max}.

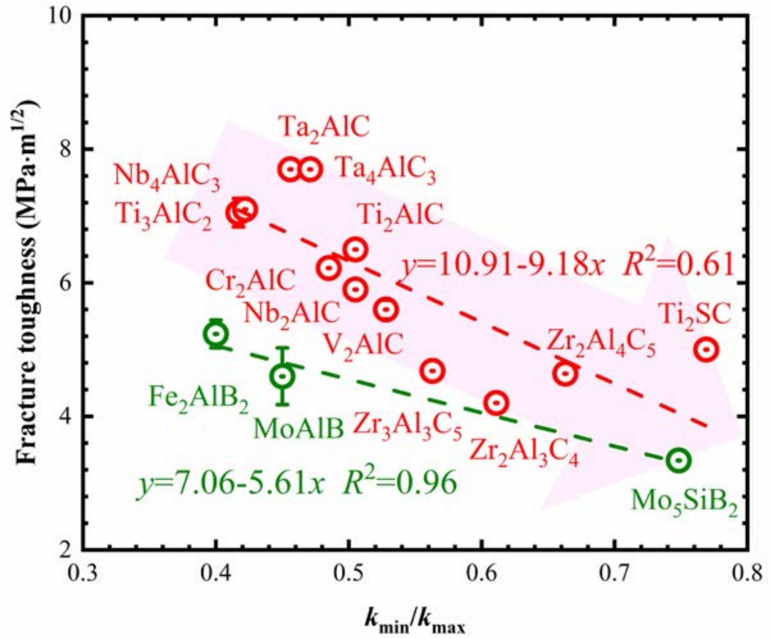

Figure 1 Experimentally measured fracture toughness by single edge notched beam (SENB) as a function of theoretically calculated k_{min}/k_{max} of some selected ternary layered compounds [1]

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Synthesis science of MAX phases: A chemist’s journey to new functional ceramics

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Keywords: synthesis science, layered solids, carbides, nitrides, carbonitrides, 2D materials, Mxenes, structure, morphology, solid-solutions

MAX phases are a chemically versatile family of materials that exhibit very interesting properties combining characteristics of metals and ceramics. They are ternary transition metal-based carbides, nitrides and carbonitrides, that typically crystallize in a hexagonal structure with alternating layers of M_6X octahedra (M = early-to-mid transition metals, X = C and/or N) and the A-element (A = main group element or late transition metal). According to the general chemical formula $M_{n+1}AX_n$ ($n = 1, 2, 3$), “211”, “312” and “413” MAX phases possess n (1, 2, 3) M_6X layers (2, 3 and 4 M-layers) between the A-layers, respectively. Historically the interest in MAX phases has been related to their intriguing mechanical properties including high-temperature and corrosion resistance and metal-like conductivity, and they are therefore not typically discussed as functional materials. In a different setting, they serve as bulk precursors for a relatively young class of 2D materials, the MXenes that can be synthesized from MAX phases by means of chemical etching.

In this talk, I will discuss our group’s efforts to synthesize new versions of MAX phases and MXenes in terms of their chemical composition and morphology. The structure of the compounds is analyzed in detail by different diffraction techniques and electron microscopy. Additional spectroscopy techniques allow insights into the chemistry of intermediate species and the final products. The functional properties of the new types of materials include magnetic and electronic properties as well as electrocatalytic performance.

Acknowledgments
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Predicting the optimal synthesis conditions and modelling the structual and electrochemical properties of MXenes

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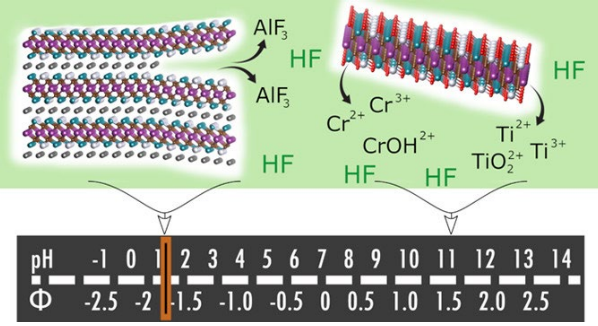
Keywords: computational modelling, MXenes, stability, energy storage, electron-phonon coupling

MXenes have shown great promise for use in a multitude of applications, and in particular in emerging electrochemical energy storage devices, including batteries and supercapacitors. It is well known that MXene surfaces are terminated by mixed –O, –F and –OH functional groups as a result of the chemical etching production process and these functional groups are randomly distributed over the surfaces, with limited experimental control over their composition. However, theoretical simulations typically assume uniformly terminated surfaces in order to minimize compuatational cost. As a result, there is limited understanding of the influence of realistic surface terminations on many structural, electronic and electrochemical properties. In this talk, I will discuss how first principles calculations can eludidate the effect of the termination groups on the structural, electronic and electrochemical properties of several common MXenes, focussing in particular on how it affects their storage capacity for future post-Li ion batteries.

I will also discuss how we can calculate the optimal conditions necessary for the chemical etching of o-MXenes – a family of layered double-transition-metal carbides and nitrides with a unique out-of-plane ordering of the two metal atoms. Their chemical versatility means they have novel applications in energy storage, catalysis, and sensing devices. I will show how Pourbaix diagrams produced from first-principles calculations can be used to determine the conditions necessary to enhance the yields of o-MXenes and will discuss how the stability of the o-MXene depends on the nature of the terminating groups.

Figures



Predicting the optimal synthesis conditions for the formation of o-MXenes.

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Radiation-induced swelling in MAX phase-based ceramics for select applications in advanced nuclear systems

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Keywords: MAX phase solid solutions, radiation-induced swelling, in-situ ion irradiation in the TEM

The nanolaminated solids referred to as the MAX phases are described by the $M_{n+1}AX_n$ general stoichiometry, where M is an early transition metal, A is an A-group element (mainly, from groups 13-15 in the periodic table of elements), X is C or N, and n = 1, 2 or 3. Their hexagonal crystal structure ($P6_3/mmc$, space group 194) leads to anisotropic swelling under irradiation, whereupon the unit cell expands along the *c*-axis and contracts along the *a*-axis. Moreover, phase-impure MAX phase ceramics are susceptible to failure by radiation-induced differential swelling (Fig. 1). This work addresses the swelling behavior of MAX phase-based ceramics for specific nuclear applications, e.g., pump impellers for Gen-IV lead-cooled fast reactors (LFRs) or accident-tolerant fuel (ATF) claddings for Gen-II/III light water reactors (LWRs). The evolution of radiation swelling in ternary (Zr_2AlC, Ti_2AlC, Cr_2AlC, etc.) MAX phases and higher-order solid solutions was monitored in-situ in the transmission electron microscope (TEM) by means of helium ion implantation (6 keV He^+, flux: 10^{14} ions/$cm^2 \cdot s$) in the 350-800°C range to a maximum damage dose of 10 dpa [1]. The two main approaches used to control radiation swelling in MAX phase ceramics strive for high phase purity and/or strong textures. The former can be achieved in compositionally tailored solid solutions synthesized with early transition metal hydride starting powders. As opposed to pure metals, the milling of metal hydrides into fine particles is easier as they fracture in a brittle manner; moreover, milling metal hydride powders is not accompanied by excessive powder oxidation similar to that observed for elemental powders, since the hydrides decompose into their respective metals, producing (in situ) powders with highly reactive metal surfaces, while simultaneously releasing hydrogen (H_2) that limits powder oxidation. The use of early transition metal hydride powders has so far enabled the synthesis of previously “impossible” to produce MAX phase compounds in the (Zr,Hf)-Al-C system.

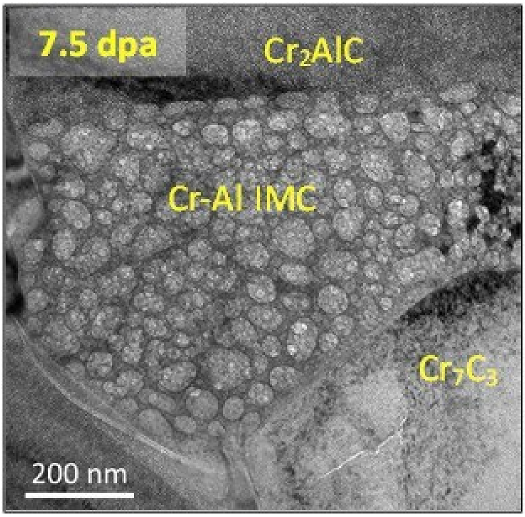

Fig. 1. Evidence of differential swelling in a Cr_2AlC-based ceramic irradiated to 7.5 dpa at 600°C with 6 keV He^+: small equiaxed He bubbles in the Cr_2AlC MAX phase, large equiaxed He bubbles in the Cr-Al binary intermetallic (IMC), and very small equiaxed He bubbles (followed by microcracking) in the Cr_7C_3 binary carbide.

Acknowledgments

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Formation and properties of MAB phase thin films

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Keywords: MAB phase, density functional theory, magnetron sputtering, phase formation, thin film

A $(Mo_{0.24}Cr_{0.76})_{0.40}Al_{0.32}B_{0.28}$ thin film was deposited by direct current magnetron sputtering at 600 °C substrate temperature. Analysis by X-ray diffraction, energy-dispersive X-ray spectroscopy, elastic recoil detection analysis, and high-resolution scanning transmission electron microscopy revealed the formation of the previously unreported $(Mo,Cr)_2AlB_2$ MAB phase, along with Cr_3AlB_4, CrB_4, and Mo, in good agreement with density functional theory (DFT) calculations. Hence, the MAB phase family in the Mo-Cr-Al-B system is extended by a novel, quaternary member. Furthermore, using spatially resolved composition and structure analysis the thermal stability of Mo-Al-B and Cr-Al-B based thin films is investigated.

Radiation effects in MAX phases

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Keywords: MAX phases, irradiation effects, phase transformations, resistance to amorphization, high entropy

MAX phase materials exhibit both metal and ceramic properties due to their unique laminated atomic structures, making them promising candidates in advanced nuclear energy systems. It is very important to understand the response of MAX relative to irradiation. In our work, an order-to-disorder phase transformation and the formation of metastable solid solution phases were observed using high-resolution STEM HADDF, ABF imaging, and X-ray diffraction under ion irradiation [1]. Combining *ab initio* molecular dynamics simulations and first-principles calculation, it is found that the phase stability of different MAX phases under irradiation is influenced by the degree of lattice distortion of the solid solution metastable phases. More recently, high entropy MAX (HE-MAX) phases have been developed and attracted much attention due to their unique properties. The mechanism of the irradiation-induced structural evolution and the point defect properties of two series of HE-MAX phases, M_2SnC (M = Ti, V, Nb, Zr, Hf) and $(Ti, M)_2AlC$ (M=Nb, Ta, V, Zr) are investigated [2,3]. It is found that the elemental species, instead of the number plays a more crucial role in the irradiation tolerance of MAX phases. This work provides a comprehensive understanding of structural evolution in MAX phases and proposes a new strategy for designing novel MAX phases with better performance under an irradiation environment.

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T4.9 CERAMIC INTEGRATION TECHNOLOGIES FOR ENERGY AND ENVIRONMENTAL APPLICATIONS

High temperature joining and mechanical testing of joints in silicon carbide-based materials: Technical challenges and opportunities

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Keywords: ceramic, ceramic matrix composite, joining, brazing, integration

Silicon carbide (SiC)-based ceramics and composites are well suited for high temperature aerospace applications. However, challenges in the fabrication of complex shapes and the need for integration with metal-based systems requires joining and integration solutions. Each joining and integration application requires a tailored solution based on material selections, properties, and incompatibilities, as well as joining or brazing conditions, component geometries, operating conditions, and service life. Once processing conditions for a joining or brazing solution are developed, thermomechanical testing is conducted to further characterize and advance the joining technologies toward targeted aerospace applications. In this presentation, joining using refractory eutectic phase bonding (from the Si-8.5Hf phase) and brazing with active braze alloys were utilized as model systems to develop mechanical test methods for characterizing and screening joints and brazes. International standard testing (ISO 13124) of bonded crossbars was used to measure interfacial bond strengths of ceramic materials under shear or tensile stresses depending on the crossbar orientation in the test fixture. Also, single lap offset testing with the use of digital image correlation (DIC) was conducted on brazes to screen shear strengths and strain evolution. Results, challenges, and advancement of bond testing will be discussed. Also, processing-microstructure-properties correlations will be emphasized. Various technical challenges and opportunities will be discussed.

A novel cost-efficient metal-ceramic-hybrid brake disc for EV's – joining challenges & friction performance

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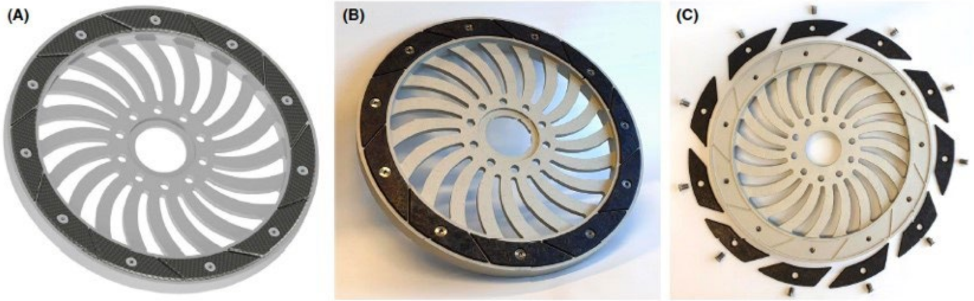
Keywords: hybrid brake disc, ceramic friction materials, joining, C/C-SiC, electric driven vehicles (EV's)

Ceramic brake discs, made of C/C-SiC (C-fiber reinforced SiC) are thermal shock and wear resistant materials with low densities (< 2.5 g/cm^3) and a high damage tolerance. Therefore, they found their application already in passenger cars as a service brake (> 300,000 parts/year) with extraordinary lifetimes and as emergency brakes for industrial applications in cranes or conveying systems. The low wear rates and fine dust emissions make ceramic discs superior compared to conventional brakes made of grey cast iron or steel. One drawback of ceramic brake is, that they are very expensive, due to the applied materials, the long processing times and the high machining costs.

To overcome these challenges a metal-ceramic hybrid brake disc is a promising approach. A cost efficient, light metallic carrier body (e.g. Al) can be applied to carry the mechanical and thermal loads. Within the Al-metal ring wear resistant C/C-SiC segments are fixed and the frictional contact was made only between these segments and their counterpart, e.g. the brake pads. Therefore, the amount of the required C/C-SiC can be decreased dramatically (about 80 %) and the costs of the whole disc as well significantly.

The joining of the ceramic segments with the metallic disc is challenging and was studied in detail. Thermal loads and corrosion must be considered. Aluminum was studied in combination with C/C-SiC segments. Joining methods like screwing and adherence were evaluated at room temperature up to 250 °C. The corrosion was studied in a salt containing solution under different conditions. One suitable glue (JBWeld) was identified. Screwing was possible as well and with special designed screws. Afterwards, an Al-ceramic-hybrid disc was manufactured and tested on a tribological test rig under realistic conditions, with a fly wheel, that simulates the mass of a car. The results show, that the coefficient of friction (COF) is mostly in a promising range of > 0.25, but the wear rate is significantly higher compared to the full ceramic disc, which is most probably due to the gaps between the segments. Nevertheless, the hybrid-disc is a promising concept for an emergency brake disc for electric driven vehicles (EV's, city cars & motorcycles), even if the design of segments needs to be improved.

Figure



Final design of the Al-metal-ceramic hybrid brake disc (outer diameter = 410 mm): (A) rendering of CAD-Design, (B) photo of the built prototype, (C) carrier body with friction segments and correspondent screws

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Material and process development for Copper-Si_3N_4 AMB-substrates

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Keywords: Si_3N_4 substrate, copper, active metal brazing, brazing paste, circuit board, power electronics

Power electronic components made of copper-ceramic composites as circuit carriers and SiC semiconductor components are at the heart of the control and regulation of high currents and voltages and are therefore key components in devices and systems for the storage and conversion of electrical energy. A focus is on the use of highly thermally conductive and temperature cycling resistant copper-ceramic composites based on Si_3N_4 ceramics in combination with SiC semiconductors for battery-powered electric vehicles and increasingly in photovoltaics. These copper-Si_3N_4 composites produced by active metal brazing (AMB) exhibit significantly increased thermal shock resistance compared to DCB substrates. At the electrical level, the composite must ensure good conductivity within the metal layer and excellent insulation through the ceramic. Mechanically, the ceramic must be stable against external loads. Thermally, the heat generated during the switching of the semiconductor chips must be dissipated and the thermal expansions in the composite.

In the German CuSiN project, material and process improvements to Cu-Si_3N_4 AMB substrates were developed along the complete production chain. An overview of the topics addressed in the project and the results achieved is presented in this contribution. Based on Si_3N_4 powders with low O and Al impurities, Si_3N_4 ceramics that possesses high thermal conductivity (> 85 W/(mK) along with high strength (> 800 MPa) have been developed that can be sintered into large blocks from which substrates with a thickness of 320 μm and also lower thickness can be efficiently cut using the multi-wire saw technology well known from photovoltaics. For the active metal brazing of Cu-Si_3N_4 composites, screen-printable silver-containing and silver-free active metal brazing pastes have been developed, which allow joint zones with thicknesses < 25 μm. To improve the process suitability of the pastes, particularly fine-grained powder qualities were evaluated. Particular attention was paid to minimizing and homogenizing the particle content of the active phases (TiH_2) to avoid the formation of titanium silicides at the interface with Si_3N_4 during the brazing process. The bond strengths of the silver-free filler metal are approximately 80 % of those of the silver-containing qualities. For copper, grades with improved microstructural stability have been evaluated against thermal stress in the AMB process up to 1050 °C. Microstructures with medium grain sizes in the range of 300 to 600 μm have proven to be more favourable in terms of achievable bond strengths than finer-grained qualities (< 100 μm) or those exhibiting an inhomogeneous microstructure with individual large grains up to 3000 μm. Based on these material- and process-specific individual results, joining processes have been developed to achieve peel strengths exceeding the strain strength of the bonded medium-grained copper and homogeneous, pore-free joint zones. The composites were characterised in terms of microstructure, bond strength (macroscopic and microscopic scale) and cycle stability. Finally, the joining process was demonstrated in scaled furnace units using graphite-based charging racks.

Joining of monolithic SiC and ceramic matrix composites with refractory transition metal-based interlayer

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Keywords: joining, silicon carbide, ceramic matrix composites, spark plasma sintering, zirconium carbide

Field Assisted Sintering Technology (FAST) was successfully applied to join monolithic CVD β-SiC and C_f/SiC ceramic matrix composites (CMC) with $ZrSi_2$-based interlayer. First, the wetting and phase interaction of molten transition metal disilicide ($ZrSi_2$) on the surface of CVD β-SiC and C_f/SiC was investigated in different atmospheres (vacuum and Argon). A significant evaporation of Si from the liquid affected the wetting behaviour of the alloy when tested under a vacuum. On the other hand, wetting behaviour and spreading of the alloy were significantly improved in argon atmosphere. The formation of ZrC phase with a high melting point partially hindered the spreading of the melt over the surface of C_f/SiC or CVD β-SiC.

The $ZrSi_2$ powder was then used as an interlayer for joining of both CVD β-SiC and C_f/SiC using FAST at different temperatures (1400 – 1650°C). A non-homologous interlayer was formed, consisting of both ZrC and remaining $ZrSi_2$. In addition, a significant reaction with SiC and C_f/SiC substrates was observed, leading to the dissolution of SiC and infiltration of the filler into the base materials. Therefore, the $ZrSi_2$-C (10 wt.%) powders mixture was used to form a uniform SiC-ZrC composite interlayer by in-situ reactions between $ZrSi_2$, C, and SiC-based ceramics. The strength of the joints significantly improved with the increasing joining temperature, and reached the initial strength of the reference, un-joined CVD β-SiC and/or C_f/SiC materials. The mechanical performance of the joints was then compared to the joints of the same base materials with a Ti foil and a Ti_3SiC_2 MAX phase as the interlayers. Unlike the joints with the Ti and Ti_3SiC_2 interlayers, no degradation of the strength of the joints up to 1400°C was observed, due to the in-situ formed refractory ZrC-SiC interlayer.

Acknowledgments

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T4.10 ENVIRONMENTAL FRIENDLY AND ENERGY EFFICIENT MANUFACTURING ROUTES FOR THE PRODUCTION ROOT TECHNOLOGY APPLICATIONS

Joining as enabling technology for energy- and resource-efficient manufacturing

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Keywords: brazing, soldering, reactive joining, nanojoining

The combination of materials with different properties in one product is crucial for energy- and resource-efficient manufacturing of high-performance products, as it enables the best match between the product requirements and local component properties. Joining, in this respect, is a key enabling technology for the manufacturing of multi-material product, in particular for the full integration of high-performance ceramics across various length scales. However, several challenges need to be overcome when manufacturing reliable dissimilar material joints. In particular, in the case of large-scale ceramic-metal joints, as for example for space or medical applcations the thermal residual stresses must be controlled [1], [2]. For miniaturized devices with heterogeneous materials combinations, such as those used in high-power electronics, the thermal management is a priority issue.

This contribution will discuss some examples of recent developments in joining techniques, from brazing and soldering to micro/nano-joining techniques [3], and their applications [4]. The emphasis will be on the materials that enable this technological progress, such as composite brazing fillers, nanoparticle-based sintering pastes, nanomultilayers, and reactive nanofoils [5]. The role of ceramics within these approaches, for example, as a functional barrier in nanomultilayers, will be stressed. The opportunities of energy-saving approaches by techniques without use of external heating sources such as reactive joining will be discussed. All the examples demonstrate that the growing energy and environmental challenges can only be addressed by a holistic approach based on integrated materials and process development.

Acknowledgments
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Low-temperature preparation and high-temperature oxidation performance of SiBCN ceramics with MA@PDC-SiBCN structure

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Keywords: SiBCN ceramics, oxidation behavior

In this study, the densification of SiBCN ceramics with an MA@PDC-SiBCN structure at low temperatures (<1600 °C) without any sintering aids was achieved by preparing a partially cured polyborazylene coating layer on the surface of MA-SiBCN nanoparticles, followed by warm pressing of coated powder and pyrolysis/sintering of powder compact. Due to the significant viscoelastic deformation behavior, the partially cured precursor layer surrounding the MA-SiBCN particles in the coated powder could merge together to form a three-dimensional precursor network that encapsulates and connects MA-SiBCN particles in a dense powder compact. Serving as a template, the structure in the powder compact transforms to dense SiBCN ceramics with MA@PDC-SiBCN structure during subsequent pyrolysis and sintering and the resulting ceramics exhibit enhanced mechanical performance and oxidation resistance. Under the same sintering condition, MA@PDCs-SiBCN ceramics demonstrate a substantial increase in density (2.62 g/cm^3>2.16 g/cm^3), compared to traditional MA-SiBCN ceramics, with flexural strength from 91.2 MPa to 285.9 MPa, and fracture toughness from 0.73 MPa·m$^{1/2}$ to 4.63 MPa·m$^{1/2}$. The presence of numerous relatively weaker interface binding in the MA@PDCs-SiBCN structure significantly facilitates stress relaxation at crack tips and deflection within the ceramic matrix, thereby markedly enhancing the mechanical properties of SiBCN ceramics.

The heterogeneous oxidation behavior and kinetics of each phase in MA@PDCs-SiBCN ceramics at different temperature range and their effects on structural evolution and oxide layer composition were analyzed by comparison with the MA-SiBCN ceramics. The significantly improved oxidation resistance of MA@PDCs-SiBCN ceramics should be attributed to the inhibition of MA@PDCs-SiBCN structure to heterogeneous oxidation, especially the consumption of *t*-C, and different oxide layer composition generated from microcrystalline structure rather than nano capsule-like crystalline structure. The kinetic calculation shows that each phase in MA@PDCs-SiBCN ceramic has a higher activation energy than that in MA-SiBCN ceramic because the oxide layer of MA@PDCs-SiBCN is a uniform borosilicate solution with more residual nitrogen and carbon elements, providing better oxygen-isolating and self-healing capacity.

Sustainable URTRIP technology: Up-cycling, recycling, and trans-cycling of industrial by-products

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Keywords: recycling, upcycling, transcycling, industrial by-product

Recycling is gaining more attention these days. Resource depletion has resulted in more energy consumption in the production of the same element from the geological minerals and more CO_2 emission. For example, iron ore contains higher Al_2O_3 and P contents than ever, so more energy is required for iron- and steel-making processes. Accordingly, the conventional blast furnace is switched to the electric arc furnace to utilize the steel scrap more efficiently. Additionally, hydrogen-based DRI production has been developed in many countries. Likely, many technological breakthroughs have been developed to recycle human-made resources: so-called urban mines. The complexity of the minerals tackles the recycling of the urban mine. Geological minerals generally contain 15 elements, whereas urban mine minerals have more than 40 elements to meet the requirements of the market for functional materials of high complexity. Therefore, engineers must overcome technological difficulties to find a solution to increase the recycling rate and save natural resources.

In order to increase the overall resource efficiency, recycling, up-cycling, and trans-cycling technologies should be considered simultaneously. When we focus on the industrial by-products, recycling in the roop of the manufacturing process should be examined first. With the addition of chemicals, the product's value can be increased. We call it up-cycling. Finally, the industrial by-products can be utilized in other business sectors as a resource, which is cited as trans-cycling. This presentation suggests strategies for URTRIP technology, and several practical use cases are introduced. Environmental friendly and energy efficient manufacturing routes could be considered as potential breakthrough for the production root technology applications.

Efficient electrocatalsyts prepared by pulsed laser ablation for water splitting

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Keywords: nanocrystal, pulsed laser ablation, oxygen evolution reaction, water splitting

Alkaline water electrolysis is a vital technology for sustainable and efficient hydrogen production. However, the sluggish kinetics of the 4 electron pathway in oxygen evolution reaction (OER) requires overpotential. Noble-metal-based electrocatalysts are commonly used but face limitations in cost and availability. Carbon nanostructures, such as carbon nanotubes (CNTs), offer promising alternatives due to their abundant active sites and efficient charge transfer properties. In this study, we investigate the effect of surface-modified carbon (SMC) via pulsed laser ablation in liquid media (PLAL) on electrocatalytic performance for the OER. We focus on different types of heterostructures prepared by PLAL. Experimental results combined with computational simulation reveal that formation mechanism of the electrocatalysts on SMC. Also, mechanism underlying the improved OER properties is suggested. This work contributes to the understanding of CNT-based heterostructures and their potential for enhancing electrocatalytic performance in alkaline water electrolysis. This study contributes to the understanding of SMC-based heterostructures and their potential for enhancing electrocatalytic performance in alkaline water electrolysis.

Design of dissimilar materials joint based on influencing factors of strength

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Keywords: dissimilar materials joint, strength reliability, design, self-piecing rivet, friction stir welding, rolling

Dissimilar materials joining is a key technology to realize innovative structures and generate new functions. For example, weight reduction of a vehicle can be achieved by rational design with concept of multi materials structure and it is effective for energy saving. Strength reliability of dissimilar materials joint is important in practical applications and strongly depending on joint process. It is important to study design method based on influencing factors on the joint strength with understanding of its joining process characteristics. In this presentation, design method of dissimilar materials joint is discussed and proposed in two different joint technologies such as self-piercing rivet joining and friction stir welding.

Self-piercing rivet, SPR joining is a mechanical joining method and applied to joining of thin plates in lap joint configuration. Lower energy is necessary for joining and dissimilar materials joining is applicable in SPR. In the process of SPR joining, a rivet penetrates an upper sheet and deforms following die shape inside a lower sheet but without penetration. Fatigue strength of dissimilar materials SPR joints were evaluated under tensile shear loading. According to results of the fatigue strength tests, fatigue strength of the dissimilar materials SPR joint depends on materials combination between an upper and lower sheet. Bending moment acted on the SPR joint under tensile shear loading and induced fatigue crack initiation around the joint part. Fatigue strengths of dissimilar materials SPR joints are well arranged by stiffness ratio between an upper sheet and a lower sheet. It is important to take effect of stiffness decided by elastic modulus and thickness of sheets into account fatigue design of dissimilar materials SPR joint.

Friction stir welding (FSW) is a solid-state welding technology and applied to dissimilar materials joining. In the process of FSW, a tool with high rotation speed penetrates to joint materials and induces plastic flow without melting. Formation of brittle reaction layers at the interface usually observed in dissimilar materials joint welded with conventional fusion welding can be solved in FSW. However, it is difficult to make a joint in thin plates because large deformation can be occurred during the joining process due to inserting of a rotating tool. In the present study, a dissimilar materials joint thin plate was produced by FSW followed by rolling. Mechanical properties and interfacial angle changed by applying rolling affected the joint strength. Lower interfacial angle can decrease normal stress acting on the interface resulted in apparently higher joint strengths, however higher stress concentration also occurs at the edge of interface between different materials. In design of the dissimilar materials joint thin plate, effect of change in mechanical properties and interfacial angle should be considered.

Acknowledgments

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A revolution in scientific research: An innovative blend of simulation, machine learning and cloud-based technology

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Keywords: AI, Simulation, platform, SaaS

Scientific research is witnessing a profound transformation underpinned by the confluence of advanced simulation, machine learning, and Software as a Service (SaaS) technologies. This integration is powerfully exemplified in the advent of platforms such as Materials Square, a virtual laboratory enabling comprehensive materials research.

Modern simulations, realized through the capabilities of high-performance computing, enable us to model intricate real-world systems, providing invaluable context and applications for machine learning algorithms. These algorithms, by utilizing the extensive data derived from simulations, can discern complex patterns and formulate remarkably accurate predictive models. The incorporation of SaaS propels this integration further by allowing users to access these specialized software tools over the internet. This ensures a more cost-effective and accessible utilization of these technologies, inducing a democratized, dynamic, and interconnected shift in the scientific research paradigm. Materials Square epitomizes this integration, thus symbolizing the vanguard of this profound scientific transformation.

In this presentation, we would like to discuss into the specifics of how the interplay between simulation, machine learning, and SaaS technologies is molding the future of scientific research. Particularly, focusing on Materials Square, exploring its capabilities as a virtual lab, and its role in fostering a more accessible and democratized research landscape.

A highly deficient medium-entropy perovskite ceramic for electromagnetic interference shielding under extreme environment

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Keywords: medium-entropy ceramic, aliovalent substitution, vacancies, electromagnetic interference shielding, extreme environment

Materials that can provide reliable electromagnetic interference (EMI) shielding in highly oxidative atmosphere at elevated temperature are indispensable in the fast-developing aerospace field. However, most of conductor-type EMI shielding materials such as metals can hardly withstand the high-temperature oxidation, while the conventional dielectric-type materials cannot offer sufficient shielding efficiency in gigahertz (GHz) frequencies. Here, we demonstrate a highly deficient medium-entropy (ME) perovskite ceramic as an efficient EMI shielding material in extreme environment. The synergistic effect of entropy stabilization and aliovalent substitution on A-site generate abnormally high concentration of Ti and O vacancies that is stable under high-temperature oxidation. Due to the clustering of vacancies, the highly deficient perovskite ceramic exhibits giant complex permittivity and polarization loss in GHz, leading to the specific EMI shielding effectiveness above 30 dB/mm in X-band even after 100 hours of oxidation at 1000°C. Along with the ultralow thermal conductivity, the aliovalent ME perovskite can serve as a bifunctional shielding material for applications in aircraft engines and reusable rockets.

T4.12 GRAPHENE AND 2D MATERIALS

Graphene doped carbide based composites prepared by SPS and flash sintering

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Keywords: boron carbide, field assisted sintering, graphene platelets, ceramic composites

Ceramic materials containing various amounts of graphene platelets within boron carbide matrix were prepared by the field assisted sintering methods, namely by spark plasma sintering (SPS) and by flash sintering methods (FSPS). Carefully prepared powder mixtures were sintered by SPS at 2200 °C, at heating and cooling rate of 100°C/min, with simultaneous application of 15 MPa pressure and with no holding time. For FSPS, the samples were discharged just for 24 seconds under a peak power of about 25 kW which is the 65% of machine power.

In B_4C/GPLs system prepared by SPS technology almost full compaction was reached for all specimens up to 5 wt.% of GPLs addition. The highest density 99.9% of ρTD was measured for the reference material. These well compacted experimental materials are the result of precise preparation of starting powders and using of the technological benefits which bring SPS processing. In FSPS technique the effect of carbon-based sintering activators was observed, when specimen with the addition of 5 wt.% of GPLs achieved 95.7% of ρTD in comparison with the carbon-free reference material which reached only 90.6% of ρTD and a higher portion of pores caused by the process.

Microstructural analysis of polished B_4C samples, cross-sections and fracture surfaces were carried using scanning electron microscopes (FIB – SEM Auriga Compact and EVO 40HV, Carl Zeiss). Fracture surfaces of reference materials show the difference of the used processing method on material densification. On the fracture surfaces of composites at relatively low magnification, the distribution of the GPLs in the B_4C matrix and the preferential perpendicular orientation of GPLs to the pressing direction during sintering process is visible. The GPLs were relatively well dispersed and arranged in boron carbide matrix. The addition of GPLs has no significant influence on the grain size of the boron carbide, but the addition of GPLs has an important role in densification of experimental materials prepared by FSPS technique.

The hardness of the composites prepared by SPS was in the range of 26.6–17.7 GPa. In the case of FSPS samples the strong effect of residual porosity on hardness values in the range of 16.9–14.0 GPa is evident.

The addition of GPLs and new processing ways had a positive effect on fracture toughness. The K_{IC} values of SPS specimens were in the range of 2.52–4.17 MPa.m$^{1/2}$ which is the improvement of 61%. In the case of FSPS specimens, fracture toughness values were in the range of 4.63–5.14 MPa.m$^{1/2}$ and the decrease could be caused by porosity.

The elastic modulus of the SPS specimens was in the range of 542–433 GPa and for the FSPS ones in the range of 519–441 GPa. All elastic moduli were slightly affected by the presence of pores.

Acknowledgments

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3D-printed graphene/porous α-Al2O3 composites and hybrid scaffolds

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Cellular ceramic materials exhibit unique properties related to their porosity, lightweight, and high specific surface area, which make them appropriate for their use as absorbers, membranes for catalysis and filtration, thermal management, and tissue engineering. The traditional fabrication methods as replica or sacrificial template are now combined with novel additive manufacturing technologies for the fabrication of complex structures, broadening the application fields. Graphene, on the other hand, has been successfully used for the development of ceramic composites and hybrids with improved properties in bulk and porous structures, and more recently in 3D printed composites by its addition mainly in the form of thin sheets.

The present contribution gathers the main results on the incorporation of graphene into 3D alumina structures through two different routes: *i)* the processing of graphene ribbons/boehmite composite inks for subsequent structure 3D printing and sintering, and *ii)* the use catalyst-free CVD with different sets of parameters for obtaining graphene networks of variable thickness (FLG-20nm) and crystallinity supported on light and robust 3D-printed porous α-Al2O3 structures.

The first approach showed the reinforcing capability of graphene as a second phase in 3D printed composite materials, achieving an increment of 14-50% in the compressive strength, concerning scaffolds based on pure alumina. As for the second route, it was the first time CVD graphene was used for coating 3D-printed ceramic scaffolds. Multi-scale porosity of 80% was obtained by the use of a grid pattern combined with partial sintering that served to create a fully contacted graphene network. Raman spectroscopy and transmission electron microscopy were used to characterize the homogeneity and quality of the film across the supports. Functional properties as electrical and thermal conductivity were also determined, achieving 10^3 Sm^{-1} and an increment of 45%, respectively, for the structure with the thicker film.

High temperature interaction of ceramic aerogels and their bulk counterparts with liquid metals and alloys

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Keywords: ceramic aerogels, Mg, wetting, adhetion, interface, bonding

Aerogels belong to a group of ultra-light porous materials having unique combination of structural, physical and utility properties. In many possible applications, aerogels are required to be joined to other materials, especially metals. For liquid-assisted joining dissimilar materials, wetting behavior and adhesion between them are the key factors responsible for integrity and properties of final products. Therefore, information on high-temperature interaction between ceramic aerogels and different liquid metals and alloys is of a great scientific and practical importance.

This work summarizes the results of comparative studies of high-temperature behavior of different types of ceramic aerogels and their bulk counterparts in contact with liquid magnesium, which is the lightest of all metals used as the basis for constructional, biocompatible and biodegradable alloys due to its lightweight, high strength and corrosion resistance.

For real-time observation of wetting behavior and adhesion of liquid Mg with porous or bulk ceramic substrates, the sessile drop method was adopted and combined with in situ removal of a native oxide film from Mg sample directly in high-temperature chamber using capillary purification procedure. Solidified Mg/substrate couples were subjected to detailed structural characterization by scanning electron microscopy, transmission electron microscopy and energy dispersive X-ray spectrometry.

The results obtained are analyzed in terms of the effects of testing conditions as well as porosity, residual oxygen, structure and chemical composition of the aerogel on its wetting, adhesion and bonding with liquid Mg.

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T5 Technology, Society and Sustainability

T5.1 GLOBAL INNOVATIONS IN BIOMATERIALS, BIOMANUFACTURING, AND BIOTECHNOLOGIES

Glass/ceramic composite coatings embedding silver nanoparticles with antipathogen properties

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Keywords: antipathogen, composite coatings, silver

Innovative solutions and approaches address the pressing issue of emerging diseases caused by bacteria and viruses emphasing their significant threats to human well-being. In response, this study aims to the design and develop smart, sustainable nanostructured materials to mitigate the effects of microbiological contaminants on indoor air quality. For this purpose, antipathogen composite coatings embedding silver nanoclusters/nanoparticles into a glass/ceramic matrix were developed using two techniques, the co-sputtering and the use of pre-ceramic polymeric precursors.

The co-sputtered coatings are composed of silver nanoparticles well dispersed and anchorated within a silica or zirconia matrix[1]. The controlled release of metallic ions from the silver nanoparticles proves highly effective in preventing the adhesion, proliferation and spread of various bacterial strains, fungi and airborne viruses, including SARS-CoV-2. The co-sputtering technique provides versatility for various surfaces including filters and membranes, scalability for industrial applications and environmental friendliness.

Pre-ceramic polymeric precursors have been explored to obtain coatings with advanced properties. The precursors transformation into ceramic materials at low temperatures generates minimal waste material. The incorporation of silver nanoparticles into the precursors marks a significant achievement for further antimicrobial applications.

Acknowledgments

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Bioceramics for healthcare: Where the future lies?

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The next generation of bioceramics in healthcare is spearheaded by two core aspects, a) better (more holistic) understanding of the quantitative interactions with the components of the biological system at multiple length and time scales; b) probing the biocompatibility of lesser-explored ceramics for biomedical applications. The biocompatibility of materials is determined by their application-specific desired responses with proteins, cells, tissues, and blood. First, the Molecular Dynamics (MD) simulation results will be described to demonstrate the temporal kinetics of the fibronectin protein adsorption on doped hydroxyapatite (HA). In substantiating the second aspect, the cell and tissue compatibility of perovskites either in particulate format or in bulk composite with HA, will be discussed. Some recent developments on blood compatible SiBCNO coatings for cardiovascular applications will be presented, in the context of the new results on blood-capillary like tube structure formation during co-culture of endothelial and connective tissue cells under electric field stimulation conditions. Towards the end of the presentation, the Data Science (e.g. Artificial Intelligence/ Machine Learning algorithms) driven 'Biomaterialomics' approach will be presented to demonstrate its capability to integrate the computational tools, databases, experimental methods, machine learning, and advanced manufacturing (e.g., 3D printing) on a single platform. The speaker will close this talk by providing a set of key recommendations, which may be highly transformative to the field, while benefitting people's well-being and advancing economic development in many nations, in their energy and momentum.

Synthesis of antibacterial nanostructured glass-ceramics from glass waste: A cost-effective approach

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Developing solutions and applications for vitreous waste is fundamental nowadays. In theory, glass is a material 100% recyclable, but the logistics and handling are the notable drawbacks of recycling. Developing materials with new properties using solid waste glass is highly desirable from a sustainability point of view [1, 2]. Flint and amber-colored glasses, often found in high quantities in municipal waste, can serve as valuable sources of raw materials. Thus, we propose an affordable pro duction process that requires just a thermal treatment of glass waste to obtain glass-based antimicrobial materials. The thermal treatment induces crystallized nanoregions, which is the primary factor responsible for the bactericidal effect of waste glass. As a result, coarse particles of in waste glass with thermal treatment. show superior antimicrobial activity than amber waste glass. Glass-ceramic materials from int waste glass, obtained by thermal treatment show antimicrobial activity against Escherichia coli just after 30 minutes of contact time. Laser induced breakdown spectroscopy (LIBS)was employed to monitor the elemental composition of the glass waste. The obtained glass-ceramic material was structurally characterized by transmission electron microscopy, enabling the confirmation of the presence of nanocrystals embedded within the glass matrix.

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Promising bioactive apatite-biopolymer composites in bone tissue engineering

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Keywords: amorphous calcium phosphates, biopolymers, biocomposites, bioactive coatings

Nowadays, it is still a key issue to provide long-term success of implanted biomaterials in both tissue engineering and other biomedical applications. To obtain this goal, a high level of biocompatibility and bioactivity are required from the applied materials, either in scaffold or in coating form. Bioactive ceramic composites (BCCs) are especially useful materials in soft and bone tissue engineering and even in dentistry. They can be the solution to many medical problems, and they have a huge role in the healing processes of bone fractures. Interestingly, they can also promote skin regeneration and wound healing. The bioactive ceramics are able to attach to the bone tissues and form an apatite layer which further promotes the biomineralization process. The formed intermediate apatite layer makes a connection between the hard tissue and the bioactive glass material which results in faster healing without any complications or side effects. The properties and biological performance of these unique composites can be adjusted to meet the standard requirements of biomedical applications. The main approach is that the bioceramic bone cements or grafts or even coatings can act as an initiative intermediate surface for the increase in bone cell attachment, growth, and proliferation as well as new bone formation. Calcium phosphate (CaP)-based ceramic–biopolymer composites can be regarded as innovative bioresorbable scaffolds or coatings on load-bearing implants that can promote the osseointegration process. The bioactive ion modified amorphous carbonated apatite (cAp) phase is the most suitable CaP form, since it has sufficient similarity to the mineral phase in human bones, and the highest biodegradability rate as well. The crystallinity or amorphous characteristic and particle size of CaP particles are strongly dependent on the preparation and post-treatment methods, such as heat or alkaline treatment of as-precipitated powders. The carbonated, ion-modified cAp particles can be embedded into different biopolymers, such as polycaprolactone (PCL) and cellulose acetate (CA). The CaP particles are to be homogeneously dispersed into the polymer solutions, and then the dispersion can be deposited onto the surface of implants.

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Therapeutic ions-doped glass with antimicrobial properties

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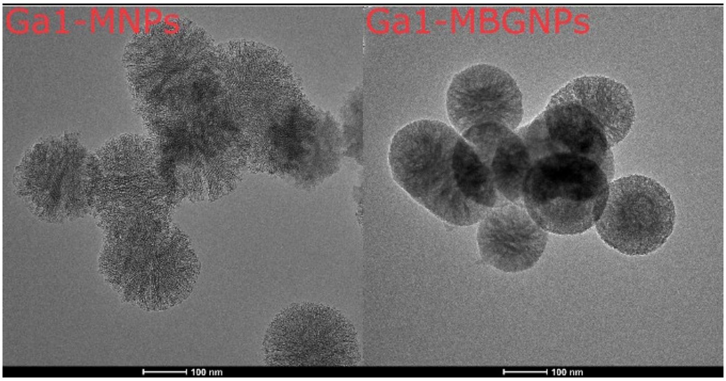
Keywords: MRSA, therapeutic ions, glass, mesoporous bioactive glass nanoparticles

The continually increasing number of strains of antibiotic-resistant pathogenic microorganisms (e.g., MRSA – Methicillin-resistant Staphylococcus aureus) poses a real threat to human health. This problem is further exacerbated by factors such as horizontal gene transfer between different bacterial strains, allowing bacteria to acquire antibiotic resistance even if they are not direct descendants of already resistant strains [1]. Additionally, pharmaceutical companies are reluctant to invest in the development of new antibiotics due to high costs. The situation is further complicated by the fact that the effectiveness of new antibiotics is relatively limited, and bacteria develop resistance faster than we can introduce new antibiotics to the market. It is, therefore, crucial to design new strategies to combat pathogenic microorganisms. An interesting alternative in this field is represented by inorganic ions, such as Ag^+, Zn^{2+}, Ga^{3+}, Ce^{3+}, etc., whose antibacterial properties are well-documented. These ions can be incorporated into the structure of various bioactive glasses, which gradually dissolve in the body environment, leading to controlled release of ions with antibacterial effects. This contribution provides an overview of joint research activities of the Institute of Biomaterials, University of Erlangen-Nuremberg, and the the FunGlass Centre, focusing on the development and testing of bioactive glasses, as well as biocomposites with a biopolymeric matrix doped with bioactive glasses containing ions with therapeutic and antibacterial effects. The antibacterial and antimicrobial activity of Zn-doped glasses prepared by conventional melt quenching, as well as Ce and Ga-doped mesoporous bioactive glass nanoparticles prepared by micremulsion method against selected Gram-positive (*S. Aureus*) and Gram-negative (*E. Coli*) bacteria and microscopic fungi is documented.

Figures



Mesoporous bioactive glass nanoparticles doped with Ga

Acknowledgments

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Size controlled hydroxyapatite particle nucleation in natural rubber latex membranes

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The generation of new bone tissue is a highly effective treatment for fractures and other bone injuries. However, the severity of the injury, the age of the patient, and other factors can sometimes result in a delayed healing process, preventing complete calcification of the affected area. In such scenarios, implant or bone transplant procedures are necessary to aid tissue repair. Synthetic hydroxyapatite (HA), a stable calcium phosphate, is commonly used in medical applications due to its structural similarity to biological apatite in bones and hard tissues. Natural rubber latex has a wide range of applications in tissue engineering and drug delivery due to its porosity, elasticity, and biocompatibility. Latex membranes combined with HA can be used in a variety of hard tissue regions, enabling effective remineralization. Incorporating HA particles into latex membranes has the potential to revolutionize the therapeutic efficacy of materials. However, some traditional techniques have constraints due to the high-temperature synthesis required. This can lead to protein decomposition and reduce the overall effectiveness of the material. Additionally, other approaches may result in the agglomeration of particles and an uneven distribution on the polymeric matrix. It is important to consider these adversities and explore alternative strategies to unlock the full potential of HA particle incorporation. To address this issue, the biomimetic method was employed to nucleate HA particles into latex membranes, resulting in nano and microstructured materials. This composite was then characterized using X-ray diffractometry and Fourier-transform infrared spectroscopy, which confirmed the heterogeneous nucleation of HA over the latex membrane. Further scanning electron microscopy analysis revealed a homogeneous deposition of HA, with an increase in particle density, roughness and size as the biomimetic incubation period progressed. The charged surface and protein adsorption were also evaluated These membranes will be applied to rabbits' broken bones to investigate the impact of HA nanostructure size on tissue regeneration.

Enhancing functional properties of bone tissue replacement materials with polyol-citrate polyesters

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Keywords: calcium phosphate cement, polyol-citrate, mechanical strength, biodegradation, in-vitro cytotoxicity

Bone tissue-related illnesses resulting from degenerative diseases, infections, trauma, or oncology, impact millions of people worldwide. While bone tissue possesses a certain ability for self-repair and regeneration, larger defects and major injuries necessitate the use of advanced solutions in the form of bone replacement materials, to treat and restore the functionality of damaged tissue.

Biomaterials based on hydroxyapatite (Hap), the main mineral component of bone tissue, find widespread clinical application due to high biocompatibility, bioactivity, osteoconductive, and osteoinductive properties. Hydroxyapatite bone cements represent a special case of moldable material. They are prepared by mixing calcium phosphate precursors with a liquid phase to form a paste that can be easily applied to defects of various shapes and can set to a hard mass with tight bond with the surrounding tissue. Despite many advantages, the main drawback of calcium phosphate cements (CPCs) lies in their lower mechanical strength due to high brittleness and lower degradation and resorption rate. To address these shortcomings, recent studies have focused on incorporating polymeric fillers into the structure of CPCs, predominantly in the form of thermoplastic polylactides. However, although polylactides are biocompatible and biodegradable, their hydrophobicity shows a limitation. Additionally, while certain polylactides exhibit relatively high strength and elastic modulus, their incorporation into the cement matrix has, in some instances, shown negligible impact or resulted in a decrease in mechanical strength due to poor bonding and mixing with the cement mixture.

Therefore, in recent years, attention has increasingly turned towards biodegradable thermosets, such as polyol-citrates, synthesized by esterification of citric acid with polyhydric alcohols. Polyol citrates offer advantages over polylactides in terms of superior elastic properties, cost-effective and simple synthesis procedures, and a hydrophilic nature, which provides a more beneficial effect on tissue response compared to traditional hydrophobic polymers. Considering the important role of citrates in the bone tissue formation and metabolism, there is a good assumption of using polyol citrates in bone tissue engineering.

A comprehensive overview of the history, recent advancements in the design, application, and ongoing development of polyol-citrate polyesters and their composites in relation to bone tissue engineering will be presented and thoroughly discussed.

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Novel additive manufacturing technologies for bio-ceramics in bone tissue engineering

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Keywords: bioceramics, additive manufacturing, multi-material

Additive manufacturing (AM) in the medical industry can be organized into several broad categories, including tissue and organ fabrication, customized prosthetics, implants, anatomical models, and pharmaceuticals. Moreover, multi-material AM technologies are fascinating in the field of tissue engineering because tissues or organs have multiple functions and are composed of multiple components. Our group recently developed an original material extrusion-based AM process for the simultaneous manufacturing of hydrogel-based cells and bioceramics for bone tissue regeneration. This novel process is performed in gel bath condition, where we could fabricate the self-standing 3D ceramic structure without any supporting structure. Our group also developed a novel stereolithography-based AM process for multi-ceramic materials. We were able to mimic both the structure and function of bone. Furthermore, we simultaneously imitated both the shape and color of teeth by manufacturing a functionally graded material structure using two types of feldspathic porcelain for applying aesthetic and restorative dentistry. We believe these new technologies may expand application market of ceramic AM technologies.

T5.2 GLOBAL YOUNG INVESTIGATOR FORUM

Rapid firing of 3YSZ: impact of the heating rate on sintering, properties and microstructure

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Keywords: ultrafast high-temperature sintering, fast firing, YSZ, additive manufacturing

Ultrafast high-temperature sintering (UHS) is currently emerging as a powerful tool to consolidate ceramics in the seconds/few minutes timescale. It employs graphite felts as resistive heating elements that, due to the low thermal capacity, can be heated to ultrahigh temperatures in a matter of seconds.

Herein, we report the ultrafast high-temperature sintering of yttria-stabilized zirconia (YSZ). The results show that effective densification can be attained in a very short time scale and at temperatures significantly lower than that required for conventional sintering. Such an effect is attributed to the microstructural refinement induced by rapid heating when treating nanograined YSZ powders (particle size about 20 nm). On the other hand, the heating rate impact on densification is reduced when considering green bodies obtained with coarser powders. In this case, analytical models extrapolated during conventional heating can be used to predict the densification also under extreme heating rates.

UHS can also be integrated with additive manufacturing techniques to produce small components with complex shapes. In particular, we show that fused filament fabricated YSZ gyroids can be debinded and sintered by UHS within one minute obtaining bodies with properties analogous to those obtained by conventional firing.

Finally, we show that “reactive UHS” of YSZ with an N2-containing atmosphere is possible, allowing a fine tailoring of the material composition, structure, and properties with a specific focus on the ionic conductivity of the sintered components.

A novel two-stage flash sintering of fine-grain 3 vol.% yttria stabilized zirconia

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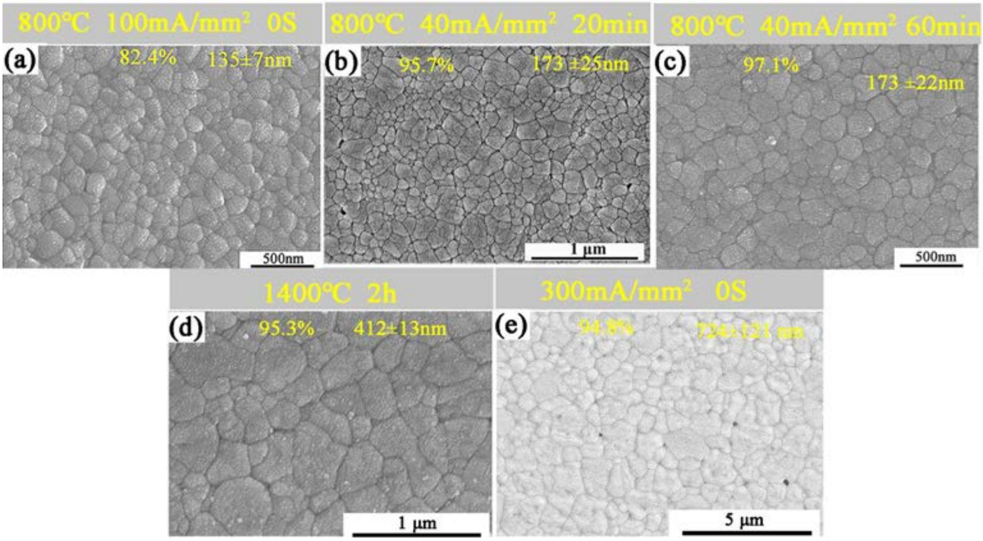
Keywords: 3YSZ, flash sintering, two-stage sintering, fine grain size

The coupling effect of rapid densification and fast grain growth caused by the electromigration and Joule heating generated during flash sintering means that it is difficult to fabricate a dense ceramic with a very fine grain size. In this paper, a fine-grain 3 mol% yttria-stabilized zirconia (3YSZ) ceramic was successfully prepared by a novel two-stage flash sintering method. This method used the current-surge stage (II stage, < 2 s) of flash sintering to obtain a relatively high-density ceramic with limited grain growth, followed by further densification in a current-control stage (III stage) with low-current-density stimulation. The dense 3YSZ ceramics were obtained with an average particle size of 170±16 nm, a relative density of 95.7%, and a hardness of 1270 Hv.

Figures



The microstructures of 3YSZ samples sintered by different methods. a) first-stage flash sintering, b) two-stage flash sintering with holding time of 20 min, c) two-stage flash sintering with holding time of 60 min, d) conventional pressureless sintering at 1400 °C for 2 h, e) one-step flash sintering without holding period (T=800 °C, E=160V/cm, J=300 mA/mm^2).

A multiscale approach for robust sintering simulation of lattice structures in 3D-printed ceramics

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Keywords: lattice, additive manufacturing, anisotropy, modeling, sintering

Most parts manufactured through 3D printing utilize a bioinspired infill strategy, incorporating a dense shell with internal lattice structures. This approach optimizes the strength-to-weight ratio of the part through topological optimization and significantly improves both printing time and quality. However, simulating such complex porous internal structures can lead to computational instabilities and a colossal increase in simulation time due to the large number of degrees of freedom involved. As a result, there is currently no robust solution for simulating the sintering of 3D-printed parts with internal lattices, despite these constituting the majority of printed objects. This study addresses this challenge through a continuum-based approach capable of simulating real parts and the intricate behavior of lattices with a computational time representing a small fraction of the sintering time. The lattice geometry is initially simulated by a sub-model that identifies their effective moduli for different porosities. These effective moduli are then used to simulate sintering in the lattice regions of the printed parts, significantly reducing the internal part's thermal conductivity. An additional sub-model is employed to extract the lattice's effective thermal conductivity through a simulation accounting for thermal conduction in the skeleton, thermal radiation, and convection in the cavities. A robust thermomechanical simulation is subsequently utilized to rapidly and efficiently predict the baking of the parts, considering developed thermal gradients, resulting deformations, and the inherent anisotropy that significantly influences the final part's dimensional characteristics. This simulation tool is illustrated through 3D/regular honeycomb lattices.

Tribological characteristics of dual-phase high-entropy ceramics: Influence of the testing methods

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Keywords: dual-phase high-entropy ceramics, wear, wear mechanisms

Wear behavior of a fine-grained dual-phase high-entropy carbide/boride ceramics was investigated using ball-on-flat dry sliding methods in air, applying rotational and linear reciprocation motion with SiC counterpart. The investigated system showed very high nanohardness of the carbide and boride grains with mean values of 37.4 ± 2.3 and 43.0 ± 2.9 GPa, respectively, with the microhardness of dual system HV1 29.4 ± 2.0 GPa. The stabilized friction coefficient values during the circular tests changing from 0.62 to 0.77. During the reciprocal test, the frictional coefficient values are very similar with an average value of .53. The specific wear rates during the circular motion were similar in the range from 4.65 × 10^{-7} to 1.68 × 10^{-7} mm^3/N m. During the reciprocal test, the wear rates at 5 and 25 N were similar as in the case of circular motion, but at 50 N load, the wear rate increased significantly to the value of 9.11 × 10^{-6} mm^3/N m. The dominant wear mechanisms in all cases were oxidation driven tribochemical reaction and tribolayer formation in boride grains and mechanical wear in carbide grains. During the linear reciprocation test, the loading mode created conditions resulted in relatively low coefficient of friction and very high specific wear rate.

Figures

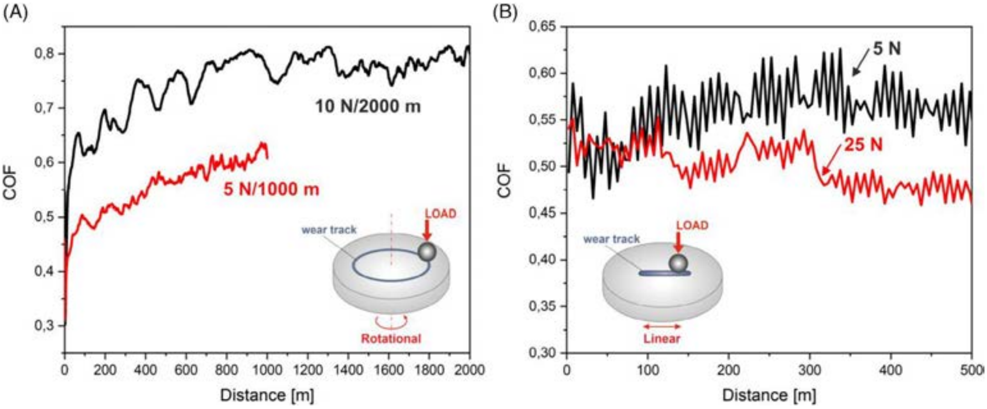

Fig.1. Evolution of the typical coefficient of friction values during the rotation (A) and reciprocation (B) wear tests, based on.

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Recycling of batteries with lithium thiophosphate solid electrolytes

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Keywords: recycling, solid-state batteries, thiophosphates

Since the first commercialization of rechargeable Li-ion batteries, this technology has become omnipresent in our everyday lives. In recent years, the exponential growth of consumer electronics and stationary battery markets, coupled with the significant advancement in electronic vehicle technology, has led to a surge in the demand for LIBs - a trend expected to persist in the coming years. However, inherent safety concerns related to the use of combustible liquid electrolytes and limited energy density have also prompted the development of various next-generation battery technologies. Among these, all-solid-state batteries (ASSBs) utilizing solid electrolytes (SEs) are considered highly promising, and different material classes including oxides, polymers, halides and sulfides are intensively studied with respect to their potential use as SEs. Owing to their high ionic conductivities in the range of 10^{-4} to 10^{-2} $S\cdot cm^{-1}$, sulfide-based electrolytes including thiophosphates such as Li-P-S (LPS)-based glasses or glass ceramics (e.g. $xLi_2S\bullet(100\ x)P_2S_5$, $Li_7P_3S_{11}$, $\beta\text{-}Li_3PS_4$), argyrodites Li_6PS_5X (X = Cl, Br, I), thio-LISICONs and $Li_{11-x}M_{2-x}P_{1+x}S_{12}$ (M = Ge, Sn, Si) have gained significant interest.[1]

With the increasing significance of such next-generation batteries, the development of sustainable recovery and recycling strategies has become a matter of growing urgency. However, so far only a limited number of studies have been conducted on ASSBs.[2] For conventional lithium-ion batteries, there is a broad variety of established approaches including pyrometallurgical, hydrometallurgical, and direct recycling methods. While these methods can be partly adapted to derive recycling strategies for ASSBs, the unique properties of ASSBs, which can be primarily attributed to the chemical nature of the SEs employed in these batteries, do not allow to apply these methods directly. For thiophosphate-electrolyte-based ASSBs, pyrometallurgical and hydrometallurgical recycling processes are not feasible since reactions with water or O_2 lead to chemical degradation of the electrolyte. Related to the potential for solution-processing of thiophosphate electrolytes, direct recycling strategies involving the dissolution and subsequent precipitation and recrystallization of the electrolyte are more promising. Such strategies may result in an efficient separation of the electrode materials from the electrolyte under retention of the thiophosphate building units. In this contribution, the feasability of a dissolution-based separation process and related challenges are discussed.[3-4]

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Design and construction of highly hard yet toughened TMB_2 based nanocomposite thin films

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Keywords: ceramic thin films, hardness, toughness, TMB_2

An enduring quest in materials research is to reconcile two of the most prominent yet often conflicting mechanical properties, hardness and toughness. Strong covalent solids like diamond exhibit superior hardness but are brittle, while ductile metals possess excellent toughness but are soft. Transition-metal (TM) borides offer a viable solution, where metal atoms provide the valence electrons to raise toughness and light elements form a covalent bonding network to build hardness. This talk will discuss the construction of highly hard yet tough films based on the transition-metal diborides, following three recent advances: (1) discovered the new robust descriptor for sorting wide-ranging TM compounds on their mechanical properties, opening a new path for rational design and optimization of hardness-toughness balance in wide-ranging materials [1,2]; (2) demonstrated a chemically tuned solid solution approach that simultaneously enhances hardness and toughness of superhard transition-metal diboride $Ta_{1-x}Zr_xB_2$[3] ; (3) constructed a dual-phase nanocomposite film that comprises a wear-resistant phase (TiB_2) and an internal lubricant source ($MoS_{1.7}B_{0.3}$) exhibits superdurable superlubricity characterized by a vanishingly small friction coefficient (0.007) and ultralow wear rate (10^{-9} $mm^3N^{-1}m^{-1}$) maintained in lubricants over an unprecedentedly long sliding distance without performance deterioration [4,5].

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T5.6 FunGlass

Cold consolidation of glass aqueous slurries: the cooperation between the chemistry of glass and basic activators

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Keywords: alkali activation, gelation, waste glass, cold consolidation

Alkali activation is often referred to as a process yielding sustainable construction materials, especially starting from reactive waste-derived alumino-silicate feedstock. Strong and chemically durable components derive from extensive dissolution of starting materials, followed by condensation reactions, realizing highly interconnected, 'zeolite-like' gels. A challenge, however, concerns the use of synthetic activators, in the form of concentrated aqueous solutions of alkali hydroxides, silicates and aluminates, and their amounts. This contribution aims at summarizing experiences concerning alkali activation of glasses of different chemical composition. Special attention is given to fine powders (<100 µm), which can still be collected as industrial waste, in very high amounts. A fundamental example is that provided by boro-alumino-silicate glass from discarded pharmaceutical containers. Suspended in alkaline solution of limited molarity (e.g. ≤3M NaOH), glass undergoes partial dissolution, followed by gelation, upon drying at 40-80 °C. This gelation is attributable to condensation reactions occurring at surface hydrated layers, leading to strong bonds (Si-O-Si, Al-O-Si etc.) as bridges between adjacent particles. Silicates, borates and aluminates, from glass dissolution, may combine with alkaline ions, in new phases. These extra phases may be leached out, upon immersion in boiling water or acidic attack; the latter attacks, however, do not compromise the integrity of the bonds between particles. The process may yield dense blocks as well as highly porous bodies, simply from slurries including additives capable of gas release (e.g. oxygen, from perborates) during drying.

The process does not depend on specific chemistries, of both glass and activators. In fact, siloxanic bridges are formed in the presence of nearly B_2O_3- and Al_2O_3-free glasses, including common soda-lime container and flat glasses; gelation can be experienced even from the limited residual glass phase of LAS glass-ceramics. Changes in the activators are an opportunity for changes in the nature of secondary phases, which may consist of gels and crystal phases of enhanced chemical stability: as an example, while NaOH generally leads to soluble Na-silicate gel and soluble sodium hydrated carbonates, by interaction with boro-alumino-silicate glass, CsOH leads to a substantial formation of stable boro-pollucite phase. The mixed attack of alkali hydroxides and NH_4OH further enhances the flexibility of the approach, by favouring the inclusion of alkali in gels instead of in carbonates.

Rare-earth-doped nanostructured and transparent glass-ceramics for enhanced photoluminiscence

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Keywords: glass-ceramics, sol-gel, SPS, photonics, RE

Transparent oxyfluoride glass-ceramics (OxFGCs) have attracted great interest in the field of photonics during the last decades. The classical processing route to obtain transparent OxGCs starts with a controlled crystallization of the precursor glass obtained by melt-quenching (MQ). The incorporation of RE ions in the crystalline phases enhances the optical emission intensity, a major property of these materials [1]. Although it is suitable for fibers and bulk glass, it is not a suitable way to make films.

On the other hand, Sol-gel (SG) method is a promising alternative process to prepare oxyfluoride glass-ceramics films avoiding the drawbacks of MQ such as loss of fluoride content associated with the high process temperatures. This talk will present the processing routes to prepare oxyfluoride glass-ceramic films through a precipitated route based on stable aqueous suspensions of doped fluoride nanoparticles and the further incorporation to silica sols. In particular, doped-LaF_3 or $Na/KGdF_4$ aqueous suspensions were prepared and characterized by different techniques, before their incorporation to a silica sol, deposition by dip-coating on glass-slide and sintering[2]. Morphological and structural characterizations of the RE doped glass-ceramics films were performed by HR-TEM, FTIR, and Ellipsometry.

On the other hand, transparent GC materials have been also obtained by spark plasma sintering (SPS) [3]. This approach combines thermal action with simultaneous compression of the material to reach full densification and high homogeneity in a short time [4]. The structural, mechanical, and optical properties were characterized and compared with GCs of the same composition prepared by melt-quenching followed by conventional heat treatment. The results confirm the suitability of the SPS processing for the preparation of highly dense and transparent oxyfluoride glass-ceramics containing nanocrystals.

Finally, optical characterization was performed by the emission spectra and the lifetimes of the excited states in all the materials obtained by both processing routes. Promising results were achieved confirming the incorporation of Re^{3+} ions into the fluoride phases and suitable luminescence lifetimes in the films as well as in SPS materials.

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FunGlass: Where we are, and where we are heading at the end of the project?

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FunGlass, or the Centre for functional and surface functionalized glass was established in 2017, as a research Centre established with financial support of the European Commission (European Union´s Horizon 2020 research and innovation programme under grant agreement No 739566), and the Slovak government (ERDF project CEGLASS, operational programme Research & Innovation). In its research activities focused on bioactive materials, glass processing, advanced functional coatings, functional glass and ceramics, upcycling of inorganic waste and additive manufacturing technologies. It cooperates closely with four international partners of the Centre, namely Friedrich Alexander Universität Erlangen Nuremberg, Germany (prof. A. Boccaccini), Friedrich Schiller Universität Jena, Germany (prof. L. Wondraczek), Institute of Glass and Ceramics, CSIS Madrid, Spain (prof. A. Durán), and University of Padova, Italy (Prof. E. Bernardo). The FunGlass symposium is aimed at presenting the latest, and the most important research activities of the Centre achieved in collaboration with, but also without our partners. This introductory lecture of the FG symposium gives a brief overview of the Centre, its structure, achievements, international collaborations, and activities.

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Progress and challenges in melt-electrowriting of polymer-inorganic phase composites

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Keywords: melt electrowriting, polycaprolactone, superparamagnetic iron oxide nanoparticles, mesoporous bioactive glass

The melt electrowriting technique is a solvent-free additive manufacturing method that uses electrohydrodynamics to produce micron-scale fiber struts [1]. The structural properties of MEW scaffolds are similar to those of extracellular matrix and interconnected porous structure, which has attracted researchers to use them in biomedical applications [1,2]. For more than a decade, these highly ordered MEW scaffolds have been widely made with polycaprolactone (PCL) owing to its outstanding processability, biocompatibility, mechanical capabilities, low melting temperature, and quick solidification qualities (relative to other polyesters) [1,3]. On the other hand, nanoparticles are interesting nanomaterials that can be used in biomedical applications, including cancer treatment, targeted drug delivery, magnetic particle imaging, and targeted drug delivery [4]. Notably, in the field of biomedical have garnered used of the distinctive physical, chemical, and biocompatibility characteristics of superparamagnetic iron oxide nanoparticles (SPIONs) [5,6] and mesoporous bioactive glass nanoparticles (MBGNs) [7]. In this research, our objective is to devise inventive strategies for manufacturing SPIONs or MBGNs-coated PCL-MEW scaffolds that can be utilized in various biomedical applications. In this sense, PCL scaffolds were first fabricated using the MEW method and further treated with alkaline surface modification to enhance their hydrophilicity and cell affinity and enable coating with MBGNs and SPIONs. Scanning electron microscopy images revealed that PCL-MEW scaffolds were unaffected by alkaline surface modification, and SPIONs and MBGNs exhibited uniformity and less aggregation within MEW scaffolds. Furthermore, ATR-FTIR spectra confirmed MBGNs and SPIONs coating. Moreover, when exposed to an alternating magnetic field, SPIONs-coated samples generated heat, which might be used to treat hyperthermia. On the other hand, in vitro cell viability assay results showed that coating MBGNs and SPIONs has no adverse effect on MC3T3-E1 pre-osteoblastic and normal human dermal fibroblast (NHDF) cells. Moreover, SEM imaging, and staining techniques using Calcein/DAPI and rhodamine-phalloidin/DAPI showed that the samples did not result in any cytotoxic effects and did not cause any abnormal cell behavior. In summary, the early findings showed the potential of coating MEW scaffolds with SPIONs or MBGNs for use in various biomedical applications.

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ORAL

T1 Ceramics for Energy Conversion, Storage, and Distribution Systems

T1.1 HIGH-TEMPERATURE FUEL CELLS AND ELECTROLYSIS

Manufacturing strategy of lightweight solid oxide fuel cell for aviation applications

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Keywords: solid oxide fuel cells (SOFCs), additive manufacturing, ceramics, lightweight design, aviation

The world's first hydrogen based commercial airplane is aiming to reach the market by 2035. The idea is to focus on the ZEROe concept aircrafts, which shows Airbus' commitment to lead the decarbonization in the aviation industry, which rely on hydrogen as a main fuel. Hydrogen boarded aircraft in a hybrid configuration power system that combines fuel cells for electrical power with modified gas turbine engines to achieve the targeted performance. Although one of the most established fuel cell types is the proton exchange membrane (PEM) technology, Airbus Central Research and Technology (CRT) is also looking at unique SOFC concepts for prospective hybrid-hydrogen configurations.

A solid oxide fuel cell (SOFC) system is an attractive candidate for aircraft application due to its capability of high efficiency when combined with gas turbine engines and fuel versatility. The tubular SOFC design principally provides fast start-up time, high gravimetric and volumetric power density compared to traditional planar stacks. However, the ohmic losses in the long tubular cell is a challenging factor due to the single end correct collection method. We have manufactured lightweight cells with an improved current collection pathway. The most promising designs are the tubular and monolithic SOFCs, so far achieved experimental tested performance at Airbus recently is about 2 kW/kg (tubular anode supported cell) in high fuel utilization testing condition. Moreover, the novel networking serially connected cell design gives a theoretical estimated power density > 3KW/kg. These cell designs' manufacturing feasibility are explored by advanced production techniques such as additive manufacturing techniques with the feature of highly porous, lightweight substrates and followed by thin film electrolyte coating for metallic and ceramic based SOFCs. Additionally, conceptual stacking design of SOFCs are explored for aviation applications.

Impact of NaCl containing air on the cathode of a solid oxide fuel cell

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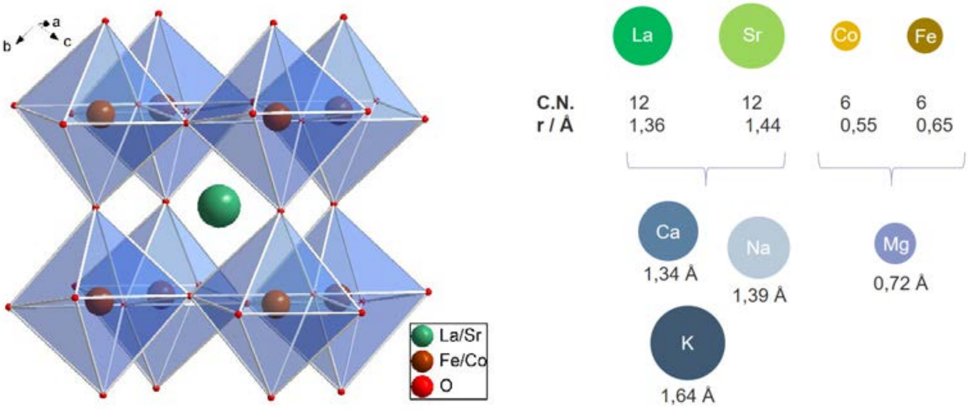
Keywords: solid oxide fuel cell, cathode, electrochemical impedance spectroscopy

The marine industry must reduce emissions to comply with existing and forthcoming regulations. In this context, solid oxide fuel cells (SOFCs) could play a significant role in ship propulsion due to their high flexibility in fuel compatibility. However, concerns regarding their durability hinder their widespread adoption in shipbuilding.

The aim of this study is to investigate the effects of the marine environment on SOFC cathodes. To this end, a mist generator has been constructed that allows the generation of different salt concentrations and humidity levels. The impact of this simulated sea air is studied on single cells with a LSCF ($La_{0,6}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$) cathode. The performance of the cell is monitored via chronoamperometry and electrochemical impedance spectroscopy. Post-mortem SEM and EDX analyses reveal the microstructural changes, caused by the simulated maritime conditions.

In order to get deeper insight into the structural and electrochemical changes of the cathode material LSCF, the material is exposed to different sea salts at different temperatures and different levels of humidity. Powder XRD and Rietveld refinement elucidate the structural changes in the material and elemental analyses evidence the changes in the materials composition.

Figures



Representation of the crystal structure of LSCF (left) and schematic comparison of the ionic radii of ions present in LSCF and those in sea-salts.

Reversible solid oxide fuel cells based on semiconductor-ionic composites: material development, structure design and performance optimization

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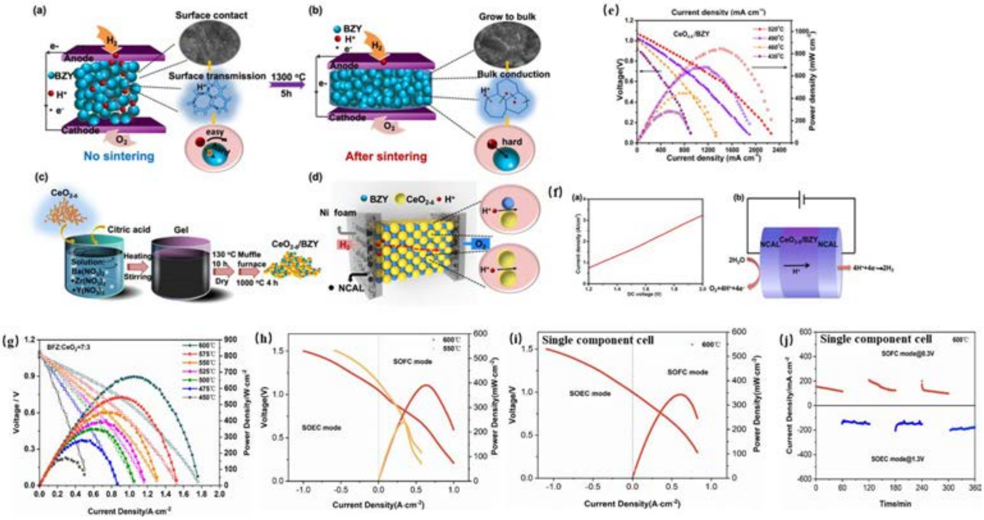
Keywords: reverisble solid oxide fuel cells, semiconductor-ionic composites, triple-conducting oxides, water electrolysis

Reversible solid oxide fuel cells (RSOFCs) are electrochemical devices based on oxide electrolyte that alternate sequentially between power-generating fuel cell and fuel-producing electrolysis cell modes for renewable energy storage and conversion. RSOFCs generally operates at high temperatures (800-1000 °C) to activate oxide-ion conduction, which not only accelerate the electrode kinetics but also affect the stability and cost of cell, thus restrict the commerical application. Lowering the temperature of RSOFC to below 700 °C has been realized by reducing the electrolyte thickness and using protonic oxide electrolytes. However, the insufficient ionic conductivity of electrolyte and catalytic activity of electrodes as well as the traditional three-layer cell structure pose a challenge to material selection and cell fabrication. To overcome the drawback of electrolyte material development through the structural design and ion-doping, oxide semiconductor-ionic materials have become promising candidates to replace traditional ionic electrolyte materials. A wide range of semiconductor-ionic materials based on mixed ionic-electronic conducting oxides and composites have been exploed to act as only electrolyte or function as both electrolyte and electrodes, thus derived single-component and symmetric three-component cell structures. However, most efforts are focused on fuel cell operation but seldom on fuel cell/electrolysis cell reversible operation due to the unsintered electrolyte layer or functional layer which can not ensure the safety of hydrogen separation.

In this study, we attempted to develop low temperature RSOFCs based on semiconductor-ionic composites. Several kinds of semiconductor-ionic composites such as $BaZr_{0.8}Y_{0.2}O_3$ (BZY)-CeO_2, $Ba_{0.875}Fe_{0.875}Zr_{0.125}O_{3-\delta}$ (BFZ)-CeO_2, BFZ-$Gd_{0.1}Ce_{0.9}O_{2-\delta}$ (GDC)-$(Li/Na)_2CO_3$ (BFZ-GDC-LN), $Ni_{0.8}Co_{0.15}Al_{0.05}LiO_{2-\delta}$ (NCAL)-GDC-LN were successfuly developed as electrolytes for low temperature RSOFC application. The ionic conductivities of these functional materials exceeded 0.1 Scm^{-1} below 600°C and the ionic conduction mechanisms were also discussed. Symmetric three-component RSOFCs and single-component RSOFCs were constructed and demonstrated excellent fuel cell and electrolytic cell performances. The introduction of molten carbonate phase into oxide semiconductor ionic composites will improve the operating stability of such RSOFCs. This work demonstrates that protonic conductors for RSOFCs can be designed by semiconductor heterojuction formed during fuel cell operation.

Figures



Schematic of the proposed design ideas for surface proton conduction enhancement, where (a) BZY without sintering was used as the electrolyte layer; (b) BZY was sintered after high-temperature treatment; (c) synthesis process of $CeO_{2-\delta}$/BZY; (d) fuel cell assembly using Ni-NCAL/($CeO_{2-\delta}$/BZY)/NCAL-Ni as the anode/electrolyte/cathode; (e) corresponding fuel cell I-V and I-P curves; (f) Performance of the water electrolysis cell (reversed PCFC, current density as a function of the applied voltage) employing the $CeO_{2-\delta}$/BZY electrolyte at 520 °C; (g) I-V and I-P curves for NiNCAL/(7BFZ-3$CeO_{2-\delta}$)/NCAL-Ni fuel cell at different temperatures; (h) I-V and I-P curves for NiNCAL/(7BFZ-3$CeO_{2-\delta}$)/NCAL-Ni in two modes; (i) I-V and I-P curve for NCAL-GDC-LN single component fuel cell and (j) short-term interval reversibility.

Acknowledgments

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Effect of thickness on the microstructure, ionic conductivity and strength of tape casted zirconia-based electrolytes for solid oxide fuel cells

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Keywords: tape-casted electrolyte, microstructure, Ball-on-3-Balls test (B3B), fractography, impedance analysis

Electrolyte supported solid oxide fuel cells (ESCs) have gained attention as electrochemical energy conversion devices due to their easy scale-up capacity and low cost mass production. Tape-casted 8 mol% yttria stabilized zirconia (8YSZ) is widely used as electrolyte component due to its high ionic conductivity and good mechanical stability. A major drawback of ESCs is their higher ohmic resistance as compared to electrode (anode, cathode) supported fuel cells. These ohmic losses are associated with the large thickness of the electrolyte layer (~>150 µm). Minimizing the ohmic losses is challenging due to the limitations in mechanical load-bearing capacity of electrolytes for ESCs. These drawbacks can be mitigated by using alternative higher ion conducting electrolyte materials or reducing the thickness of electrolytes while maintaining sufficient mechanical integrity. Hence, the fabrication of thin electrolytes with good mechanical integrity and high ionic conductivity is one of the key research directions for SOFCs.

In this study, the microstructure, ionic conductivity and mechanical strength of tape-casted 8YSZ as a function of electrolyte thickness are investigated. In this regard, 8YSZ electrolyte sheets with a thickness ranging from ~70±5 to ~350±5 µm are fabricated through tape casting followed by debinding at 600 °C for 2 h and sintering at 1400 °C for 2 h. Scanning electron microscopy (SEM) is used to evaluate porosity and grain size distribution in sintered electrolytes. The mechanical strength distribution of sintered electrolytes with different thicknesses is investigated using the Ball-on-3-Ball biaxial bending tests, supported by fractographic analysis to reveal the fracture origin and type of critical defects. Strength results are analyzed in the framework of Weibull statistics. In addition to the mechanical testing, impedance measurements are carried out to study the effect of different thicknesses on the ionic conductivity of tape casted 8YSZ electrolytes.

Isothermal degradation of porous Ni-3YSZ in solid oxide cells: Occurrence, challenges, and solution

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Keywords: tetragonal zirconia, solid oxide cells, degradation, durability

Hydrothermal degradation in transformable tetragonal zirconia ceramics is a well-known issue. The phenomenon occurs at temperatures below ≈ 400 °C and embrittles the ceramics. Nevertheless, it is widely believed that the degradation does not occur at higher temperatures.

Solid oxide fuel and electrolysis cells (SOCs) demonstrate great potential in the green transition due to their high efficiency. Fuel electrode-supported cell based on a Ni(O)-3YSZ (3 mol% yttria doped zirconia) support is one of the most common SOC designs. The excellent fracture toughness and strength of the support in this design, resulting from the transformation toughening in 3YSZ, enables scaling up the cell size. Although 3YSZ has a transformable (metastable) tetragonal phase, since SOCs typically operate at temperatures well above 600 °C, the 3YSZ-containing cells have been considered resistant to hydrothermal degradation in operation.

In this work, we present our studies on the isothermal degradation of Ni-3YSZ at various temperatures, from room temperature to 820 °C. The high-temperature degradation observed in several long-term tested cells – tested for more than 8,500 to 10,000 h and under various conditions (including temperature, atmosphere, and testing mode) – are discussed. We further report a comprehensive study of the degradation of Ni-3YSZ at room temperature, 134 °C, and from 350 to 550 °C. Moreover, the effect of the grain size of 3YSZ on the degradation behavior of supports and the impact of the degradation on the fracture strength are presented.

The findings of this work indicate that the isothermal degradation of metastable tetragonal zirconia poses a significant challenge to the long-term durability of SOCs containing this class of zirconia materials. Ni-3YSZ supports are highly vulnerable to degradation at low and high temperatures. The degradation studies provide a clearer understanding of the degradation behavior of Ni-3YSZ ceramic and the effect of porosity on its degradation kinetics. The results further show that degradation drastically embrittles the supports. In addition, it is concluded that supports with fine-grained 3YSZ (with grain size smaller than 200 nm) have excellent resistance to degradation at different temperatures.

Upscaling of proton conducting ceramic cells

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Keywords: proton conduction ceramics, electrolysis, hydrogen production, processing, upscaling

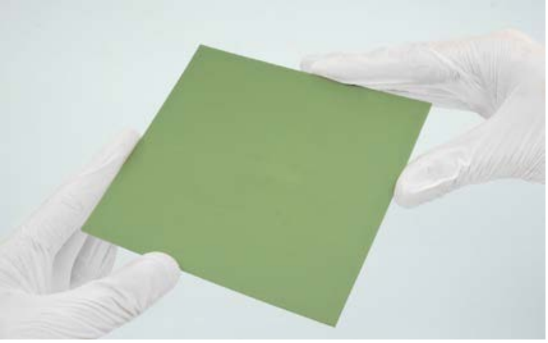
Ceramics based on proton-conducting oxides are promising for a variety of applications, including fuel cells, electrolysis, hydrogen pumping, or chemical synthesis, but up-scaling of cells and stack remains a challenge.

In this presentation, we will give an overview of ongoing activities at the Technical University of Denmark (DTU Energy) to address this challenge.

The latest results on upscaling planar proton-conducting ceramic cells (PCCs) based on Ba(Ce, Zr)O_3 will be presented. Symmetrical and asymmetrical cells with an area of <140 cm^2 can be produced (Figure 1), and the geometry and composition of the electrolyte and electrodes can varied/optimized for different applications.

Also, the development of auxiliary components like interconnects and glass ceramic sealants needed to build stacks will be discussed. Furthermore, potential stacks design, which can circumvent challenges arising from the thermal expansion mismatches of the different materials used in PCC stacks, will be highlighted.

Figures



Proton Conducting Cermauic Cell produced at DTU.

Operation-specific electronic leakage in protonic ceramic electrolytes for solid oxide cells

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Electronic conduction through proton-conducting electrolytes significantly impairs the efficiency of protonic ceramic cells (PCCs). In this study, we explore the electron and ion mixed transport properties of four common protonic ceramics, $BaZr_{0.8}Y_{0.2}O_{3-\delta}$ (BZY82), $BaZr_{0.7}Ce_{0.2}Y_{0.1}O_{3-\delta}$ (BZCY721), $BaZr_{04}Ce_{0.4}Y_{0.1}Yb_{0.1}O_{3-\delta}$ (BZCYYb4411) and $BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$ (BZCYYb1711). It marks the first instance of investigating these properties under operation-specific scenarios: fuel side of electrolysis cell, air side of electrolysis cell, fuel side of fuel cell, and air side of the fuel cell. BZCYYb1711 exhibits the highest ionic conductivity, but 2-3 times higher electronic leakage when exposed to oxygen-containing environments than the others. BZY82 exhibits ~2 times higher electronic leakage in hydrogen-containing environment. BZCY721 demonstrates excellent ion transport numbers (~0.95) across these four operating conditions. BZCYYb4411 behaves quite similarly to BZCY721. The most challenging operating environment for all candidates is the air side of fuel cell mode. This mode leads to a high initial electronic leakage, followed by a significant increase with polarization. The probable cause for this behavior is a H_2-free, polarization-induced reduction that leads to the formation of $V_O^{\bullet\bullet}$. The electron small polaron associated with $V_O^{\bullet\bullet}$ is released by the electrical field due to the Poole-Frenkel effect. ZnO and NiO sintering aids are found to be detrimental to the ionic conductivity of the electrolytes. In particular, NiO substantially lowers the ion transport number. The correlation of these operation-specific electronic leakage to full cells is discussed. It is suggested that a rational PCCs design should synergistically couple BZCYYb1711 at fuel side with BZCY4411 at air side to deliver a well-balanced performance and faradaic efficiency simultaneously, and the high temperature sintering process with a NiO fuel electrode should be shortened or replaced by ultra-fast sintering techniques or using a fuel electrode scaffold-infiltration fabrication strategy.

Development and performance evaluation of honeycomb based and planar based anode supported intermediate temperature solid oxide fuel cell for power generation

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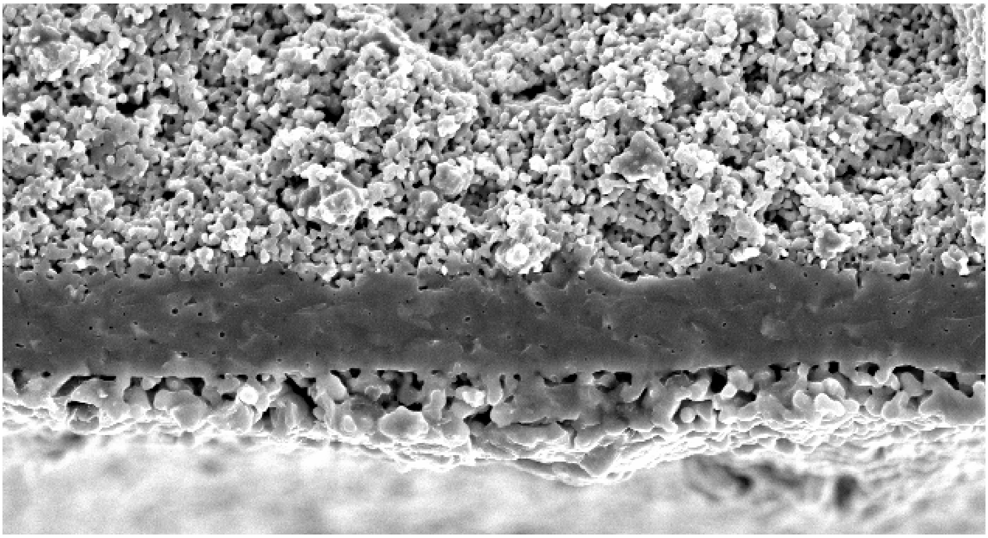
Solid oxide fuel cells (SOFC's) are the interesting energy production systems because of their high efficiency, versatility in fuel usage and environmental friendliness. Currently the reduction of the operating temperature is very important issue for commercialization. Though extensive efforts are in progress to address this issue, reducing the operating temperatures to the intermediate temperature range of 500-800ºC with traditional SOFC materials is still exists as a challenge. Lowering the operation temperature of SOFC will resolve a series of problems such as sintering of electrodes, high reactivity between cell components and strict requirements on interconnected materials, which will often happen in conventional SOFCs. The decrease in operating temperature however increases the cell over potential, and the main contributor to this increase is the ceramic components such as ceramic cathode, ceramic anode and ceramic electrolyte materials. Hence the development of solid oxide fuel cell with low polarization resistance is of great importance to achieve high power densities at reduced temperatures.

ARCI has started working on SOFC on a typical design of honeycomb structures for specific application. NiO-8YSZ ceramic anode powders are mixed with binder and made into dough, which is passed through specially designed and fabricated dies to achieve anode ceramic honeycombs with more than 16 no. of channels. Alternate channel are given an electrolyte coating using dip coating process and heat treated anode honeycombs along with coated electrolyte material. The dense electrolyte coated channels were coated with LSM cathode using dip coating process. Further, dual chamber interconnect is used to seal the channels with high temperature glass sealant. Thus, anode supported ceramic honeycomb SOFC has fabricated and tested the performance of the Honeycomb SOFC and proved the concept. The cross sectional image of the honeycomb SOFC single cell shows clearly the dense and thin 8YSZ electrolyte sandwiched between LSM cathode and Ni-8YSZ anode. ARCI indigenous produced nano-powders of LSM cathode used for SOFC by spray pyrolysis process. Cross sectional image of the honeycomb sofc cell developed is shown here with dense and thin electrolyte.



Further, to the above design, ARCI jointly with CGCRI and HPCL in a consortium project is establishing a pilot scale facility for the development of SOFC systems and fabricating indigenous solid oxide fuel cell single cells with 8YSZ electrolyte, LSM-8YSZ cathode functional layer, LSM cathode and Ni-8YSZ anode as support as well as anode support layer using tape casting process. The results will be presented and discussed during the presentation.

Sinterability of NiO added $BaZr_{0.8}Yb_{0.2}O_{3-\delta}$ perovskite as an electrolyte of Protonic Ceramic Fuel Cell

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Keywords: proton ceramic fuel cell, $BaZr_{0.8}Yb_{0.2}O_{3-\delta}$ perovskite, sinterability

Protonic Ceramic Fuel Cell (PCFC) can exhibit a power generation efficiency more than 70 % by high H_2 fuel utilization[1)]. $BaZr_{0.8}Yb_{0.2}O_{3-\delta}$ (BZYb) perovskite is considered as one of the most promising material for an electrolyte of PCFC. Since BZYb perovskite is well known to be quite poorly sinterable, BZYb perovskite is fired with NiO which is a fuel electrode component during PCFC fabrication process to obtain dense electrolyte. Further understandings of the sintering mechanism of NiO added BZYb during the fabrication process of PCFC are essential in controlling the material properties.

Fig. 1 shows relative densities of 1 wt. % NiO added BZYb perovskite as a function of firing temperature and holding time. The relative density of the sample significantly increased at firing temperature at 1300 °C and was 95 % at firing temperature at 1500 °C. Fig. 2 shows TG-DTA results of $BaCO_3$-NiO with equimolar ratio after heating at 1100 °C for 15 min. The endothermic peak at 1243 °C is corresponded to the melting point of the $BaNi_xO_y$ eutectic product It is considered that this product is formed and promotes the sinterability of NiO added BZYb perovskite during the firing process. Further effects of NiO addition on sintering characteristics of BZYb perovskite will be discussed in the conference.

Figures

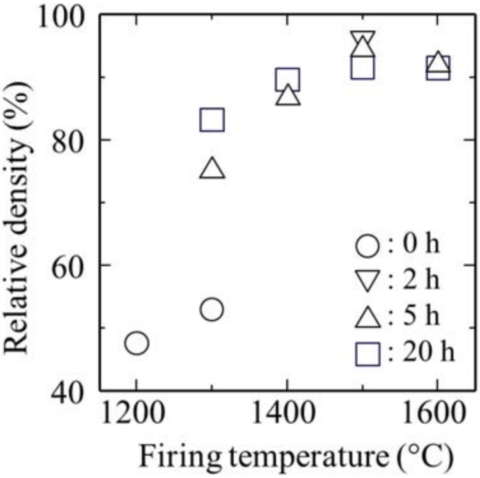

Fig. 1 Relative densities of 1 wt. % NiO added BZYb perovskite as a function of firing temperature and holding time.

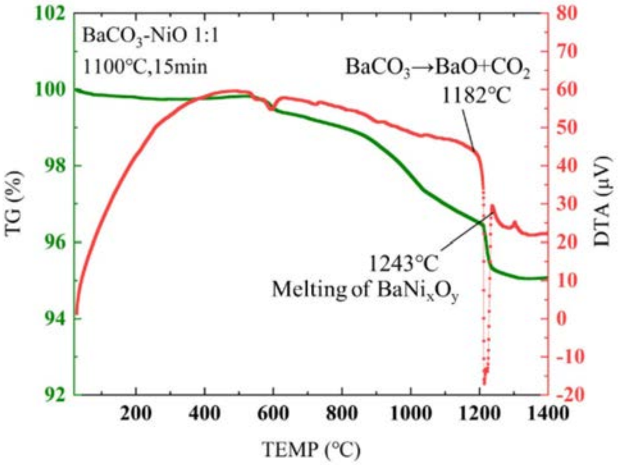

Fig. 2 TG-DTA results of BaCO$_3$-NiO with equimolar ratio after heating at 1100 °C for 15 min.

Acknowledgments

This work has been supported by the New Energy and Industrial Technology Development Organization (NEDO) Japan via the project “Development of Ultra-High Efficiency Protonic Ceramic Fuel Cell Devices (JPNP20003)”.

References

K. P. Li *et al., Energy Convers. Manag.*, 296 (2023) 117678.

Creep behavior of glass-ceramic sealant in amorphous and crystalline phases for SOEC stack sealing

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Keywords: creep deformation, glass-ceramic sealant, crystallization, SOEC stack

The Solid-Oxide Electrolysis Cell (SOEC) is recognized as the most efficient electrolysis technology for Power-to-X solutions, despite its relative immaturity at the industrial level. A key factor in enhancing the competitiveness of this technology is extending the SOEC stack's lifespan, as the benefits of conversion efficiency can only offset installation costs over extended periods. To this end, SOEC stacks are designed to operate at high temperatures (>700°C) for several years, positioning creep as a crucial determinant of stack structural durability.

The long-term behavior of the glass-ceramic sealant is particularly critical, as it meets two fundamental design requirements: bonding stack components and preventing gas leakage. Given that glass ceramics are multi-phase materials, often featuring an amorphous phase coexisting with multiple distinct crystalline phases, it is valuable to characterize the creep behavior of each phase individually.

In this study, we have experimentally investigated the creep properties of glass-ceramic sealant material under varying temperatures and loads, within the stack's operational conditions. We have also examined the impact of crystallization on creep deformation. Furthermore, a creep constitutive material model has been utilized to predict glass sealant deformation at elevated temperatures, with these predictions subsequently compared to experimental results. The obtained results indicate that crystallization significantly reduces the creep deformation of the glass-ceramic material.

The findings of this work provide detailed information about the creep deformation of the Glass-Ceramic sealant material under stack working temperatures and are highly beneficial for the development of durable and high-performance SOEC stacks.

Acknowledgments

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Innovative architectures and nanostructures of composite oxygen electrodes for SOC application

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Keywords: solid oxide cells, oxygen electrode, electrostatic spray deposition, lanthanum nickelate composites

One strategy to limit the chemical reactivity between SOC (solid oxide cell) materials consists in lowering the operation temperature (~ 800 °C). This however also reduces reaction kinetics of oxygen species and the charge transport properties, especially at the oxygen electrode. An improvement of the charge transfer of oxygen species has been reported by optimizing the microstructure, composition of the oxygen electrode, and the quality of interfaces between ionic and electronic conducting layers using Electrostatic Spray Deposition (ESD).

In this work, we offer an innovative solution to create new nanostructures and architectures of LNO ($La_2NiO_{4+\delta}$) and CGO ($Ce_{0.9}Gd_{0.1}O_{2-\delta}$) composites by ESD and screen-printing. The electrochemical properties (measured by impedance spectroscopy) of these advanced electrodes are shown to be strongly dependent on (i) the unique coral-type microstructure (high porosity and specific surface area), and (ii) the architecture (chemical composition either homogeneously distributed through the electrode volume, or distributed in form of a gradient, or in a triple layer configuration). Temperature-dependent acquisition of impedance spectra in synthetic air allow to correlate the improvement of the polarization resistance with the microstructure and the oxygen electrode architecture [1].

Figures

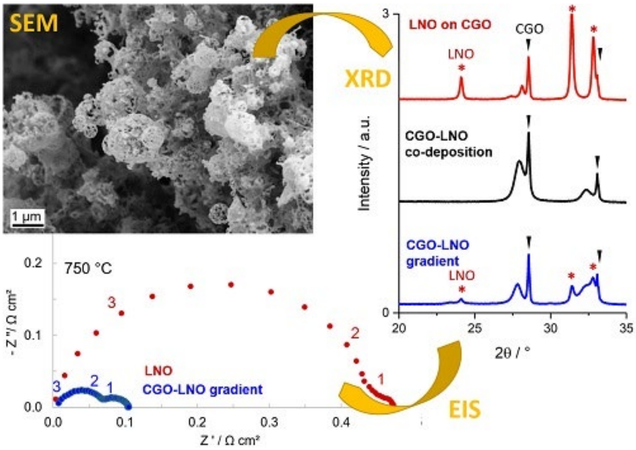

Figure 1: Impedance spectra of CGO-LNO electrodes related to their structural and microstructural properties.

Acknowledgments

This work benefited from state support managed by the Agence Nationale de la Recherche under the France 2030 program, referenced ANR-22-PEHY-0008.

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Mechanical properties of thin zirconia substrates, mechanisms of degradation and reduced performance

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Keywords: zirconia substrates for SO(F)C, mechanical properties, reliability, degradation

One of the most critical issues in solid oxide cell and stack manufacturing is the mechanical failure in ceramic electrolyte. In operation, drastic performance losses and a reduced stack lifetime can be observed, if cells are mechanically destroyed.

In this study strength, fracture toughness and the influence of subcritical crack growth (SCCG) has been investigated for different zirconia electrolytes with thickness <200 µm. Strength has been determined by tensile tests at room temperature and B3B tests up to a maximum stack temperature of 850 °C. The determination of fracture toughness via notched samples (ISO21113) is not suitable for substrates <200 µm and materials of lower strength, due to specimen failure during notch polishing. Alternatively, evolution of crack length from Vickers hardness indentations up to 850 °C has been evaluated. The results show for T>400 °C a decreasing crack propagation resistance i.e., lower transformation toughening, for partially stabilized zirconia (3YSZ and 6ScSZ).

The mechanical measurements have been repeated after aging zirconia substrates by annealing. Pure 3YSZ and cathode-coated 3YSZ were annealed both in air and in a dual atmosphere (air and N_2 + 40 % H_2) for 100 h at 835 °C. Based on investigations of these samples, mechanisms, which lead to mechanical degradation of the electrolytes, will be discussed.

Development of ceramic-supported Solid Oxide Cells with LSFNT-based fuel lectrode

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Keywords: solid oxide cell, fuel electrode, ceramic-supported cells, LSFNT

The Solid Oxide Cell (SOC) technology holds significant promise for efficient energy conversion and the production of green chemicals and fuels. However, it faces challenges related to durability and cost, particularly concerning the fuel electrode. Ni/8YSZ (Nickel/8 mol.% yttria-stabilized zirconia) is widely used as the fuel electrode in SOCs due to its high electrocatalytic activity and conductivity. However, challenges such as nickel migration reduce its performance and can hinder long-term operation.

To develop cells with improved fuel electrodes, low-Ni content fuel electrodes made of perovskites such as $La_{0.49}Sr_{0.31}Ti_{0.94}Fe_{0.03}Ni_{0.03}O_3$ (LSFNT) have received significant attention. LSFNT is a material of interest, being an A-site deficient lanthanum-substituted $SrTiO_3$, which has garnered attention in recent years. LSFNT fuel electrodes have shown promising performance and durability when integrated into metal-supported solid oxide cells. Still, their integration into 3YSZ-based supported cells and their performance at typical operating temperatures of such cells (>650°C) is not well investigated. Ceramic-supported LSFNT cells with infiltrated electrocatalysts could offer the potential for operation at higher temperatures and current densities with improved electrochemical performance.

In this work, we have developed ceramic-based fuel electrode-supported cells and investigated the performance of this cell configuration for SOEC operation. The cells have a multilayered structure, comprising a mechanical support layer of 3 mol.% yttria-stabilized zirconia (3YSZ), an LSFNT fuel electrode, a 10 mol.% scandia, and 1 mol.% yttria-stabilized zirconia (10Sc1YSZ) electrolyte, a gadolinia-doped ceria (CGO) barrier layer, an LSC ($LaSr_{1-y}CoO_{3-x}$)/CGO air electrode, and an LSC contact layer. These layers were fabricated using conventional ceramic processing techniques, such as tape casting and screen printing.

The microstructure evolution of the LSFNT fuel electrode as a function of sintering temperature (1200°C, 1225°C, and 1250°C) is studied. Additionally, phase stability at the interfaces between the support and electrode was assessed using Raman spectroscopy. Following the co-sintering process, intact cells were manufactured, and the cells exhibited appropriate microstructure, particularly regarding sinterability and adhesion of the fuel electrode with the 10Sc1YSZ electrolyte and Ni-3YSZ support layers. Electrochemical impedance spectroscopy (EIS) measurements were conducted on 4×4 cm² single cells, comparing pure LSFNT cells with those infiltrated with CGO and Ni-CGO catalysts. Cell reduction was carried out over 5 hours at 850°C in a diluted hydrogen atmosphere (5% H_2/95% N_2). EIS measurements were performed at three temperatures (700°C, 750°C, and 800°C) and with three different gas compositions (90/10, 50/50, and 20/80) of H_2O/H_2, while air was consistently introduced into the oxygen electrode. Durability tests were carried out at 750°C with 90/10% H_2O/H_2, air in the oxygen electrode, and a current density of -0.5 A/cm². EIS measurements and durability results are discussed, and the effects of catalyst infiltration are evaluated.

Effect on structure and performance of potassium-substituted barium-strontium-cobalt-ferrite materials as air electrode for proton-conducting fuel cells

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Keywords: protonic ceramic fuel cell, electrochemical performance, XRD, air electrode

Among the solutions for accelerating SOFC development, lowering the operating temperature to an intermediate range (IT) (600°C-800°C) with proton-conducting ceramic fuel cells is widely recognized. Potassium-substituted barium-strontium-cobalt-ferrite ($K_xBa_{0.5-x}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$, $x = 0.00 - 0.20$, BKSCF) was studied as air electrode materials for IT-SOFCs. BKSCF was synthesized by auto-combustion reaction using glycine as fuel. In this study, the effects of K doping on phase formation (XRD), microstructure and composition (SEM and EDX), surface area, lattice oxygen content, hygroscopicity and electrochemical performance are investigated.

K-doping during synthesis improves crystallization and stabilization of the perovskite phase. The XRD pattern shows that BKSCF has an ABO_3 cubic perovskite structure (Pm-3m)[1]. The refined lattice parameters were found to decrease non-linearly with K^+ doping concentration, which can occur[2]. This non-linear behavior could be related to the formation of anion vacancies[3] due to the aliovalent substitution of A^{2+} by K^+. Potassium doping also improves hydration properties and we observe that the sample with the highest K^+ doping exhibits high hygroscopic property.

The electrochemical performance of BKSCF was characterized by EIS using a symmetric cell configuration (BKSCF/BZCY/BKSCF). The area specific resistance at different temperatures, a valuable parameter for characterizing the catalytic oxygen reduction activity of the air electrode material, decreased with increasing K content.

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Vacancies and electron holes triggers hydration reaction in Mn-based perovskite for Proton Ceramic Electrochemical Cells

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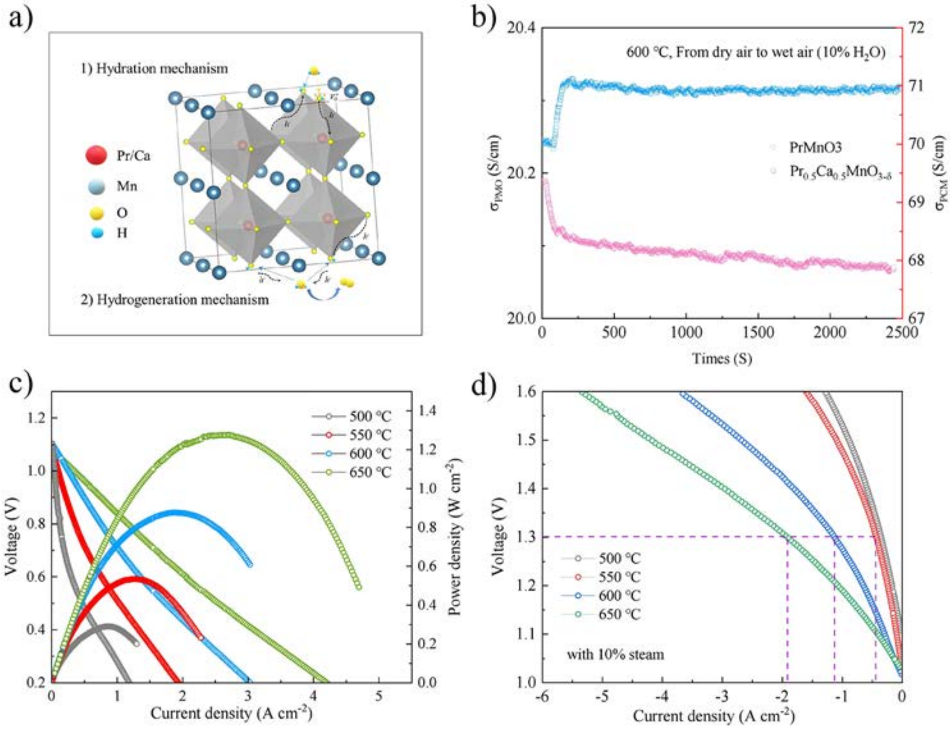
Keywords: proton ceramic cells, Mn-based perovskite, hydration mechanisms, water tolerance

Proton ceramic electrochemical cells (PCECs) are an efficient energy conversion device, which can operate in fuel cell (PCFC) and electrolysis modes (PCEC) at medium temperatures (450-650 °C)[1, 2]. To improve the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) kinetics, many perovskite-based triple-conductor ($H^+/e^-/O^{2-}$) oxides have been developed. Here, we design a $PrMnO_3$-based perovskite by Ca incorporation into the Pr-site, leading to a change of intrinsic propetrties due to the introduction of oxygen vacancies and electron holes. Electrical conductivity relaxation (ECR) tests reveal that $PrMnO_3$ primarily undergoes a hydrogeneration mechanism during water absorption, characterized by a slow kinetic process. Conversely, Ca-doped $Pr_{1-x}Ca_xMnO_{3-\delta}$ (PCM) demonstrates a higher concentration of electron holes and oxygen vacancies, thereby contributed to a more rapid water uptake by encompassing both hydrogeneration and hydration mechanisms. Electrochemical test results show that PCM5 has the best electrochemical performance. In fuel cell mode, the single cell with PCM5 electrode delivers a peak power density of 1.28 Wcm^{-2} at 650 °C; in electrolysis mode, a current density of 1.95 A cm^{-2} at 1.3 V is achieved under 10 %H_2O-air. Moreover, the single cell demonstrates excellent fuel cell stability at 600 °C and water tolerance under high water pressure of 75 %. These studies reveal that the incorporation of low-valence metals into the A-site of Mn-based perovskite can significantly enhance the electrochemical properties of air electrodes.



a) Schematic representation of the migration of four carriers during water uptake. b) ECR curves for PMO and PCM5. c) I-V-P curves of PCFC with PCM5 at 500-650 °C. d) Typical I-V curves of PCEC at 500-650 °C.

Acknowledgments

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T1.2 CERAMICS-RELATED MATERIALS, DEVICES, AND PROCESSING FOR HEAT-TO-ELECTRICITY DIRECT CONVERSION AND THERMAL ENERGY HARNESSING

Low-angle grain boundaries-advanced high thermoelectric performance in Bi_2Te_3-based alloys

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Keywords: Bi_2Te_3, thermoelectric materials, low-angle grain boundaries, thermoelectric performance

Bi_2Te_3-based thermoelectric materials are widely used in near-room temperature refrigeration fields. Tuning the microstructure, such as introducing dislocations, grain boundaries, and so on, can suppress the thermal conductivity, and thus optimize the figure of merit (*zT*). Low-angle grain boundaries(LAGBs) which consist of dislocation arrays, can effectively scatter the medium-frequency phonons and thus suppress the lattice thermal conductivity while maintaining a weak effect on the carrier transport.[1,2] Developing more strategies to reliably introduce LAGBs into Bi_2Te_3-based materials and systematic investigations into how LAGBs affect the electrical and thermal transport properties are still elusive. Here, we explore a new method that can introduce a high fraction of LAGBs in Bi_2Te_3-based alloys and reveal its formation mechanism. Finally, a high room temperature *zT* with good mechanical properties is obtained. This work puts forward a paradigm of enhancing the thermoelectric properties via microstructure modulations and is significant to the industrialization of manufacturing Bi_2Te_3-based alloys and thermoelectric devices.

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Synthesis and thermoelectric properties of polycrystalline $YbMnSb_2$

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Keywords: semimetals, anisotropic, impurities, high mobility

Topological semimetals with exotic electronic structures have been discovered in recent years, which provide a new platform to further explore new thermoelectric candidates. Topological semimetal $YbMnSb_2$ possesses a 2D Dirac band and its single crystal has been reported to have a large power factor[1-3], attracting research attention as thermoelectric candidates. To further engineer the electronic structure using chemical doping or alloying, the easily fabricated high-quality polycrystals are a good platform. Here, we find $YbMn_2Sb_2$, as a secondary phase, could be found in the synthesized single-crystalline and polycrystalline $YbMnSb_2$, the latter prepared by the conventional melting method. By further employing mechanical milling and Spark Plasma Sintering, high-purity polycrystalline $YbMnSb_2$ samples with high purity can be obtained. Further analysis revealed that $YbMnSb_2$ is sensitive to oxygen during the heating experiment, with a reaction equation as $4YbMnSb_2+O_2=2Yb_2O_3+4MnSb+4Sb$. Finally, the Seebeck coefficient of the $YbMnSb_2$ sample reaches a maximum of 154 μV/K at around 250 K, comparable to the single crystal. This study highlights the synthesis method of high-purity polycrystalline $YbMnSb_2$, paving the way to further optimize its thermoelectric performance.

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Reversible room temperature brittle-plastic transition in $Ag_2Te_{1-x}S_x$ inorganic thermoelectric semiconductors

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Keywords: plastic semiconductors, silver chalcogenides, phase structures, thermoelectric performance

Inorganic semiconductors with superior plasticity are highly desired in current flexible electronics, which however were rarely discovered owing to their intrinsic covalent and ionic bonds. The $Ag_2Te_{1-x}S_x$ semiconductors have recently been reported to exhibit plastic deformability [1-3]. Here, we report the reversible brittle-plastic transition in this inorganic semiconductor and we find that the plasticity of the $Ag_2Te_{1-x}S_x$ compounds is highly related to the phase structures [4]. The $Ag_2Te_{1-x}S_x$ with a monoclinic phase exhibits a brittle behavior, while the one with a cubic-crystalline/amorphous structure shows exceptional plasticity with a compressive strain of over 80%. Significantly, the reversible plastic-brittle transition in $Ag_2Te_{1-x}S_x$ inorganic semiconductors can be achieved by simple heat treatment. Besides the plasticity, the cubic-crystalline/amorphous $Ag_2Te_{0.6}S_{0.4}$ composites also possess good TE performance. This study uncovers the influence of phase structure on the mechanical properties of $Ag_2Te_{0.6}S_{0.4}$, which will facilitate its prospective application in flexible/wearable electronics.

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Low-grade thermal energy harvesting using organic materials

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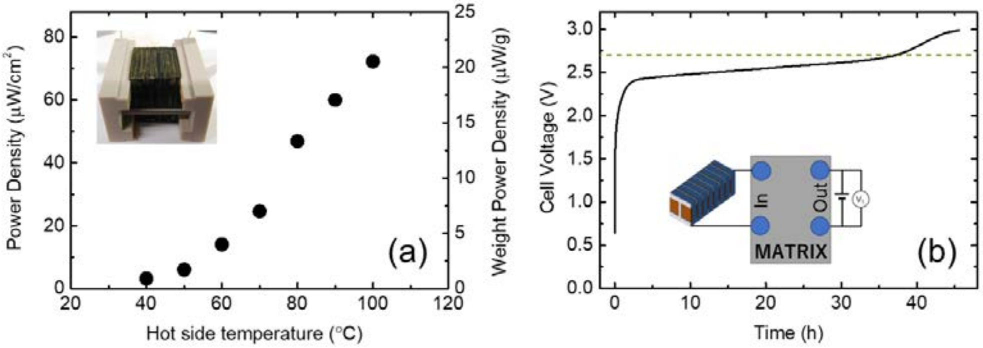
Keywords: conducting polymers, lamination, contact resistance, natural cooling

In our daily lives, a substantial amount of valuable heat energy goes to waste, primarily in the temperature range from room temperature to approximately 200 °C. Harnessing this low-grade thermal energy presents several challenges, including issues related to efficiency and energy payback during fabrication. Additionally, environmental considerations are crucial when devising solutions for broad applications. We aim to introduce thermoelectric devices based on organic materials to capture and utilize this untapped low-grade thermal energy resource.

The organic thermoelectric device introduced in this presentation, capable of operating within the temperature range of up to 200 °C. These devices are fabrciated by laminating ultrathin films of poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT/PSS) with Ni foils. Careful consideration is given to the shape and size of the Ni foil to optimize thermal and electrical resistance matching while minimizing contact resistance between PEDOT/PSS and Ni.[1] Thanks to the inherently low thermal conductivity of organic materials, these devices exhibit impressive power density, achieving 72 μW/cm^2 at 100 °C under natural cooling conditions without the need for a heat sink. Remarkably, a mere 5-gram device can fully charge a commercial Li-ion battery within just two days.[2] Furthermore, these organic thermoelectric devices can seamlessly replace CR2032 coin cells to power a wide range of commercial sensors, including those for acceleration, geomagnetism, and illuminance.[3]

Figures



(a) Power density and weight power density of the device as a function of the hot-side temperature. The mass density of the device is ca.1.6 g/cm^3. The inset is a photograph of the module. (b) Charging curve of a Nichicon SLB03070LR35 commercial Li-ion battery obtained for a process whereby the herein-manufactured organic thermoelectric module was used at 100 °C. In the inset is the block diagram.

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T1.3 Emerging Materials and Technologies for Solar Cells and Solar Fuel Technologies

Multiscale modelling of the thermal radiative properties of a CeO_2 ceramic pellet for solar H_2 production at high temperature

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Keywords: H_2, ceria, dielectric model, 2-flux approximation, emissivity

Solar thermochemistry is a green way to produce hydrogen (H_2) at high temperature. This technology is based on a two-step redox thermochemical cycle, heated by a concentrated solar power device. The most commonly used material is cerium oxide, or ceria (CeO_2). The reduction step is done at 1500°C, and the oxidation step at 900°C with the introduction of water in the reactor. The oxide reduces the water vapor, forming dihydrogen. Experimentations approaching the industrial production scale use heliostat field (50 kW) concentrating solar radiation to a reactor in a solar tower, but this process has a limited yield of 4% [1].

To enhance the H_2 production, one of the main challenges is to reduce the temperature gradient in the reactor. This latter is due to the front face exposure of the CeO_2 3D structure to the concentrated solar radiation. To cope with this issue, one way consists in the numerical optimization of the 3D architecture in order to obtain the most homogeneous volume distribution of the solar flux in the porous reactor, which can be designed furthermore by additive manufacturing [2]. The validity of these modelling depends on the exact knowledge of the thermal radiative properties of CeO_2 in the conditions of the H_2 production process, i.e. 900 to 1500°C, $pO_2=10^{-5}$ atm. Currently, the radiative properties are known only at room temperature [3]. However, the electronic transport properties in the ceria induced by the redox cycle can generate absorption mechanisms of infrared radiation when the temperature grows up, and its impact on the radiative properties is little known.

To establish a firm link between these two physical features, spectral reflectance and transmittance measurements has been firstly performed on a dense CeO_2 pellet by infrared and visible spectroscopy at room temperature, from 600 to 20000 cm^{-1} (i.e 0.5 to 16.7 µm). Electrical conductivity characterizations on the CeO_2 sample has been secondly done from 900 to 1500°C on a large pO_2 range (from 1 to 10^{-23} atm.). Thirdly, a multiscale modelling of the normal spectral emissivity of a CeO_2 ceramic bulk is proposed. The parameters injected in the model are extracted from the latter experiments. It combines a modified 2-flux approximation to describe the effective radiative behavior of the grains constituting the pellets, and a Drude-Lorentz model to take into account the electronic contributions. The computed spectra are compared to spectral emissivity measurements carried out at high temperature by infrared spectroscopy. The calculated emissivity is high (0.85) in the temperature range of interest (900-1500°C). The multiscale modelling also shows that the role of the ceramic microstructure on the spectral emissivity becomes negligible at 900°C and beyond. This suggests that the high temperature radiative behaviors of single crystals and dense ceramics of CeO_2 would be rather closed.

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Lead free photoactive $BiFeO_3$-$BaTiO_3$ solid solutions as solar water splitting photoelectrodes

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Keywords: photoelectrode, ferroelectrics, thin films, water splitting

As the world transitions to a carbon neutral future, it is generally accepted that hydrogen plays an essential part as a fuel source. The use of solar energy as means of water splitting is among the most attractive prospects for generating green hydrogen. However up until now, large market deployment of photocatalytic and photoelectrochemical systems has not materialised owing to relatively low energy conversion efficiencies. The use of ferroelectric polarisation as a means of enhancing charge separation and thus improving energy conversion efficiency of these systems has been well reported. $BiFeO_3$-$BaTiO_3$ solid solutions have attracted widespread interest in recent years as a lead-free alternative to lead zirconate titanate (PZT), with both displaying enhanced ferroelectric polarisation within morphotropic phase boundary regions. With few ferroelectric materials attracting as much interest as $BiFeO_3$ for photocatalytic systems it is surprising $BiFeO_3$-$BaTiO_3$ has remained almost completely unexplored.

This work presents photoelectrochemical performance of $BiFeO_3$-$BaTiO_3$ solid solution thin films and powders as a photocatalyst for hydrogen generation under visible light irradiation. The charge transfer behaviour is explored by considering photoelectrochemical data as well as electrochemical impedance spectroscopy. Ferroelectric properties and photoperformance of this material system are thoroughly examined to elucidate the link between ferroelectric polarisation and photocatalytic performance.

Acknowledgments

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T1.4 MATERIAL SCIENCE AND TECHNOLOGIES FOR ADVANCED NUCLEAR FISSION AND FUSION ENERGY

Investigation studies of WNbMoVTa and WNbMoVTa$Cr_{0.5}$Al refractory high entropy alloys as plasma-facing materials

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Keywords: refractory high entropy alloy, wear resistance, microhardness, He^+ irradiation

Tungsten (W) is used chiefly as plasma-facing material. However, it has some problems, such as brittleness after plasma exposure. High-entropy alloys (RHEAs) are a new opportunity for this deficiency. So, the neutron shielding behavior of WNbMoVTa and WNbMoVTa$Cr_{0.5}$Al compositions were examined against He^+ irradiation in this study. The mechanical and irradiation properties of the WNbMoVTa base composition were investigated by adding the Al and Cr elements. The mechanical alloying (MA) for 6 hours was applied to obtain RHEA powders. According to the X-ray diffraction (XRD) method, the body-centered cubic (BCC) phase and NbTa phase with a small amount of WC impurity that comes from vials and balls were determined after 6 h MA. Also, RHEA powders were consolidated with the spark plasma sintering (SPS) method (1500 ºC, 30 MPa, and 10 min). After the SPS method, (Nb,Ta)C and $W_2C_{0.85}$ phases were obtained with the decomposition of WC and stearic acid that is added during MA based on XRD results. Also, the BCC phase was obtained for both samples. While the Al_2O_3 phase with a small intensity was seen for the WNbMoVTa$Cr_{0.5}$Al sample, the Ta_2VO_6 phase was determined for the base sample. These phases were observed as three different regions according to scanning electron microscopy (SEM). All elements were distributed homogeneously on the white region by measuring of electron probe micro-analyzer (EPMA) coupled with a wavelength dispersive spectroscope (WDS). Also, the grey region of the WNbMoVTa sample was rich for Ta, V, and O elements. However, the amount of Al and O elements was higher for the grey region of the WNbMoVTa$Cr_{0.5}$Al sample. The high amount of Nb, Ta, and C elements were determined for both samples. Archimedes' densities that were measured with alcohol media were closer to the theoretical densities of RHEAs. These values were important for the microhardness and irradiation resistance of compositions. While the Vickers microhardness value of the WNbMoVTa sample was measured as ~11 GPa, this value increased to nearly 13 GPa with the WNbMoVTa$Cr_{0.5}$Al sample. These values were compatible with the wear behavior. The wear volume loss was decreased to 0.16×10^{-4} from 1.25×10^{-4} mm^3 by the addition of Al and Cr elements to the WNbMoVTa. The He^+ irradiation was conducted on the samples to observe surface damage. After irradiation, the XRD patterns were shifted to the left because of defects and dislocations. He^+ ions were infused under the surface, so they created the lattice expansion. The peak shifting of the WNbMoVTaCr$_{0.5}$Al sample was less than the WNbMoVTa base sample, thanks to less impact. A small amount of fuzz was observed for the base sample. This structure was removed and transformed to a wavy structure with the addition of Cr and Al elements. Also, the deformation hardening was actualized after irradiation. A lower amount of hardening was obtained with the WNbMoVTaCr$_{0.5}$Al sample based on the changing microhardness values. The surface deformation was decreased in the WNbMoVTaCr$_{0.5}$Al sample.

Thermochemical simulation of the behavior of a nuclear fuel in space reactors

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Keywords: nuclear fuels, themochemistry, propulsion, CALPHAD

Simulation of the thermochemical behavior of materials play a crucial role in understanding their durability in nuclear thermal propulsion (NTP)[1] and power related applications. Currently, NASA's Space Nuclear Propulsion (SNP) and Fission Surface Power (FSP) projects are focusing on the development of nuclear thermal propulsion and power technologies to meet future space exploration missions. Knowledge gained in computing properties have important implications for development of reliable fuel forms required for these technologies. Ceramic-ceramic (cercer) UN-based fuels have been considered for NTP and power related applications.[2-4]. In the cercer fuel system, ceramic UN fuel kernels are dispersed in a ceramic matrix, such as ZrC. For NTP, U-235 fission reactions in the reactor core generate the thermal energy required to heat the propellant to high exhaust temperatures for rocket thrust.[2] For FSP, U-235 fission reactions generate the thermal energy necessary for a power conversion system such as a Stirling or Brayton engine, to convert that heat into electricity.

We summarize and discuss in this presentation our current calculations of the thermochemical behavior of graphite-coated UN fuel kernels during nuclear reactor operation. For the calculations, we used the Thermo-Calc software together with the Thermodynamic of Advanced Fuels-International Database (TAF-ID version 9) providing thermodynamic functions for the fuel. The fcc $UC_{1-x}N_x$, β - U_2N_3, and graphite phases in equilibrium were found to be relatively stable up to ~2810 K where α - U_2N_3 begins to form. A liquid phase forms above 2891 K where extensive reactions take place. The β - U_2N_3 and α - U_2N_3 phases are stabilized by the high N_2 pressure built up in the enclosed kernel porosity, delaying their decomposition to higher temperatures. The fcc $UC_{1-x}N_x$ phase was found to be the major product of the reaction between UN and graphite coating with the vapor phase dominated by carbon-nitrogen gas species. The implications of these results for predicting the operation of NTP and FSP reactor systems are discussed.

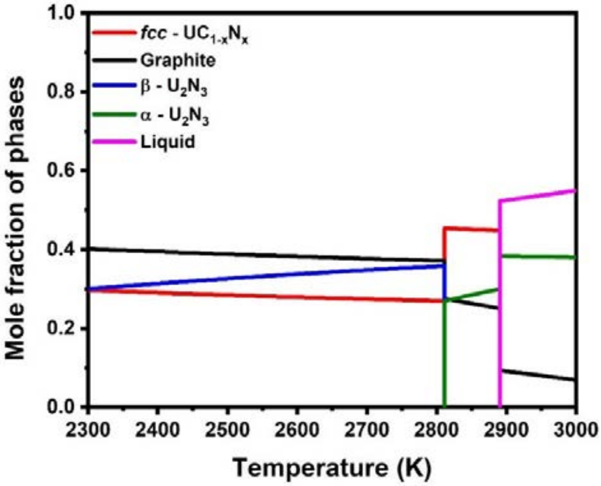

Figure 1. Calculated total amount of phases in the UN-C kernel

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Outstanding performance of PLD-grown amorphous alumina coatings dedicated for advanced nuclear applications

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Keywords: nuclear materials, amorphous materials, alumina coatings, high temperature applications, nanoindentation, X-ray diffraction, radiation damage

Lead-cooled fast reactor (LFR) is one of Generation IV concepts, allowing to close the fuel cycle and thus to reduce the uranium consumption and to limit the volume of high-level wastes for disposal. The main drawback of the advanced lead or lead–bismuth eutectic (LBE) cooled energy systems is the issue related to corrosion degradation of structural materials exposed to the heavy liquid metal. It is widely recognized that all available corrosion resistant metallic materials are not suitable for use in liquid lead and LBE environment, at temperatures above 500 °C. One of the considered strategies to mitigate the issue consists in deposition of an external coating on the steel substrate. The leading candidate for the coating material is alumina. Pulsed laser deposition (PLD) is one of the physical vapor deposition techniques which can be used to grow thin alumina films and permits the deposition at low substrate temperatures. In the past decade, a growing interest of the nuclear community in PLD-grown amorphous alumina coatings have been observed. Available literature data prove that PLD-grown Al_2O_3 coatings show excellent corrosion resistance in HLM and exhibit a number of features desirable for nuclear applications. One of the biggest reasons for that lies in metal-like mechanical properties and strong interfacial bonding of the system.

Presented work is a part of the ongoing research on this topic. Performed studies focus on the influence of high temperature and radiation damage on the coating properties. To determine the effect of the anticipated service conditions (up to 550 °C and 200 dpa) on materials performance a series of room and high temperature tests were performed. 1 μm PLD-grown amorphous Al_2O_3 coatings deposited at room temperature were ion irradiated. Comprehensive post-irradiation characterization comprising microstructural and mechanical analysis was performed using X-ray diffraction, transmission electron microscopy and nanoindentation. Additionally, to study the evolution of the coating under high temperature, in situ nanoindentation (up to 650 °C) and X-ray diffraction (up to 1100 °C) measurements were carried out. It has been demonstrated that as the temperature increases (up to 650 °C), the amorphous alumina experiences a constant gradual decrease in hardness and an increase in plasticity. The phenomenon that has been reported is crucial since it indicates that the alumina coating-steel substrate system is mechanically well-suited for use at high temperatures. The XRD work shows the importance of phase transformation control in amorphous alumina, as it is critical to the performance of the system and a crucial point for understanding the damage behavior of such coatings. Overall, the results obtained so far are very promising and show that the system retains its integrity under the conditions investigated.

Acknowledgments

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Investigation on failure mechanism of multilayer SiC accident tolerant fuel claddings by *in situ* high-temperature X-ray computed micro-tomography

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Keywords: silicon carbide, nuclear fuel cladding, X-ray computed micro-tomography, C-ring compression

Silicon carbide (SiC) ceramics are promising candidates for accident tolerant fuel claddings in light water reactors due to their outstanding high-temperature strength and excellent corrosion resistance under severe accident conditions. SiC fibre reinforced SiC matrix (SiC_f/SiC) composites can effectively mitigate the inherent brittleness of monolithic SiC with the fibre acting as the reinforcement phase to prevent catastrophic failure. In this work, SiC claddings with a novel multilayer design were investigated. This cladding consists of a sintered inner SiC monolith, a SiC_f/SiC composite intermediate layer fabricated by Polymer Infiltration and Pyrolysis (PIP) method, and a thin SiC outer layer coated by Chemical Vapour Deposition (CVD) process. An i*n situ* synchrotron X-ray computed tomography (XCT) imaging study of C-ring compression test specimens at room temperature, 800°C, and 1050°C was conducted to determine the deformation and fracture mechanism of the SiC multilayer tubes. Specifically, the crack initiation and propagation processes in the multilayer cladding material have been captured. The failure load and ultimate hoop strength at 1050°C have been found to be higher than those of room temperature indicating an improved load bearing capability at higher temperatures under C-ring compression configuration. In addition, the results also revealed crack toughening mechanisms within themultilayer SiC cladding, where the SiC_f/SiC composite functioned effectively enabling non-brittle fracture behaviour at room and elevated temperatures.

Acknowledgments

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T1.5 Nanostructured, and Hybrid Functional Materials for Energy and Sustainability

3D OS FeRAM constructed by stacking Vertical OSFET and ferroelectric trench capacitor

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Keywords: low-power device, ferroelectric device, oxide semiconductor

Data centers demand more power with the development of Information and Communications Technology (ICT), which presumably causes an explosive increase in power consumption [1]. The increased power consumption might accelerate global warming. Considering the above situation, measures need to be taken in hardware. Widely-used DRAMs and flash memories have problems in power consumption and cycle characteristics. In view of this, non-volatile memories (NVMs) are promising as a low-power device. Among NVMs, HfO_2-based FeRAM has been attracting attention.

The HfO_2-based FeRAM has features such as high endurance (> 1E+11 cycles), long data retention time, and non-volatility [2]. Meanwhile, FeRAM has a problem of high driving voltage. To obtain ferroelectricity, a HfO_2 film needs to be thick in many cases, leading to high driving voltage. An oxide semiconductor (OS) FET is a minute device with high breakdown voltage and can be formed over a Si FET [2]. Thus, in fabrication of a memory, a peripheral circuit can be placed under memory cells, so that the area efficiency of a non-volatile memory is increased. In addition, like conventional DRAM, FeRAM requires a high-density capacitor array, and thus a ferroelectric trench capacitor [3] has been also considered.

In fabrication of a memory cell, we combined a trench capacitor with a vertical channel FET (VFET) including an OS; the VFET is suitable for reducing the cell size [4]. Since the VFET has a vertical channel, a lower electrode of the VFET can be used also as an electrode of the trench capacitor, which facilitates connection.

For the purpose of reducing the total device area, we formed a ferroelectric trench capacitor under a vertical OSFET utilizing the above features (Figs. 1(A) and 1(B)). Both FET characteristics (Fig. 1(C)) and ferroelectric characteristics (Fig. 1(D)) are favorable, from which operation of the 3D OS FeRAM has been demonstrated.

Figures

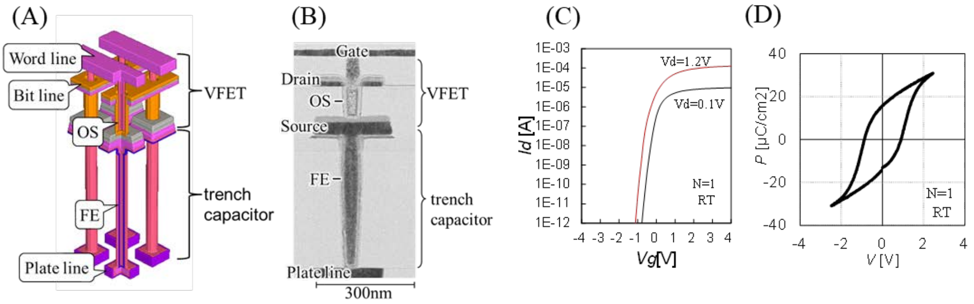

Fig. 1 3D VFET/trench capacitor structure

Schematic view of 3D VFET/trench capacitor structure. (B) Cross-sectional STEM image of VFET/trench capacitor structure. (C) VFET's *Id−Vg* curve. (D) ferroelectric trench capacitor's *P−V* curve.

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Insight into energy conversion properties of MOCVD-deposited eu-doped barium fluoride thin films: A comprehensive analysis

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Keywords: MOCVD, energy conversion, photovoltaic

In recent years, a significant push towards the development of novel functional materials has been observed, driven by the quest to enhance the efficiency of photovoltaic (PV) devices while maximizing the utilization of solar radiation. One advanced approach to enhance the efficiency of PV systems involves the conversion of photons with energies that lie beyond the absorption capabilities of the photoactive material, typically silicon, into a more suitable optical region. Within this landscape, lanthanide (Ln)-doped fluoride materials have emerged as highly promising contenders for energy conversion (EC) applications, owing to their unique luminescent properties upon exposure to light irradiation. Previous research indicates that fluorides serve as more efficient inorganic hosts for EC processes compared to other inorganic matrices. BaF_2 stands out as a promising host for incorporating luminescent Ln^{3+} ions, thanks to its low phonon energy (similar to or even lower than commonly used hosts like $NaYF_4$), high chemical stability, wide transparency, and versatile synthesis methods. Trivalent lanthanide ions can be easily integrated into the BaF_2 crystal structure due to their comparable coordination sphere, but a charge compensation mechanism is essential to offset the additional charge.

This study delves into the fabrication of Eu-doped BaF_2 thin films using the metalorganic chemical vapor deposition technique (MOCVD), focusing on the production process and down-shifting (DS) luminescent properties (see the scheme of figure 1). The production of BaF_2 thin films doped with Eu^{3+} employs a multicomponent mixture of metalorganic adducts in an appropriate molar ratio to finely tune the chemical compositions of the films.

Structural, morphological, and compositional characterization of the films was conducted using X-ray diffraction (XRD), field-emission scanning electron microscopy (FE-SEM), and energy-dispersive X-ray analysis (EDX). Finally, luminescence spectroscopy was employed to assess the functional properties of the films.

These MOCVD-grown luminescent thin films hold great promise as downshifting layers in photovoltaic cells, allowing harnessing of the UV component of the solar spectrum.

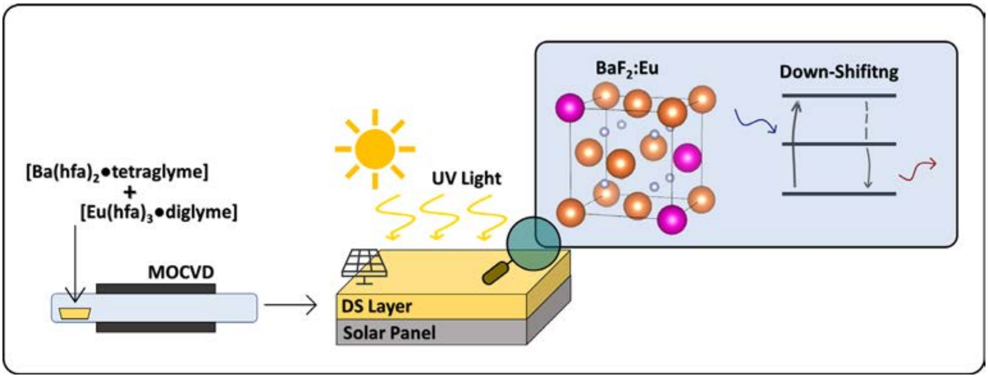

Figure 1. MOCVD approach adopted to produce Eu-doped barium fluoride thin films.

Acknowledgments

This work has been partially funded by the European Union, through the MUR-PNRR project SAMOTHRACE (ECS00000022).

Synthesis of the lead-free piezoceramic potassium sodium niobate (KNN) via an aqueous route

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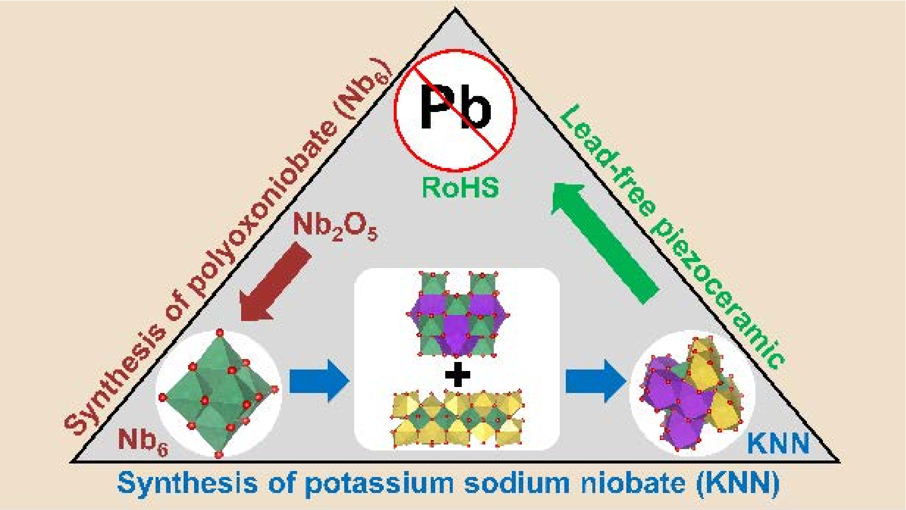
Keywords: lead-free, piezoceramic, KNN, hexaniobate

The use of PZT has continued despite the restriction of hazardous substances (RoHS) directives being passed by the European union (EU) to limit the use of hazardous materials – such as lead (PZT) – in electronic equipment. This is influenced by a lack of available substitutes that can be implemented and scaled in a reasonable time to eliminate the use of PZT (RoHS Annex III). The lead-free alkali-niobate, potassium sodium niobate ($K_xNa_{1-x}NbO_3$, KNN), is a potential replacement for PZT, since it can exhibit equivalent, if not better, piezoelectric properties without compromise at temperatures >120 °C. The challenges in the synthesis of KNN, however, have hindered its use as an alternative. A notable challenge includes difficulty in achieving the 50% K^+ and Na^+ occupancy required to make stochiometric KNN (i.e., $K_{0.5}Na_{0.5}NbO_3$) and a lack of control in the formation of phase boundaries. Therefore, developing a reproducible method for synthesising stoichiometric KNN, bodes well for the implementing KNN as a commercial piezoceramic. Most syntheses of KNN continue to be based on procedures which encompass either solid-state, hydrothermal, spray pyrolysis or sol-gel techniques. The solid-state syntheses may include reacting Na_2CO_3, K_2CO_3 and Nb_2O_5 in a molten salt reaction to yield a precursor oxide that can be sintered to obtain KNN. Notably, the use of a molten salt is to overcome the inertness of Nb_2O_5. The hydrothermal route circumvents the use of molten salt via the use of alkali hydroxides and Nb_2O_5, to similarly yield precursors to KNN. However, the solid-state and hydrothermal routes still require prolonged heating to yield KNN. Likewise, a molten salt reaction is challenging to control. Herein a simple and robust method for synthesis of the lead-free piezoceramic material KNN has been developed via an aqueous route. Stochiometric KNN ($K_{0.5}Na_{0.5}NbO_3$) was prepared by combining alkali-nitrate solutions ($NaNO_3$ and KNO_3) with the nano-sized, water-soluble, niobium precursor hexaniobate ($[H_xNb_6O_{19}]^{8-x}$, Nb_6), followed by sintering at elevated temperatures for at least one hour. Limitations associated with stochiometric control and selectivity, that are inherent to conventional methods of solid-state, sol-gel and hydrothermal based KNN synthesis, can be obviated with the use of this water-soluble niobium precursor.

Graphical abstract



Schematic representation of the synthesis KNN from the water-soluble hexaniobate species (Nb$_6$)

Acknowledgments

The Knut & Alice Wallenberg Foundation and Magnus Bergvalls Stiftelse (PANLA:2023-453) are acknowledged for financial support. Companhia Brasileira de Metalurgia e Mineração (CBMM) is acknowledged for a generous gift of niobic acid.

T1.6 ADVANCED BATTERIES AND SUPERCAPACITORS FOR ENERGY STORAGE APPLICATIONS

Comparative study on the electrochemical and physical properties of water-based electrodes via manufacturing process: Screenprinting *vs.* conventional coating

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Keywords: Li-ion battery, biobased polymers, electrode process

Energy storage has been vividly studied over the past few years as one of the solutions to climate change. This domain covers a vast variety of systems, from mechanical storage devices that involve complex systems with numerous tools, to lighter electrical energy storage systems such as batteries. The lithium-ion battery remains essential in electrical energy storage and is globally used for various applications, including laptop computers and, most prominently, portable devices. Many components of batteries are currently under investigation to achieve better performance for an efficient and cost-effective processing method. Electrodes (more specifically composite electrodes) are one of the key components in batteries. They are the primary components responsible for the electrochemical reactions that occur during the charging and discharging cycles. Many strategies to enhance the electrochemical performance of batteries seek to discover new redox active materials. Electrodes manufacturing processes are another strategy to improve practical properties such as energy density, recharge time, lifetime and safety. These properties are correlated to the electrode mesostructured, which depends on the fabrication parameters.[1]

The conventional processing method for electrodes involves a coating technique using a doctor blade or slot-die instrument for the slurry, a mixture of materials containing the active material, polymeric binder, and some carbon additives, with a solvent. New methods of manufacturing such electrodes are now being explored to efficiently process them. One of these processes is the printing process. The growing interest in printing methods lies in the use of architectural freedom, in addition to achieving higher filling degrees with a reduced amount of solvent. Moreover, this field facilitates the sustainability of this technique, being well-suited for both prototype construction and scaling process.[2]

The focus of this study is to highlight the impact of manufacturing battery composite electrodes on their actual physical and electrochemical properties. Here, we will emphasize the differences between ink formulations in both techniques according to the ink's rheological characteristics. After processing the composite electrodes, comparative study will focus on electrode morphology and topology and the impact of such microstructure on the electrochemical properties. This research focuses on the actual porosity obtained with these manufacture processes and the intrinsic dispersion of the active material ($LiFePO_4$) in the composite electrode system (carboxymethyl cellulose (CMC) and carbon black).[3] This work is a preliminary approach towards understanding the impact of the manufacturing process on the final properties of our system.

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Enhancing supercapacitor performance: A novel approach to high-purity activated carbon using a solvothermal process with urea

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Keywords: supercapacitor, activated carbon, high-purity, oxygen content

This study addresses the challenge of oxygen group-induced conductivity reduction in activated carbon, a material known for its extensive surface area and chemical stability, and commonly used as an electrode in supercapacitors. These oxygen groups, introduced during manufacturing, not only reduce conductivity but also lead to gas generation and oxidation of the electrolyte solution. To overcome these issues, we developed a novel solvothermal process using urea to reform activated carbon, aiming to achieve high purity with minimal functional groups. X-ray Photoelectron Spectroscopy (XPS) analysis revealed a significant decrease in oxygen content to 0.15 atomic percent in the modified carbon, with little to no change in the specific surface area compared to the raw material. Electrochemical assessments, including coin cell tests, showed a consistent specific capacitance of 15.6F/cc. In a 1300F-class cylindrical cell format, the modified carbon exhibited a low Direct Current-Equivalent Series Resistance (DC-ESR) of under 0.7 milliohms, maintaining stable performance across a wide temperature range (-40 to 75 °C). Notably, a 500-hour high-temperature durability test at 65 °C demonstrated marked improvements in capacity and resistance characteristics. This research indicates that high-purity activated carbon, produced through our method, has the potential to significantly expand the applications of supercapacitors by enhancing performance and reliability.

Acknowledgments

This work was supported by the Technology Innovation Program (RS-2022-00156080, Development of electrical double layer capacitors for power supplement of hydrogen forklift) funded by Ministry of Trade, Industry and Energy.

Hybrid polymer-ceramic electrolytes: opportunities and challenges

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Keywords: type your, keywords here, separated, by commas

Hybrid solid composite electrolytes, comprised of polymeric and ceramic fractions, have been proposed as a means of circumventing common pitfalls that are associated with either polymer (lower ionic conductivity, low mechanical strength) or ceramic (large interfacial resistance with electrodes, brittle) electrolytes. Despite this premiss, previous studies have revealed uncertainty as to whether both phases participate in ion conduction and whether interactions between phases cause electrolyte degradation via surface reactions, interfacial resistance, or corrosion. In this presentation, we will address important parameters to consider when investigating hybrid composite electrolytes. Using different examples, we will demonstrate how to get a better understanding of the polymer-ceramic interaction and its impact on the ionic conductivity of these complex systems.

Iron and sulfate based positive electrode materials for Na-ion batteries

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Keywords: batteries, electrode materials, abundant elements, na-ion batteries, inorganic synthesis

Concept of Na-ion batteries is among the most emerging battery technologies to deal with the issue of critical and scarce elements used in Li-ion batteries. Portable applications demand high energy density, favoring use of V- and Mn-based Na-ion positive electrode materials. In contrast, for stationary applications where battery weight is less important, the price of the components plays main role. In 2023 Mn has been classified as a critical raw material by EU committee, which promotes search and development of new materials based on abundant Fe. Stable polyanionic frameworks ensure longer cycling life as well as greater safety in comparison to layered oxides. Among different polyanionic electrode materials, phosphates are extensively explored, leaving room for search of new pure sulfate and mixed phosphate-sulfate based phases.

From this point of view, we revisited already presented $NaFe_2PO_4(SO_4)_2$ (NFPS), which crystallizes in NaSICON structural type [1-4]. High-purity samples of NFPS were synthesized and studied by means of X-ray, neutron and electron diffractions, scanning electron microscopy and electrochemical methods. Thorough investigation allowed us to propose a new structure description and to discuss the relationship between synthesis conditions, stoichiometry and electrochemical performance. Theoretical capacity was obtained at C/30 cycling rate due to optimization of morphology and electrode formulation. Step-by-step up-scaling allowed to synthesize 8 g of NFPS per batch.

As NFPS contains Fe in the oxidation state 3+, it is worth trying to obtain by direct synthesis the sodiated compound. New series of phases of the same element composition with Fe^{2+}, adopting different structural type than NFPS, were synthesized via newly established easy up-scalable solid-state procedure. Exploration of other synthesis methods, also enabling to obtain this series of materials, would be discussed. Challenges of different synthesis strategies linked to control of stoichiometry and promising electrochemical performance will be presented.

A new phase based on only abundant elements, such as Na, Fe and S, obtained via simple ball-milling procedure, could be suggested as a cheap and efficient positive electrode material for stationary storage. Advantages of this synthesis method are necessity to use only two easily-available precursors, while neither solvent, nor heating is not required. One of the main advantages of this material is excellent stability of cycling. Structure and electrochemical experiments would also be presented.

Acknowledgments

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Exploring aluminum (Al^{3+}) ion insertion in vanadium bronze ($NH_4V_4O_{10}$) for aqueous rechargeable aluminum-ion batteries

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Keywords: aqueous, multivalent-ion, solvation, interlayer expansion, electrolyte additives

Aqueous rechargeable batteries have garnered significant attention for their safety, cost-effectiveness, and the simplicity of utilizing water as a solvent. Multivalent-ion batteries featuring Zn^{2+}, Ca^{2+}, and Al^{3+} ions present a compelling alternative to conventional monovalent-ion systems (Li^+ and Na^+), offering higher energy density due to their higher valency and abundant mineral reserves in the earth's crust. Despite their potential, the high charge-to-size ratio of multivalent ions poses challenges, such as susceptibility to larger hydration shells hindering rapid diffusion into the active charge storage material. This presentation delves into a systematic exploration of the insertion/de-insertion dynamics of Al^{3+} ions within ammonium-ion (NH^{4+}) pillared vanadium oxide, utilizing aqueous aluminum chloride ($AlCl_3$) electrolyte in a three-electrode setup. The NH^{4+} ion serves a dual purpose by expanding interlayer spacing to accommodate hydrated ions and stabilizing the oxide framework. The $NH_4V_4O_{10}$ cathode exhibited an initial discharge capacity of ~300 mAh/g, with a gradual capacity fade during cycling. Post-cycling XRD analysis revealed an expanded interlayer spacing, indicating the successful intercalation of hydrated Al^{3+} ions by displacing NH^{4+} ions within the interlayer.

Modified aqueous electrolytes with targeted additives were employed to address capacity fade and enhance coulombic efficiency. Incorporating ammonium salts, along with aqueous $AlCl_3$ and organic solvents, significantly improved the reversible shuttling of Al^{3+} ions within the cathode. The presentation will comprehensively discuss the electrochemical performance and mechanism of Al^{3+} ion incorporation into $NH_4V_4O_{10}$, drawing insights from experimental observations.

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Ruddlesden-Popper structured $Li_2La_2Ti_3O_{10}$ for lithium ion battery anode

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Keywords: lithium ion battery anode, Ruddlesden Popper structurre, perovskite

In the current landscape of energy storage technology, research into innovative anode materials for enhancing the energy density and lifespan of lithium-ion batteries (LIBs) is gaining increasing momentum. In this study, Ruddlesden-Popper structured $Li_2La_2Ti_3O_{10}$ (RPLLTO) is presented as a new anode material for LIBs. The material was synthesized through an ion exchange reaction method, and as a result of powder XRD Rietveld refinement, it was confirmed to have a layered perovskite structure including a Li ion path layer. As a result of electrochemical property evaluation, it showed a unique charge/discharge reform with a capacity of 170 $mAh \cdot g^{-1}$ and two plateau voltages. XANES was analyzed to identify the Li ion storage reaction corresponding to the two plateau voltages, and the reduction reactions of Ti^{4+}/Ti^{3+} and Ti^{3+}/Ti^{2+} were confirmed, respectively. Analysis of crystal structure changes during lithiation using In-situ XRD and EXAFS revealed that RPLLTO undergoes complementary expansions along the a/b axes and contractions along the c axis, leading to about a 1.8% volume change. This structural stability is evidenced by an 88% capacity retention after 1000 cycles. This study is a report on the Li ion storage ability of RPLLTO and contributes to the development and scalability of perovskite anode materials of various compositions and structures.

Acknowledgments

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Synergetic impact of dual substitution on anionic–cationic activity of P2-type sodium manganese oxide

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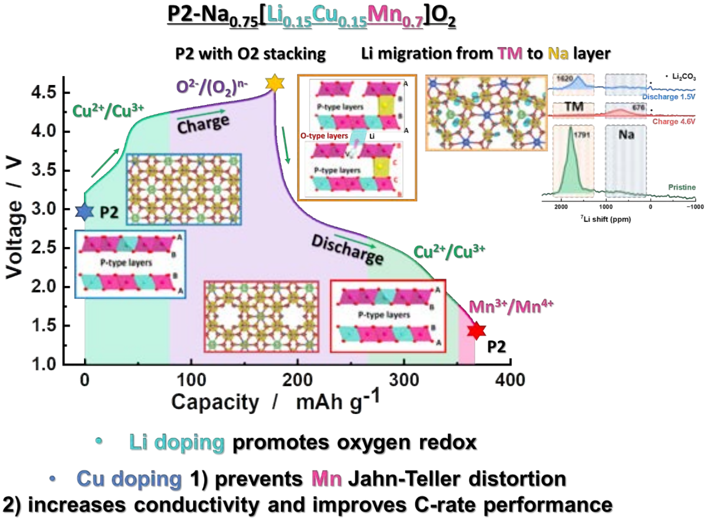
Keywords: oxygen, redox, sodium, cathode, battery

P2-type sodium-deficient cathodes with the local Na–O–A configuration (A=Li, Mg, Zn, and vacancy) have attracted great interest due to their high capacity, stemming from the additional contribution of the oxygen-redox chemistry. However, such materials suffer from irreversible oxygen redox, oxygen release, structural distortion, and capacity fading. Herein, we introduce a dual-doping Li/Cu strategy to improve the properties of P2-Na_xMnO_2 cathode material. The unique sodium-storage mechanism in P2-$Na_{0.75}[Li_{0.15}Cu_{0.15}Mn_{0.7}]O_2$ is verified using *operando*-XRD (*o*-XRD), X-ray absorption, X-ray photoelectron spectroscopy, and magnetic susceptibility methods. *o*-XRD and ^{7}Li NMR analysis reveal that mainly the P2 phase is maintained within charge and discharge; however, at high voltage, a small portion of O-type stacking faults are present due to the migration of Li to octahedral Na sites. Furthermore, various spectroscopy and magnetometry techniques combined with density functional theory calculation demonstrate the stable activity of cationic Cu^{2+}/Cu^{3+} and Mn^{3+}/Mn^{4+} and anionic $O^{2-}/(O_2)^{n-}$ redox processes. This work highlights the efficacy of Li and Cu doping in P2-type layered materials and the contribution of oxygen redox to additional capacity at high voltages, suggesting the potential for future development of cathode materials for Na-ion batteries with oxygen redox.



- Li doping promotes oxygen redox
- Cu doping 1) prevents Mn Jahn-Teller distortion
2) increases conductivity and improves C-rate performance

Figure 1. Schematic illustration of influence of Li/Cu doping in P2-$Na_{0.75}[Li_{0.15}Cu_{0.15}Mn_{0.7}]O_2$ material.

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Tailoring mesoporous and macroporous structures in activated carbon from NaOH-pretreated oak for superior supercapacitors

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Keywords: lignocellulose, NaOH pretreatment, physical property, carbonization, chemical activation, pore structure

The growing need for sustainable and efficient energy storage solutions has intensified research efforts into eco-friendly materials such as activated carbon (AC) derived from lignocellulosic biomass. Herein, we present a method to enhance the physical characteristics of AC from oak via NaOH pretreatment. The NaOH-pretreated oak was converted into AC through carbonization and chemical activation using KOH as the activating agent. The AC tended to develop mesopores (2–50 nm) and macropores (> 50 nm) as the pretreatment ratio increased (0%, 1%, 2%, and 8%), achieving a specific surface area of up to 2706 $m^2\ g^{-1}$ and a pore volume of up to 1.97 $cm^3\ g^{-1}$. This result is due to the transformation of the structure of lignocellulosic biomass into a more advantageous structure for pore development through the reactions of delignification and deacetylation that occur during NaOH pretreatment. The mesoporous and macroporous structures offer efficient ion diffusion pathways and reduce resistance, which leads to superior rate capability, capacity retention, and a gravimetric specific capacitance of 44.5 $F\ g^{-1}$ at a current density of 1 $mA\ cm^{-2}$ in supercapacitors. These results underscore the potential of NaOH-pretreated oak as a sustainable and effective precursor for high-performance AC in energy storage applications, offering new insights into the optimization of material properties for supercapacitors.

Acknowledgments

We acknowledge the support of the Technology Innovation Program (20012763, Development of petroleum residue-based porous adsorbent for industrial wastewater treatment) funded by the Ministry of Trade, Industry & Energy (MOTIE, Korea).

Composition optimisation for dry-processed solid-state $LiFePO_4$ electrodes

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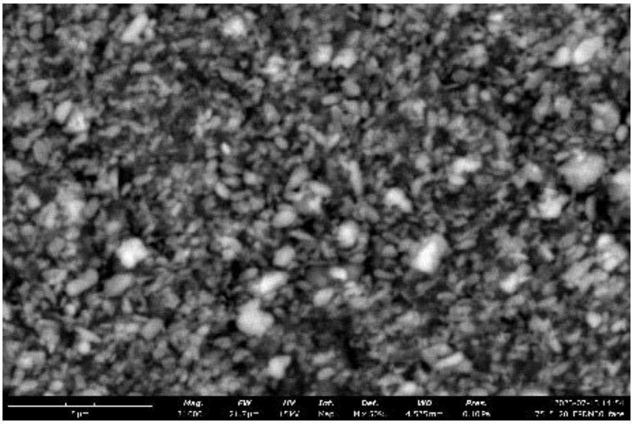
Keywords: solid-state batteries, formulation, electrochemistry, polymer extrusion

Lithium batteries are one of the pillars of the green energy transition as their large scope of applications makes them an attractive alternative to fossil fuels, particularly in the transportation sector. While the operation of a lithium battery may not be considered harmful to the environment, the large-scale production of batteries involves the use of toxic organic solvents and an energy consuming drying process. Polymer extrusion represents an effective alternative that allows for the homogenous mixing of active battery materials, conducting carbon additives and polymer electrolytes. The extrusion of polymers with a twin-screw extruder, also called melt-processing, eliminates the need for organic solvents as the melted polymers act as the solvent, allowing a homogenous dispersion of active material[1,2]. The process eliminates the need for solvents and therefore the subsequent drying step, decreasing overall energy consumption. Despite these advantages, there are challenges and limitations associated with melt-processing. The maximum amount of active material that can be incorporated into a formulation tends to be lower than what is possible with solution casting. It is therefore essential to tune the proportion of active material, conductive carbon and polymer binder to obtain the best possible combination of electronic conductivity, ionic conductivity and capacity while being processable through extrusion[3].

This work focuses on optimizing the composition of dry-processed electrodes to obtain the best performances in solid-state batteries. Every electrode composition must be balanced between powder content and polymer matrix as mixing the active materials and carbon additives with the molten polymer requires high torque. This represents the biggest limitation of melt-processing. Coupling scanning electron microscopy to investigate electrode microstructure (see Figure) and galvanostatic cycling to investigate battery performances, the main objective is to increase active material content. This is required to obtain high mass loading, while maintaining a sufficient electronic conductivity without affecting the diffusion of lithium ions through the composite electrodes.

Figure



Cross-section SEM image of a melt-processed $LiFePO_4$ electrode

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New halide-based Na-ion conductors: $NaNbCl_6$, $NaTaCl_6$, and some more

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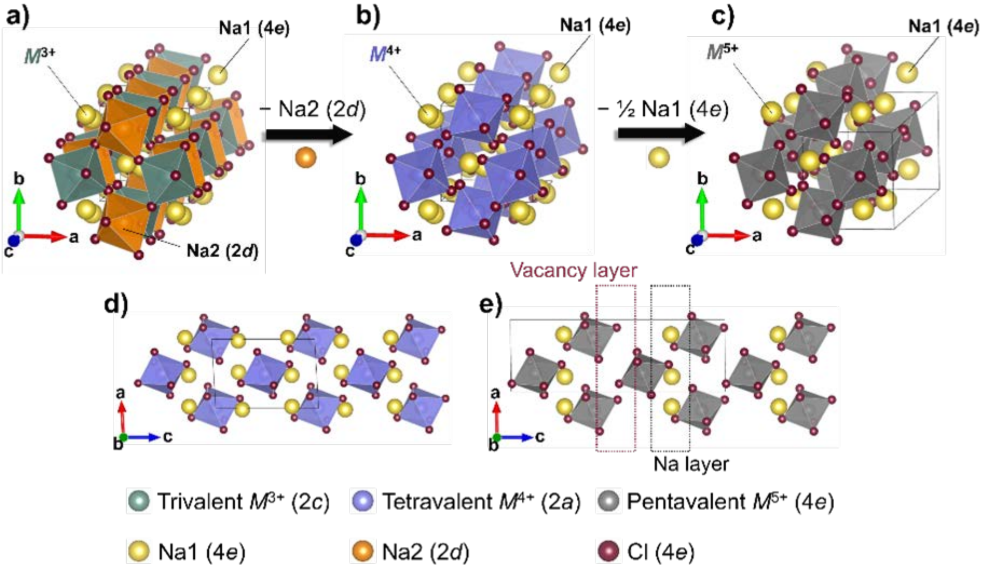
Keywords: solid electrolytes, solid state batteries, Na-ion batteries

All-solid-state sodium-ion (Na-ion) batteries are promising candidates for the post-lithium-ion (Li-ion) batteries owing to their improved safety and earth abundance, enabled by less- to non-flammable solid electrolytes (SEs). Ion-conducting halides are an emerging class of materials for solid electrolytes that may satisfy all requirements with their balanced ionic conductivity (> 1 mS cm^{-1} at room temperature), oxidation stability (~ 4 V), and room temperature processability. Ion-conducting halides first stepped into the spotlight in 2018 with the report of mechanochemically synthesized Li_3YX_6 (X = Cl, Br). Up to date, a wide variety of Li-ion conducting halides have been reported, e.g., $Li_3M^{3+}X_6$ (M^{3+} = In, Sc, Ti, Y, Ho, Er, Yb and X = Cl, Br, I), $Li_2M^{4+}X_6$ (M^{4+} = Zr, Hf and X = Cl, Br, I), $LiM^{5+}Cl_4O$ (M^{5+} = Nb, Ta) and $LaCl_3$-based Li-ion conductor. Many exhibits room-temperature ionic conductivity higher than 1 mS cm^{-1} and demonstrated stable cycling with the state-of-the-art cathode active materials operating > 4 V.

Despite the success in Li-ion conducting halides, only a few Na-ion conducting halides have been found to date, e.g., $Na_3M^{3+}Cl_6$ (M^{3+} = Y, Er, In), Na_2ZrCl_6 and $NaAlCl_4$, and their reported room-temperature ionic conductivity are mostly less than 0.1 mS cm^{-1}. With the less polarizing nature of Na ions, Na-ion conducting SEs tend to possess higher ionic conductivity than their Li-analogues, and indeed, higher ionic conductivity is generally reported in Na-ion conducting oxides and sulfides than those in Li-ion conducting counterparts. Inspired by the fact that the known Na-ion conducting halide-based SEs exhibit much inferior ionic conductivity to the Li-analogues, here we explore the new Na-ion conducting halides, $NaM^{5+}Cl_6$ (M^{5+} = Nb, Ta), achieving 0.1 mS cm^{-1} at 30 °C. This high ionic conductivity is attributed to the beneficial inductive effect and improved migration entropy and is one of the highest among the crystalline monoanionic Na-ion conducting halides.

Figures



Here the structural framework consists of MCl_{6x}^{-} is extended from tri- and tetravalent ions to the pentavalent ions, forming alternating Na-layers as with additional structural freedom on the metal sites.

Acknowledgments

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Looking for new electrode material for K-ion batteries: the case of K_3MnO_4

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Keywords: K-ion batteries, manganese oxides, K_3MnO_4

Potassium batteries, with improved lifespan and capacity, will become advantageous compared to lithium due two major advantages: the low cost of potassium, the 7th most widespread element in the earth's crust, and it's low redox potential, similar to that of lithium[1–3]. To successfully develop commercially relevant potassium-ion batteries (KIBs), it is necessary to find new cathode materials with a reasonable potassium diffusion to improve the capacity[4]. For these reasons we decide to explore the inexpensive and non-toxic K-Mn-O system.

Hereby, we report for the first time the electrochemical behaviour of K_3MnO_4 phase[5]. This material, first reported by Hagenmuller[6], could be described as an non-dimensional structure built of isolated $[MnO4]^{2-}$ tetrahedra surrounded by complex potassium ion polyhedra. Till now, only two polymorph's type were reported. The first one, obtained at high temperature (1100°C), called γ-K_3MnO_4 with disordered $[MnO_4]^{2-}$ arrangement and the second one, β-K_3MnO_4 with ordered $[MnO_4]^{2-}$ synthetized at low temperature (300°C). We use commercial precursors KO_2 and MnO with a ratio 3.1:1 placed in a vacuum furnace at 450°C for 12h. Thus, pure $K_3Mn^{+V}O_4$ is obtained with a characteristic duck-blue colour common for the Mn^{+V}. The structure was refined using it's iron analogue: K_3FeO_4 due to the zigzag $[MnO4]^{2-}$ arrangement. This tetrahedral configuration was never reported, so we proposed to label it α-K_3MnO_4. The phase crystalizes in the orthorhombic space group *Pnma* with the following cell parameters: $a = 7.75(4)$, $b = 8.96(1)$, $c = 7.91(8)$ Å and volume of $V = 550.99$ Å^3. The charge-discharge profiles of α-K_3MnO_4 were measured by incremental galvanostatic cycling at C/20 (corresponding to the (de)insertion 1 K^+ per unit formula in 20 h) in the potential window 1.6–3.5 V versus K^+/K. Two phenomena can be clearly distinguishing. On the potential window 3.1 – 1.6 V, a reversible phenomena is observed with the exchange 0.6K^+ i.e. a capacity of 70 mAh/g at 2.37 V vs. K^+/K with a Coulombic effiency of 97.3%. Once the charge is extended above 3.1V, the process is no longer reversible. The potentiostatic intermittent titration (PITT) curve shown in Fig. 2b. reveals a dominant bell shape-type response at 2.7 V, which characterizes a biphasic process, a second similar but shorter process located at 2.9 V and then a third one at 3.47 V vs. K^+/K.

In our presentation, we will discuss the structure/properties relationships of this family of materials.

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LFP 3D printed mesh electrodes for lithium-ion batteries

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Keywords: mesh electrodes, FFF printing of ceramics, LiB LFP electrodes, performance enhancement

Lithium-ion batteries (LiBs), as a key energy storage technology in industrial applications such as electric vehicles (EVs) and portable electronics, must face several challenges to consolidate their position. Apart from the effort on the searching for novel compositions, alternative manufacturing routes may significantly maximise volumetric and gravimetric energy density. Conventional LiBs electrodes consist of a mixture of active material, conductive agents, and polymeric binders (e.g. PVDF). This approach results in reliable batteries with basic geometries. However, the use of non-electrochemically active additives (up to 50 vol%) causes a dramatic decrease in the volumetric energy density.

Recently, several alternative strategies have emerged to overcome such limitations. Among them, additive manufacturing (AM) technologies are at the forefront to reach the benefits related to the freeform fabrication. Indeed, a wide variety of geometries has already been explored via direct ink writing (DIW) or stereolithography (SLA). These techniques perform high resolution electrodes, but they showed several drawbacks related with the handling and preservation of the inks and resins used.

Fused Filament Fabrication (FFF) uses solid thermoplastic-based filaments that do not demand special preservation requirements in the long-term. This combined with the ease of use and the low cost of equipment, justify the research efforts towards the development of LiBs using this technology. To date, the number of applications via FFF is rather limited, with filaments containing high loadings of inactive polymeric binders (e.g. PLA) that cannot be removed from the printed parts. We have recently produced $LiCoO_2$, $Li_4Ti_5O_{12}$ and $LiFePO_4$ full ceramic printed electrodes based on a specifically designed and optimised composite polymer-ceramic filaments [1]. These electrodes showed an electrochemical performance fairly close to the state-of-the-art electrodes [2,3].

Currently, we are exploring non-conventional geometries to maximise energy density via higher surface to volume ratio printed structures [3]. Furthermore, several thick mesh geometries (up to 300 μm) have been produced to explore the impact upon performance in thick electrodes, which exhibited longer cycle life and higher capacities, especially at high current densities, compared to solid thick counterparts.

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Investigations on the Ca-ion intercalation characteristics in molybdenum trioxide electrode of an aqueous Ca-ion rechargeable battery

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Keywords: aqueous batteries, calcium-ion, intercalation, MoO_3, electrolyte, ion-solvation

Rechargeable batteries are being increasingly explored for deployment in large and mass scale applications such as the electric mobility and grid integration. State-of-the-art advanced lithium-ion batteries (LiBs) offer good energy and power density however, these are unlikely to meet the performance consistency, cost and safety expected in electric transportation and grid power management. Additionally, ever-increasing emphasis on sustainability have led to shift in focus towards the development of alternative battery systems, so-called the "beyond Li-ion" technologies. Utilization of earth-abundant and low-cost materials (based on Na, Zn, Ca, Al*)* coupled with aqueous electrolytes in an electrochemical cell is a novel and effective strategy, which has great potential to replace the more than half a century old LiBs based on non-aqueous liquid electrolytes. Despite the advantages, the aqueous rechargeable batteries too come with several fundamental challenges which impedes it's widespread commercialization.

Our research group has explored organic and inorganic electrode materials in monovalent (mixed Na^+-ion and Li^+-ion) and multivalent (Zn^{2+}-ion) aqueous batteries. The electrode function has been extensively investigated using the combination of diverse experimental techniques and first principles density functional calculations.[1, 2] In this presentation, we focus on the performance and intercalation mechanism of Ca^{2+}-ions into a model layered compound, such as molybdenum trioxide and simualtaneously discuss the fundamental challenges associated with aqueous Ca^{2+}-ion chemistry. Detailed mechanistic studies of the Ca^{2+}-ion intercalation coupled with electrolyte solvation studies and DFT calculations will be discused**.**

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Enhancing lithium-ion battery cycling performance and recycling efficiency through laser texturing of metallic current collectors

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Keywords: laser texturing, current collector, cathodes, NMC, recycling, Li-ion battery

Lithium-ion batteries (LIBs) have emerged as the primary energy storage solution for numerous portable electronic devices, electric vehicles, and renewable energy systems. The potential benefits of recycling spent lithium-ion batteries are immense, promising economic and environmental advantages while recovering critical raw materials. Various processes have been explored for battery recycling, yet a crucial challenge remains the separation of the metallic current collector from the electrode composite film [1]. In this framework, the present study focuses on laser texturing of aluminum current collectors (CCs) to introduce a microscale surface architecture. The asymmetric surface pattern facilitated a controlled and directional adhesion, enhancing attachment to manage the significant volume variation of the active material (NMC811) during charging and discharging cycles [2]. Additionally, it enabled an easy separation of the electrode composite layer from the current collector, during recycling, by applying a force in a specific direction. As a result, the laser-treated cathodes displayed low electrode polarization and increased cycling performances, with a capacity retention of 67.6 % after 300 cycles at 1C, thanks to the increased interfacial adhesion that reduced the active material delamination from the current collector upon cycling.

Figures

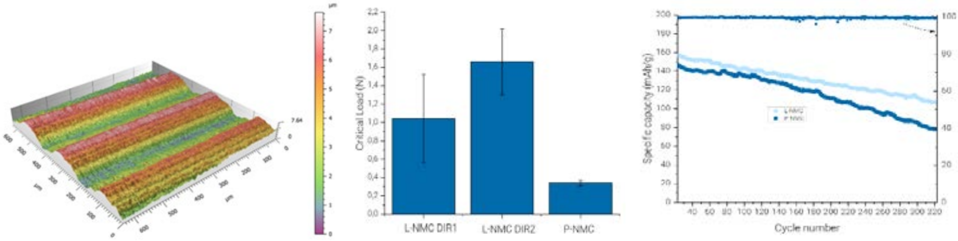

Figure 1. (a) Optical profilometry image of the laser textured surface. (b) Critical load values measured by micro-scratch. (c) Galvanostatic cycling showing the different capacity retention between the pristine and the laser textured electrode.

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Reactive flash sintering of High entropy oxides $(Mg_{0.2}Ti_{0.2}Zn_{0.2}Cu_{0.2}Fe_{0.2})_3O_4$

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Keywords: hardness, reactive flash sintering, grain size, solid state reaction

High Entropy Oxides (HEOs) are a relatively new material class that has attracted significant attention in recent years. They are a type of ceramic material consisting of five or more metal cations with equal molar ratios. The idea behind HEOs is to create a material with a high degree of structural disorder, which can result in enhanced mechanical, electrical, and optical properties. There are several synthesis techniques for HEOs, such as solid-state, Sol-gel, Co-precipitation, and Mechanical alloying, among which the solid-state synthesis technique is most used. Reactive flash sintering could be the alternative synthesis technique for HEOs, which can lead to further property enhancement. Reactive Flash Sintering (RFS) is a novel sintering technique that has emerged in recent years, which combines electrical current and a reactive atmosphere to produce rapid and efficient sintering of ceramic powders. It has several potential advantages over traditional sintering methods, including reduced energy consumption, improved densification, and enhanced microstructural control. In our work, we will be synthesizing and densifying (reaction sintering) High entropy oxides, such as $(Mg_{0.2}Ti_{0.2}Zn_{0.2}Cu_{0.2}Fe_{0.2})_3O_4$, via flash sintering in one minute at a 950 °C furnace temperature. On the other hand, solid-state synthesis requires about 1000 °C temperature and about 24 hours. The resultant high entropy has superior mechanical properties in hardness compared to one synthesized via solid-state reaction.

T1.7 Materials for Solar Thermal Energy Conversion and Storage

Porous advanced ceramics utilized to produce “green hydrogen” via concentrated solar thermal power: the Hydrosol experience

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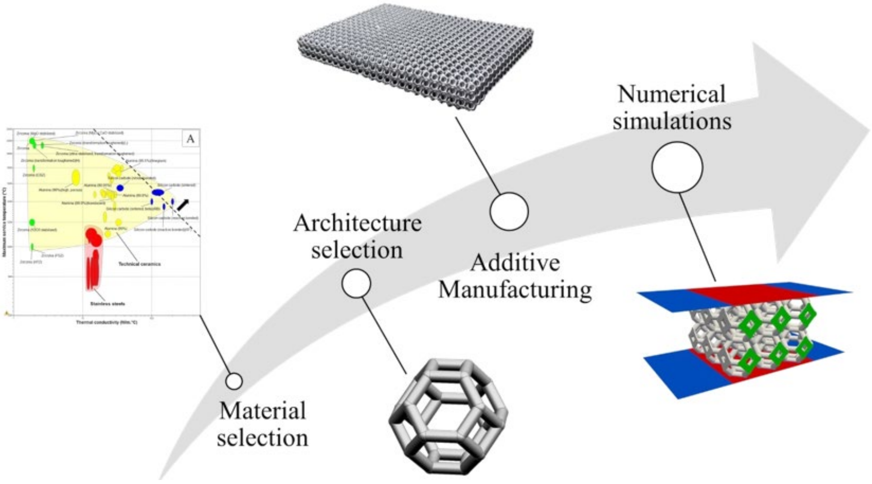
Keywords: SiC, toplogy optimization, additive manufacturing, concentrated solar energy

There are many ways to produce hydrogen gas, many of which are not emission free. Generating hydrogen gas from renewable energy sources results in so-called 'green hydrogen', and it is the focus of the EU-funded HYDROSOL-beyond project. HYDROSOL, an Horizon 2020 project, is here presented. It aims to optimise an hydrogen production plant that produces hydrogen via concentrated solar thermal power. This presentation delves into the use of porous advanced ceramics utilized to reach the final goal.

Figures



Schematic approach of the Hydrsol heat exchanger development

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Silica-based rocks and refractories for thermal energy storage – Characterization of phase composition, microstructure and thermal conductivity

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Keywords: silica (quartz, cristobalite, tridymite), thermal conductivity (thermal diffusivity), quartz sandstone, refractory materials, optical microscopy (polarizing microscope), laser flash technique, transient plane source technique

Silica-based materials can be useful for thermal energy storage (TES). Some of them, like quartz sand, are popular materials for intermediate-temperature TES at temperatures below 1000 °C, especially around 600 °C, while silica refractories, consisting mainly of cristobalite and tridymite, are promising candidates for high-temperature TES up to approximately 1600 °C. On the other hand, quartz sandstone has not been considered for TES applications so far, although also this material might be a viable low-cost alternative in specific cases. This work investigates and compares the phase composition, microstructure and thermal conductivity of quartz sandstone and silica refractories. Thin sections of both materials are studied with a polarizing microscope in transmitted light (with and without crossed Nichols). Results from stereology-based image analysis concerning the phase composition and porosity are compared with results of helium pycnometry, the Archimedes method and X-ray diffraction (XRD). Based on XRD results (phase composition), SEM micrographs and microstructural descriptors (porosity, grain size, pore size and shape), digital random microstructures are created via the GeoDict® software package, and the effective thermal conductivity of these computer-generated microstructures are calculated numerically via GeoDict® software and compared with analytical predictions and experimental data. For obtaining the latter, two different transient measurement techniques are applied, the laser flash technique (a non-contact technique) and the transient plane source technique (a contact technique), including the so-called modified transient plane-source technique. Using the bulk density experimentally determined (via the mass-to-volume ratio and the Archimedes method) and the specific heat from the literature (calculated on the basis of the phase composition experimentally determined via XRD), thermal conductivities are calculated from the thermal diffusivities experimentally measured via the laser flash technique. The temperature dependence of the thermal conductivity is compared up to 300 °C.

Acknowledgments

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T1.8 High Temperature Superconductors: Materials, Technologies and Systems

High temperature annealing effects on $La_{1.84}Sr_{0.16}CuO_4$ superconductor made by Spark Plasma Sintering

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Keywords: LSCO, superconductor, annealing effect, SPS, J_c

$La_{2-x}Sr_xCuO_4$ (LSCO) is a typical type II high-temperature cuprate superconductor. Since its discovery in 1986 [1], it has been studied in details. It includes CuO_2 planes forming single layers in which the superconducting charge carriers are located and is characterised by an orthorhombic to tetragonal stuctural phase transition in the superconductive temperature range. While the critical current density measured in optimally doped LSCO single crystals can reach about 7×10^5 A/cm^2 [2, 3], this parameter is significantly suppresed in polycrystalline samples due to limitations originating from grain broundaries, low ceramic density, etc. The aim of this work is to improve the critical current density of polycrystalline LSCO samples by means of a heat treatment combining high pressure and high temperature.

During several decades of development, the spark plasma sintering (SPS) process has demonstrated its high value for the synthesis of ceramics with very high density. SPS offers rapid and uniform densification, revolutionizing the fabrication of intricate structures. In this research, the SPS method has been used to synthesize high-density and high quality LSCO superconductive polycrystalline ceramic pellets. By tuning the processing parameters, we achieved densities up to 6.5 g/cm^2, corresponding to 92 % of the crystallographic density of LSCO. As a result, the percentage of porosity is significantly reduced in comparison with samples produced via standard solid state techniques. A further step consisted in applying post-SPS high-temperature annealing to modify the grain size of the LSCO ceramics and suerpconductive properties.

Previous studies related to cuprate superconductors post-annealing mostly focused on the lower temperature range from 300 to 500 °C. In the present research, we conducted annealing in oxygen with a higher temperature range up to 1300 °C. Due to this post-treatment, the grain size of SPS-treated samples was increased from the sub-micrometers range to over 100 μm and the critical current density has been improved by about two orders of magnitude and can be as high as 6×10^5 A/cm^2, which is in a range comparable to values reported for single crystals.

Acknowledgments
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T1.9 RECYCLING

Selective separation of ultrafine active material particles applying particle-fluid interactions for the recycling of high temperature water electrolyzer cells

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Keywords: particle separation, recycling, critical raw materials, sustainability

Green hydrogen, which is considered one of the keys to realizing carbon neutrality, can be obtained through water electrolysis technology. Consequently, Germany aims for 10 gigawatts of electrolysis capacity by 2030 to reach the high demand for green hydrogen. For the high performance of the system, critical raw materials such as rare earth elements and nickel composites are used as active materials in the High-Temperature ELectrolyzer (HTEL) cell. For a sustainable supply and application of these valuable materials, the development of recycling processes after the large utilization phase is necessary, especially the efficient mechanical separation on the fine particle scale. Different ceramic materials used in a HTEL cell have similar surface properties such as wettability. For this reason, the application of surfactants on the fine particle surface plays an important role in selective separation processes of fine particles based on heterocoagulation spearation.

In this study, the particles from before and after the use of HTEL cells are investigated. Since the characterization of representative particles and several separation experiments have been successfully studied in our previous investigations, the methodology is able to be further developed and applied. Physical properties of the particles from before and after the operation have been characterized. Different reagents have been applied to selectively render the particle surface hydrophobic. By the method of liquid-liquid micro-particle separation, which also addresses the wettability of the particles, has been applied to separate valuable materials from the particle mixture. Comparing the results, how the operation of the electrolysis cell affects the separation of the particle mixture could be explained and it will provide a guide for future separation process design in large-scale processes.

Acknowledgments
The authors would like to thank the German Federal Ministry for Education and Research (BMBF) for funding of the project ReNaRe – Recycling – Nachhaltige Ressourcennutzung (code: 03HY111D, FeinElSep) as part of the technology platform H2Giga. The authors thank Institut für Energie- und Klimaforschung (IEK), Forschungszentrum Jülich GmbH for supplying HTEL particle samples and Subrina Islam for her experimental work and data that she made.

Selective separation method for re-use of solid oxide electrolyser & fuel cell materials

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Keywords: solid oxide cell, critical materials, recycling, hydrometallurgy

In the hope of a low-carbon future, innovation is our best asset for reducing today's economic footprint. Growing interest in hydrogen as an alternative fuel for mobility and the decarbonisation of industries, leads to the development of ever more efficient and sustainable solutions for producing green hydrogen. Among known, high-temperature solid oxide electrolysers achieve hydrogen production yields from 60 % for the system-total efficiency, to 90 % for stack efficiency[1]. However, Solid Oxide Electrolysis Cell (SOEC) is made of critical or strategic resource and mining industries[2]. To contribute to overcome this dependence, the European project "NOUVEAU" aims to develop a more sustainable electrolysis cell with less critical elements. To achieve this objective, several academic and industrial partners, including the group of Nantes (IMN), have been brought together to find new materials and eco-responsible processes to recycle them.

The term "recycling" in solid oxide cells (SOCs) is still quite new in the research community, and publications on the subject propose separation and extraction strategies inspired by the Li-ion battery (LIB) and waste printed circuit board (WPCB) recycling industry[3,4]. The processes used are mainly based on the hydrometallurgical route, which involves dissolving the target elements in solid matrices using caustic or acid attacks. This step is typically followed by separation via precipitation, solvent extraction, distillation, ion exchange, cementation or filtration[5]. The latest works use the leaching process to dissolve materials contained in the electrodes in aqueous form (Ni, La, Sr, Co cations) and thus separate them from the electrolyte, which is fortunately stable in nitric acid and remains in a solid state[6].

Using this method, the process can be extended by varying the leaching conditions, using nitric acid as a leaching solvent at different concentrations, or mixing with an oxidising agent (Figure 1). After a case-by-case study, it was found that the $Ca_2(Fe,Co)_2O_{5+\delta}$ air electrode (CFCO), is completely dissolved at RT in slightly concentrated nitric acid (0.5M). This is not the case for Ni and NiO from the hydrogen electrode, which needs to be dissolved in concentrated nitric acid (14M) and at a higher temperature (60°C). The rest of the solids, $Ce_{0.9}Gd_{0.1}O_{1.95}$ (GDC) and $Zr_{0.84}Y_{0.16}O_{1.92}$ (YSZ), are separated using a mixture of 10M nitric acid and 1M hydrogen peroxide. This solution allows us to completely dissolve GDC, without altering YSZ, which remains in solid form. The use of the different solutions containing ions of various elements, and allowing the recovering of starting products, will be then discussed.

Figures

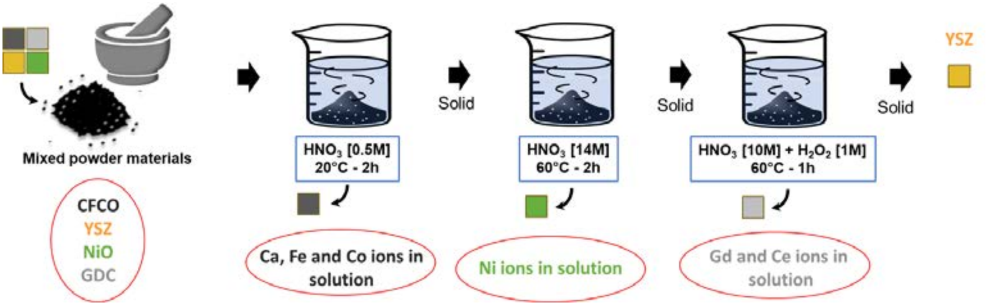

Figure 1. Step-by-step dissolution of the different materials that make up a SOC.

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Innovative transformations of coal combustion by-products from challenges to industrial applications

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Keywords: coal ash by-products, bituminous Fly Ash, processing, recycling, ash mineralogy and properties

This work explores the diversity of coal combustion by-products, emphasizing their transformation from challenges into opportunities for innovative industrial applications. It provides a short overview of various by-product types and their complexities in direct utilization. In the example of High Si bituminous Fly Ash it is demonstrated how average by-products can be strategically processed and modified to yield diverse sub-products with qualified properties. These tailored materials can find their usage in various applications across industries, showing the potential for ecological sustainability and resource optimization. A modification of the presented technology can enable the transformation and enhancement of various combustion by-products bringing benefits to the numerous branches.

Ultrasonic decoating of solid oxide electrolyzer cells for raw material recycling

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Keywords: solid oxide cell, electrolyzer, recycling, decoating

In the current context of energy transition, hydrogen is considered to play a key role as an energy carrier. Therefore, worldwide hydrogen production capacity, electrolyzer capacity respectively, is being greatly expanded. Based on the announced projects, global electrolyzer capacity could increase from the current 0.6-3 GW to 170-365 GW by 2030 [1].

Solid oxide electrolyzers (SOELs) are the subject of intense research due to their high efficiency. However, their degradation and short lifetime remain key issues [2]. Given the critical raw materials involved in SOELs, the development of a viable recycling process is of crucial importance.

The solid oxide cell (SOC), which consists mainly of oxide ceramics and has a micrometer-scale layered structure, is the central part of SOELs. These layers are rich in nickel and various rare earths, which is why SOCs are attracting increasing attention in recycling research.

Given the layered structure, selective decoating has been shown to be an effective recycling method. This technique involves the selective removal of layers under defined stress. Ultrasonic decoating, where the stress is applied through a sonotrode, has been shown to be effective in removing perovskite material from some types of SOC [3]. With this approach, very pure product streams of up to 99% purity or higher can be achieved without the need for complex separation processes or the use of additional hazardous materials.

This study presents methods for integrating ultrasonic decoating into SOC recycling. Two approaches are discussed: surface decoating and particle decoating. During surface decoating, the full planar SOC is scanned with the sonotrode. The perovskite layers detach, leaving the remaining cell undamaged. This approach is simple in theory, but automation can be challenging because of the high risk of breakage due to the brittleness combined with the very thin cell thickness.

Particle decoating stresses cell particles rather than the entire cell. For this purpose, the SOC is first coarsely comminuted with the aim of obtaining processable particles with as intact a layer structure as possible. The decoating of the particles is achieved through the ultrasonic treatment of these coarse particles and the additional particle-particle friction. Although particle decoating provides greater flexibility in terms of cell size and cell condition, i.e. broken or not, the selectivity of the process is reduced. This adds the need for a subsequent separation process for high purity products that can be reused for new cells.

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Direct recycling of Li-ion battery production scraps by pressurized fluids

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Keywords: Li-ion battery recycling, direct recycling, positive electrode material, pressurized fluids

Due to the lack of adapted competitive recycling methods for lithium-ion batteries (LIB), production scraps are currently treated as end-of-life (EOL) batteries, despite their significant difference in characteristics. However, with the drastic increase in LIB production and consequently, the generation of scraps, various innovative recycling techniques have emerged and gained significant attention, aiming to offer greener and more direct recycling routes. Production scraps can constitute a significant proportion (5 to 30 wt.%) of electrode production [1,2], making their recovery crucial. Moreover, the limited availability and high cost of key materials like cobalt and nickel underscore the need for effective recycling. Current methods such as pyro- and hydrometallurgy have drawbacks including low yield and environmental concerns. A more promising alternative is the direct recycling strategy, which mitigates purity issues and aligns with sustainability goals by reducing energy consumption and acid usage. Positioned as a credible pathway to sustainable battery recycling, the direct recycling strategy represents a significant advancement in resource efficiency and environmental responsibility for energy storage technologies, especially applicable to the pristine state production scraps.

This communication focuses on employing pressurized fluids for the direct recycling of positive electrode production scraps of LIB [3]. Illustrated in Figure 1, our objective is to separate all electrode components while preserving their properties and integrity using a carbon dioxide (CO_2)-based technology. The study investigates the influence of various optimized parameters, such as temperature, time, co-solvent ratio, and consumption, to achieve the successful delamination of 100% of the active material. Multiple characterization techniques are employed to assess the structure, chemical composition, and physical properties of the recycled active material, specifically $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ (NMC622). Finally, the electrochemical performance of the recycled NMC622 electrode material in new batteries will be highlighted. This research aims to contribute valuable insights in the feasibility and efficacy of the CO_2 process in the direct recycling of LIBs positive electrodes production scraps.

Acknowledgments

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Closing the loop: Advancing solid oxide cell ceramics in the circular economy

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Keywords: high-temperature electrolysis, solid oxide cells, ceramic recycling, circular economy

The adoption of fuel cell and hydrogen technologies will play a crucial role in facilitating the shift towards decarbonization and meeting the EU's goal of achieving zero net greenhouse gas emissions by 2050. In the coming years, particular emphasis will be placed on expanding the deployment of suitable hydrogen electrolyzers, such as solid oxide electrolysis cells (SOECs), which currently have a moderate technology readiness level (TRL 5-7). To support market entry and promote resource recovery, early-stage development and implementation of recycling strategies are imperative. Efforts are underway to address the reuse and recovery of components from high-temperature electrolyzers, focusing on the reprocessing of ceramic components from End-of-Life solid oxide cells (SOCs).

Establishing closed-loop recycling processes is highly desirable, with a focus on scalability. In line with this objective, a recovery route has been devised for the well-established fuel electrode-supported cell design (**Figure 1**). The primary goal is to reprocess more than 80% of the cell material into new substrate, directly applicable in the SOC device. Therefore, a prerequisite step involves the separation of the oxygen electrode and any potential contact layer, which can be achieved through mechanical and/or hydrometallurgical approaches. Subsequently, the sintered bodies undergo reprocessing into ceramic powder, substrate slurry, and ultimately the pre-sintered substrate. Components of the separated oxygen electrode are recovered as precursors, suitable for SOC applications (e.g., manufacturing oxygen electrodes or contact layers) or alternative uses.

In addition to presenting the properties of the recycled substrate, full cells were manufactured based on substrates containing 0%, 25%, and 50% recyclate by weight. Electrochemical tests were conducted to determine whether these substrates meet the functional requirements, including gas distribution, electrical conductivity, and mechanical stability.

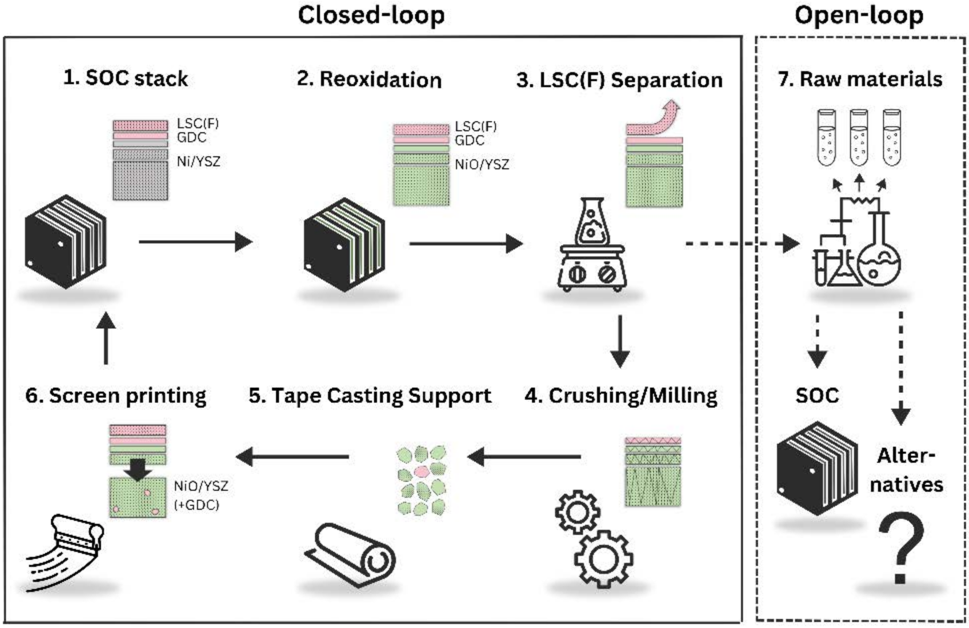

Figure 1. Recycling concept for fuel electrode-supported cell ceramis.

Refractory recycling: A contribution for raw materials, energy and climate efficiency in high-temperature processes (GRK 2802)

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Keywords: MgO, recycling, metal ceramic composite, high-temperature application

Every year, approximately 28 million tons of used refractories are generated worldwide. The majority of the consumed refractories are primarily used for foreign applications, such as aggregates for road construction (downcycling) or deposited in landfills. The recycling of such materials played a rather subordinate role until now. For ecological reasons and due to the risen landfill costs, an increased research potential to deal with the application of refractory recyclates was identified in the last few years. The objective of the Research Training Group GRK 2802 is to research and develop new sophisticated recycling options for used refractories. Within the scope of the Research Training Group, fundamental knowledge should be developed, allowing both the recycling (re-utilisation in similar high-temperature materials) and the upcycling (material upgrading) of refractories in metallurgical processes. The main objectives of the GRK 2802 are an interdisciplinary and structured training of PhD students in the fields of recycling and upcycling of refractories as well as the research and development of a new generation of coarse-grained high-temperature materials based on refractory recyclates with particular functional properties for high-temperature processes in the metallurgy (figure 1).

This will be applied to 2 core ideas:

1. Core idea I: Recycling - Novel refractories based on refractory recyclates and environmentally friendly binders (resin-free, pitch-free) with an application as lining material for steel ladles
2. Core idea II: Upcycling - Novel metal ceramic composites based on refractory recyclates with an application as electrode material for aluminium fused-salt electrolysis

The interdisciplinary team of the Research Training Group GRK 2802 comprises 12 PhD students, 1 Mercator Fellow, 12 Principal Investigators and several Associated Members. The training and qualification programme of the Research Training Group GRK 2802 is being developed and organised by a scientific coordinator. The administrative coordinator is responsible for the fund management and accounting.

The presentation will provide insights into the technical motivation of this long-term project and will give an overview of the results of each subproject of the past one and a half years.

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T2 Ceramics for Energy Conservation and Efficiency

T2.1 ADVANCED FIBER REINFORCED COMPOSITES FOR TURBINE ENGINES

Basic science questions on SiC/SiC composites with applications in aircraft propulsion

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Keywords: SiC/SiC composites

SiC/SiC composites are now increasingly recognized as game-changing materials for hot parts of next-generation aircraft turbines. In conjunction with increasing efforts in TRL scale climbing, basic questions arise concerning their processing and their behavior in the envisaged environments.
This talk will give an overview of recent results obtained by LCTS on SiC/BN/SiC composites foreseen for use in aircraft turbines. Fundamental questions on gas-route (CVI) and liquid-route (MI) processing, on the influence of the BN interphases, ont he design of Environmental Barrier Coatings (EBC) and on the mechanical behavior and testing will be addressed.

Acknowledgments
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Machinability and surface integrity in grinding of C/C-SiC composites with different fibre volume content

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Keywords: C/C-SiC, fibre volume content, grinding force, surface roughness, flexural strength

Carbon fibre reinforced silicon carbides (C/SiC, C/C-SiC) represent a group of Ceramic Matrix Composites (CMCs) already well-established in several high-performance applications. Although they were originally developed for aerospace and defence industries, the advances made in the manufacturing of CMCs over the past few decades have further expanded their spectrum of applications, e.g. as advanced friction systems, furnace charging devices or thermal energy storage systems. As their use in industrial applications increases, the need for a more effective processing arises.

In this respect, the final machining stage plays a crucial role. Machining of C/C-SiC is a challenging task owing to their hardness, anisotropy, and brittle behaviour. Significant effort has been made in optimizing the process by improving factors such as the machining method, the tool material/geometry, or the cutting parameters. The material microstructure and composition play an important role as well. The majority of studies in this regard focused on the effect of the fibre orientation, yet the influence of material composition variations on the machining performance has not been reported so far.

The presented work investigated the effect of different fibre volume content of woven reinforced C/C-SiC on the machinability and the surface integrity using different grinding conditions. The C/C-SiC composites were fabricated by the liquid silicon infiltration method. The physical and mechanical properties, as well as the microstructure and the phase composition of the different materials were assessed and compared. The machining experiments were conducted in a CNC machining centre with different diamond grain size tools at varying feed rates. The effect on the cutting force and the dimensional accuracy was examined.

Results revealed that the surface integrity is more influenced by the microstructure than by the grinding process. In contrast, the process stability is mainly driven by the machining conditions. Little influence on the three-point-flexural strength was observed after machining. Samples with lower fibre content exhibited decreased flexural properties, and higher cutting forces and surface roughness due to the presence of significantly higher porosity and free silicon content. On the other hand, both the cutting forces and the surface roughness gradually increased with the increase of the feed rate. Grinding with finer diamond grain size tools led to smoother surfaces.

Rare earth silicates as oxidation resistant interphase for SiC_f/SiC CMC: Inspiration from model composites investigation

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Keywords: SiC_f/SiC CMC, rare earth silicates, interphase, interfacial parameters

Rare earth (RE) silicates have attracted considerable attention as advanced interphase materials for SiC_f/SiC CMC due to their better resistance to high temperature oxidation and hot steam corrosion than traditional interphase materials. In the present work, model composites consisting of SiC fiber embedded in Yb_2SiO_5 or $Yb_2Si_2O_7$ matrix are processed by Spark Plasma Sintering and the feasibility of these silicates as interphase in SiC-based CMCs are estimated. Fiber push out experiment clearly shows the different debonding mechanisms in model composites. The weak $SiC_f/Yb_2Si_2O_7$ interface exhibits low sliding stress and debonding energy, which are comparable to those of PyC or BN interfaces and ensure the well-recognized crack deflection criteria of energy release rate. $SiC_f/Yb_2Si_2O_7$ interface also possesses semi-coherent structure, proving excellent chemical stability between $Yb_2Si_2O_7$ and silicon carbide. While, SiC_f/Yb_2SiO_5 interface exhibits high interfacial strength and debonding energy, which do not satisfy the crack deflection criteria. Raman spectrum analyzation indicates that the thermal expansion mismatch between Yb_2SiO_5 and SiC contributes to high compressive thermal stress at interface, and leads to high interfacial parameters. The results indicate that $Yb_2Si_2O_7$ is qualified for advanced interphase and the interfacial parameters could be adjusted to reach optimal mechanical fuse mechanism in SiC_f/SiC CMC.

Validaton of progressive damage models of ceramic matrix composites for turbine engine applications

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Keywords: progressive damage modeling, ceramic matrix composites, damage tolerance design

Ceramic matrix composites (CMCs) are enabling for future highly efficienct gas turbine engine concepts that require materials with use temperatures beyond currently availible Ni-based superalloys. However, the progressive damage modeling approaches needed for system design, certfication and sustainment are lacking. Here we consider a variety of progressive damage modeling approaches to enable damage tolerance based design [1-9]. Specifically, a set of thermo-mechanical validation experiments were performed to support an independent evaluation of the a sampling of current state-of-the-art damage and life prediction modeling tools for assessing time-dependent behavior of SiC/SiC ceramic matrix composites in relevant environments for aerospace turbine engine applications. The models were exercised through a specifically designed set of seven challenge problems designed to test capability to accurately describe damage development, retained mechanical properties, as well as behavior and life. Included were tensile, creep rupture, fatigue, and flexure fatigue loading regimes at elevated temperatures, with a unique material architecture and/or stress concentrating geometrical features. Here we will describe the materials studied, the procedures used, and results recorded from the thermo-mechanical validation experiments performed in the laboratory.

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CVD-fiber coating (BN + SiC) for hot gas stable SiC/SiC

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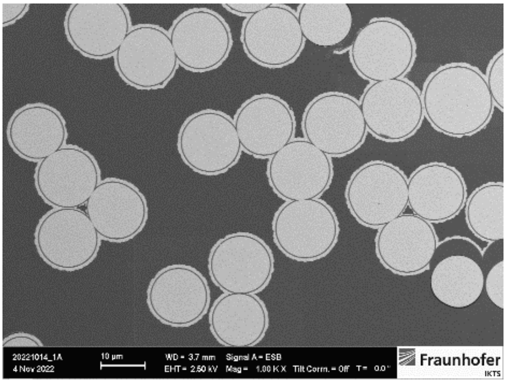
Keywords: SiC/SiC, fiber coating, CVD

Hot gas stable SiC/SiC composite materials require a dense matrix to prevent degeneration effects caused by hot gas contact. Toughness-enhancing mechanisms for the composite material, like crack deflection and fiber pull-out, require an interphase between the fiber material and the matrix acting as a predetermined breaking point.

State of the art interphase materials are coatings of the fiber materials applied by wet-chemical processes or gas phase processes as chemical vapor deposition (CVD), like PyC or BN. The layered crystal structure of the materials favors a deformation due to slip processes. However, the limited stability of the interphase material in oxygen containing atmospheres at elevated temperatures (> 900 °C) is critical. At these conditions oxygen migration through microcracks in the matrix or by diffusion leads to oxidation of the interphase material (borate glass formation) resulting in a decrease of the material strength and an enhancement of brittleness. Therefore, it is crucial for applications in hot gas atmosphere to develop an interphase material which is more advantageous compared to currently available BN fiber coating.

Within the present contribution, initial results for modified BN fiber coatings in combination with a SiC top coating by thermal CVD processes are presented. Changes in the structure and their effects on oxidation resistance are discussed. Finally, first results of these interphase materials within the siliconization process are presented.

Figures



BN/ SiC coating on Hi Nicalon S fiber.

Acknowledgments
project is funded by BMWi 20T2108C.

Design and manufacture of liquid silicon infiltration based SiC/SiC nozzle guide vanes for high-pressure turbines

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Keywords: ceramic matrix composites, CMC, SiC/SiC, nozzle guide vane, liquid silicon infiltration

Increasing the efficiency of jet engines is essential for more environmentally friendly air transport. Higher temperature resistance and lower weight of the combustor and turbine components are key requirements for new materials. Along with adapted environmental coating systems and cooling features, ceramic matrix composites (CMC) are strong candidates for aircraft applications. They can withstand high temperatures in an aggressive environment, while their density is two-thirds lower than that of conventional nickel-based alloys, leading to savings in cooling air and potential improvements in engine efficiency.

As part of the DLR project “3DCeraTurb”, turbine vanes made of silicon carbide fiber-reinforced silicon carbide composites (SiC/SiC CMC) are developed. One aim of 3DCeraTurb is to design and manufacture ceramic nozzle guide vanes (NGV) for a high-pressure turbine (1st stage), experimentally investigate the vane behavior in a wind tunnel, and evaluate performance, damage and lifetime for later application in an aircraft engine.

The focus was the enhancement of the manufacturing process from plate dimensions to more complex three-dimensional components. A ceramic-based design served as a basis for the development and manufacture of a new NGV geometry, considering material- and manufacturing-specific constraints. The liquid silicon infiltration (LSI) process was used to manufacture the SiC/SiC vanes. The process began with the draping and CVI fiber coating of woven fabric layers. During this stage, shaping occurred, and the final component contour was defined. The fiber preform was then infiltrated with a phenolic resin, which acted as a carbon source, using resin transfer molding, followed by high-temperature pyrolysis. The resulting porous carbon matrix was infiltrated with a silicon-boron melt, leading to the conversion of carbon into a SiSiC matrix. The surface was ground, to meet the high requirements for surface roughness and geometric and positional tolerances. Cylindrical, laser-drilled cooling holes were introduced for cooling the trailing edge. In the final step, an environmental barrier coating system (EBC) consisting of yttrium disilicate and yttrium monosilicate layers was applied using PVD processing.

Thermal simulations were performed at the highest loads (Take-off End of field). Therefore, computational fluid dynamics (CFD) simulations were coupled with a finite element analysis (FEA). For the determination of thermal and mechanical properties, SiC/SiC plates were manufactured. Safety factors were calculated using the Tsai-Wu criterion. Wind tunnel testing under TRL 4 will be performed and vane performance will be evaluated.

T2.2 ADVANCED CERAMIC COATINGS FOR POWER SYSTEMS

Comparison of thermal-sprayed YbDS coatings for better durability in 1400°C steam

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Keywords: EBC, steam-exposure testing, thermal-spraying

SiC_f/SiC_m Composites is one of the candidate materials for high-pressure turbine components for its light weight and high heat-resistance. However, it is known that SiC is easily oxidized or vaporized as $Si(OH)_4$, and Environmental Barrier Coating (EBC) must be coated for long-term durability. Ytterbium disilicate (YbDS) has the similiar CTE with SiC and is expected as the barrier against water vapor. In this presentation, we prepared the thermal-sprayed YbDS coupon with different process conditions, conventional spray methods for APS/SPS, and a novel spray medhod, and steam-exposure testings were also conducted at 1400°C with each coupon.Detail characterization results of the each coupon are showing, and the relationship between the microstructure and the property against water vapor is discussed. From these insights, we have developed the bilayer EBC system, and further severe testing results and future tasks are also introduced in short.

Acknowledgments
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Mechanical, microstructural, and fretting wear behaviour of Al_2O_3-ZrO_2-CNT based composite coatings

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In the current work, bimodal thermal barrier coatings (TBC) were deposited via atmospheric plasma spraying (APS) using Al_2O_3 as a matrix, reinforced with 20 wt% of ZrO_2 and 4 wt% of carbon nanotubes (CNT) over Inconel 718 substrate. The objective is to study the effect of bimodality and reinforcements on the mechanical and tribological behavior of Al_2O_3-based TBC. Al_2O_3–ZrO_2, Al_2O_3–ZrO_2-CNT, and micro-Al_2O_3 coatings are named as AZ, AZC, and Al_2O_3, respectively. The presence of partially melted and solid-state sintered nanostructured region (NR) with fully melted and re-solidified microstructured regions (MR) showed bimodal microstructure. Reinforcements lead to enhanced nano-hardness from (12.8 GPa) for Al_2O_3 to (14.7 GPa) for MR of AZ and (14.1 GPa) for AZC, which is attributed to a higher amount of α-Al_2O_3 and t-ZrO_2 present in the coatings. NR reduces shear stress generation during fretting wear in AZ (293.8 MPa) and AZC (298.7 MPa), resulting in a more uniform surface and reduced wear rate. Additionally, the higher aspect ratio and lubrication effect of CNTs in AZC generates the least energy dissipation (92.9 J) and wear rate (0.9×10^{-6} $mm^3N^{-1}m^{-1}$). SEM and EDS analysis of worn surfaces in coatings revealed abrasive, adhesive wear is dominant in Al_2O_3 coatings due to the higher amount of material transfer from coating to Si_3N_4 body than AZ and AZC. Overall, the synergistic effect of bimodality and reinforcements leads to improved mechanical properties and reduced shear stress generation during wear making APS-AZC coating a potential material for wear and high temperature applications.

Neutron diffraction based investigation on the origin of low thermal expansion coefficient for multicomponent RE_2SiO_5 and its correlation with coating thermal cycling lifetime

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Keywords: neutron diffraction, pair distribution function, rare-earth silicates, environmental barrier coating, burner rig tests

Owing to the large thermal expansion coefficient (CTE) of rare earth monosilicate (RE_2SiO_5) topcoat, limited thermal cycling lifetime has become the main challenge of multi-layered environmental barrier coating. Using neutron powder diffraction and total scattering, current work explored the physical mechanisms of thermal expansion in RE_2SiO_5 and contributed to understanding the correlations between CTE and thermal cycling lifetime. It is revealed that it's effective to reduce the distortion degree of [ORE_4] tetrahedrons by introducing Y^{3+}, Ho^{3+} and Er^{3+} into Yb^{3+} sites of Yb_2SiO_5, and the lower the distortion degree of [ORE_4], the lower the CTE. The [ORE_4], with less deviation from the regular tetrahedrons, exhibits improved high-temperature resistance to thermal deformation, resulting in a lower CTE. The more CTE-matched $(Y_{1/4}Ho_{1/4}Er_{1/4}Yb_{1/4})_2SiO_5$ topcoat presents reduced residual tensile stress by 17%, compared to Yb_2SiO_5 topcoat, which substantially reduces the tendency for mud crack initiation and the energy release rate for crack extension, and make significant contributions to the improved durability in service. The present study would give new insights into the physical mechanisms of thermal expansion of RE_2SiO_5 and further provide some practical information towards selection of RE-doping strategy in RE_2SiO_5 to get matched-CTEs to Si-based ceramic.

T2.3 Engineering Ceramics: Advanced Processing, Properties, and Applications

Cold sintering of ZSM-5 zeolite ceramics with superior physical properties

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Keywords: zeolite ceramics, ordered microporous structure, thermal properties, compressive strength, cold sintering process

The cold sintering process, thermal insulating performance and compressive strength of ZSM-5 zeolite ceramics were investigated. Densification of ZSM-5 zeolite ceramics could be achieved by cold sintering process at 393 K under a pressure of 450 MPa for 0~60 min by adding 3 mol/L NaOH solution. X-ray diffraction (XRD), high resolution transmission electron microscopy (HRTEM) image, N_2 adsorption/ desorption measurements and fourier transform infrared (FT-IR) spectra demonstrated that zeolite framework was preserved without collapse of ordered microporous structure in the present ceramics. The thermal conductivity as low as 0.88 W/m·K was achieved together with a high compressive strength up to 315 MPa, which was attributed to ordered microporous structure, amorphous phase and porosity in zeolite ceramics. The ZSM-5 zeolite ceramics prepared by cold sintering process could be expected as promising thermal insulating materials, since the low thermal conductivity was comparable with typical porous ceramics while the compressive strength was much higher than that of them.

Process and characterization informatics of silicon nitride ceramics with engineered microstructural characteristics

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Keywords: artificial intelligence determinations, process informatics, Si_3N_4 and microstructures

This presentation reviews process and characterization informatics to produce silicon nitride (Si_3N_4) ceramics with engineered performances. Si_3N_4 ceramics are generally composed of complicated microstructures including elongated grains dispersed in a matrix of fine grains and grain boundary as well as pores with various sizes, leading to tailored mechanical, thermal and electrical properties. Due to modulated sintering technologies with various conditions selected carefully, Si_3N_4 ceramics with engineered microstructural characteristics have been expected for a practical industrial use in insulated heat-dissipating substrates for power modules which can control mortor driven units in such as electric vehicles, leading to an enormous amount of carbon dioxide emissions reduction by further popularizing electronic vehicles. In this presentation, the engineered properties of the Si_3N_4 substrates required for this application will be comprehensively summarized, in terms of four important engineering aspects: thermal conductivity, mechanical strength, fracture toughness, and dielectric breakdown strength. Second, the sintered reaction-bonded Si_3N_4 technologies strategically selected and the resultant engineered microstructures with various grain boundary characteristics will be mentioned, in comparison with those produced by the other conventional methods. Third, the detail of dielectric breakdown for Si_3N_4 will be introduced, although that has been hardly reported, in which large elongated grains work as severe defects. Finally, their artificial intelligence (AI) determination technologies including process and characterization informatics will be proposed through the process conditions such as types of raw materials, sintering additives and sintering conditions by using a conventional machine learning and microstructural images with various grain and grain boundary configurations as well as porosity via deep learning respectively, demonstrating relatively high AI-determination accuracy of the processes and engineered performances.

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Preparation and characterization of CMAS corrosion resistance of nanostructured lutetium silicate coating

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Keywords: Lu_2SiO_5, $Lu_2Si_2O_7$, CMAS corrosion, environmental barrier coating

In order to improve the CMAS (CaO-MgO-Al_2O_3-SiO_2) corrosion resistance of environmental barrier coatings (EBCs) of SiC_f/SiC composite materials, nanostructured lutetium silicate feedstocks were first prepared in this work. Subsequently, nanostructured Lu_2SiO_5/$Lu_2Si_2O_7$/Si environmental barrier coatings were fabricated via atmospheric plasma spraying (APS). Finally, the CMAS corrosion performance of EBCs in the Lu_2SiO_5/$Lu_2Si_2O_7$/Si system was studied. The microstructure and phase structure of CMAS coatings before and after corrosion were characterized and analyzed using SEM, TEM, and XRD. The results showed that the tendency of Lu to react with CMAS in the nanostructured Lu_2SiO_5/$Lu_2Si_2O_7$/Si environmental barrier coating increased, and a dense layer of apatite was rapidly formed, which slowed down the penetration rate of CMAS and enhanced its corrosion resistance to CMAS.

Functional properties of additive-free silicon carbide ceramics

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Keywords: silicon carbide, additive-free, electrical conductivity, thermal conductivity

Fully dense (t. d. > 99 %) silicon carbide ceramics without any sintering additives were succesfully prepared by combination of freeze granulation of silicon carbide powder, annealing of granulated powder and subsequent rapid hot pressing at 1900°C with dwell time from 5 to 80 minutes (Fig. 1). Thermal and electrical conductivity of prepared materials considering the ratio of SiC polytypes was investigated. Different ratio of alpha and beta silicon carbide has been achieved by adjusting dwell time during sintering. Thermal diffusivity, specific heat capacity, thermal conductivity, electrical conductivity, density, microstructure of additive-free SiC with various α/β content has been investigated. The electrical conductivity of SiC decreased from 104 S/m to 8 S/m as a content of α-SiC increased from 63 to 94 %. Opposite trend, when thermal diffusivity increased from 47.3 to 68.4 mm^2/s as a content of α-SiC increases from 63 to 94 %, was observed.

Figures

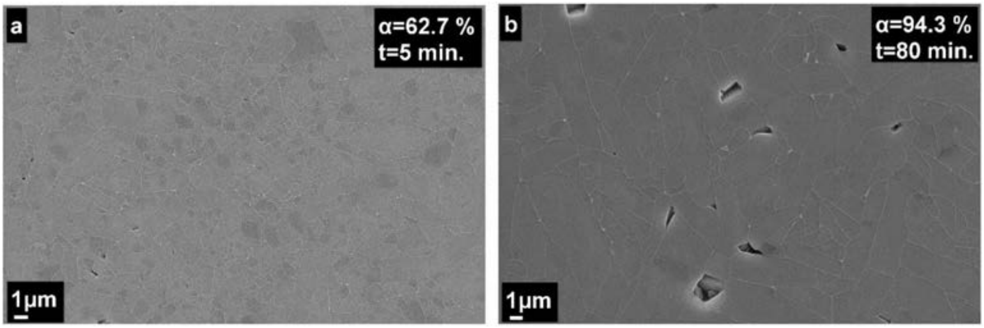

Fig. 1. Plasma etched surfaces of samples with shortest and longest holding time.

Acknowledgments
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Enhanced thermal stability of dielectric and energy storage properties in 0.4BCZT-0.6BTSn lead-free ceramics elaborated by sol-gel method

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Keyword: sol-gel, ferroelectrics, lead-free, perovskites, energy storage

Polycrystalline lead-free Ba0.85Ca0.15Zr0.10Ti0.90O3 (BCZT), BaTi0.89Sn0.11O3 (BTSn) and 0.4Ba0.85Ca0.15Zr0.10Ti0.90O3–0.6BaTi0.89Sn0.11O3 (0.4BCZT–0.6BTSn) ferroelectric ceramics were prepared via sol-gel process and their structural, dielectric and energy storage properties were studied. Pure perovskite structure was confirmed by X-ray diffraction analysis. The evolution of energy storage performances with temperature was studied. A Significant recoverable energy-storage density of 137.86 mJ/cm3 and high energy-storage efficiency of 86.19% under a moderate electric field of 30 kV/cm were achieved in the composite 0.4BCZT–0.6BTSn ceramic at 353 K. Moreover, excellent temperature stability (70–130 ◦C) of the energy storage efficiency (less than 3%) was achieved.

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Solid oxide cells: From 3D microstructure to comprehensive quantification

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Performance and durability of solid oxide cell (SOC) electrodes are closely linked to their porous microstructure properties and the microstructure evolution during the cell's lifetime. Thus, comprehensive characterization of three-dimensional (3D) microstructures is essential for SOC electrode optimization. Using Plasma FIB-SEM (PFIB-SEM) microscopes, which offer accessed material volumes thousandfold larger than those of traditional Ga^+ FIB-SEMs, along with the latest implementations of automated serial sectioning, multidetector SEM imaging techniques, and SEM auto-functions, make PFIB-SEM an ideal platform for investigating SOC microstructures and other porous materials.

This contribution addresses the major areas of SOC characterization, for the first time, and proposes a complete characterization workflow from 3D microstructure to comprehensive quantification: triple-phase boundary, (non-) percolating Ni and pores. As a practical example in this study, we characterize a fresh solid oxide fuel cell (NYDC-55-3-0) manufactured and prepared for investigation by Northwestern University. We utilize the Plasma FIB-SEM platform (Helios 5 PFIB) and automated serial sectioning software (Auto Slice and View 5 – ASV5) to collect a large 3D volume of $180 \times 150 \times 30\ \mu m^3$ with a voxel size of $32 \times 32 \times 50\ nm^3$.

We developed automated Avizo recipes that take control of the data processing and analyses and allow consistent and reliable data quantification and 3D visualization. The recipes calculate spatial parameters of tortuosity, triple-phase boundaries (total length, length/volume), phases volume fractions, percentage of non-percolating for each phase, and surface area/volume for Void|YSZ, Void|Ni and YSZ|Ni.

This study presents a new and comprehensive characterization workflow leveraging deep-learning predictions, covering the entire spectrum from 3D microstructure analysis using PFIB-SEM to thorough quantification, as demonstrated through the examination of a freshly prepared solid oxide fuel cell. Our advancements resulted in a thousandfold increase in the volume of image data acquisition compared to prior studies, all while maintaining a consistent voxel size (or resolution). To ensure robust identification of material constituents, we implemented the simultaneous acquisition of back scattered electron and secondary electron images, guaranteeing 99.99% confidence.

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SiC-based ceramics for high-temperature applications on oxidizing environment: prepared with mere amount of carbide additives and liquid phase routes

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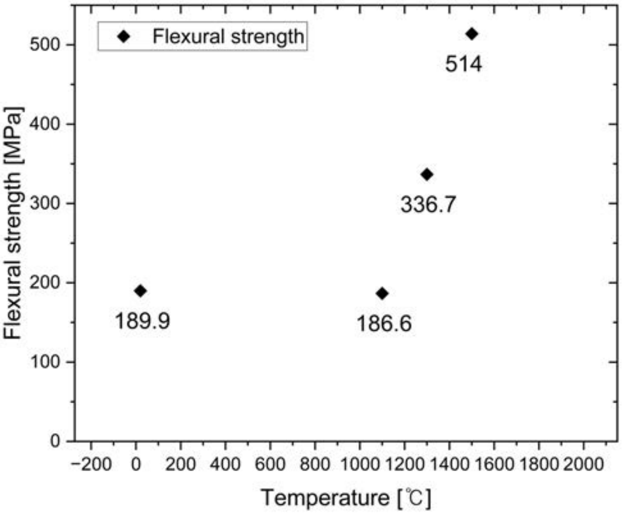
Keywords: SiC, B_4C, rare-earh (RE) carbides, precursor infiltration and pyrolysis (PIP), Spark plasma sintering/field assisted sintering technology (SPS/FAST), aqueous slurry

Silicon carbide (SiC) and SiC-based materials are representative engineering ceramic for high-temperature environment applications. Due to SiC's excellent thermal stability and mechanical properties at high-temperature environments, SiC-based materials are actively applied to industries under extreme thermal environment like aerospace and turbine materials.

However, one of the major tasks for SiC specialist is to materialize SiC's suitable high-temperature properties, which could be possible with fabrication processes to control defects, and undesirable components like oxides or residues in the material. Applying high solid loading SiC slurry could minimize the above problems. High concentration slurry (over 60 vol%) reduces shrinkage of green body and precursor infiltration and pyrolysis (PIP) method operates further densification without residues. For most high-temperature applications, operating environment contains oxygen gas that oxidation behaviour should be considered. SiC is basically stable and excellent on oxidation resistance, however, it could turn into active oxidation mode at above certain level of oxygen gas. Environmental barrier coatings (EBCs) are applied to prevent this critical phenomenon.

We add carbide additives (including rare-earth (RE) carbides) on preparation of SiC-based materials. Despite the final portions are less than 1 vol%, additives show promisiong or noticeable effects on high-temperature properties of SiC-based ceramics. For instance, SiC-B_4C showed 514 MPa at 1500 °C, and SiC-YC_2 also showed interesting results. With the advantage of flexible shaping and fast densification, this approach could efficiently contribute to SiC-based materials' high-temperature application in various operating environments, both with or without EBCs.

Figures



In-situ flexural strength of SiC-B_4C fabricated using high concentration slurry and PIP method.

Role of boron nitride nanosheets on the crack growth resistance of zirconia composites obtained by environmentally friendly processes

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Keywords: boron nitride nanosheets, zirconia, composite materials, microstructure, R-curve, bridging

In the last years, a great interest in new composite materials with 2D nanomaterials as fillers has been developed as they could meet the multifunctional properties required for application on the environment, medicine, space, or energy industries. Among the inorganic graphene analogues, 2D hexagonal boron nitride (2D-hBN) has gained relevance as filler in ceramic composites since it possesses comparable mechanical properties to those of graphene, but showing some advantages over it, such as its chemical stability up to 800-1000 ºC or its white color. In fact, with the incorporation of this nanomaterial to advanced ceramics, the composites are expected to attain greater structural stability. However, despite the interest of these materials, the studies approaching the mechanical performance of ceramic composites with 2D-hBN as filler are still scarce.

In this work, the role of the incorporation of boron nitride nanosheets (BNNS) on the microstructural and mechanical features of 3 mol.% yttria-stabilized tetragonal zirconia polycrystal (3Y-TZP) ceramics has been analyzed. To that end, BNNS were exfoliated by two different simple and environmentally friendly processes: hydroxide-assisted planetary ball milling and shear exfoliation in a kitchen blender. The composite powders were spark plasma sintered at 1250 °C for 5 min with an applied pressure of 75 MPa. The microstructural features have been assessed through scanning and transmission electron microscopy, X-ray diffraction and Raman spectroscopy. Besides other classical mechanical properties- hardness, Young's modulus and single edge V notched beam (SEVNB) fracture toughness-, the resistance to stable crack growth (R-curve) of the composites containing either type of exfoliated BNNS have also been evaluated on SEVNB by three-point bending tests. Inspection of the crack paths revealed the mechanisms responsible for toughening in the composites.

Acknowledgments

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Hardness anisotropy of HfC and TaC ceramic grains

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Keywords: hardness anisotropy, slip systems, transition metal carbides, nanoindentation

The anisotropy of hardness and indentation modulus of grains of low-index crystallographic orientations ({001}, {101} and {111}), mapped by electron backscatter diffraction, were investigated by nanoindentation in polycrystalline HfC and TaC ceramics. It was revealed that the hardness anisotropy exhibited different trends for the HfC and TaC ceramics while the indentation modulus did not show detectable anisotropy. The {101} and {111} facets of HfC is found to be harder (~32 GPa) than the {001} orientation (~30 GPa) while, in the case of TaC, higher hardness corresponds to the {111} facet (~23 GPa) in comparison with the {001} and {101} orientations (~22 GPa) as shown in Figure 1. The different hardness anisotropies are attributed to the different dominant slip activation reported in the literature, providing a quick and efficient tool for the distinction between the <1-10>{110} and <1-10>{111} type active slip systems in rock salt structure transition metal carbides.

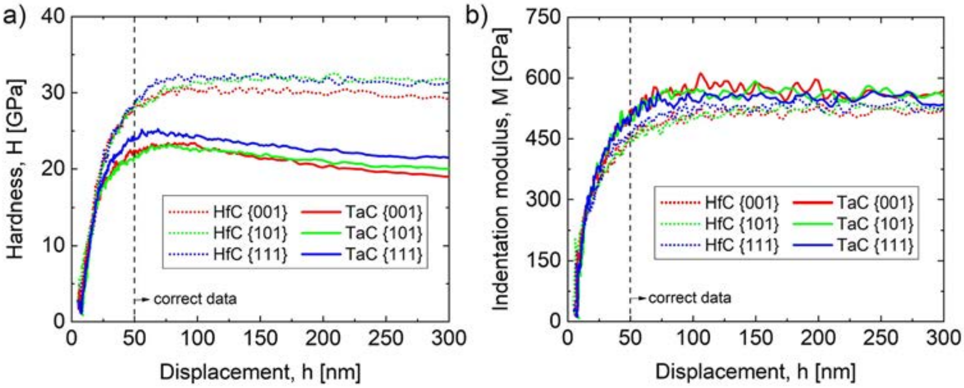

Figure 1: Typical a) hardness - and b) indentation modulus - depth curves of HfC and TaC grains measured on low index crystal facets.

Acknowledgments

This research was supported by the Slovak Grant Agency for Science via the projects APVV-19-0497 and APVV-22-0493 and by the Slovak Academy of Sciences via the projects: Seal of Excellence – Strengthecs and IMPULZ IM-2022-67.

Vat photopolymerization of ceramic multi-material systems

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Keywords: vat photopolymerzation, multi-material, mechanical properties

Combining different materials in additive manufacturing (AM) is garnering widespread attention due to the wide range of possibilities that it provides to realize parts with increased functionality. This talk presents the status quo of multi-material AM on the basis of lithography-based ceramic manufacturing (LCM), a technology belonging to the family of vat photopolymerization (VPP) techniques, which is capable of realizing high resolution 3D printing for ceramics. Beside the technological principles the focus of this presentation will also be on the results and current challenges in terms of co-printing and co-sintering of different ceramic materials as well as ceramic and metals. Different material combinations have been investigated including hydroxyapatite (HA)/tricalcium phosphate (TCP), porous/dense alumina, porous/dense HA, alumina (A)/zirconia-toughened-alumina (ZTA), and copper (Cu)/glass ceramic. In more detail, this contribution will showcase the use of this multi-material AM approach to combine ZTA sandwiched between pure alumina, yielding a characteristic strength higher than 1 GPa on the laminate multi-material system, compared to 650 MPa in the monolithic alumina. It will also present the outstanding thermal shock resistance of such AM produced multi-material components owing to the embedded compressive layers, which leads to a significant performance enhancement compared to the monolithic reference. This article also discusses the main issues and future possibilities of ceramic-ceramic and metal-glass ceramic multilayer fabrication by LCM technology. The initial results show that this technologicy holds great potential to path the way from classical single material structures to multi-material and functionally-graded ceramics.

Figures

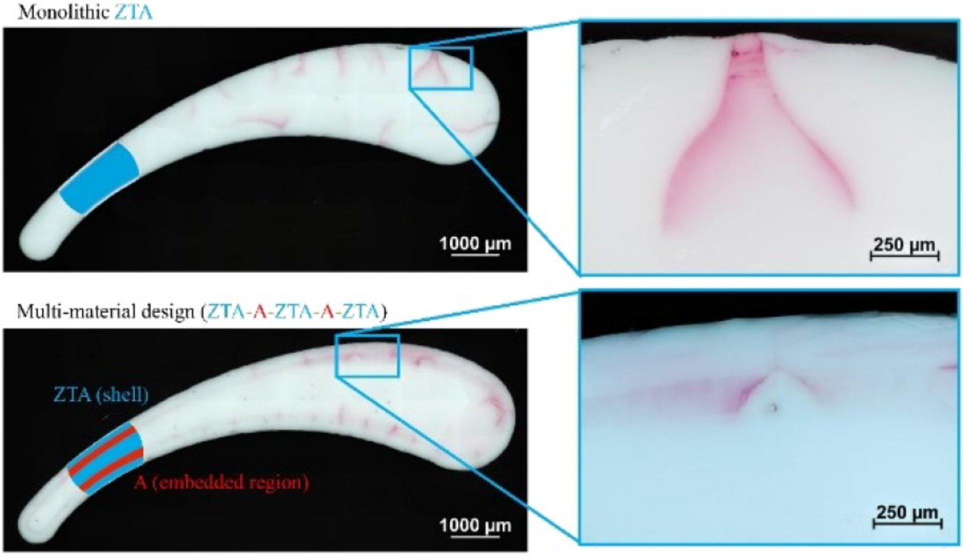

Figure 1: Schematic image showing the improved thermal shock resistance of a ceramic turbine blade fabricated by multi-material VPP compared to the monolithoc counterpart due to crack arrest within the embedded layers

Acknowledgments

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Treatment of oil sands process-affected water using a induced gas flotation with submerged ceramic membrane filtration system

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Keywords: oil sands process-affected water, induced gas flotation, submerged ceramic membrane, oil removal

In a previous study, we conducted research on the removal of oil from oil sands process-affected water using a coalescing filter (CF). The CF efficiently removed oil wastewater from 100 to 200 mg L^{-1} down to 10 to 20 mg L^{-1} within a short period. However, beyond this range, the removal of low concentrations of oil took significantly more time, leading to a sharp decrease in efficiency. Therefore, the application of alternative oil separation technology suitable for efficiently removing oil in the range of 10 to 20 mg L^{-1} is necessary. In this study, we aimed to effectively remove extremely low concentration oil from oily wastewater using a induced gas flotation with submerged ceramic membrane (scmIGF). The scmIGF injects gases such as N_2 and CO_2 to float oil droplets and skims them through the skimmer module. Simultaneously, it employs submerged ceramic membrane technology to remove ultrafine oil droplets. This enables the effective removal of free oil, unlike the CF, and proves to be effective in removing oil in wastewater with low concentrations of 20 mg L^{-1} or less. We tried to achieve process optimization of the scmIGF by evaluating oil removal efficiency based on various operating conditions, such as the type of gas, bubble size, and pore size of the ceramic membrane. From an operational perspective, it was observed that the oil removal efficiency of scmIGF varied significantly depending on the type of gas (N_2, CO_2, etc.) and the pore size of the submerged ceramic membrane. The results showed that the ceramic membrane enabled complete oil removal before going to next treatment step and the injected bubbles effectively removed the oil-contaminated fouling layer formed on the surface of the membrnae.

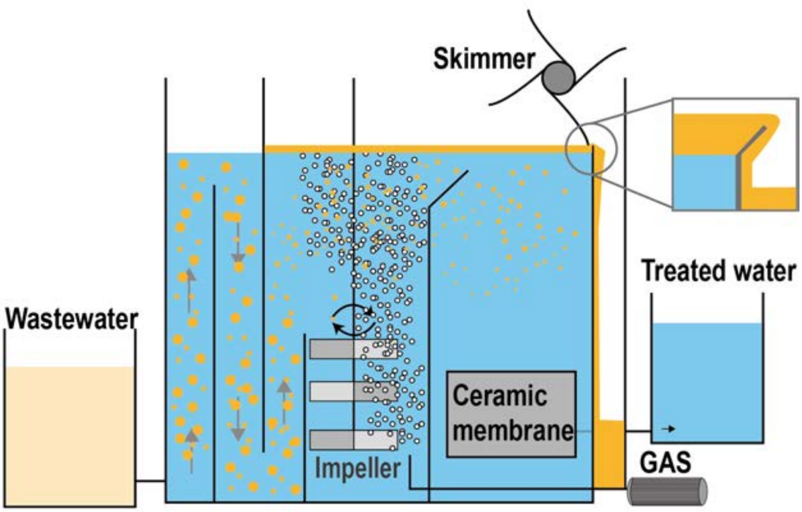

Figure 1. A schemaic diagram of scmIGF.

Acknowledgments

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Step-by-step designing of A and B-site doped high-entropy perovskite oxides for thermoelectric applications

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Keywords: high-entropy, thermoelectrics, figure of merit, material design, etc.

Ceramic oxides were subjected to immense scientific scrutiny for thermoelectric (TE) applications because of their high thermal and chemical resistance at high temperatures. However, their mediocre electrical conductivity and/or high thermal conductivity limit the material design for practical commercial applications [1]. Interestingly, the high entropy oxides (HEOs), a subset in the family of high entropy materials, are considered potential candidates for practical TE applications because they can offer a pathway to partially decouple the electronic and thermal conductivities to significantly enhance the TE properties [2,3]. HEOs are formed by a random and homogeneous distribution of nearly equimolar cations at a crystallographic site in a single phase due to the dominance of configurational entropy over enthalpy at high temperatures [4-6]. A strong lattice distortion in a highly symmetric structure may allow for an overall enhancement in the figure of merit ($zT= \alpha^2T/\rho\kappa$) via a reduction in phonon thermal conductivity (κ_{ph}) and optimization of the power factor (α^2/ρ) [2]. Microstructural engineering through advanced sintering and/or processing methods will then allow exploring a widely expanded chemistry-structure-property space for HEO-based thermoelectric material optimization. HEOs may thus form the foundation of a technology roadmap for highly efficient and versatile thermoelectric devices. In the present work, we focus on a step-by-step feedback-based designing of A- and B-site doped perovskite (ABO_3) HEOs to study their structural, magnetic, electronic, and thermoelectric behavior.

Fe and Mn-based (having free electrons in *d*-shells) B-site modified [$A_1(5N)_1O_3$] HEOs were first prepared to systematically understand the effects on the material properties such as carrier concentration, density of states, valence state, matrix effect, and structural distortion. This understanding was then escalated to the design of A and B-site doped [$(5M)_1(5N)_1O_3$] HEOs. Accordingly, first single-phase $BaBO_3$ (B= Y, Fe/Mn, Ti, Zr, Hf, Nb, Zn, W, and Ta) with variable Fe/Mn content (0, 0.2, 0.3, and 0.4) was prepared via solid-state synthesis method. The low-temperature magnetic behavior of 0.4Fe was analyzed with dc/ac-magnetic, neutron, and µSR measurements to confirm the short-range order owing to the competitive ferromagnetic-antiferromagnetic correlations [7]. Further, spark plasma sintering (SPS) at 1000-1200°C with a pressure of 100 MPa was used to prepare engineered 0.4Fe samples for thermoelectric applications. We observed enhancement in the electrical conductivity and the Seebeck coefficient increased significantly to a relatively large value of $\sim 10^5$ µV/K at 75°C in correlation with the structural phase transition observed in the temperature-dependent x-ray diffraction and electrochemical impedance spectroscopy measurements.

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Synthesis and 3D printing of carbon coated lithium iron phosphate (C/LFP) cathodes

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Keywords: LFP/C synthesis, solid-state reaction, 3D printing, cathodes, lithium-ion batteries, fused filament fabrication (FFF)

Synthesis of carbon coated lithium iron phosphate (LFP/C) cathodes for lithium-ion batteries (LiBs) has been optimised to produce novel configurations by advanced fabrication methods such as 3D printing[1]. Synthesized LFP/C exhibits a pure phase with an orthorhombic structure with lattice constant equal to: a=10,3676Ǻ, b=5,9987Ǻ, c=4,71312Ǻ in the Pnma space group [2]. According to morphological analyses, as synthesised LFP appears as agglomerates that were sonicated to obtain nanometric grain sizes, around ≈ 30 nm, improving the morphology observed for commercial LFP/C powder, with a larger grain size (approximately 1 µm). Solid state synthesis under reducing conditions leads to the production of a 49 nm coating to improve the electronic conductivity of the cathodes.

Such nanometric powder was used to fabricate polymer-ceramic filaments with up to 65% of ceramic loading, which were subsequently fed to a desktop FFF-3D printer. After debinding and final sintering at 500 °C, these electrodes have been electrochemically tested and compared with commercial LFP/C. Thus, cycling of new 3D printed LFP/C electrodes yields up to 128 mA/g at C/10 which is almost a 85% of the theoretical capacity. Such variation may be attributed mostly to the the synthesis process followed, particularly the carbon coating.

Therefore, further investigation, such as the impact of carbon coating, particle size and electrode fabrication procedure on the electrochemical performance of LFP/C cathodes would provide a novel perspective for the development of improved cathodes for lithium-ion batteries.

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Microstructure and physical properties of plasma-sprayed nanostructured $Yb_4Hf_3O_{12}$ thermal and environmental barrier coatings

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Keywords: rare earth hafnate, physical properties, plasma spraying, nanostructure, thermal/environmental barrier coating

Ceramic matrix composite (CMCs) is expected to replace superalloy as the ideal high temperature structural material for the new generation of high thrust-weight ratio aero engine. However, CMCs faces severe challenges such as water oxygen and CMAS in the service process. Thermal and environmental barrier coatings (TEBCs) technology should be used for thermal protection and corrosion protection of ceramic matrix composites. Nanomaterials are widely used in coating because of their excellent thermodynamic properties and the introduction of nanostructures into coating has become one of the research hotspots. In this work, we compared the microstructure and nanomechanical properties of nanostructured and conventional $Yb_4Hf_3O_{12}$ coatings prepared by atmospheric plasma. The nanostructured $Yb_4Hf_3O_{12}$ coatings exhibited a bi-modal distribution in microstructure. Due to the existence of phase transition, the mechanical properties of the two annealed coatings after annealing were investigated. Both types of coatings demonstrated increased nanomechanical properties after heat treatment, but the nanostructured $Yb_4Hf_3O_{12}$ coatings showed a more significant increase in elastic modulus and nanohardness than the conventional $Yb_4Hf_3O_{12}$ coatings. The thermal properties of nanostructured and conventional $Yb_4Hf_3O_{12}$ coatings were also investigated, and the nanostructured coatings showed lower thermal conductivity. Furthermore, the thermal expansion behavior of two types of coatings was investigated. Although there is a phase transition in the spraying process, the thermal expansion coefficient of phase δ and phase F is not very different, which does not affect the use of the coating.

Preparation of non-ablative elastic insulation materials with maintainable shape properties

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Keywords: ceramic, insulation materials, thermal conductivity, elasticity

Non-ablative ceramic insulation materials play an important role in aerospace field. However, the traditional rigid insulating ceramic tile material has inherent brittleness, while the flexible insulating felt material has weak dimensional ability, which limits their application in some fields. This report puts forward a new idea from the construction of elastic micro-junction units to the realization of macroscopic elastic properties, and innovatively develops a new type of thermal insulation material with both maintainable shape and strong elasticity. The advanced elastic insulation materials exhibited low density (~0.15 g cm^{-3}), high compressive stress (~0.36 MPa), and low thermal conductivity (~0.04 W m^{-1} K−1). The fascinating material may provide new insights for candidate materials in thermal insulation and other fields.

Acknowledgments

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The enhanced thermal conductivity of Si_3N_4 ceramics prepared by using metal hydride

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Keywords: silicon nitride, thermal conductivity, sintering, metal hydride

In this work, two kind of metal hydride, namely YH_2 and ZrH_2 were used to prepare the high thermal conductivity of Si_3N_4 ceramics. The metal hydride additives involved two step sintering. For YH_2, the native SiO_2 was eliminated, and Y_2O_3 was in situ formed by a metal hydride reduction reaction. The Y_2O_3/SiO_2 ratio increased with the increase of YH_2 content. Full densification of YH_2-doped samples could be achieved after sintering at 1900°C for 4h. The Y_2O_3/SiO_2 ratio had a significant influence on the composition of crystalline secondary phases. Besides, the increased Y_2O_3/SiO_2 ratio is conducive not only to the grain growth but also to the reduction of activity of SiO2 in the liquid phase, resulting in enlarged purified grains, reduced volume fraction of intergranular phases and increased Si_3N_4-Si_3N_4 contiguity, the thermal conductivity increased by 29% from 95.3 to 123.0 $W·m^{-1}·K^{-1}$ after sintering at 1900 ℃ for 12h by the substitution of Y_2O_3 with YH_2.

For ZrH_2 , the metal hydride reduction reaction in the first step sintering allows the in situ generation of ZrO_2 and the elimination of native SiO_2. A smaller amount of liquid phase with reduced oxygen content was produced during the second step sintering as a result of the replacement of ZrO_2 by ZrH_2. The inherent oxygen in those ZrH_2-doped samples was removed via a route of $SiO_2 \rightarrow ZrO_2 \rightarrow SiO(g)$. Consequently, the densified Si_3N_4 ceramics with larger volume percent of elongated purified β-Si_3N_4 grains and less glassy phase were obtained. Ultimately, the optimal thermal conductivity of 116.4 $W·m^{-1}·K^{-1}$ was achieved after sintered at 1900℃ for 12h by using 3wt% ZrH_2 and 1.5wt% MgO as additives.

T2.4 Materials for Solid State Lighting

Development of transparent and fluorescent α-SiAlON ceramics by adding various rare-earth additives

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Keywords: transparent ceramics, α-SiAlON, controlling microstrucuture

α-SiAlON ceramics are expected as novel optical materials because of their excellent thermal, mechanical properties and intrinsic transparency due to high band gap energy. However, most of fabricated α-SiAlON ceramics has been opaque because of scattering and absorption sources (pores, secondary phases, coarse particles, and SiAlON glassy phase) developed through the liquid phase sintering process, which is derived from the rare-earth additives. In the present study, the influence of rare-earth additives on transparency of α-SiAlON ceramics was investigated.

At first, the samples using 15 different rare-earth oxide powders were prepared by firing at 1600℃ for 4 h in 0.9 MPa N_2. As shown in Fig. 1, the α-SiAlON ceramics fabricated by adding rare-earth oxides whose rare-earth ions have small ionic radii: Y_2O_3, Ho_2O_3, Er_2O_3, Tm_2O_3, Yb_2O_3, and Lu_2O_3, showed high α-SiAlON fraction and high relative density related to wider composition for formation of α-SiAlON single phase[1]. In addition, these samples were consisted with fine microstructure associtated with low temperture sintering. These microstructure, which have fewer scattraing sources, resulted in high transparency showed in Fig. 2(a).

Based on these insights, Ce-doped α-SiAlON ceramics fabricated by co-doping with Lu^{3+},which is the smallest rare-earth ion, is resulted high transparency and fluorecence corresponding to Ce^{3+}. Furthermore, the in-line transmittance of Lu-α-SiAlON:Ce^{3+} ceramics using fine raw powders of rare-earth oxides was 50% at 600 nm (Fig. 2(b)).

Figures

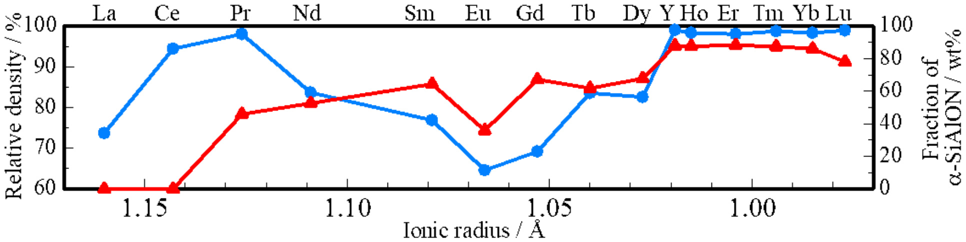

Fig. 1 Relative densities and fractions of fabricated α-SiAlON ceramics.

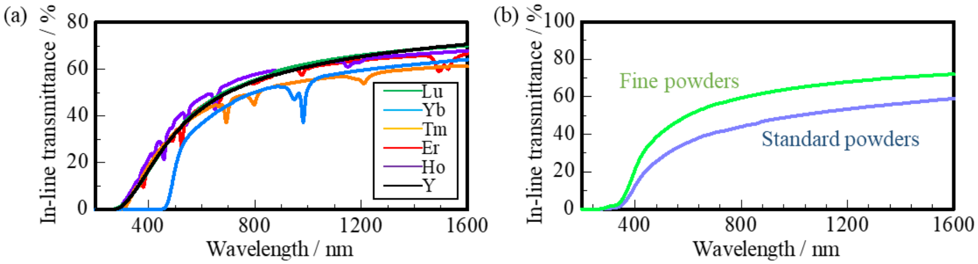

Fig.2 Transparency of α-SiAlON ceramics (thickness:100µm). (a) single doped (b)codoped with Lu and Ce

Acknowledgments

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Utilizing rare earth element-modified smectites for the synthesis of photoactive ceramics with up-conversion properties

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Keywords: smectites, cation exchange, rare earth elements, high temperature transformation, solid state phosphors, up-conversion, terahertz time-domain spectroscopy, additive manufacturing

Synthetic layered clay minerals with smectite structure and different chemical composition were used for synthesis of ceramic materials after their modification by stochiometric mixture of Er^{3+}/Yb^{3+} (REE) cations. The behavior of selected smectites was systematically investigated before and after modification using REE and heating up to temperatures ensuring the sample dehydration (400 °C), dehydroxylation (800 °C) and formation of new high temperature phases (1200 °C). The effect of temperature on the samples was investigated by thermogravimetry (TG), powder X-ray diffraction (PXRD), terahertz-time domain spectroscopy (THz-TDS) and UV-VIS-NIR fluorescence spectroscopy. The samples undergo phase transformation immediately after dehydroxylation and new phases are starting to be formed already at 800 °C. At this stage only main diffractions of forsterite Mg_2SiO_4 and/or enstatite $Mg_2Si_2O_6$ ceramics can be observed. The heating at 1200 °C enabled detection of erbium silicate $Er_2Si_2O_7$ and/or ytterbium silicate $Yb_2Si_2O_7$ by PXRD as important phases used in up-conversion of electromagnetic radiation or photonic components such as optical waveguide amplifiers [1]. Interestingly, the forming of new products was detected also by THz-TDS spectroscopy in the far-infrared region [2], by the detection of the increase of frequency dependent index of refraction and decrease of absorption coefficient compared to the pristine clays. Prepared ceramic materials revealed typical emission bands after irradiation by 980 nm laser located within green (540 nm) and red (670 nm) emission. The averaged integrated intensity ratios between green and red emissions were 0.43 and 0.51, dependent on the smectite material used for modification. The results achieved indicate that the functionalized ceramic structures prepared from modified smectites can be processed also using additive manufacturing technologies based on composites photopolymerization.

Acknowledgments

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T2.5 ADVANCED POLYMER DERIVED CERAMICS (PDCS) AND RELATED MATERIALS FOR ENERGY APPLICATIONS

Downshift of the Ni d band center over Ni nanoparticles in situ confined within an amorphous silicon nitride matrix

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Keywords: d band center, electronic metal-support interaction, amorphous silicon nitride, nickel nanoparticle, nanocomposite

Hydrogen (H_2) has been widely used in chemical processes. Most of these reactions generally can be facilitated by the transition metal (TM) catalyst because its d-electrons play a central role in the adsorption and dissociation of H_2. In general, binding strength between hydrogen and TM highly influences the subsequent catalytic performance. Based on the d band theory, the d band center (ε_d) is found to show a correlation with the binding strength between TM and adsorbates[1]. The down (up) shift of the (ε_d) means that the less (higher) availability of empty antibonding states between the TM and adsorbate results in weaker (stronger) interactions between them[1]. The weak (strong) binding strength between them makes the chemisorption (desorption) difficult, thus there is an appropriate binding strength to maximize the catalytic activity. As a general trend, the d band center of TM shifts down from left to right, and from 3d to 5d TMs in the periodic table. Thus, downshifting the d band center of 3d TMs such as nickel is one of the reasonable strategies to approach the catalytic performance of noble metals.

The construction of electronic metal–support interaction (EMSI) is a promising strategy for modifying the electronic structure of TM[2]. Therefore, the choice of catalytic support is crucial for developing novel active catalysts. Silicon nitride (Si_3N_4) is an attractive catalytic support because its nitrogen atoms can electrically interact with the loaded TMs. In our previous study, the successful formation was achieved under anhydrous conditions for the Ni nanocrystallites embedded within the amorphous Si_3N_4 (Ni/a-Si_3N_4) through the polymer-derived ceramics (PDCs) route[3]. Moreover, the embedment structure of TMs within catalytic support generally facilitates the EMSI because the structure has a larger contact area between TMs and support matrices.

Herein, to investigate the influence of Si_3N_4 catalytic support on the EMSI, we synthesized polymer-derived Ni nanoparticles embedded within an amorphous silicon nitride matrix (Ni/a-Si_3N_4) and an amorphous silicon dioxide matrix (Ni/a-SiO_2) samples[4]. In both compounds, the Ni/Si atomic ratio (0.06–0.07), average Ni nanocrystallite size (7.0–7.6 nm), and micro/mesoporosity of the matrix were rigorously fixed. Hydrogen (H_2)-temperature-programmed desorption (TPD) profile analysis revealed that the activation energy for H_2 desorption at about 100–130 °C evaluated for the Ni/a-Si_3N_4 sample (47.4 kJ mol^{-1}) was lower than that for the Ni/a-SiO_2 sample (68.0 kJ mol^{-1})[4]. Mechanistic study with XPS analysis and DFT calculations revealed that, at Ni nanoparticle/matrix heterointerfaces, Ni becomes more covalently bonded to N atoms in the a-Si_3N_4 matrix compared to O atoms in the a-SiO_2 matrix. Based on experimental and theoretical studies, we elucidated that Ni–N interactions at the heterointerface lead to remarkable Ni d band broadening and downshifting of the d band center relative to those generated by Ni–O interactions at the heterointerface. This facilitates H_2 desorption, as experimentally observed in the Ni/a-Si_3N_4 sample[4].

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Merging self-assembly and additive manufacturing for hierarchically structured ceramics

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Amongst macromolecules, preceramic polymers (PCPs) are unique in their ability to be converted from a workable polymeric material to ceramics via heat treatment. The flowable nature of many PCPs lends these materials to additive manufacturing, including direct ink writing (DIW). Several research groups have explored the DIW of both neat and filled PCPs to create relatively complex ceramic components (post pyrolysis). In this presentation, we will discuss our efforts to merge the PCPs with self-assembling molecules and DIW printing, to produce hierarchically-structured materials. Block copolymers (PNBA-PMMA-PNBA) were utilized in this work to direct the structure of the PCPs as well as serving as sacrificial porogens that are lost from the structure during pyrolysis. Ink formulations and printing parameters can be tailored to provide a variety of nanostructures within the confines of the printed components and mechanisms of structure development will be discussed. Structural, chemical, and mechanical characterization of the final ceramics will also be presented. The final nanoporous and nanostructured ceramics may have potential for a variety of energy-related applications, including catalyst supports.

Hierarchically porous ceramic materials via vat photopolymerization-induced phase-separation as catalysts for CO_2 methanation

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Keywords: polymer-derived ceramics, vat photopolmyerization, phase separation, catalysis

Hierarchically porous ceramic materials combine excellent thermal and mechanical properties with suitable media flow characteristics and high active surface areas, thus rendering them materials of interest for a large variety of applications in the fields of energy and environment, as well as in catalysis. However, the formation of complex-shaped parts exhibiting these characteristics is highly challenging, often requiring multiple steps.

In this contribution, we present a novel approach for the preparation of hierarchically porous ceramic and metal-ceramic hybrid materials by combining the concepts of polymer-derived ceramics, vat photopolymerization, and polymerization-induced phase separation. By a systematic developement of phase-separating polysiloxane-based preceramic resin systems, a spinodal decomposition between the preceramic polymer and a sacrificial acrylate phase can be achieved via the photopolymerization step taking place during DLP-based 3D printing. Upon selective removal of the sacrificial phase during pyrolytic conversion, complex-shaped SiOC ceramic parts exhibiting sub-micron sized, continuous porosity are obtained.

Furthermore, we showcase the potential of precursor-based ceramic processing by modifying the preceramic starting resins with organometallic compounds, thus facilitating an in-situ generation of metal nanoparticles (e.g., Ni or Co) within the resulting SiOC matrices.

Finally, we demonstrate the proof-of-concept of our materials design approach for applications in the field of catalysis, focusing on CO_2 methanation. Hierachically porous SiOC materials decorated with up to 20 wt.% Ni nanoparticles are employed as catalyst reactors, evaluating their respective catalytic activity. While untreated pyrolyzed materials exhibited rather limited performance due to limited accessibility of active metal nanoparticles, an oxidative post-treatment facilitated excellent conversion rates and selectivities in the CO_2 methanation model reaction.

We consider our processing approach as a straightforward and highly versatile tool toward the structural and chemical design of novel ceramic materials, not only limited to catalytic applications, but also providing a high applicability in the fields of energy storage, energy conversion, or environmental remediation.

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Atmosphere effect on the organic-to-inorganic transformation of PDC

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Keywords: SiOC, polymer-derived ceramics, microporosity, mechanical properties

Si-based polymer-derived ceramics (PDCs) are a family of advanced inorganic compounds obtained through pyrolysis in a controlled atmosphere of organosilicon polymers. They are of interest for a variety of structural and electrochemical devices due to their unique mechanical and functional properties. Moreover, they offer a great flexibility in terms of shaping processes and possible morphology as they can be integrated with any polymer-manufacturing technology.

Most of the research has been focused on the organic-to-inorganic conversion into an inert (usually Ar) atmosphere. Herein, we investigate the ceramization process in different atmospheres including Ar and reactive CO_2, some samples were also pyrolyzed in Ar/H_2 and air for comparison.

The obtained amorphous SiOC ceramics were extensively studied from a mechanical and chemical point of view showing that the pyrolysis atmosphere impacts their structure and composition and, interestingly, also the evolution of the transient microporosity developed during the pyrolysis process. Furthermore, the resistance to de-vitrification and the mechanical properties (elastic modulus and Vickers hardness) were investigated. The results indicate that pyrolysis in CO_2 leads to a glass more similar to SiO_2, characterized by lower hardness, elastic modulus, and lower stability of the microporosity compared to the SiOC obtained in an inert environment. As such, the pyrolysis atmosphere can be used as a tool to provide a fine-tuning of PDCs properties and strucutre.

Engineering high-entropy carbide nanocomposites for oxygen reduction electrocatalysis in alkaline media

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Keywords: high entropy carbides, oxygen reduction reaction, nanocomposites, single source precursor

High entropy carbides (HECs) are the new class of materials that have generated considerable interest in the recent times due to the remakable improvement in properties compared to their binary couterparts. The materials have generated interest for potential applications as ultra high temperature ceramics and high hardness materials [1]. However, their usage in the applications such as catalysis has been restricted because of low surface area and agglomeration [2]. Moreover, the synthesis of HEC ceramics with controlled size, phase composition, morphology and shape remains a significant challenge.

To address this challenge single source precursor (SSP) derived ceramic route has been employed to synthesize HEC containing high surface area nanocomposites through in situ crystallization of the (VTaNbMoW)C nanoparticles in SiOC matrix. Extensive characterization of these materials revealed that the nanostrucutral features have been significantly affected by varying heat-treatment conditions indicating the possibility to tailor the properties of these ceramics. By changing the heat-treatment ramp rate from 100 °C/h to 1200 °C/h to reach a temperature of 1400 °C, the crystallize size of the high-entropy carbide increased from ~10 nm to ~25 nm accompanied by an increase in graphitization of the free carbon present in the matrix. Furthermore, these ceramics were evaluated for their electrocatalytic performance for oxygen reduction reaction (ORR). These studies exemplify the ability of compositionally complex ceramic systems to enhance electrocatalytic activity and stability by careful selection of appropriate elements. By adding Fe to the HEC lattice, the onset potential for ORR increased from 0.82 V to 0.87 V with a concomitant high stability of >97 % after 10000 s of operation. Thus the present study emphasizes that the cocktail effect in high-entropy carbides and the feasibility to get tailorable microstructures by using SSP derived PDC route can be leveraged to attain favorable electrocatalytic properties.

Acknowledgments

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Polymer-derived silicon oxycarbide as support material for ionic liquid phases for heterogeneous catalysis

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Keywords: polymer-derived ceramics, ionic liquids, freeze-casting, CO_2 utilization, catalysis

Supported ionic liquid phases (SILPS) are highly promising catalysts for a wide variety of organic synthesis reactions, but require suitable carrier structures for high performance. In this work, polysiloxane-derived silicon oxycarbides (SiOCs) were investigated as novel, alternative carrier materials and compared to conventional SILPs using mesoporous silica (SiO_2). The heterogeneous SILP catalysts were tested for the production of limonene carbonate by cycloaddition of CO_2 to limonene oxide, stating an interesting high value product. In a first step, a screening of SiOCs derived from precursors after pyrolysis at various temperatures (300-900 °C) was conducted. The particulate support materials were impregnated with tetrabutyl ammonium halides (TBAX, X = Cl-, Br-, I-) and were investigated in batch mode for the model reaction, yielding excellent selectivities of 97-100 % and yields of 53-62 % for SiOC-SILPs. Differences in the surface characteristics and the affinity to water between SiO_2 and SiOC were correlated with the effect that SiO_2-SILPs triggered the formation of diol as a by-product, leading to a lower selectivity of 87 % and a lower yield of 48 %, respectively. Subsequently, macroporous monolithic SiOC-SILPs with suitable permeability characteristics ($k_1 = 10^{-11}$ m^2) were produced via freeze-casting and successfully used as base for monolithic reactors for the selective and continuous production of limonene carbonate in supercritical CO_2. Constant product output over 48 h without concurrent catalyst leaching was achieved, rendering these polymer-derived support materials highly promising for future SILP-related applications owing both to their catalytic performance as well as their immense flexibility in shaping and structural tailorability.

Acknowledgments

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Development of a lamellar Zn-Mg-Al base coating for corrosion protection of steel in salt water

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Keywords: corrosion protection, lamellar Zn-Mg-Al coating, saltwater corrosion, preceramic polymer derived coating

Lamellar zinc coatings are widely used in automotive industry to protect steel parts from corrosion. They often consist of flake like or spherical shaped zinc fillers in combination with aluminum and/or magnesium in an epoxy resin matrix. The advantage of such lamellar coatings is the high corrosion protection of steel in salt water environments while the coating thicknesses can be kept low. The matrix materials of such coatings are often epoxy resins. They show a limited application temperature and chemical resistance which entails a restricted field of applications. Polymer derived ceramic (PDC) precursors like polysilazanes are an interesting class of material which stand out due to their chemical inertness and good adhesion to metals. At a few hundred degrees of Celsius, polysilazanes convert gradually into ceramic materials with a high temperature stability. Furthermore, they can be easily applied by spray coating methods with adjustable coating thickness. These properties make them an interesting candidate for an alternative matrix material for corrosion protection coatings.

Therefore, this study focuses on the development of a lamellar zinc coating using the polymer derived ceramic route. First, the amounts of the zinc, magnesium and aluminum fillers were varied in order to achieve the best corrosion protection performance showing the strong influence of the magnesium content on the corrosion protection performance in salt water. The highest protection was achieved at a magnesium content of 30 vol.%. Subsequently, the emphasis was placed on the investigation of the influence of a thermal curing on the microstructure and the corrosion protection properties of the lamellar coating system. SEM images showed a densification of the porous base coat with increasing treatment temperature. Only from 400 °C onwards, an oxidation of zinc and a dissolution of the zinc magnesium phase were observed by XRD measurements. This demonstrates the coatings can be used up to a temperature of 400 °C. Additionally, artificially scratched samples were tested in the salt spray corrosion test according to DIN EN ISO 9227. After a duration of 240 h red rust was formed in the scratch while Simonkolleite and a zinc aluminum carbonate hydroxide hydrate were the main corrosion products on the coating surface.

T3 Ceramics for Environmental Systems

T3.1 PHOTOCATALYSTS FOR ENERGY AND ENVIRONMENTAL APPLICATIONS

Synthesis and application of high entropy oxides nanoparticles for photocatalytic hydrogen production

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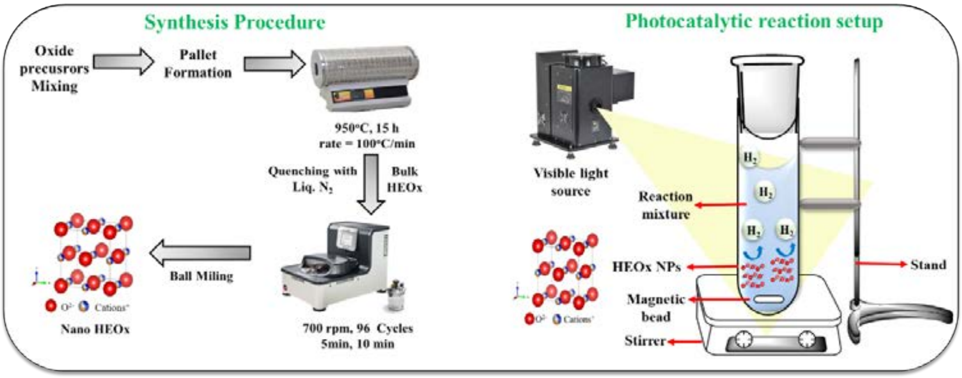
Keywords: HEOx, hydrogen production, photocatalysis, nanoparticles, water spliting, visible light

Hydrogen has been widely recognized as a potential source of clean energy for the next generation due to its ultra-high energy density and zero emission. However, the conventional methods utilized for hydrogen production (e.g., methane reforming and biogas stream reforming) are accompanied by the releases of greenhouse gases (e.g., CO_2) into the environment. Therefore, the photocatalysis of water to produce green hydrogen has been considered as an ideal option from economic and environmental viewpoints. In recent years, the high entropy oxides (HEOx) with five or more cations randomly distributed in the cationic site of the structure have gained growing attention in the area of catalysis/photocatalysis mostly attributed to highly tuneable optical properties [1, 2]. Moreover, the synergy between multi-element in HEOx provides a diverse range of adsorption and defects sites (e.g., oxygen defects) to facilitate the catalytic process [3, 4].

In this respect, the present work describes the photocatalytic potential of rock-salt HEOx nanoparticles for photocatalytic hydrogen production with visible light. The materials were synthesized via a new and easy-to-implement process combining solid-state high temperature reaction and mechanical ball-milling. A series of HEOx nanoparticles were formed by varying the process conditions and their impact on optical properties and hydrogen production will be discussed. Overall, It was observed that the HEOx NPs exhibited 8-fold higher photocatalytic activity relative to bulk HEOx.



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Photocatalyst materials for green hydrogen production and CO_2 utilization

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Keywords: photocatalyst, artificial photosynthesis, green hydrogen, carbon dioxide

Photocatalytic water splitting is a challenging reaction because it is an ultimate chemical reaction to create a carbon neutral society and to solve resources, energy and environment issues [1]. Photocatalytic CO_2 fixation has also attracted attention from a viewpoint of carbon capture and utilization (CCU) to contribute to the carbon neutral. These reactions can be regarded as artificial photosynthesis, because light energy is converted to storable chemical energy. In the present paper, photocatalyst materials for water splitting and carbon dioxide reduction have been introduced.

Rh, Ir, Ru-doped $SrTiO_3$ functions as a single particulate photocatalyst for water splitting to produce green hydrogen under visible light irradiation and simulated sunlight irradiations. Rh-doped $SrTiO_3$ photocatalyst responded to 500 nm [2]. Moreover, Ir and Ru dopants made $SrTiO_3$ visible light responsive to 600-700 nm.

$SrTiO_3$:Rh of a H_2-evolving photocatalyst and $BiVO_4$ of an O_2-evolving photocatalyst constructed various type of Z-schematic photocatalyst systems with $[Co(bpy)_3]^{3+/2+}$ and a conductive reduced graphene oxide (RGO) as an electron mediator and even without an electron mediator [3]. Metal sulfide photocatalysts that are normally unstable for water splitting into H_2 and O_2 in the absence of an electron donor were able to be employed for a Z-schematic photocatalyst system and a photocathode for water splitting [4].

Ag/$NaTaO_3$:Ba photocatalyst gave ca. 90% of the selectivity for the CO_2 reduction to form CO using water as an electron donor without any sacrificial electron donors [5]. It was also found by further surveying of cocatalyst that Rh-Ru/$NaTaO_3$:Sr continuously produced CH_4, H_2, and O_2 under UV irradiation [6]. The selectivity for CH_4 formation based on the number of reacted electrons was about 10%. An e^-/h^+ ratio estimated from obtained products was almost unity and TON based on the CH_4 formation to Rh and Ru cocatalysts was 2.0. These results have proven that CH_4 was obtained by photocatalytic CO_2 reduction using water as an electron donor over the Rh-Ru/$NaTaO_3$:Sr. Thus, an uphill reaction of CO_2 reduction accompanied with water oxidation was achieved using the Ag-loaded metal oxide photocatalysts with wide bandgaps.

A Z-scheme system employing the bare $(CuGa)_{0.5}ZnS_2$ photocatalyst and RGO-(CoO_x/$BiVO_4$) as an O_2-evolving photocatalyst produced CO of a CO_2 reduction product accompanied with H_2 and O_2 in a simple aqueous suspension system without any additives under visible light irradiation and 1 atm of CO_2 [7]. The selectivity for the CO formation of the Z-schematic CO_2 reduction reached 10 – 20% even in an aqueous solution and without loading any cocatalysts on the $(CuGa)_{0.5}ZnS_2$ metal sulfide photocatalyst. It is notable that CO was obtained accompanied with reasonable O_2 evolution indicating that water was an electron donor for the CO_2 reduction.

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Ultrahigh piezocatalytic performance of perovskite ferroelectric powder via oxygen vacancy engineering

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Keywords: piezocatalysis, oxygen vacancy, perovskite ferroelectrics, degradation

Piezocatalysis, utilizing the piezopotential and piezoelectric activity of catalysts, has emerged as a promising strategy for green catalysis, with applications ranging from hydrogen production to wastewater treatment. Despite its potential, the practical application of piezocatalysis is hindered by the low activity of existing materials. In this study, we propose a novel approach to significantly enhance the piezocatalytic activity of a high-piezoelectricity perovskite ferroelectric, Sm-doped $0.68Pb(Mg_{1/3}Nb_{2/3})$-$0.32PbTiO_3$ (Sm-PMN-PT), through the introduction of oxygen vacancies (OVs).

The results show that the presence of OVs promotes the production of reactive oxygen species while enhancing the adsorption and activation of organic pollutants to improve piezocatalytic performance. The OV-Sm-PMN-PT is found to possess a superior piezocatalytic degradation rate constant of 0.073 min^{-1} under ultrasonic vibration, which is approximately 4.9 times higher than that of pristine Sm-PMN-PT. Furthermore, the OV-Sm-PMN-PT can efficiently remove RhB under 400 rpm stirring, making it a promising candidate for water purification using low-frequency mechanical energy from nature. This research sheds light on the design of piezocatalytic materials through defect engineering, opening avenues for the development of high-performance catalysts with applications in sustainable energy and environmental remediation. The synergistic combination of high piezoelectricity and oxygen vacancy engineering showcases the potential of perovskite ferroelectrics for advancing the field of piezocatalysis.

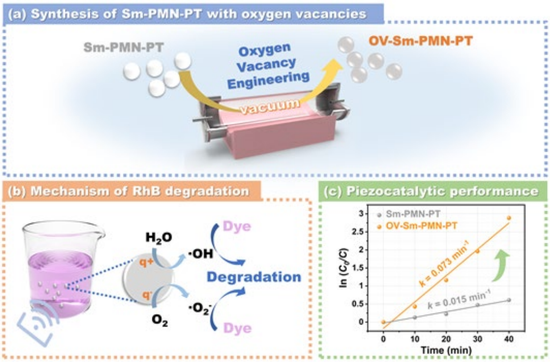

Figure 1. (a) Schematic illustration of the synthetic method of Sm-PMN-PT with oxygen vacancies; (b) Piezocatalytic mechanism diagram of RhB degradation; (c) Plots of ln(C_0/C) versus ultrasonic time and corresponding first-order rate k constants of the degradation reaction when Sm-PMN-PT and OV-Sm-PMN-PT are used as piezocatalysts.

Gas-phase CO_2 photoreduction over capped vapor–liquid–solid-grown bilayer molybdenum vanadium disulfide continuous films

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Keywords: VLS, TMDC, photocatalysis, CO_2 reduction

Towards the net zero carbon goal and to keep global warming to no more than 1.5 °C, engineering the interaction of CO_2 molecules with the surface of catalysts is the very first important step toward efficient artificial photosynthesis [1,2]. Here, we grow wafer-scale bilayer S_{vac}-$Mo_{1-x}V_xS_2$ (where S_{vac} stands for sulfur vacancy) film using an capped vapor–liquid–solid (VLS) method. The growth parameters, i.e., the thickness of the silicon dioxide capping layer, growth temperature, and layer thickness of sandwiched solid precursors in nanometer-size space, are systematically optimized (Figure 1). We show that the SiO_2 capping layer plays a triple role: (i) preventing the escape of vanadium, (ii) supplying S/H_2 into the eutectic liquid, and (iii) assisting symmetric 2D growth of grains. Cs-corrected ADF-STEM images unveil the film consists of micron-size grains. High-resolution AFM images display that the films, consisting of interconnected grains in agreement with the ADF-STEM images, have a coverage of > 97% and a Gaussian probability distribution for the height profile with an average thickness of 2.3L. Experimental observations and theoretical calculations revealed a strong correlation between V– S_{vac}, i.e., the density of S_{vac} is proportional to the amount of V, resulting in the charge density transfer from vanadium to the S and Mo atoms and significant photoluminescence quenching. 2L S_{vac}-$Mo_{1-x}V_xS_2$ demonstrates an enhanced CO_2 to CO reduction yield of ~5 times larger than the pristine MoS_2 under sunlight. We further measured the internal quantum efficiency of the photocatalytic process at 0.017% under the solar light intensity of 0.5 sun and stability of 20 h. Theoretical calculations attributed the observed photocatalytic performance mainly to the presence of a catalytic V– S_{vac} active site.

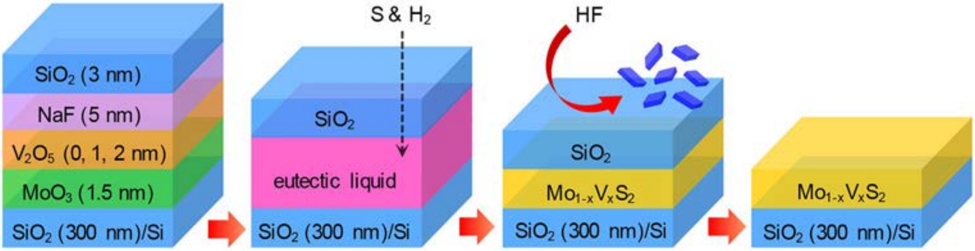

Figure 1. Geometry of the solid precursors and the growth steps.

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Enhanced photocatalytic activity of Flash-Sintered Co-doped materials

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Keywords: Flash Sintering, Co-doping, photocatalysis, Fe and Cu-doped-TiO_2**,** sustainable energy

Flash Sintering, a rapid and effective technique in materials synthesis, has exhibited promising avenues for enhancing the photocatalytic activity of materials by co-doping. For the very first-time flash sintering has been used for co-doping in any material. This method, employs intense electric field-induced heating, presents an expedited approach to fabricate co-doped materials with improved photocatalytic properties. Through the precise introduction of dopants, such as transition elements, Flash-Sintered materials demonstrate enhanced light absorption, reduced recombination of photo-generated charges, and increased surface area, thereby amplifying their photocatalytic efficiency for environmental remediation, water splitting, pollutant degradation, and other solar-driven applications. This abstract elucidates the mechanisms behind the augmented photocatalytic activity of Flash-Sintered doped materials, discusses the influential factors governing their performance, and delineates potential pathways for leveraging these materials in advancing sustainable energy and environmental technologies.

T3.2 Ceramics for Carbon Capture and Storage Technologies

A-site substitution of $Sr_{1-x}A_xTi_{0.8}Fe_{0.2}O_{3-}\delta$ perovskite in single and dual phase in combination with CGO for OTM applications

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Keywords: ceramic materials, perovskite, dual-phase materials, OTMs

Oxygen Transport Membranes (OTMs) have gained a lot of attention in recent years thanks to their wide range of applications from industrial processes to reactors for chemical production. Another promising feature is their potential to create less pollutant systems for the production of energy. OTMs are ceramic materials which should be thermo-chemically and -mechanically stable in harsh conditions such as high temperatures and reducing environments. Moreover, their stability should be guaranteed for a long time. For such reason when designing the composition of such membranes, there are a lot of conditions to take into account. [1] Dual-phase composites have gained a lot of attention since they allow highly efficient membranes by combining good and stable ionic and electronic conductors. [2] One of the most studied materials for OTMs is the well-known perovskite LSCF, which exhibits high permeability towards oxygen. However, degradation occurs when the material is exposed to high temperatures for a long time. [3]

We chose substituted $SrTiO_3$ (STO) perovskite to be the focus of our research. STO exhibits oxygen permeability when titanium is partially substituted by iron. However, high dopant levels reduce the stability of the material. In literature, a lot of works discuss further substitution of the B-site whereas A-site substitution is investigated less. Therefore, in this study 20 mol% Fe at the B-site and A-site substitution with calcium was selected, aiming in higher stability compared to full Sr-occupancy at the A-site. $Sr_{1-x}Ca_xTi_{0.8}Fe_{0.2}O_{3-}\delta$ with x = 0, 0.1, and 0.4 were synthesized and their stability and performances are studied. In addition, dual-phase membranes by adding 60 wt% of $Ce_{0.8}Gd_{0.2}O_{1.9}$ (CGO), a well-known and good ionic conductor, with the perovskites prepared. [4]

Preliminary results reveal that $Sr_{0.9}Ca_{0.1}Ti_{0.8}Fe_{0-2}O_{3-}\delta$ shows the best compromise between permeability and stability and, thus, will further be studied in more detail.

Acknowledgements
Special thanks for support to Y. Tang (IEK-1) for sample preparation and support, Dr. D. Sebold (IEK-1) for SEM-analyis, S. Heinz (IEK-1) for permeation tests. E. Malgrati (RSE) for SEM-Analysis and F,Drago (RSE) for suppoort.

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Ni-doping influence on functional properties of $SrTi_{0.65}Fe_{0.35}O_{3-\delta}$ for use as oxygen transport membranes

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Keywords: oxygen transport membrane, mixed ionic-electronic conductivity, strontium titanate, STFN

Mixed ionic-electronic conducting (MIEC) materials are promising candidates of oxygen transport membranes (OTMs). They have attracted great interests in scientific research field over the last two decades due to the high purity and energy efficiency of oxygen separation from air for different applications in catalytic membrane reactors such as partial oxidation of methane (POM). For application, the structural stability of MIEC membranes under operating conditions is a very important factor.

Pure strontium titanate, $SrTiO_3$, exhibits excellent thermodynamic stability but negligible electronic and ionic conductivity in a wide range of temperatures and oxygen partial pressures. In order to improve the conductivity, B-site doping strategy is used in this work. The $SrTi_{0.65-x}Fe_{0.35}NixO_{3-\delta}$ (x=0, 0.05, 0.075, 0.1) (STFNx) powders were synthesized by a solid-state reaction method at 1200 °C and then sintered into membranes at 1350/1400 °C for 5 h. Functionality, i.e. mixed ionic and electronic conductivity, is introduced by substitution of Ti by Fe and Ni. In addition, Ni is proven to improve the catalytic performance by exsolution phenomenon. The XRD patterns show that the materials are single phase after sintering in air. The oxygen permeance and the ionic conductivity of STFNx increase with an increasing Ni content and are close to benchmark $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ at around 850 °C, which increases with an increasing Ni content. Thermochemical stability tests were performed by annealing samples in syngas with/without H_2S and clean H_2. XRD analysis and thermogravimetry analysis (TGA) reveal that STFN005 exhibits good thermochemical stability in reducing atmospheres and the stability of STFNx decreases with increasing Ni content. Well distributed Fe/Ni exsolution can be found even with the lowest Ni amount doped material $SrTi_{0.6}Fe_{0.35}Ni_{0.05}O_{3-\delta}$ after annealing in reducing atmosphere, which will be beneficial to catalytic performance in a membrane reactor. Therefore, 5% Ni doped STFN005 can be a promising material in catalytic membrane reactors, e.g. for partial oxidation of methane (POM), due to its high oxygen permeation rate, Ni exsolution and good stability in reducing atmosphere.

T3.4 Porous and Cellular Ceramics: Porosity Design and Engineering Applications

Ceramic aerogel's porosity manipulation

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Keywords: ceramic aerogels, porosity, mesoporous structure

Ceramic aerogels are high porosity materials with nanometer-range pore sizes, resulting in low density, high surface area, low dielectric constant and low thermal conductivity. Attributable to the described properties, ceramic aerogels and their composites have many potential applications. Aerogels are prepared through sol-gel process followed by CO_2 supercritical drying to remove the solvent within the gels. As dried ceramic aerogels can have porosity as high as 97%. This research aims to manipulate the chemistries of ceramic aerogels to retain the mesoporous structure at high temperatures, for example, ratio of water/ceramic precursor, ratio of different ceramic precursors, and types of ceramic precursors. We developed aerogels that retain mesoporous structure at 1000^{o}C, or even as high as 1200^{o}C. N_2 adsorption/desorption and Scanning electron microscope (SEM) were used as the tools to characterize the pore structures of the as dried aerogels and those at high temperatures.

Novel method for characterising the porous microstructure of nuclear grade graphite materials at multiple length scales

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Keywords: fine-grained nuclear graphite, μXCT and FIB-SEM tomography, porosity, deep learning segmentation

Advanced ceramics, under various circumstances, have multiple phases and a complex porosity network across many length scales that can affect the thermo-mechanical properties of these materials. The morphological features, population, spatial distribution, and sizes of these porous microstructures can be intricate and very challenging to characterize and quantify in three-dimensional space at high spatial resolution. One of the typical examples of these porous ceramics is the high purity nuclear-grade graphite material that plays a vital role in advanced fission reactor systems and multi-megawatt (MW) class proton accelerators around the world. This work, by using industrially mass-produced nuclear-grade graphite ceramic composite material as an example, demonstrates the development and application of advanced experimental characterization techniques to study the complex porous microstructure and multiple phases over several length scales in porous quasi-brittle ceramic/composite nuclear graphite materials.

The sub-micrometer to micrometer-scale porosity in many grades of fine-grained nuclear graphite has been faithfully characterized by using a multi-length scale approach, including state-of-the-art X-ray computed micro-tomography (μXCT) and focused ion beam-scanning electron microscopy tomography (FIB-SEM tomography), providing notable findings. The developed experimental methodology has also been successfully implemented in characterizing the porosity evolution in proton-irradiated fine-grained graphite material that has experienced truly complicated irradiation conditions at Fermi National Accelerator Laboratory (Fermilab), including irradiation damage, steep thermal gradients, thermal cycling, helium/hydrogen gas production damage, and irradiation creep. A novel deep learning-based porosity segmentation method has been established to directly segment and reconstruct the sub-micrometer scale porosity, revealing porosity volumetric reduction after proton irradiation. Transmission electron microscopy has been applied to study proton irradiation damage mechanisms at the crystal lattice scale to investigate the amorphization processes at crystal lattice scale. The established experimental and computational methods are applicable to characterizing other porous ceramic materials that play crucial parts in safety-critical and advanced applications in aerospace, nuclear, electrodes, and automobile industries, just to name a few.

Tailoring microstructure via freeze-casting and gelcasting

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Keywords: gel-casting, freeze-casting, alumina, porous ceramics

Well-established techniques for tailoring the microstructure and enhancing the properties of porous ceramics are freeze-casting and gelcasting, which offer a wide range of technological applications such as thermal insulation, filtration or biomedical implants.

These techniques were used to produce porous alumina samples with varying amount of macroporosity. Within the samples the amount of solid content, equivalent to the ceramic powder content was varied between 25 – 55 vol% and thus the porosity, compressive strength and thermal conductivity were investigated. In order to avoid the lamellar pore structure resulting from static freezing in the freeze-casting process, cooling down under continuous motion was also investigated. A porosity of 38% resulted in a compressive strength of 7 MPa for static freezing, whereas an increase to 54 MPa was observed for freezing under continuous motion. In addition, an increase of 1.45 W/mK was observed in the thermal conductivity of the porous alumina from 8.89 W/mK for static freezing to 10.34 W/mK using the continuous motion approach. Compared to gelcasting, which is also a proven method for producing ceramics with porosities between 40 and 95%, the properties of the pore network can differ in terms of size, morphology and connectivity and freeze-casting. The mechanical and thermal properties of porous samples produced by the different methods are analysed and compared.

Rapid prototyping of ceramic filters via negative additive manufacturing

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Keywords: gel casting, porous ceramics, additive manufacturing, ceramic filters

The work "Rapid prototyping of ceramic filters using negative additive manufacturing" was using an innovative route to fabricate ceramic parts of high complexity by combining polymer additive manufacturing to produce sacrificial moulds and gel casting of ceramic slurries followed by use of various sintering techniques including both pressure-less and pressure-assisted techniques to optimise final characteristics of the ceramic parts. The moulds are removed through melting process or dissolving in water. The intended application for the manufactured ceramic components is for ceramic filters used in metal casting. These filters play a crucial role in the metal casting industry, as they help to remove impurities and ensure the production of high-quality metal products.

Gel casting is a colloidal forming technique that is relatively inexpensive, produces high yields with minimal defects, and has fast forming times. In this method, a ceramic suspension with organic monomers is poured into a mould which polymerizes in-situ to act as a binder. Depending on the gelling agent, the green body ideally should hold the mold cavity shape and be strong enough to handle for subsequent processing steps.

The work is also in line with Materials 4.0 scope, as it will help ceramic industry with faster manufacturing and testing of their new products/designs with the aim of moving toward mass production of those complex parts via indirect or direct AM technologies, with the latter being more readily scalable for high volume production, whilst still enabling relatively complex geometries, including functional grading, and keeping the ability to customise each part independently.

Interaction of water with heteroatoms in zeolite framework by synchrotron X-ray spectroscopy

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Keywords: zeolite framework, heteroatom, water, interaction, X-ray spectroscopy

Zeolites have a variety of catalytic properties, such as solid acidity, by controlling the framework structure, morphology, and substitution of heteroatom. Since the primary process in solid catalytic reactions is molecular adsorption, investigating the chemical state of heteroatoms during molecular adsorption is an essential issue in understanding the catalytic reaction of zeolite. In this study, the chemical state and local structure of the heteroatom (Fe) in the zeolite framework were analyzed by synchrotron X-ray spectroscopy, and the interaction of adsorbed water with Fe was discussed.

The Fe-containing MWW (Fe-MWW) type zeolite was synthesized by the mechanochemical (MC) method[1,2]. An amorphous precursor was prepared by ball-milling SiO_2 and α-FeOOH powders. A mixed aqueous solution of N, N, N-trimethyl-1-adamantylammonium hydroxide, and hexamethylenimine was mixed with an amorphous precursor to prepare the gel. The prepared gel was hydrothermally treated and calcined to obtain Fe-MWW. Characterization of the Fe-MWW was performed using XRD, UV-vis, and BET. Fe *K*-edge and O *K*-edge X-ray absorption fine structure (XAFS) spectra were measured at SPring-8 BL01B1 and BL27SU, respectively.

Only peaks attributed to the MWW structure were observed in the XRD pattern of the synthesized sample, and peaks attributed to mononuclear Fe species were observed in the UV-vis. We judged that the MWW-type zeolites with Fe incorporated into the framework could be synthesized based on these results. The difference spectrum was obtained from the O *K*-edge XAFS spectra before and after annealing at 80 ºC (Fig.1), and it was found to be similar to the XAFS spectrum of the ice type H_2O [3]. This suggests the presence of strongly hydrogen-bonded H_2O in Fe-MWW. The chemical state of the heteroatom (Fe) was traced by in situ XAFS measurement during heat treatment. Then, the spectral change with and without water showed reversible behavior, suggesting that adsorbed water strongly interacts with Fe in Fe-MWW zeolite.

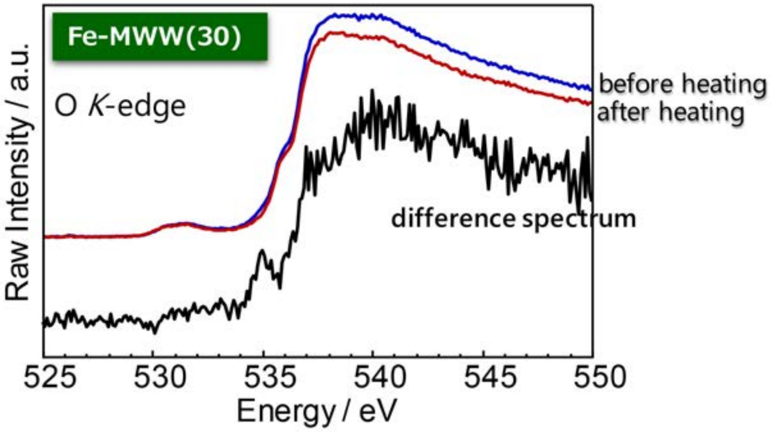

Fig. 1 O *K*-edge XAFS spectra before and after heat treatment at 80°C and their difference spectrum

Acknowledgments

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Methylated silica xerogels as self-cleaning, multifunctional materials with bacteria-repelling properties for environmental protection and biomedical applications

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Keywords: silica xerogels, hydrophobicity, oil adsorbents, bacteria-repelling ability

Hydrophobic silica xerogels (SXs) are sol-gel derived nanoporous materials synthesized via energy-efficient ambient pressure drying technique. Due to their highly developed porous network and water-repelling ability, they have been proven to be efficient as adsorbents and thermal insulators in environmental and energy-related applications. Besides that, the hydrophobic/superhydrophobic behavior of SXs can also impart some special side benefits to these materials such as "easy-to-clean" property due to the lotus effect or “bacteria-repellent” ability as a result of inhibition of biofilm formation on the material’s surface. Considering recently emerging applications of silica-based materials in the biomedical field as biocompatible scaffolds, implantable devices, or drug carriers, developing SXs with enhanced bacterial anti-adherent activity based on superhydrophobicity stands as an attractive strategy that has been rarely reported before [1].

In this study, methyl modified hydrophobic SXs were developed as multifunctional adsorbents which not only act as oil/organic solvent sorbents but also possess additional properties such as self-cleaning and bacteria-repelling abilities. SXs were synthesized via a facile two-step sol-gel method involving co-condensation reactions of a methyl functional alkoxysilane (methyltriethoxysilane (MTES)) and a tetraalkoxysilane (tetraethylorthosilicate (TEOS)). The further methylation of the samples was satisfied via surface silylation with a monofunctional silane after gelation. The impact of the application of post-gelation silylation and performing heat treatment at 200 °C after the drying stage on the hydrophobicity were investigated as process parameters. The physicochemical, textural, microstructural, and hygroscopic properties of the SXs were characterized by FTIR, SEM, N_2 sorption analyses, and contact angle measurements. The results have shown that increasing the degree of methyl substitution altered the morphology of SXs from a micro/mesoporous to a hierarchical macro/mesoporous nature and increased the size of the secondary silica particles. Applying silylation slightly increased the samples’ hydrophobicity whereas post-drying heat treatment has not caused a significant impact on the hydrophobic behavior of the SXs. The samples obtained with a low density (<0.1 g/cm^3), high porosity (> 95 %), and enhanced hydrophobicity ($\theta>139°$) were then tested on batch oil sorption set-up to reveal their adsorptive performance on the removal of several oils and organic solvents from wastewater. The sorption results confirmed their efficiency as adsorbents with high oil/organic solvent sorption capacity (15.2 g/g) and regeneration ability (up to 8 cycles). The xerogel with the highest hydrophobicity (150°) has also exhibited excellent self-cleaning behavior. Bacterial anti-adhesive properties of the SXs were also investigated via dip-inoculation in bacterial suspensions containing model bacteria E. coli and S. aureus. Bacterial growth on the xerogel surfaces was observed via SEM analysis and results confirmed the drastic inhibition of the bacterial attachment on the superhydrophobic samples compared to hydrophilic SXs. In conclusion, methyl modified silica xerogels with superior hydrophobicity were found to be highly promising both as adsorbents in environmental remediation applications and as multifunctional hygienic materials for biomedical applications in the future.

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T3.5 Advanced Sensors for Energy, Environment and Health Applications

Layered MBene-MoB for sensitive electrochemical detection of heavy metal ions Cd^{2+}, Pb^{2+}, Cu^{2+} and Hg^{2+}

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Keywords: MoAlB, MBene, etching, electrochemical sensor, heavy metal ions

The emerging transition metal boride layered nanomaterials, known as MBenes, have attracted considerable attention due to their remarkable electronic conductivity, stability, and diverse surface chemical properties. However, a comprehensive exploration of their synthesis techniques and electrochemical applications remains imperative. This study presents a novel approach involving the controlled etching of MoAlB in fluoride-free acidic/alkaline solutions. Under hydrothermal conditions, complete aluminum removal was achieved in dilute alkaline solutions, leading to the fabrication of pristine single/few-layer Mbene-MoB for the first time. In acidic media, etching rates reached a maximum of 33%. We elucidate the viable reactions in dilute acid and alkali etching at room temperature through thermodynamic and kinetic analyses. XRD refinement, tracking aluminum removal from 0% to 100%, unveiled transient metastable phases of $MoAl_{1-x}B$ ($x<0.5$) in the initial etching stages, evolving into relatively stable pure Mo_2AlB_2 structures with 50% aluminum consumption, serving as a precursor to Mbene formation. The subsequent loss of aluminum resulted in a two-dimensional MBene-MoB structure. Density functional theory (DFT) calculations confirm excellent conductivity for MoAlB, $MoAl_{1-x}B$ ($x=0\sim1$), and MBene-MoB.

The MBene-MoB modified glassy carbon electrode (GCE) exhibits excellent detection limits for heavy metals, including divalent cadmium, lead, copper, and mercury, in water. Due to its unique multilayer structure and outstanding conductivity, it can detect concentrations below drinking water standards. In the future, we aim to extend its application to the simultaneous detection of various heavy metals and organic pollutants.

Figures

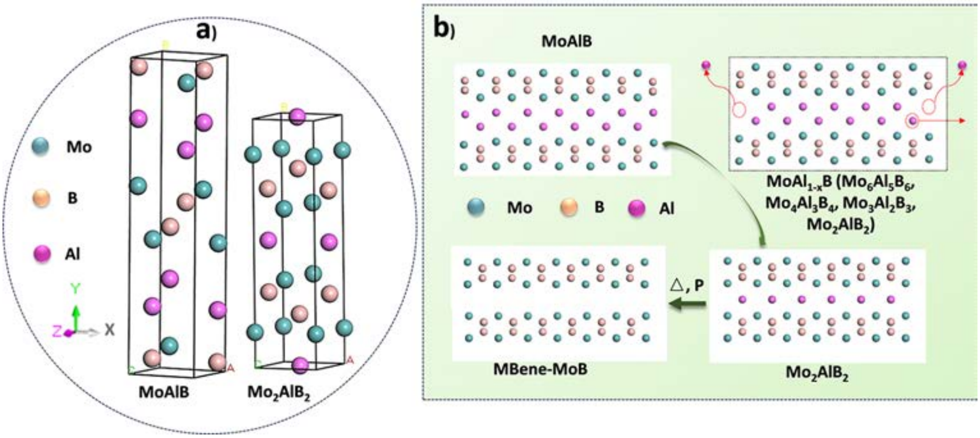

Figure 1 a) Crystal structures of MoAlB and Mo_2AlB_2, b) schematic diagram of the aluminum removal process from MoAlB.

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T3.6 Advanced Materials and Membrane Technologies for Sustainable Water Purification and Desalination Systems

Application of ceramic membrane in advanced oxidation process (AOP) for removing contaminants of emerging concern (CECs) in wastewater

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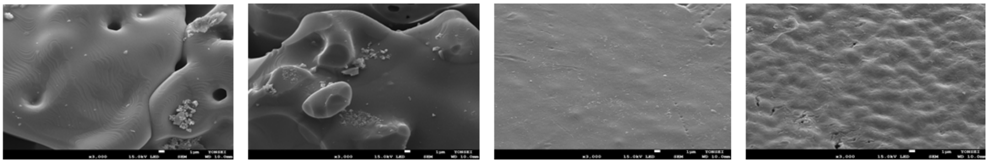
Keywords: ceramic membrane, AOP, CECs, wastewater

Residual pharmaceuticals and perfluorinated compounds that are newly discovered in the water system are causing serious harm to humans and the ecosystem, and to this end, there is a growing movement in developed countries to legally regulate and dispose of these substances[1]. These substances have clear limitations in commonly applied biological treatments, and recently, various advanced oxidation processes have been proposed to be applied at the end of biological treatments. However, the indiscriminate oxidation of OH radicals generated in AOP has the disadvantage of making it difficult to apply organic membranes, which have excellently effecient for turbidity in treated water. We were to solve this drawback by using a ceramic membrane that is resistant to oxidation. Therefore, in this study, to evaluate the oxidation resistance of organic and ceramic membranes in ozone based AOP, ozonated water injected with ozone gas at a concentration of 10 g/m^3 was filtered through membranes for 5 days, respectively. The operated membranes were analyzed through field emission scanning electron microscopy (FESEM), energy dispersive spectrometer (EDS) and fourier transform-infrared (FT-IR) spectroscopy. Results showed more severe structural changes of the organic membrane surface. In addition, for the long-term effects of residual ozone on the ceramic membrane for 30 days, structural changes were evaluated using the same experimental methods at NaOCl 3000 mg/L having the same ORP with ozone 0.5 mg/L. Finally, based on the study of these structural changes, it was confirmed that the operation of a ceramic membrane containing residual ozone in real wastewater from a sewage treatment plant was improved through a significant delay in cleaning periods compared to the operation of a ceramic membrane in the absence of ozone.



after 24 hr after 120 hr after 24 hr after 120 hr
Ceramic membrane Organic membrane

Figure 1. FESEM image comparing ceramic membrane and organic membrane

Table 1. EDS results showing element changes of organic membrane after ozone exposure

Membrane Material	Ozone exposure time	% elemental analysis		
		Carbon	Oxygen	Nitrogen
Polyacrylonitrile (PAN)	Control (0 hr)	58.7	29.3	12.0
	24hr	68.4	4.5	27.1
	120hr	68.9	4.7	26.9

Acknowledgments

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T4 Cross-Cutting Materials Technologies

T4.1 COMPUTATIONAL DESIGN AND MODELING

Characterization and simulation by discrete elements of the early sintering stages of silica-based ceramics shaping by additive manufacturing and uniaxial compaction

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Keywords: silica, sintering, simulation, discrete elements, microstructure

The aim of this research is to perform discrete-element modeling of the sintering behavior of silica-based ceramics produced by additive manufacturing. These silica-based refractory structures are designed as thermal insulators for high temperature applications. Discrete-element modeling is developed to well understand sintering behavior of produced ceramics and to optimize sintering conditions, ultimately ensuring the quality and reproducibility of the manufactured parts. The development of this numerical tool is based on a detailed characterization of the material's sintering behavior and an in-depth understanding of material transport processes and driving forces. These forces affect granular rearrangement and interparticle bridge formation during the early stages of consolidation. It is essential to predict consolidation and densification kinetics by understanding the laws of micromechanical interaction between particles. These numerical developments will be carried out within the GranOO discrete-element calculation code [1].

A commercial amorphous silica powder has been selected. It exhibits spherical particles and a quasi-monodisperse size distribution around a mean value of a few µm. The first part of this work has been devoted to: finely characterize the raw powder; study its shaping by stereolithography and compare it to compaction by uniaxial pressing without additives; analyze and compare the thermal and sintering behavior of the raw materials obtained. The glass transition has been identified in the temperature range 880-960°C by thermogravimetry. No crystallization is detected up to 1300°C. Analyzes of measured shrinkage kinetics have allowed to verify a viscous flow densification mechanism over the selected temperature range and to estimate the associated apparent activation energy. The microstructure evolution during sintering has been finely characterized using FIB-SEM micrographs of samples sintered at different stages. The second part consists in adapting the solid phase sintering model available in the literature in order to be applied to the case of viscous flow sintering in the discrete element method. The reliability of the built model has been validated by comparison with experimental data. A good match is noticed at the macroscopic scale with dilatometric analyses. The effect of the shaping mode is analyzed on the evolution of the microstructure in the early stages of sintering (evolutions of particle shape, particle size distribution, size of interparticle bridges and porous architecture). Figure 1 shows 3D representation of a pellet sintered at 1200°C at a rate of 10°C/min, the bridge size distribution is shown in color with a maximum size value of 30% of the particle radius. This oral presentation will focus on the second part of this work, dedicated to numerical aspects.

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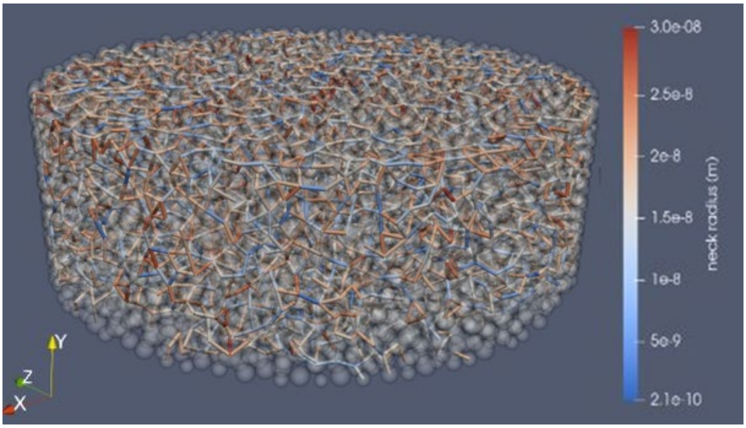

Figure 1: 3D view of the sintered granular stack

Effect of extrinsic and intrinsic defects on halide ion migration in Lead-Iodide perovskite

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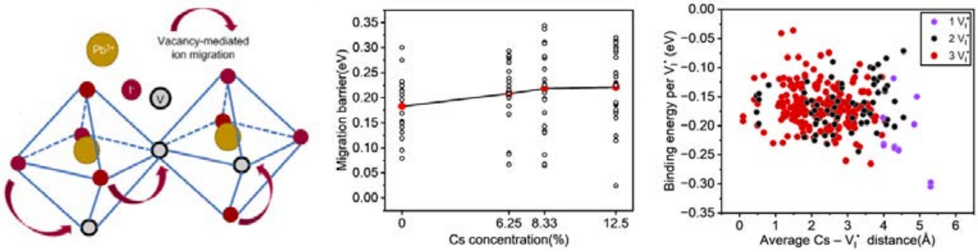
Keywords: atomistic modelling, defects, ion migration, perovskite

Since the advent of discovery of halide perovskite, defect chemistry in Methylammonium Lead Iodine($MAPbI_3$) has played a significant role in determining the potential of this material towards photovoltaic applications. Various partial cation[1] and anion substitutions have been reported to study and suppress ion migration phenomenon and attempts have been in the direction to achieve a more stable perovskite structure. In the current work, force field based atomistic simulations are performed in GULP to understand the effect of Cs concentration on ionic migration in Methylammonium Lead Iodide. Nudged Elastic Band simulations were used to calculate the Iodine ion activation barrier varying the size of supercell to obtain different Cs concentrations. Iodine migration in $CH_3NH_3PBI_3$ is conventional vacancy hopping through immediate neighbouring positions[2](figure 1a). The activation energy barrier of Iodine jumps which occur within the octahedral is found to increase in the doped Cs-MAPI(figure 1b) when compared with the un-doped one at different concentrations of Cs(x = 6.25%, 8.33%, 12.50%), thus ion migration is suppressed which is due to the favouble V_I– defect binding(figure 1c) leading towards a more stable structure of perovskite. Experimental validation has been conducted for the Cs-doped perovskite films.

We also calculate the energetics of formation of various intrinsic defects namely Lead antisite, Lead interstitial, Methylammonium vacancy, Lead vacancy, and Iodine vacancy in $MAPbI_3$ through force field based atomistic simulations and first principles calculations[3]. Effect of these defects on halide ion migration is investigated. The creation of Iodine vacancy becomes relatively easier in the defected system when compared with pure $MAPbI_3$, which is due to lesser breaking of bonds in the defected system and also the electrostatic attraction between the charged defects. Energetically favourable defect complexes are formed which cause binding of Iodine vacancy with these defects thus leading to a higher activation energy values of Iodine ion migration in the defected systems. First principle analysis of the charge distribution shows effective polarization near to the defect centre which causes defect-induced structural distortions. Interestingly, from the electronic structure calculations, we find that the defects do not perturb the valance and conduction band edge states and therefore, are not detrimental for the optoelectronic properties.



(a) **(b)** **(c)**

Figure 1. **(a)** Schematic picture of vacancy mediated ion migration process in perovskite. **(b)** Scatter plot of Iodine migration barriers as function of Cs concentration. Multiple point for a single concentration correspond to different ionic jumps and red filled circles correspond to the average value of migration barrier. **(c)** Binding energy per iodine vacancy for defect clusters of one Cs_{MA} and one to three V_I. Negative values indicate energetically favourable binding.

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Compositional design and phase formation capability of multicomponent rare-earth disilicates via machine learning

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Keywords: high entropy, stability, rare earth disilicate, environmental barrier coating

Rare earth disilicates ($RE_2Si_2O_7$) exhibit great potential for environmental barrier coating (EBC) application due to their excellent resistance to molten CaO-MgO-Al_2O_3-SiO_2/water vapor, low thermal conductivity, and compatible thermal expansion coefficients with SiC_f/SiC ceramic matrix composites substrates [1-5]. A crucial approach to design environmental barrier coatings involves incorporating multiple rare-earth (*RE*) components into *β*- and *γ*-$RE_2Si_2O_7$ for achieving multifunctional performance optimization. Nevertheless, the polymorphic phase presents significant challenges for the design of multicomponent *RE* disilicates. Here, a machine learning (ML) method based on decision fusion is developed to identify multicomponent *RE* disilicates, demonstrating remarkable accuracy in prediction. Well-trained ML models assess the phase formation capability of 118 unreported $(RE1_{0.25}RE2_{0.25}Yb_{0.25}Lu_{0.25})_2Si_2O_7$ and $(RE1_{1/6}RE2_{1/6}RE3_{1/6}Gd_{1/6}Yb_{1/6}Lu_{1/6})_2Si_2O_7$, further validated by first-principles calculations. Model visualization elucidates essential factors governing the formation of $(RE1_{0.25}RE2_{0.25}Yb_{0.25}Lu_{0.25})_2Si_2O_7$, such as the average radius of RE^{3+} and variations in different RE^{3+} combinations. On the other hand, $(RE1_{1/6}RE2_{1/6}RE3_{1/6}Gd_{1/6}Yb_{1/6}Lu_{1/6})_2Si_2O_7$ formation requires the consideration of the average mass and electronegativity deviation of RE^{3+}. This work integrates material-oriented ML methods with the formation mechanisms of multicomponent *RE* disilicates, facilitating the efficient design of superior materials with exceptional properties for EBC applications.

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Revealing ion velocity effect on ionization-induced recovery in defective $KTaO_3$

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Keywords: $KTaO_3$, defect analyses, defects simulation, velocity effect

Interest in ion beam modification of potassium tantalate ($KTaO_3$) properties has rapidly expanded in the last decade[1,2], fueled by the tunability of its optical and electronic properties through irradiation-induced defects[3], which makes $KTaO_3$ a promising candidate for future optoelectronic and spintronic applications [3,4]. All these applications require effective control of the structural modification, but this is an extremely difficult task, since it demands in-depth knowledge of the interactions of ions with the local defect states in the corresponding material and the resulting evolution of radiation damage[5]. In this regard, effects of electronic to nuclear energy losses (S_e/S_n) ratio on damage evolution in defective $KTaO_3$ have been investigated by irradiating pre-damaged single crystal $KTaO_3$ with intermediate energy O ions (6 MeV, 8 MeV and 12 MeV) at 300 K. By exploring these processes in pre-damaged $KTaO_3$ containing a fractional disorder level of 0.35, the ion channeling results demonstrate the occurrence of a precursory stage of damage production before the onset of damage annealing process in defective $KTaO_3$ that decreases with O ion energy. In addition, the reduction of disorder level is accompanied by the broadening of the disorder profiles into greater depth with increasing ion fluence, and enhanced migration is observed with decreasing O ion energy. Since S_e (~ 3.0 keV nm^{-1}) is nearly constant at all 3 ion energies, the difference in behavior is a natural consequence of the "*velocity effect*". As consequence of the so-called "*velocity effect*", the S_e is confined to a smaller volume in case of the low velocity ions leading to a higher energy density. Therefore, for equal values of S_e, enhanced ionization-induced annealing process is expected for the smaller ion velocity/energy (i.e., 6 MeV O). The inelastic thermal spike calculation has further confirmed the existence of a velocity effect, not previously reported in $KTaO_3$ or very scarcely reported in other materials for which the existence of ionization-induced annealing has been reported.

Acknowledgments

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DE-AC07-05ID145142. Zarkadoula was supported by the Center for Nanophase Materials Sciences, (CNMS), which is a US Department of Energy, Office of Science User Facility at Oak Ridge National Laboratory.

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T4.2 ADDITIVE MANUFACTURING & 3D PRINTING TECHNOLOGIES

Feasibility of coupling novel rapid sintering technologies with additive manufacturing

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Keywords: additive manufacturing, debinding, sintering, rapid

Usually, ceramics are fabricated and consolidated by sintering powder compacts, but structures with complex geometries are difficult to produce due to limitations in the mould design. Additive manufacturing (AM) allows fabricating complex geometries with fewer constraints compared to the conventional fabrication techniques. On the other hand, it is becoming more evident that the bottleneck of these technologies is not represented by the printing process itself, but also by the slow thermal debinding and sintering, typically requiring several hours or days. In the recent years, ultrafast sintering techniques have gained popularity as a way to reduce the processing time and energy consumption of the ceramic industry.

In light of this, the discussion will concentrate on the outcomes that were accomplished via the use of innovative sintering procedures for the purpose of achieving quick debinding and sintering of additively manufactured components fabricated with different techniques. Additionally, the difficulties that were involved with the procedure will be discussed. In fact, this approach of shaping and sintering complex-shaped ceramics has the potential to provide an energy-efficient alternative to conventional techniques such as pressureless sintering, hot pressing, etc.; hence representing a small step in the direction of addressing the current energy crisis. Such a flexible, economically viable approach could be extended to a wide range of complex geometries and compositions.

Acknowledgments

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Advances in additively manufactured sodium-beta-alumina solid state electrolytes

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Keywords: sodium-beta-alumina, additive manufacturing; 3D printing; ceramic electrolytes, energy storage

Additive manufacturing (AM), also known as 3D printing, has the potential to revolutionise battery production by offering precise control over material properties and enabling the creation of intricate geometries. This project investigates the use of AM to fabricate solid-state electrolyte structures using sodium beta-alumina ceramic oxides.

Two prominent AM techniques for ceramics – Direct Ink Writing (DIW) and Digital Light Processing (DLP) – were employed to create a variety of solid electrolyte structures. High-solids-loading feedstocks with suitable rheological properties were developed specifically for each AM process.

The 3D-printed test structures, along with conventionally densified counterparts, underwent comprehensive characterisation using various techniques to evaluate their physical, structural, and electrochemical properties relevant to battery performance. This research aims to advance our understanding of AM's potential to improve battery technology.

Acknowledgments

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Fabrication of 8-YSZ/LSM SOFC symmetric cells by 3D-printing

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Keywords: electrolyte, cathode, symmetric cCells, 8-YSZ, LSM, 3D-printing, SOFCs

Fuel cell technologies are expected to substantially reduce oil dependency and hence the greenhouse gases emissions. Among the different types, Solid Oxide Fuel Cells (SOFCs) can be fed with different types of fuels exhibiting high energy efficiency, especially when high temperature exhaust gases are used for cogeneration or hybrid applications [1]. Currently, 3D-printing technologies offer several advantages compared to conventional manufacturing processes, including the development of alternative geometries to improve the volumetric and gravimetric energy density and optimise the Triple Phase Boundary (TPB), in addition to reduce the fabrication costs and waste disposal. Focusing on Fused Filament Fabrication (FFF) 3D printing, we have fabricated electroactive components for SOFCs to assess its potential application as alternative manufacturing procedure [2].

We have produced thermoplastic filaments the state-of-the-art electrolyte (YSZ) and cathode (LSM) [3].The rheological characterisation in the 180-220 °C temperature range, i.e. 3D printing range, revealed that the store modulus, G’ is higher than loss modulus, G’’, the complex viscosity, η*, increased with the temperature. Symmetric LSM-YSZ cells were fabricated using two alternative printing designs: first, sequential printing of LSM-C electrodes on both sides of the YSZ electrolyte, and second, one-step printing of LSM-C+YSZ+LSM+C layers in the search for improved interfacial adherence. Optimised debinding and co-sintering rendered high quality electrolyte-electrodes interfaces (Fig. 1). The 3D printed symmetrical cells exhibited R_s and R_p **values of 0.26** $\Omega cm^{-1}$and 0.30 Ωcm^2 at 900 °C in air, respectively, close to the commonly accepted reference, i.e. 0.27 Ωcm^{-1} and 0.4 Ωcm^2 [4].

Figure

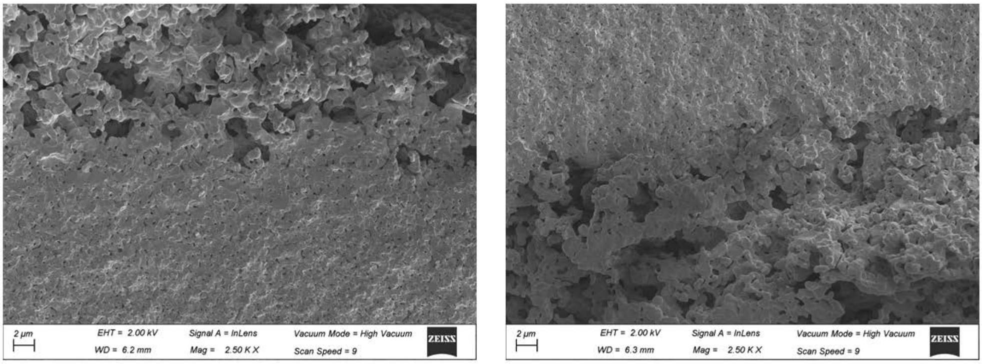

Figure 1: Interface LSM/YSZ after co-sintering process.

Acknowledgments

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T4.3 Novel, Green, and Strategic Processing and Manufacturing Technologies

Surface modifications of soda lime silicate glasses to achieve silky matte glass surfaces

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Keywords: soda lime glasses, silky matte glasses, wet coatings, surface roughness

Glass products are widely used in the automotive, white goods and construction fields. Among these, especially the glasses used in the white goods industry has gained importance today. A lot of research is conducted on resistance to staining with the development of touch panels. The degree of mattnes on the surface reduces staining caused by fingerprints. Today HF acid etching, sandblasting and other mechanical etching methods are the most commonly used surface mattification methods. Sandblasting methods reduce the mechanical properties because they modify the surface by scratching it. On the other hand acid etching method has many harms to humans and nature and waste generated after process. The aim of this study was surface modification with wet coating application. The method includes the stages of coating the prepared mixture on the surface and heat treatment. The most important contribution of this process is being environmentally friendly and eliminating the risk of diseases due to manufacturing process when we think of conventional routes like acid etching. This being more important day to day in this era. Another attractive point of this environmentally friendly process is its compatibility with manufacturing route. The working temperatures were close to tempering temperatures and the heat treatment process can be carried out in the tempering furnace. It doesn't require any extra steps which can increase the energy consumption and cost of the production. The working temperatures were close to tempering temperatures and the heat treatment process can be carried out in the tempering furnace.

As a result of the experimental studies, surface roughness, gloss measurement, Uv- Vis Transmission performance and SEM analyzes were applied to determine the related properties. According to the test results, the best results were obtained for talc mixtures after heat treatment at 625 °C for 1 hour. In addition, water solubility resistance of the layer on the surface after the applied method was evaluated by examining the effects of ultrasonic cleaning process on the surface roughness.

Carbon contamination prevention during spark plasma sintering of transparent MgO and YAG

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Keywords: MgO, YAG, transparent ceramics, SPS

Optically transparent ceramics are essential for a variety of optical applications. Spark plasma sintering (SPS) enables rapid sintering at relatively low temperatures, which limits grain growth during densification and can improve transparency. Carbon contamination from graphite molds during SPS significantly affects the materials properties, especially their transparency. Here, we present two approaches that address this issue: 1) using LiF as a sintering aid and physical buffer against carbon contamination; 2) applying Ta and Mo foils as diffusion barrier against carbon.

Highly transparent MgO and YAG ceramics were prepared via SPS by optimal incorporation of LiF. The effect of LiF content on the microstructural and optical properties of MgO will be presented with emphasis on its function as a densification aid and an agent for minimizing residual carbon contamination. Fully dense MgO discs, 20 mm in diameter and 2 mm thick, with ~80% in-line transmission at 800 nm and >85% transmission in the infrared range (2−6 µm), are attained. These results demonstrate outstanding transparency only 7% below the theoretical value. In addition, this work strengthens the understanding of LiF action mechanism during sintering as a lubricant and as a gas-phase buffer minimizing inward diffusion of carbonaceous gasses.

A second approach to minimize carbon contamination using metallic foils of tantalum and/or molybdenum adjacent to the samples will be discussed as well, and demonstrated on transparent YAG. These findings pave the way for fabrication of large, fully dense transparent MgO and YAG samples with nearly theoretical transparency.

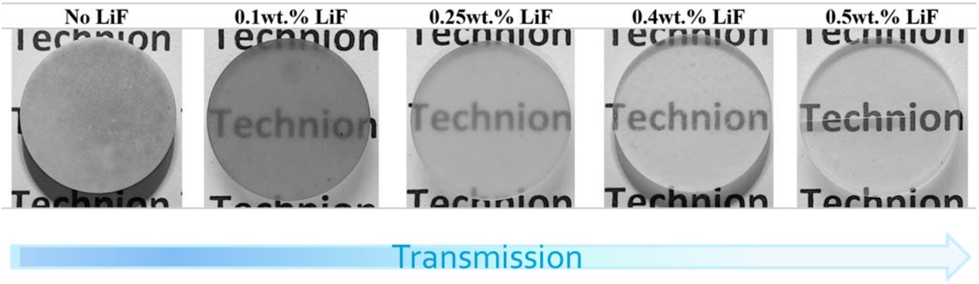

Figure 1: Polished MgO discs sintered with different LiF concentrations of 0–0.5 wt % (Ø = 20 mm, H = 2 mm).

Mechanical properties of cold sintered ceramics

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Keywords: cold sintering, strength, fracture toughness, scaling up, fractography

Among the different alternative low temperature sintering techniques, the cold sintering process (CSP) enables densification of ceramics at temperatures below 350°C. The process is driven by a chemo-mechanical effect activated by a compatible transient liquid phase and high pressure. This study aims at optimizing the processing conditions in CSP, taking into consideration the effect of liquid phase chemistry, heating rate and homogeneity of applied pressure on the density and structural integrity of cold sintered parts. A combination of biaxial bending and fractographic analyses were employed to identify macroscopic strength-limiting flaws. It was found that the strength of cold sintered samples can be remarkably compromised by improper processing conditions associated with temperature and/or pressure gradients related to insufficient tooling quality, resulting in delamination effects. The prevention of such defects is demonstrated by appropriate selection of the processing parameters in CSP, resulting in structurally reliable cold sintered ZnO samples with strengths exceeding 100 MPa. Based on these findings, scaling-up the CSP was successfully demonstrated– an important step toward its industrial implementation.

Development of rice husk composite ceramic sphere with enhanced radiation heat transfer for high temperature

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Keywords: rice husk, ceramics, rapid heat storage and release, radiation heat transfer, regenerative burner systems

As global greenhouse effects become increasingly severe, a significant amount of carbon dioxide is produced annually, with the industrial sector contributing the largest share[1, 2]. Additionally, a considerable portion of energy generated during industrial production processes is not utilized effectively[3]. Consequently, the development of Thermal Energy Storage systems has become a focal point. Currently, mid to low temperature range applications have been extensively researched and explored. However, the study of high-temperature applications, specifically those involving storage temperatures exceeding 600°C, remains insufficient and faces numerous challenges. Therefore, Regenerative burner Systems have been gradually developed and applied. The capability of heating ambient air in a short time, and the advantage of energy saving through alternating heat storage and release states. The key to enhancing the efficiency of regenerative burners lies in the heat storage medium within the heat storage tank. Currently, alumina solid spheres are widely used, but there are still issues such as low total heat storage and heat storage density, as well as slow heat transfer rates. Therefore, developing a heat storage medium with high heat storage capacity, fast heat transfer rates, and low consumption is very necessary.

In pursuit of developing a cost-effective technology for rapid high-temperature heat storage and release, This study innovatively uses rice husk ash as the raw material to develop a rice husk composite ceramic (RHC) sphere thermal storage material, which is simple to prepare, has a greatly reduced cost and compared with conventional thermal storage materials used in commercial regenerative burner systems, such as SiC and Al_2O_3 ceramic spheres, RHC demonstrates comparable rapid heat storage and release rates to SiC and is significantly faster than Al_2O_3. In addition, RHC exhibits an impressive radiation absorptivity of 0.93 in the 600-1200°C range, which is higher than the 0.85 of SiC ceramic spheres and 0.25 of Al_2O_3 ceramic spheres. The distribution of high radiation absorptivity carbon and SiC particles within RHC is a key factor for its strong radiation properties, facilitating overall rapid heat storage and release through radiation heat transfer. This technology not only significantly enhances the efficiency of rapid heat storage and release from an industrial perspective, playing a role in energy saving and emission reduction, but also serves as an excellent example of recycling waste resources and advancing the development of a greener Earth.

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Lipopolysaccharide (LPS) on bacterial surface stabilizes ionic colloids and promotes biomineralization

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Keywords: lipopolysaccharide (LPS), biomineralization, ionic colloids, bacteria

Biomineralization is associated with a wide range of bacterial species. Mechanisms and applications of bacteria-induced biomineralization have been investigated in various fields. The formation of biominerals is templated and promoted by biomolecules under the control of chemical, physical, morphological and structural mechanisms. In aqueous solutions, metal ions can present in forms of single ions or ionic colloids. Brownian motion drives collisions between particles and facilitates colloidal formation. The surface of colloids electrostatically attracts oppositely charged ions to form a boundary of ionic atmosphere, or an electric double layer, which will exert repulsive forces toward similar particles and prevent colloids from aggregation. Biomineralization on bacterial surfaces is regulated by ionic colloids as follows: (1) ionic supersaturation results in colloidal formation; (2) ionic atmosphere rearranges are promoted by electrostatic interactions when colloids attach to negatively charged bacterial surfaces; (3) the colloidal structure is maintained in a thermodynamically unstable status that is easily interfered and results in precipitation (e.g., Ag^+/Cl^- colloids) or colloidal disintegration with the depletion of OH^- (e.g., Fe^{3+}/OH^- colloids). Therefore, stabilizing ionic colloids is an important issue for biomineralization. Lipopolysaccharide (LPS) is the main and outermost component on the cell surface of Gram-negative bacteria. Ionic colloids with positively charged metal ions on the surface interact with negatively charged LPS, which prevents ionic colloids from aggregation as well as regulates the formation, deposition, and development of mineral crystals.

In the present study, interactions between LPS and various metal ions as well as ionic colloids (Ag^+/Cl^-, Fe^{3+}/OH^-) were evaluated, which showed that LPS increases the energy barrier for the collapse of ionic colloids and prevents ionic colloids from aggregation. The roles of LPS stabilized ionic colloids in inducing biomineralization were explored, which showed that reducing colloidal stability by increasing the ionic strength significantly inhibited biomineralization of ionic colloids. The molecular mechanism of LPS in affecting biomineralization of Ag^+/Cl^- colloids was further investigated by taking advantages of two LPS structural deficient mutants of *Escherichia coli* that were generated by impairing the expression of *waa*P or *wbb*H genes with CRISPR/Cas9 technology that induced deficient polysaccharide chain of O-antigen (Δ*wbb*H) or phosphate groups of core oligosaccharide (Δ*waa*P) in LPS structures. There were significant changes of the cell morphology and surface charge of the two mutants in comparing with that of wild type cells. LPS from Δ*waa*P mutant showed increased ΔH_{ITC} upon interacting with free Ag^+ ions than LPS from wild type cells or Δ*wbb*H mutant, implying the binding affinity of LPS to Ag^+ ions is affected by the phosphate groups in core oligosaccharide. LPS from Δ*wbb*H mutant showed decreased endotherm (ΔQ) upon interacting with Ag^+/Cl^- colloids than LPS from wild type or Δ*waa*P mutant cells, implying LPS polysaccharide chain structure is critical for stabilizing Ag^+/Cl^- colloids. Biomineralization of Ag^+/Cl^- colloids on Δ*wbb*H mutant cell surface showed distinctive morphology in comparison with that of wild type or Δ*waa*P mutant cells, which confirmed the critical role of O-antigen of LPS in biomineralization.

This study provides a novel insight into interactions between LPS and ions or ionic colloids in influencing biomineralization on bacterial cell surface.

Acknowledgments

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A novel high-entropy $(Y_{0.2}Gd_{0.2}Ho_{0.2}Er_{0.2}Yb_{0.2})_3Al_5O_{12}/Al_2O_3$ eutectic with outstanding crystallographic texture formation capability and CMAS corrosion resistance

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Keywords: high entropy eutectic ceramic, directional solidification, crystallograohic texture, CMAS corrosion resistance

Al_2O_3-based directionally solidified eutectic (DSE) ceramics have been regarded as promising structural materials for long-term service in ultrahigh temperature oxidizing environments due to their outstanding oxidation resistance and superior high-temperature mechanical properties. In this work, high-entropy Al_2O_3-based DSE ceramic was prepared using the optical floating zone melting method. And both crystallographic texture control and high-temperature corrosion ability are recognized as the critical issues in the exploration of potential DSEs. Here a new $(Y_{0.2}Gd_{0.2}Ho_{0.2}Er_{0.2}Yb_{0.2})_3Al_5O_{12}/Al_2O_3$ ($(5RE_{0.2})AG/Al_2O_3$) DSE with excellent crystallographic texture formation capability and calcium–magnesium–aluminosilicate (CMAS) corrosion resistance was fabricated under the high entropy design conception. We prepared this DSE via optical floating zone and single-crystal $(5RE_{0.2})AG$ and Al_2O_3 phases are obtained within a growth distance of 15 mm, which is much shorter than those of single rare earth containing $RE_3Al_5O_{12}/Al_2O_3$ counterparts (typically ≥80 mm). Besides, the true recession depth of $(5RE_{0.2})AG/Al_2O_3$ is about 219.5 μm after corroded by CMAS at 1500 °C for 200 h. The current results can cast light on new mechanisms and strategies to multilevel optimization to develop novel high-temperature structural materials with tailored microstructure and enhanced CMAS corrosion resistance ability.

T4.4 POWDER PROCESSING TECHNOLOGY FOR ADVANCED CERAMICS

Synthesis of ZrB_2 rod crystals and exploration of their alignment behavior under strong magnetic field

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Keywords: ZrB_2 rod crystals, textured ceramic, strong magnetic field

Zirconium boride (ZrB_2) is an important ultra-high-temperature ceramic in the aviation and aerospace fields due to its low theoretical density, high melting point, hardness, and thermal and electrical conductivity. Poor fracture toughness is a critical deficiency which is the main issue of current research. In view of the prospective to enhance the performance of ZrB_2 ceramics by tailoring microstructure, this study tried to fabricate textured ceramics by aligning rod-like ZrB_2 grains using a strong magnetic field.

In this work, rod-like ZrB_2 grains were prepared by a salt-assisted boro/carbothermal reduction technique using NaCl as flux. A comprehensive thermal analysis of raw materials composed of different boron and carbon sources as well as the morpologies of products illustrated the importance of interproduct B_2O_3 to the anisotropic growth of ZrB_2 crystals. Besides, the addition of NaCl decreased the synthesis temperature and improve the products morphology by introducing more liquid phase to reactants. X-ray diffraction and scanning electron microscopy confirmed that the heat-treatment temperature of 1550 °C and the addition of 50 wt.% NaCl were the most effective in the preparation of ZrB_2 grains with a high aspect ratio. The products have diameters and aspect ratios of approximately 1 μm and 30, respectively, as shown in Fig.1a.

With the help of rod-like ZrB_2 grains, submicron ZrB_2 irregular grains were used as starting materials, polyethyleneimine (PEI) was employed as dispersant. A stable slurry with low viscosity was formulated by investigating different solvents, dispersant content, pH values, and solid loadings in details. Due to the hexagonal crystal structure and anisotropic magnetic susceptibilities along a, b and c axes ($x_c > x_{a,b}$), rod-like ZrB_2 grains in the slurry can rotate under strong magnetic field (12T), until the c axis parallel to the direction of magnetic field. After solidification and pre-treatment in cold isostatic pressing (CIP), highly c-axis oriented ZrB_2 ultrahigh-temperature ceramic was quickly sintered by spark plasma sintering SPS, as shown in Fig.1b.

Figures

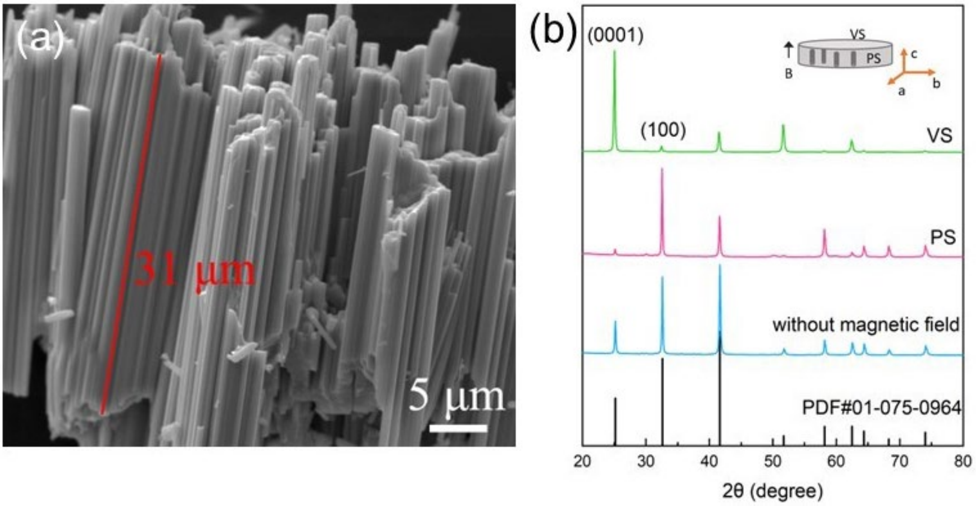

Figure 1 (a) SEM image of ZrB_2 rod crystals with 50 wt% NaCl; (b)XRD patterns of ZrB_2 bulks with and without strong magnetic field.

Effect of inert atmospheres on the resistance of graphite heater

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Keywords: graphite heater, electrical resistivity, atmosphere control, energy saving

Graphite materials have been widely used as important industrial furnace parts to attain high temperature above 2000 °C. For example, graphitization furnace to produce anode powder for LIB is one of such furnaces using many graphite parts. In many cases, indirect heating system with graphite heater has been adopted to these furnaces.

It has been known that the intrinsic electrical resistivity of graphite shows monotonical increase with increasing temperature up to 3000 °C after reaching a minimum at around 500-1000 °C1).

Our group also revealed that the resistivity of graphite by direct heating system shows linear increase above 1000 °C, in which no reduction of resistivity up to 3000 °C was observed2). However, as shown in Fig. 1(a), a remarkable decrease in resistance of heater above 2500 °C has been observed for indirect furnace in Ar atmosphere3).

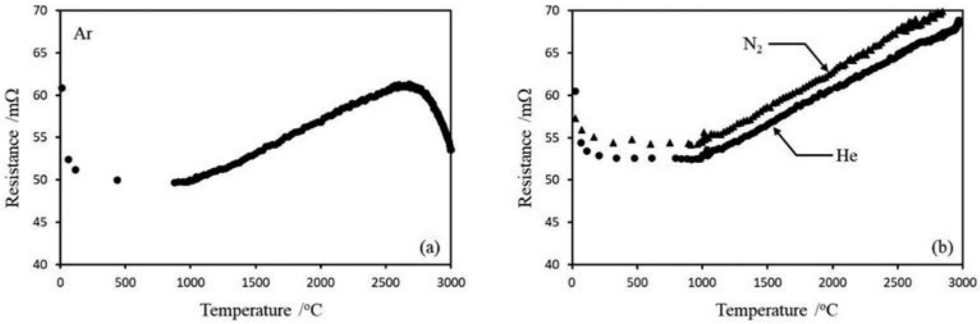

Fig. 1 Effect of furnace atmosphere on heater resistance during heating process: (a) Ar, (b) N_2 and He atmosphere. Graphite material: IG-110U (Toyo Tanso Co. Ltd.) purified after machining under halogen gas flow at a high temperature

Resistance fading temperature depends on the pressure of Ar gas, fading shifts to high temperature side by increasing pressure, but the fading occurs apparently at lower temperature by lowering pressure. In addition, the reduction in resistance of the heater was accelerated by the presence of vapors which came from carbon parts/carbon materials loaded in the furnace.

On the other hand, as shown in Fig. 1(b), no such reduction behavior was observed in N_2 and He atmosphere3). In He, much higher power was necessary to obtain the high temperatures close to 3000 °C steadily, however in N_2, heating up to 3000 °C with sufficient stabilities in temperature and power supply was possible for the present system4).

From these results, resistance reduction in Ar atmosphere above 2500 ^{o}C was supposed to be due to the formation of conduction path by ionized Ar, which could be accelerated by the coexistence of vaporized gases from carbon materials generated in the furnace during the heat treatment. The reduction of resistance was avoidable by mixing the appropriate amounts of He or N_2 in Ar, which may be important for energy saving of electricity for heating in the practical usage of furnace.

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Experimental considerations on selective gilling of two-component composite materials with attritor-type mill

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Keywords: selective grinding, attritor mill, composite material

In the recycling field, crushing and sorting technologies for composite materials are of great importance. Once selective grindding is achieved, it is possible to separate each component from the composite material in combination with classification operations. Despite these bachground, the conditions under which only certain components of the composite material can be ground are still unclear, and in the actual recycling field, conditions are often set by empirical rules. In this study, therefore, we conducted grinding experiments on glass mixed with metals and ceramics, and discussed the conditions under which selective grinding of glass can be achieved.

An attritor-type mill (POWDER LAB, Nippon Coke & Engineering Co., Ltd.) was used in our grinding experiments. The mill capacity was 180 ml and the total volume of material was adjusted to 40 ml. The agitation speed was 800 rpm and the grinding time was 10, 20, and 40 minutes. The samples were glass, steel, alumina, and lead. Glass was assumed to be the material to be ground and steel, alumina, and lead was assumed as simulated grinding media. All samples were prepared with spherical particles of 0.9-1.1 mm in diameter. Experiments were conducted with three combinations: glass and steel, glass and alumina, and glass and lead.

The results of the experiments showed that the most efficient grinding of glass proceeded in the glass-alumina combination, and about 70% of the glass was ground to a particle size of 0.5 mm or less. On the other hand, no progress was made in grinding alumina. In steel and lead, the glass grinding speed was significantly reduced, and the percentages of glass ground to 0.5 mm or less were about 20% and 10%, respectively. In addition, no steel or lead grinding/crushing occurred. Steel and lead balls avoided breakage by deforming due to metallic ductility, and for lead in particular, the surface was observed to deform significantly during the experiment.

The fact that even lead which has extremely low-hardness could make grinding of glass confirms that grinding process is not simply defined by the value of the Vickers hardness. In this presentation, we will discuss the conditions under which selective grinding of glass can be achieved by impact mitigation due to metal ductility and/or differences in impact time.

Acknowledgments

We are grateful to Kobe Steel, Ltd. for providing of sample.

An investigation into the influence of Al_2O_3 particulate morphology on processing conditions in industrial contexts

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Keywords: alumina, particle flow, rheology, rheological behaviour, industrial processing, statistical analysis

Alumina is a key material within the advanced ceramics field. It's chemical and thermal inertness ensure its valuable use within most industries globally. From it ultra-high purity and controlled microstructure allowing for IR transparency, to its uses within electrical components and as an emerging matrix material within aircraft engines.

The processes used to form alumina parts from powders, slurries and slips are varied and require a high degree of chemical engineering before components with the desired microstructure and properties can be achieved. The aim of this research was to highlight a factor commonly overlooked. Alumina particle size and its impact on processing is well studied, but the variation of particle shape and morphology is yet to be fully realised. The research aims to characterise key differences in morphology with a view on demonstrating this practice. From here the alumina with varying morphologies were analysed for their dry and as standard flow properties via powder rheology and methods such as Angle of Repose. A statistical analysis was conducted on the morphology to allow for a quantifiable differentiation to accompany the qualitative data collected.

The powders were then subject to flow conditions that mimic various processes in industry while suspended within polymers used for processing alumina in the advanced ceramic industries. Key trends were detected via the analysis of their flow behaviours and a novel process for imaging the movement of the particles was conducted to allow for an understanding of the interesting flow behaviours seen.

This research establishes that alumina morphology alone influences the methods in which the powder can be processed into ceramic components and aims to allow for further work to be conducted on a comparison of alternative particle sizes in the future.

Interparticle photo-cross-linkable Pickering emulsions for rapid processing of 3D-strcutured porous ceramics

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Keywords: photocurable suspension, porous ceramics, 3D structring, stereolithography

Porous ceramics are indispensable materials applied for filters, heat exchangers, and catalyst supports because of their large accessible surface area, thermal insulation properties, and corrosion resistance. Three dimensional (3D) structuring of such porous ceramics, using photocurable suspensions, have recently attracted wide attention toward material property design based on on-demand shaping. However, most protocols suffered from long processing time for drying and debinding/sintering of the photocured bodies to avoid structural collapse.

In order to realize an efficient production of tailored porous ceramic components, here, we introduce our newly designed Pickering emulsion-based suspensions[1-2] which can be photocured using reduced amounts of organic additives. Briefly, ceramic raw powder was dispersed into continuous-phase solvent with the aid of functionalized polyethyleneimine (PEI) as reactive polymer dispersant. After dissolving small amounts of acrylates with photo-radical initiators, the obtained suspension was vigorously mixed with dispersed-phase solvent. With an appropriate structural design of reactive polymer dispersants, flowable Pickering emulsions which can be photocured through interparticle photo-cross-linking reaction were successfully prepared. In this presentation, the effects of functionalized PEI structures on the flowing behavior, photo-responsiveness, and shaping (molding) properties of the designed interparticle photo-cross-linkable Pickering emulsions will be systematically discussed. Further, the 3D structuring of porous ceramics through digital light processing (DLP) printing of the designed Pickering emulsions and/or green machining of the photocured bodies will be demonstrated. Owing to the reduced amounts of organic additives used to form the photocured bodies, the 3D structured green components were processable through rapid heating for debinding/sintering without occurring any structural collapse.

Acknowledgments

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T4.5 ADVANCED MATERIALS, TECHNOLOGIES, AND DEVICES FOR ELECTROOPTICAL AND BIOMEDICAL APPLICATIONS

Characteristics of $MgGa_2O_4$ films grown by oxygen radicals assisted pulsed laser deposition

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Keywords: ultrawide bandgap, $MgGa_2O_4$, pulsed laser deposition, oxygen radicals

Magnesium gallate ($MgGa_2O_4$), a ternary oxide semiconductor with an ultrawide bandgap of approximately 4.9 eV, is explored as a promising material for high-power electronic devices and deep ultraviolet (DUV) photodetectors. Galazka et al. successfully produced bulk $MgGa_2O_4$ single crystals and observed that $MgGa_2O_4$ is a thermally stable at elevated temperatures [1]. Hou et al. employed metal organic chemical vapor deposition (MOCVD) to grow $MgGa_2O_4$ films on sapphire substrate at a substrate temperature of 650°C, demonstrating the favrication of a DUV photodetector using the oxygen-annealed $MgGa_2O_4$ film [2]. Pulsed laser deposition (PLD) is known for its efficacy in the low-temperature growth of films due to the relatively high kinetic energies of the ablated species [3]. In our previous experiments, $MgGa_2O_4$ films were grown on (0001) sapphire substrates using PLD at various substrate temperatures [4]. Remarkably, (111) oriented $MgGa_2O_4$ films were obtained at a low growth temperature of 200°C, surpassing the capabilities of other growth methods such as MOCVD. Photodetectors based on the $MgGa_2O_4$ films grown at 500°C exhibited excellent peak responsivity around 220 nm, along with a high rejection ratio and reproducibility. However, films grown below 300°C exhibited poor crystal quality, resulting in photodetectors with no peak responsivity and a very low rejection ratio. To align with established Si based integrated circuits for novel optoelectronic applications, achieving a lower growth temperature is preferable. Oxygen radicals have been identified as effective assistant species for decreasing the growth temperature of thin films. Thus, the combination of PLD and oxygen radicals assistance proves to be a highly effective method for low-temperature film growth.

In this work, the $MgGa_2O_4$ films were grown on (0001) sapphire substrate using oxygen radicals assisted PLD. A KrF excimer laser with a pulse of 2 Hz ablated a $MgGa_2O_4$ ceramic target in the growth chamber, evacuated to 5×10^{-6} Pa with a turbo molecular pump before deposition. Oxygen radicals were generated by passing high purity oxygen gas into the plasma cell with an RF power of 300 W. The growth chamber was maintained at 0.1 Pa by controlling the flow rate of the oxygen with a mass flow controller. Fim thickness was determined by using a step profile analyzer, and structural properties were characterized by X-ray diffraction. Optical transmittance spectra were measured by a spectrophotometer. Our results demonstrate that (111) oriented $MgGa_2O_4$ films can be obtained at a remarkably low growth temperature of 100°C, and the crystal quality of the films using oxygen radicals is significantly improved compared to films grown by conventional PLD.

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Photoluminescence and scintillation properties of Dy-doped $GdVO_4$ Single Crystals for X-ray detection

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Keywords: scintillator, radiation detection, photoluminescence

Scintillators can immediately convert incident ionizing radiation into UV–visible photons with low energy. Scintillators are coupled with photodetectors, which can convert the UV–visible photons into electric signals, to utilized for radiation detectors. The radiation detectors have been widely used in various applications, including medical, security, oil logging, non-destructive research in cultural objects. Since the performance of the radiation detectors mainly depends on the that of the equipped scintillators, new scintillators with better properties have been continuously developed.

$GdVO_4$ is researched and utilized for a host material for phosphors and lasers because of high chemical and thermal stability [1]. In addition, since $GdVO_4$ is relative high effect atomic number (55.9) and density (5.47 g/cm^3), it has been also subject of researches as scintillators. Particularly, it has been reported that the light yield (*LY*) of the undoped $GdVO_4$ is 12,000 photons/MeV [2]. In this study, in the purpose of further improvement of *LY*, we fabricated $GdVO_4$ single crystals doped with Dy^{3+} ions, whose emission wavelength were well-matched with photodetectors such as Si-photodiode, and evaluated photoluminesce and scintillation properties.

Fig. 1 shows the scintillation spectra of the Dy-doped $GdVO_4$ single crystals. Some emission lines were observed at 480, 570, and 660 nm. Such emission lines were due to the 4f–4f transitions of Dy^{3+} ions [3]. In addition, a broad emission band was observed in the state of overlapping with the emission line at 480 nm. This emission band was due to the charge transfer from V^{5+} ions to O^{2-} ions inside $[VO_4]^{3-}$ [3]. Fig. 2 shows the pulse height spectra of the Dy-doped $GdVO_4$ single crystals and $Bi_4Ge_3O_{12}$ (BGO) under γ-ray from ^{137}Cs. BGO was utilized for a reference sample with *LY* of 8,000 ph/MeV. All the samples showed the clear photoabsorption peak at 288 (0.05% Dy), 270 (0.1% Dy), 283 (0.5% Dy), 262 (1.0% Dy), 83 ch (BGO). From the comparison of the peak channel with BGO and the quantum efficiency of photodetector which takes the spectral shape and wavelength of scintillation spectra in account, the *LYs* were calculated by 34000 (0.05% Dy), 37000 (0.1% Dy), 48000 (0.5% Dy), 44000 (1.0% Dy). The *LY* of 0.5% Dy-doped $GdVO_4$ was the best value among the samples and 4 times higher than that of the undoped $GdVO_4$ [2].

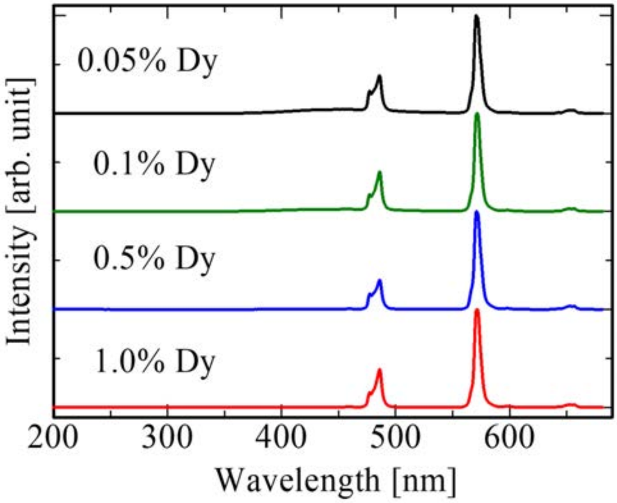

Fig. 1 Scintillation spectra of Dy-doped GdVO4 single crystals.

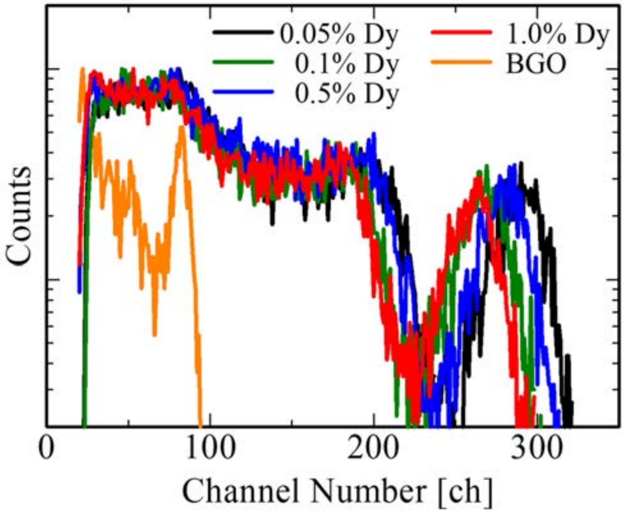

Fig. 2 Pulse height spectra of Dy-doped GdVO4 single crystals and BGO under γ-ray from 137Cs.

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Development of NIR emission phosphor for the anti-counterfeiting and certication materials

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Keywords: NIR emission, phosphor, certication material

Near-infrared (NIR) emissions are highly important in anti-counterfeiting, secret signals, medical, pharmaceutical, and agricultural industries. As counterfeiting technology for security materials develops, the importance of anti-counterfeiting and authentication technology increases, and new materials need to be developed. Recently, certification materials for waste plastic recycling and application products using eco-friendly Global Recycling Standard (GRS)-based materials are attracting attention. These anti-counterfeiting and certification materials can be applied as NIR materials with high efficiency, high thermal stability, and NIR-excitation to NIR-emission beyond existing UV-excitation.

Among the luminescence ions, Yb3+ has been widely used for developing NIR-emission phosphors due to the simple electronic structure with two multiplets: the 2F5/2 level in the excited state and 2F7/2 level in the ground state. In this study, therefore, we used Yb3+ as the luminescence ion to develop new NIR emission phosphor with high thermal stability for use in the anti-counterfeiting and certication materials. Yb^{3+}-doped NIR phosphors were synthesized by the conventional solid-state reaction method. The NIR phosphors showed a broad NIR emission which was attributed to the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition of Yb^{3+} ions in NIR region excitation. The excitation spectrum shows two bands in the UV and NIR regions. The thermal degradation behavior of NIR phosphors was measured up to 300 °C. As a result, the NIR phosphor showed excellent thermal stability and recovered close to 100% of the initial emission intensity at room temperature after cooling. Finally, it was confirmed that significant NIR emission was detected by adding near-infrared phosphors to produce a master batch for application to fiber products. These results suggest applicability to advanced anti-counterfeiting and certification applications.

Figures

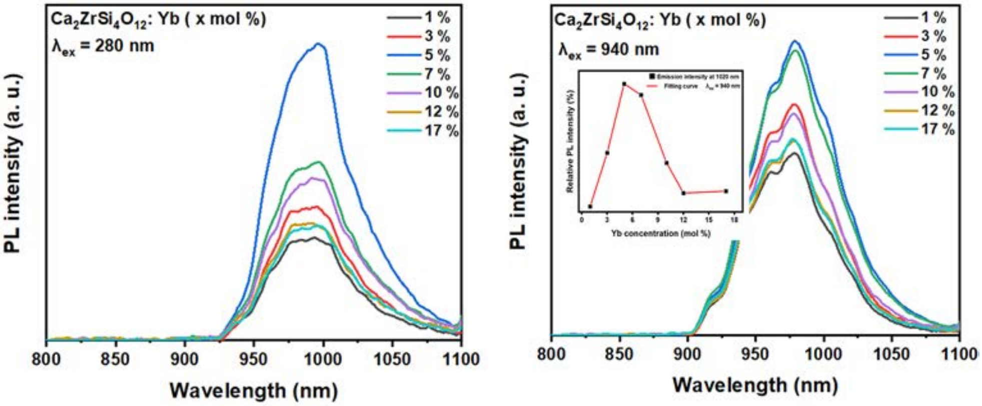

Fig. Emission spectra of Ca2ZrSi4O12:Yb3+ phosphor for excitation at 280 and 940 nm

Acknowledgments

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Red to deep red luminescence of 3d transition metal ions in fluorine-doped lithium aluminates

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Keywords: 3d transition metal ions, deep red luminescence, fluorine, lithium aluminate

Luminescence in the red to near-infrared region between 640 and 2000 nm has attracted attention in applications such as medical diagnosis, health monitoring, agriculture, and night vision; the 3d transition metal ions Cr^{3+}, Mn^{4+}, and Fe^{3+} can serve as luminescent centers for phosphors in such applications. The luminescence of these 3d transition metal ions is due to d-d transitions; the energy levels of the d orbitals and the probability of the transitions are significantly affected by the local symmetry around the center ion, so the luminescent depend on the combination of the luminescent center ion and the type of host material. We have recently reported phosphors based on fluorine-doped lithium aluminates [1-3]. According to the phase diagram [4], Li_2O and Al_2O_3 form several lithium aluminate compounds with different Li/Al ratios. We have focused on $LiAlO_2$ and $LiAl_5O_8$ because they provide both octahedral and tetrahedral substitution sites for Cr^{3+}, Mn^{4+}, and Fe^{3+} and can be good host materials for each of these cations. Fluorine doping was carried out on these lithium aluminates using LiF as the starting lithium source. Trace amounts of fluorine incorporated into the crystal lattice by substituting oxygen resulted in structural modifications, allowing various emissions in the red to deep red region.

Figure 1 shows the luminescence of Mn^{4+}, Cr^{3+}, and Fe^{3+} in $LiAlO_2$. $LiAlO_2$ has several crystallographic polymorphs, and heating in the atmospheric conditions usually yields α-$LiAlO_2$ or γ-$LiAlO_2$. γ-$LiAlO_2$ is the high temperature form and has a crystal structure consisting of corner-sharing tetrahedra of AlO_4 and LiO_4. In contrast, α-$LiAlO_2$ has a crystal structure consisting of alternating stacks of edge-sharing AlO_6 and LiO_6 octahedral sheets. α-$LiAlO_2$ forms at low temperatures below 600 °C and usually has low crystallinity, so this phase has not been used as a host material for phosphors. The introduction of fluorine stabilized α-$LiAlO_2$ with high crystallinity above 800 °C, leading to the new application of this phase in phosphors (**Figure 1**).

We will present the realization of variations in luminescence in the red to deep red region by combining the luminescent center ions Mn^{4+}, Cr^{3+}, and Fe^{3+} with the host materials lithium aluminates containing a trace amount of structural modifier (fluorine in this case).

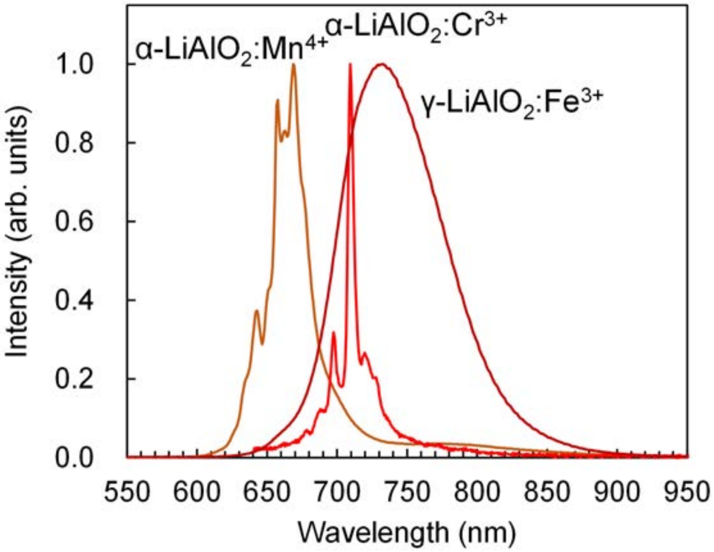

Figure 1 Red to deep red luminescence of Mn^{4+}, Cr^{3+} and Fe^{3+} in $LiAlO_2$.

Acknowledgments

This work is in part based on KAKENHI (20K05658) and the Cooperative Research Project of Research Center for Biomedical Engineering.

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Development of Er-doped $Bi_4Ge_3O_{12}$ single crystalline scintillators

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Keywords: scintillator, single crystal, near-infrared photons

Scintillators are functional materials that immediately convert ionizing radiation such as X- and γ-rays into thousands of low-energy photons after absorbing the energy of radiations. Scintillators emitting visible photons have been mainly studied up to the present because conventional photodetectors such as photomultiplier tubes have high wavelength sensitivity at 400–600 nm. In recent years, near-infrared (NIR)-emitting scintillators have attracted attention owing to the development of detectors sensitive to the NIR region. With such progress, NIR-scintillators have been gradually developed for bio-imaging and high-dose field monitoring applications [1] owing to their high penetration power with low invasiveness to human soft tissues [2] and the ease to distinguish from Cherenkov light [3]. Despite the high demand of NIR scintillators from applications, the number of reports is still few compared to UV–visible scintillators. In this study, we aimed to explore candidates for scintillators emitting NIR photons that can be applied in practice. X- and γ-rays interaction probabilities of NIR scintillators were improved by using a heavy host material; thus, we focused on $Bi_4Ge_3O_{12}$ (BGO). As a NIR luminescence center, Er was selected because it can emit photons at 1500–1600 nm owing to electric dipole-forbidden transitions between 4f orbitals [4]. Er-doped BGO single crystals were grown by the Floating zone method, and their photoluminescence and scintillation properties were investigated.

Figure 1 shows the scintillation spectra of Er-doped BGO. Broad emission peaks due to electronic transitions of Bi^{3+} were observed at 400–600 nm [5]. Sharp emission peaks appeared at 550 and 1550 nm. They originated from 4f–4f transitions of Er^{3+} [4]. Figure 2 shows the dose-rate relationships of Er-doped BGO. The vertical and horizontal axes were respectively scintillation outputs in NIR regions and irradiated dose rate. The lower detection limit was 6 mGy/h confirmed by all the prepared samples. The value was superior to those of Nd-doped BGO measured with the same setup [6].

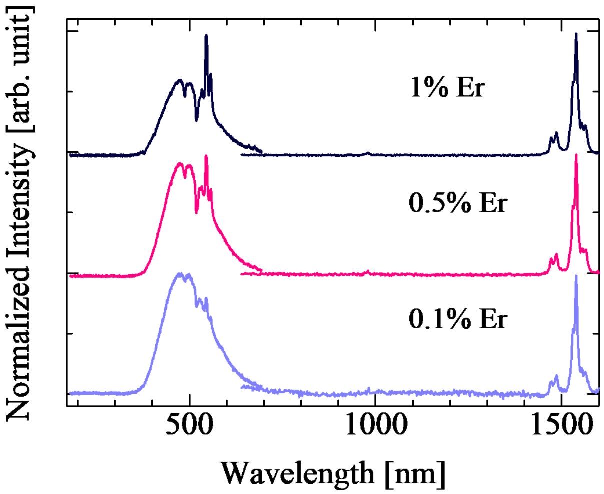

Fig. 1. Scintillation spectra of Er-doped $Bi_4Ge_3O_{12}$.

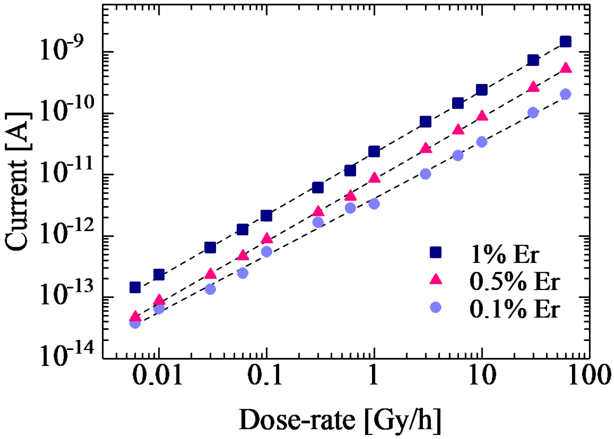

Fig. 2. Dose-rate relationships of Er-doped $Bi_4Ge_3O_{12}$.

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T4.6 Multifunctional Coatings for Energy and Environmental Applications Applications

Microstructural investigations on aerosol-deposited calcium cobaltite films revealing the outstandig thermoelectric properties and the deposition mechanism

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Keywords: powder aerosol deposition, thermoelectric material, microstructure, misfit-layered oxides, film formation, deposition mechanism

Powder aerosol deposition (PAD) is a coating process that can be used to produce ceramic coatings at room temperature. In this process, powder aerosols generated in an aerosol generator are accelerated through a nozzle into a vacuum chamber. In the vacuum chamber, the ceramic particles hit a substrate and form a dense layer of a nanocrystalline ceramic.

This process works with most technical ceramics such as aluminum oxide or yttria-stabilized zirconia (YSZ). It is also possible to produce films of functional ceramics [1]. Examples are the cathode active material nickel manganese cobalt oxide (NMC), ion conductors such as sodium super ionic conducters (NASICON) or lithium lantanum zirconium oxide (LLZO), or thermoelectric materials bismuth telluride, copper-iron delafossite or the misfit-layered oxide calcium cobaltite $Ca_3Co_4O_9$ (CCO)[2]. The latter are particularly notable for their very high deposition rate in the PAD process.

In this work, CCO powder is prepared via the mixed oxide route and films are produced by the powder aerosol deposition method. The microstructure of these films is investigated by scanning electron microscopy (SEM) and X-ray diffraction (XRD) and these results are correlated with the resulting thermoelectric properties (Seebeck coefficient and electrical conductivity).

The results show that the films do not have a typical PAD microstructure, but that the crystals are significantly larger and platelet-like shaped. XRD investigations confirma strong fiber texture of the PAD-CCO films.

The fiber texture is expressed in the fact that the vast majority of crystals are oriented with the [001] direction perpendicular to the substrate plane. This explains the comparatively high electrical conductivity and the comparatively high Seebeck coefficient of the CCO-PAD film investigated in-plane direction, as the electrical conductivity in CCO crystals in the (001) plane is many times higher than perpendicular to it.

Finally, considerations on the possible deposition mechanism for materials with layered and misfitted crystal structure are presented, through which the texture of the films is achieved.

Acknowledgments

The authors are indebted to the department of metals and alloys (Prof. Uwe Glatzel) of the University of Bayreuth for providing the X-ray diffractometer and the Bavarian Polymer Institute (BPI) for the SEM measurements.

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Challenges of metallic coatings from failure analysis perspective in automotive industry

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Keywords: Sn coating, electrochemical migration, intermetallic compounds, whiskers

Metallic coatings (*e.g.* Sn based) of design elements used in electronic control units (ECUs) built for automotive industry play an essential role with respect to their impact on the electrical functionality and performance. Depending on the environmental conditions, various challenges in terms of failure modes and processes occur either on coating surface, such as electrochemical migration (ECM) and whiskers growth or at coating interface like the growth of intermetallic compounds (IMCs). Under humidity conditions, the movement of metal ions between two electrods in an electrical field through moisture or any other liquid electrolyte can lead to ECM, which causes further different failure modes like corrosion/oxidation of metals and formation of dendrites and precipitates. On the other hand, whiskers, known as metallic protrusions that grow spontaneously on the coating surface during storage or use, do not require any electrical field for their growth, therefore they can not be confused with products of ECM. In contrast to whiskers and ECM, IMCs develop at the metallic interfaces (*e.g.* Cu/Sn, Ni/Sn) via difussion processes of the atoms depending on different temperature conditions and time. For instance, IMCs growth leads to voids formation and micro-structural coarsening while an increased IMCs layer thickness results in an increased electrical resistance and consequently low currents flow. Thus, this work presents selective results with typical failures related in particular to Sn coatings of different design elements, which were characterized by means of optical microscopy, scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) methods.

Powder aerosol deposited $Na_3V_2(PO_4)_3$/C composite cathode films for next generation of energy storage systems

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Keywords: aerosol deposition, sodium vanadium phospate, post-lithium batteries

The increasing demand for lithium and the local distribution of its sources on the Earth crust led to drastically increased prices of its resources. Therefore, researchers worldwide are in search of low-cost alternatives to state-of-the-art Li-ion battery architectures. Sodium batteries with sodium vanadium phosphate (NVP) electrodes have gained attention as a promising solution due to affordability, structural stability, high ionic conductivity, and theoretical energy density.

Dense films of functional materials on a wide variety of substrates can be fabricated directly at room temperature by the so-called powder aerosol deposition (PAD) method. Therefore, this unique spray coating method enables the deposition of composite cathode active materials on current collectors ensuring a tight contact in a relatively short processing time.

In the current work, we synthesized NVP/C composited cathode powders using the mixed oxide technique. The calcined powders were characterized by X-ray diffraction analyses including Rietveld refinement. The carbon content of the synthesized powder was determined by thermo gravimetric analysis (TGA).

The powders with the desired phase were sprayed on aluminum substrates via PAD to serves as cathodes. In addition, for comparison, a part of the powder was used for producing tape-casted cathodes. Coin cells of both cathodes were assembled (using 1M NaPF6 in EC:EMC 30:70 wt.% as an electrolyte, Whatman GF/B as a separator, and Na metal as the anode) and their cycling performances were compared. The effect of annealing on the capacity of PAD-produced cathode films was also investigated.

Our results demonstrate the successful deposition of composite cathode active materials on aluminum substrates and provide a comparative study to conventional tape casting. This work may pave the way for an easier production of low-cost and high performance electrodes for post-lithium batteries.

T4.7 Materials for Extreme Environments: Ultrahigh Temperature Ceramics (UHTCs) and Nano-laminated Ternary Carbides and Nitrides (MAX Phases) Applications

Atomic scale morphology of high-entropy metal carbides

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Keywords: high-entropy, atomic-scale STEM characterization, MAX

Mixing multiple transition metals opened a new way to explore the attainable chemistries and led to the discovery of new properties of the MAX & MXene family. Compared with a single transition metal composition, multiple principal elements increased system configurational entropy and decreased the total free energy, stabilizing the material. It has been reported that high entropy (HE) MXene shows higher conductivity, charge storage capacity, and catalytic ability. Our latest result indicates that HE MAX has superior mechanical properties compared to single transition metal MAX. The unprecedented physicochemical properties are not only an 'average' result of a combination of multiple principal elements but also excess quantities owing to complex synergetic mechanisms among multiple principal elements, such as high mixing entropy, local lattice distortion, sluggish diffusion, and cocktail effect.

This work introduces the atomic-resolution scanning/transmission electron microscopy (S/TEM) characterization of HE MXene & MAX materials and provides fundamental information on structural & chemical configuration at the atomic scale. The STEM shows a hexagonal crystal structure of the MAX phase (Figure 1), and stress analysis indicates a strong correlation between lattice distortion and configurational entropy. Atomic resolution energy dispersive X-ray spectroscopy (EDS) mapping shows the detailed chemical arrangement of multiple transition metals. High-angle annular dark field (HAADF) Z-contrast imaging shows the top-down view of the HE MXene lattice and defect configuration. The apparent atoms exhibit a stochastic arranged variation in brightness, revealing the random multiple principal atomic occupancies. Our result promotes a deeper understanding of the complex mechanism among multicomponent HE MAX & MXene materials.

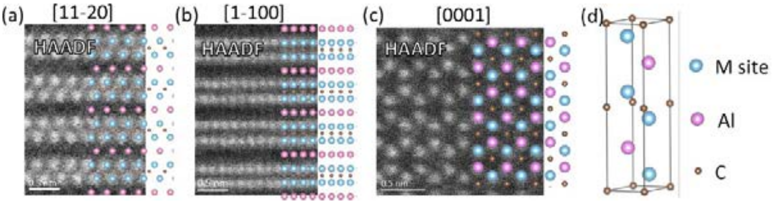

Figure 1. Atomic-resolution Z-contrast STEM images of HE-MAX (TiZrNbTa)2AlC.

Acknowledgments

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Influence of boron concentration on oxidation behavior of magnetron sputtered Hf-Al-B thin films

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Keywords: hafnium diboride, oxidation, coatings, magnetron sputtering

The isothermal oxidation behavior of single-phase solid solution Hf-Al-B coatings with compositions $Hf_{0.13}Al_{0.23}B_{0.64}$ and $Hf_{0.13}Al_{0.18}B_{0.69}$ at 700 °C for up to 8 h was studied. Both coatings were deposited using one compound HfB_2 and AlB_2 target along with an elemental Al target via direct current magnetron sputtering (DCMS). The power supplied to the latter was varied to change the B (and Al) concentration. While both films grew with columnar grains, the B-poor film was under-dense at the column boundaries. The B-rich film was finer-grained and dense with no visible porosity, showing a 44% higher Young's modulus and 100% higher hardness compared to the B-poor film.

Despite the morphological differences, the oxidation behavior of both films was indistinguishable. Passivating, dense, and X-ray amorphous oxide scales of thicknesses 33 ± 9 nm in the B-poor coating and 31 ± 9 nm in the B-rich coating, formed after 8 h at 700 °C. The scales contained roughly 30 at.% Al, 20 at.% B and 10 at.% Hf, and the growth kinetics at 700 °C followed a sub-cubic rate.

The oxidation behavior at 700 °C contrasts with isostructural Ti-Al-B coatings[1], in which overstoichiometric B concentrations lead to the formation of non-passivating oxide scales. The decelerated oxidation kinetics in overstoichiometric Hf-Al-B is attributed to the relatively limited thermal mobility at 700 °C of heavier Hf in comparison to Ti in the oxide scale, which also hinders the formation of crystalline phases.

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T4.8 Design, Processing, and Applications of Nanolaminated Ternary Transition Metal Carbides/Nitrides/Borides and MXenes and Mbenes

Magnetocaloric properties of bulk Fe_2AlB_2 synthesized by reactive hot isostatic pressing

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Keywords: Fe2AlB2, MAB phases, magnetocaloric effect, hot isostatic pressing, magnetic properties

This study outlines a new single-step synthesis of Fe_2AlB_2 at 1150°C for 4 h using the hot isostatic pressing (HIPing) technique. The material is characterized using microscopy and XRD to be largely in single phase. The suggested metallographic etching (0.005 M NaOH + 0.01 M NaOCl solution) revealed the grain boundaries and enabled the vizualization of predominant equiaxial Fe_2AlB_2 grains (~30 µm) alongside of a few unreacted boron particles and Al-rich zones located at grain boundaries. Magnetocaloric properties were assessed through isothermal magnetic field sweeps and heat capacity measurements, yielding similar results. The Gaussian fit of the average results of these two methods led in an impressive isothermal entropy change of 2.9 J/kg.K at 2 T and 6.8 J/kg.K at 5 T, with corresponding adiabatic temperature changes of 1.1 K and 2.8 K at 2 T and 5 T, respectively. Comparatively, the Fe_2AlB_2 HIPed sample exhibited slightly lower results (~15%) than other synthesis reported in the literature. However, regarding studies lacking post-treatments (acid etching and annealing) or doping the outcomes are comparable. In a broader context, the values were reduced than those of well-known first-order transition (FOMT) giant magnetocaloric effect (GMCE) materials with T_C in the same range such as $Gd_5Si_2Ge_2$ [1] and MnFe(P, Si, B) systems [2]. Moreover, considering the GMCE materials undergoing a second-order phase transition (SOMP) such as $ErMn_2Si_2$ [3] and $GdMnO_3$ [4], again Fe_2AlB_2 presented a weak performance. In this former case, however, the transition temperatures are far and less than room temperature (<160 K). Nevertheless, compared to other SOMT materials exhibiting transitions close to room temperature, the HIPed Fe_2AlB_2 demonstrated equivalent values while boasting an abundant and costless chemical composition. Fe_2AlB_2 stands out as a promising material for environmentally friendly magnetocaloric cooling due to its rare-earth-free composition and near room temperature second-order magnetic transition. Additionally, the HIPing method allows for a straightforward single-step synthesis process, shaping Fe_2AlB_2 into its final form without additional manufacturing steps. These characteristics render the HIPed Fe_2AlB_2 an appealing and cost-effective choice for magnetic refrigeration applications, offering enhanced energy efficiency and a simplified manufacturing process for future refrigeration technologies.

Acknowledgments

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Innovative synthesis approaches to prepare new solid-solution MAX phases

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Keywords: MAX phases, microwave heating, hybrid solid-state methods, (carbo)nitrides, magnetism

The world of MAX phases has rapidly evolved over the recent years and now comprises more than 340 different phases.[1] A big part of this number is represented by solid-solution MAX phases, which enable to specifically tune and influence the materials properties of the respective parent phases. However, still, most of the general synthesis approaches of MAX phase compounds are mainly based on traditional solid-state preparation techniques exhibiting significant drawbacks regarding their energy- and time efficiency. One promising approach to circumvent these drawbacks is to use microwave heating due to a direct interaction of the reactants with the electromagnetic radiation. This is exemplarily shown with the synthesis of a new *M*-site solid-solution system $(V_{1-x}Cr_x)_2GaC$ $(0 \leq x \leq 1)$. Besides the synthesis, magnetic measurements have revealed that this system almost matches the Stoner criterion at $x = 0.80$. These findings provide a necessary starting point for the challenging synthesis of new magnetically ordered MAX phases.[2]

While carbide-based *M*-site solid-solution phases form the biggest part of the current reported solid-solution members, *X*-site solid-solution phases are a rare species. For instance, less than ten phases are represented by carbonitride MAX phases and less than twenty phases are nitrides in general. These low numbers can be related to a more demanding synthesis procedure due to the high stability and low diffusion rate of nitrogen-containing compounds. However, by combining non-conventional solid-state methods, such as the liquid ammonia method, or the so-called "urea-glass method", with conventional solid-state preparation techniques, it is possible to approach the field of nitrogen-containing MAX phases using an efficient two-step synthesis process.[3] This has enabled the synthesis of new materials such as $V_2GaC_{1-x}N_x$, $Cr_2GaC_{1-x}N_x$, and $V_2GeC_{1-x}N_x$, respectively. Particularly, the latter example impressively shows how the nitrogen content in the MAX phase can specifically influence materials properties, such as magnetism or transport behavior, and thus strongly supports the potential of these types of materials.

Acknowledgments

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Comparative oxidation behavior of columnar and equiaxed Cr_2AlC coatings

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Keywords: MAX phase, oxidation, alumina, microstructure

The oxidation behavior of Cr_2AlC coatings with columnar and equiaxed grain morphologies is studied. Synthesis of phase pure Cr_2AlC coatings of identical thickness with distinct grain morphologies are carried out by magnetron sputtering. The coatings are oxidized in ambient air up to 990 °C and held for 1, 2 and 3 hours. The oxidation protocol includes a 33-minute transient oxidation phase during the initial heating of the furnace from room temperature to 990 °C. The oxide scale growth in the coatings with equiaxed grain morphology is observed to follow the parabolic law. A 259 ± 62 nm thick oxide scale is measured after 3 h of oxidation. In contrast, coatings with a columnar structure exhibit accelerated oxide scale growth, resulting in the formation of a thicker oxide layer measuring 535 ± 107 nm after 3 hours of oxidation, which is approximately twice as thick as that on equiaxed coatings. The difference in the oxidation behavior could be traced back to the varied oxide phase formation during the transient oxidation phase. In the equiaxed structured coatings, direct nucleation of the passivating α-$(Al,Cr)_2O_3$ occurs, and the further growth of the oxide is controlled by the oxygen diffusion via the oxide grain boundaries. In the case of columnar structured coatings, fast diffusion of Al facilitated by the short-circuit diffusion paths offered by the columnar grain boundaries leads to the formation of pure Al_2O_3 scale. During the transient oxidation, the pure Al_2O_3 crystallizes into metastable alumina polymorphs, transforming to α-Al_2O_3 during the subsequent isothermal oxidation.

T4.9 CERAMIC INTEGRATION TECHNOLOGIES FOR ENERGY AND ENVIRONMENTAL APPLICATIONS

Design and integration of novel sodium-zinc batteries

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Keywords: joining, glass, glass-ceramic, high temperature, sodium-zinc batteries

The SOLSTICE project (European Union's Horizon 2020, grant agreement No 963599, www.solstice-battery.eu) has developed two different designs of Sodium-Zinc batteries. One design is composed of Solid Electrolyte Cells (SECs) based on the ZEBRA technology and operates at approximately 300°C. The other design is composed of All Liquid Cells (ALCs) which are expected to operate at around 600°C and to withstand corrosive environments. For both technologies, and high-temperature devices in general, sealing the cell pack is a challenging and crucial step. This presentation will focus on the process for designing, characterizing, and optimizing the sealing process for both configurations of Na-Zn cells. The potential of glass and glass-ceramic sealants in high-temperature and harsh environments will also be addressed.

In particular, for the SEC a modified commercial glass and an original silica-free glass were extensively characterized through thermal, chemical, and morphological analyses. The optimized compositions were then applied to join α- and β-alumina components in the cells, resulting in a lower sealing process temperature compared to the state-of-the-art solution. The sealant deposition process has been automated through robocasting, and the ink recipe has been optimized for this process. The cell assembled using the designed solutions was tested under operating conditions.

Considering the ALC, where a metal-to-ceramic joining is foreseen, different glass ceramic solutions were considered, along with the surface modification of the metallic component, to enhance the compatibility with the glass ceramic sealants. Following the optimization of the sealing process, the initial cell prototypes were produced and submitted to both electrochemical characterization and post-mortem analysis.

Acknowledgments

This work is part of the "SOLSTICE" project (Sodium-Zinc molten salt batteries for low-cost stationary storage) which received funding from the European Union's Horizon 2020 research and innovation program under grant agreement No 963599.

Ceramic to metal joining for high temperature oxygen separation membrane applications

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Keywords: joining, sealant, glass-ceramic, Oxygen Transport Membranes, ceramic, metal

The integration of Oxygen Transport Membranes (OTMs) in industrial processes can lead to energetic and economic advantages, but proof of concept membrane modules are highly necessary to demonstrate the feasibility of this technology.

This study identifies innovative materials to be used to join ceramics to metals, with a specific focus on joining materials for the integration of OTMs in metallic modules for high temperature applications.

Perovskite-based membranes have been selected for the oxygen separation, since they can ensure robustness, reliability and resistance in high temperature operation.

Glass-ceramic joining materials (or sealants) are widely employed in the energy production sector, as they avoid gas mixing and consequent device failure. The sealants are characterized by high gas tightness, thermo-chemical and thermo-mechanical compatibility with metallic and ceramic materials, as well as stability in the relevant operating conditions (800-950 °C, thousand hours).

The housing of the membrane component is a metallic case joined to the ceramic membrane employing custom developed glass-ceramic sealants, that exhibited a remarkable thermo-chemical compatibility both with metal and ceramic.

In this work is presented the development and high temperature characterization carried out on glass-ceramic sealants selected to join ceramic membranes (LSCF) to the metallic part.

First of all the glass ceramics have been produced and analyzed to evaluate their thermal properties as sealant materials for the application. Then glass-caramic pastes have been developed and tested, to be employed in a robocasting deposition technique. The robocasting deposition has been implemented to overcome some issues related to the slurry deposition of the sealant.

Furthermore the thermo-mechanical compatibility of the selected sealants, with the ceramic membrane and the metallic case, has been tested, after joining, with X-ray thermography analysis and SEM observation of the interfaces. In addition to this, the produced joints have been subjected to relevant condition ageing tests (800-950°C, 1 to 3 weeks) and microstructurally analyzed afterward. In the end, gas tightness tests of the joints, and scale-up to a final module configuration, have also been performed.

As a conclusion, the selected glass-ceramic proved to be a good candidate to join ceramic membranes to metal case for Oxygen Transport Membrane applications.

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T4.10 Environmental Friendly and Energy Efficient Manufacturing Routes for the Production Root Technology Applications

Development of smart metal powder manufacturing system with an add-on module

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Keywords: Root technology, AI-based manufacturing, add-on modules, gas atomizing system

Korean goverment adressed the importance of advanced manufacturing platform utilizing artificial intelligence (AI) not only for enhancing the production efficiency, but also for reducing the expensive labor cost. Unfortunately, the Root industry, which supply a valuable products to the Korean industry i.e. Samsung Electronics, meets a great deal of challenges in digital transfromation due to its low budget for revolutionizing their own infrastructure. Among them, the gas atomizing system, which produces fine metal powder, suffered both low-efficieny and labor-intensive works due to its complex equipment. Particulary, the coarse and massive working condition in small and medium size company hinders the field workers to digitization of their process, thus the digitally recording know-how in operating steps remains to be unsolved. Ironically, as the equipment become more productive, their field work dependency became considerable, which fails to transforming into the next-generation manufactures.

Here, we suggested the digitiation process of gas atomizaing system by the sensors and add-on modules. The add-on modules, which is data collecting system, captured the step-by-step data logging by controlling their process, the operating condition has been successfully logged during operation. Furthermore, we also developed the on-line particle size analyzing (on-line PSA) system for in-situ production condition of the fine metal powder. Thus, the add-on modules, which collapsed both inputs(the preparation step) and outputs(metal powder diameters and variables etc.) process could be transformed into the AI-data sets in real-time condition, where the field workers forecasts and analyze their own operating condition. As an example, one company has been benefited from our works, showing their high accuracy by add-on modules data.

This experimental and theoretical research would pave the way not only for the customer-demand powder dimension in high quality, but also for the high-efficient and the profitable powder production in the relative industry.

Innovative synthesis of hierarchical porous nano ceramic structures using organic template and maximization of active sites

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Keywords: porous ceramic, hierarchical porous structure, active site

In this study, we present an innovative synthesis method for hierarchical porous nano ceramic structures using an organic template. Initially, utilizing naturally hierarchical porous structures of the organic template, ceramic thin films of sub-nanometer thickness are deposited onto the surface of the organic template using ALD (Atomic Layer Deposition) technique. Subsequently, atmospheric annealing decomposes the organic template while simultaneously forming nano-sized pores within the ceramic thin film of sub-nanometer thickness. This straightforward method enables the synthesis of hierarchical porous nano ceramic structures. The synthesized nanostructures were characterized using various analytical techniques, including X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The results indicate that the synthesized ceramic nanostructures exhibit hierarchical morphology with high crystallinity and purity.

Moreover, taking advantage of the exposed surfaces of the synthesized nanostructures, their catalytic properties were evaluated. The results demonstrate excellent catalytic properties with high sensitivity. The outstanding catalytic properties of the synthesized nanostructures are attributed to their hierarchical morphology, which provides a large surface area and a high number of active sites for target.

Overall, the results of this study showcase the potential of hierarchical porous nanostructures. The innovative synthesis method using organic templates offers a promising approach for the large-scale production of nanostructures with high exposed surface areas.

Development of a single-step process for cemented carbide powder fabrication using self-propagating synthesis method with carbonization/reduction

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Keywords: cemented carbides, self-propagating synthesis, metal carburation, metal reduction, ceramic powder

Selection of appropriate tool materials in manufacturing and machining is essential for enhancing product quality, increasing productivity, cost reduction, and achieving a more efficient competitiveness. Key requirements for tool materials include wear resistance, hardness, and high-temperature stability, which are crucial properties for tool performance. Therefore, WC-based cemented carbides are widely utilized, and WC-Co alloys (WC-Co, WC-TiC-Co, WC-TiC-TaC-Co) are predominantly used in cutting, excavation, and wear-resistant tools due to their mechanical properties. TaC is commonly used in WC-Co alloys as a particle growth inhibitor, offering high melting point, high strength, excellent electrical conductivity, and resistance to oxidation.

Self-propagating synthesis method was employed to manufacture WC and TaC materials. The self-propagating synthesis method utilizes the exothermic heat of reactants without external energy supply to form desired compounds in a short reaction time. This method offers advantages such as high purity of products, low production cost, simple process, and high thermal efficiency. Therefore, this study investigated the evaluation of properties and development of a single-step process for cemented carbide powder fabrication using self-propagating synthesis method.

The raw materials used in this study included WO_3 with a purity of 98.15% and a particle size of 41.24 μm, Ta with a purity of 98.88% and a particle size of 8.91 μm, Mg as the reducing agent with a purity of 98% and a particle size of 35.66 μm, and Black carbon as carbon source. Subsequently, the process of sample mixing, shaping, synthesis, and post-treatment was conducted to carry out the self-propagating synthesis process.

Prior to the self-propagating synthesis experiment, thermodynamic calculations such as adiabatic temperature and ignition temperature were performed using HSC Chemistry program. The experimental variables were set as the molar ratio of Black carbon for WC and the pressure of final product for TaC to examine their effects on the properties. WC monoclinic phase was confirmed under the condition of WO_3+3Mg+3C after acid treatment, with a purity and particle size analyzed to be 96.59% and 12.24 μm, respectively. TaC monoclinic phase was observed without post-treatment under the condition of Ta + C, with a purity and particle size analyzed to be 99.3% and 1.242 μm, respectively, surpassing the properties of commercial powders. Both materials were manufactured to commercial powder level using the self-propagating synthesis method, which utilizes the metal carburation/reduction reaction as a single process.

Polymer-Assisted Deposition of Al-doped HfO_2 high-k Dielectric Thin Films

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Keywords: polymer-assisted deposition, Al-doped HfO_2, high-k, dielectric

As transistors scale down, demands for high-k dielectric materials have increased. Among various high-k dielectric materials, HfO_2 have been considered as a promising material due to its large band gap, high dielectric constant, and excellent physical/chemical stability. Although several cost-effective solution-based deposition methods have been developed, their dielectric performances are inferior to those obtained by vacuum processes (e.g., atomic layer deposition, sputtering). This study demonstrates a solution-processed polymer-assisted deposition (PAD) of high-k Al-doped HfO_2 thin films exhibiting remarkable dielectric properties. The PAD ensures the control of film thickness (≥3 nm) and even Al distribution in the entire thin film. The key is HCl-mediated coordination of metal precursor and polymer. Thorough analysis on the structure and chemical composition of the dielectric layer is carried out. It is found that the phase transition from monoclinic phase to a mixture of tetragonal and amorphous phases results in excellent dielectric properties. The 7.8 nm thick thin film doped with 4.1 at% of Al exhibits a high dielectric constant of 30.2 with a high areal capacitance (674 nF cm^{-2} at 1.0 kHz), a low leakage current (3.3×10^{-9} A cm^{-2} at 2.0 MV cm^{-1}), and a high breakdown voltage (7.7 V).

Oxidation behavior of NdFeB magnet scraps under selective oxidation combined with roasting

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Keywords: NdFeB permanet magent, rare earth elements, recycling, selective oxidation, selective leaching

Since the advent of NdFeB magnets in 1984, their usage has prevailed in the field of permanent magnets by replacing existing Sm-Co permanent magnets due to their outstanding magnetic properties. In addition, big growth in electric vehicles and wind power industries has boosted their usage, concerning supply risk of rare earth elements such as Nd, Dy and Tb as Nd permanet magnets consume nearly 22 % of rare earth oxides produced all over world. However, the concentrated characteristic of REEs in the magnets, at leat 20 wt% REEs could solve the supply risk through recycling spent magnets.

In this study, special heat treatment, namely selective oxidation was introduced to make only REEs elements in the spent magnet oxidized. Based on Pourbaix diagram, Nd_2O_3 and Fe_2O_3 preferred for the selective leaching and it is common to apply roasting in air to form these oxides, allowing the selective leaching. However, it is not easy for the simple roasting to get only Nd_2O_3 and Fe_2O_3 system. If the temperature was not enough, Fe_3O_4 would form, while the excessive temperature would cause $NdFeO_3$. The pre-formed Nd_2O_3 by the selective oxidation would provide a chance to get the desired phase system for the selective leaching. So, for the pre-formed Nd_2O_3, the oxdiation behavior during the selective oxidation was first analyzed. Only Nd oxide was sucessfully formed through the selective leaching, where the oxidation rate of the Nd element and resultant Nd oxide size were dependant on the temperature of the selective oxidation. The activation energy for the oxidation under the selective oxidation condition was lower than that under the roasting in air due to the absence of the barrier for oxygen diffusion. The selectivly oxidized magnet, composed of the Nd_2O_3 and metallic Fe, could withstand higher roasting temperature without the formation of $NdFeO_3$. As a result, the desired phase system for the selective leaching could be obtained when the roasting at 660 °C was applied.

Figures

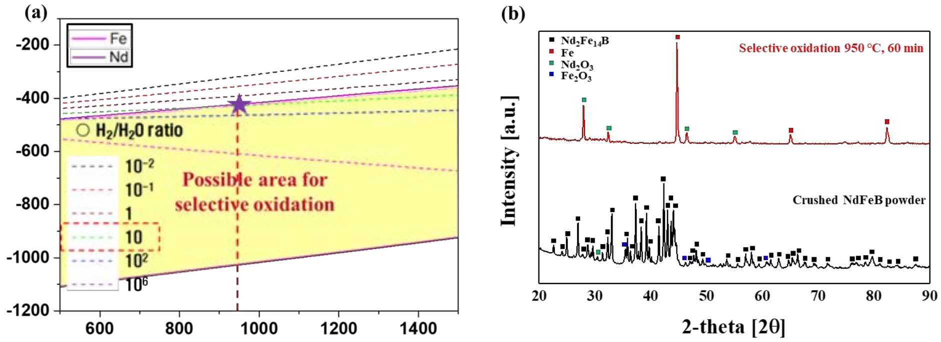

Fig. 1. (a) schematic illustrating possibility of selective oxidation for NdFeB magnet and (b) XRF patterns of crushed NdFeB magnet and selectively oxidized NdFeB magnet.

Acknowledgments

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Recycling and refining of rare metals by using molten salt electrolysis

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Keywords: electorlysis, rare metal, rare earth, recycling, refining

In this study, molten salt electrolysis process for the recycling of rare metals and rare earth elements is introduced. Molten salt electrolysis is efficient for electrolyzing various elements and alloys with high ionization tendencies without the influx of oxygen, as it involves melting inert electrolyte salts at high temperatures. Leveraging these process characteristics, this study aim to extract and refine various rare metals and rare earth materials, such as secondary battery materials, titanium, and magnetic materials from scrap or oxides.

To refine the characteristics of off-grade titanium scrap, it was aimed to decrease the oxygen concentration by using a $MgCl_2$ single molten salt process. When using Mg as a reducing agent, the oxygen removal rate is lower than that of high cost reducing agents such as Ca, La, and Y due to thermodynamic limitations. However, by continuously removing MgO from the reaction products through intended overvoltage electrolysis, it is confirmed oxygen removal efficiency exceeding the theoretical limit. Consequently, it was confirmed that oxygen levels was significantly decreased to 1000 ppm which corresponding to Grade 1 titanium.

For the recycling of large quantities of spent lithium-ion batteries from electric vehicles, lithium was recovered by using carbonate (K_2CO_3-Na_2CO_3) molten salt electrolysis. The waste cathode material, acting as the cathode, accepts electrons to be reduced to Li_2O, while CO gas formed at the anode reacts to form Li_2CO_3 within the molten salt. Leveraging the difference in solubility in water, Li_2CO_3 was separated and recovered, yielding carbonate lithium with over 99% purity from spent lithium-ion battery cathode materials.

Rare earth element were extracted from NdFeB magnets using molten magnesium halides. Magnesium halide and spent NdFeB magnet reacted to produce rare earth halide, which is used as a raw material for the electrolysis process of REE metals. Based on thermodynamic calculation, magnesium fluoride were confirmed as an extraction reagent and binary halides compositions with alkali metal salts were selected in order to reduce the process temperature. The extraction was proceeded by reacting crushed spent NdFeB magnet with molten halides at temperatures of 900°C in an argon atmosphere. As a result, using the extracted of rare earth halide with alkali halides, neodymium with a purity of more than 99 wt% was obtained.

Various rare metals and rare-earth elements were recovered and refined through molten salt electrolysis processes. All processes were validated for the electrochemical tendencies through various analytical methods, and the characteristics of the final products were utilized to evaluate the efficiency of the molten salt electrolysis process.

3D interconnected NaCl microstructures for sacrificial templates in the fabrication of porous film

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Keywords: sacrificial template, porous film, composite, self-assembly, electric field

The sacrificial template method, similar to the root technology of casting, is widely used in the preparation of porous films. It involves obtaining a material with a specific shape by removing a part of the mixed whole (template/model). The preparation of porous polyimide films typically involves using SiO_2 particles as sacrificial templates to disperse into the polyacyl acid solution. After acylation, the SiO_2 is removed by immersing the composite film in hydrogen fluoride, resulting in the formation of porous films. However, this sacrificial template method is environmentally unfriendly and the SiO_2 particles cannot be reused. To address these issues, a new environmentally friendly method for the preparation of porous films is presented in this study. The water-soluble compound NaCl is used as a sacrificial template. After it is dissolved in water, the NaCl can be recrystallised for further use, which greatly reduces the loss of NaCl and prevents pollution. The size and content of the pores can be controlled by adjusting the particle size and the amount of filler. However, if the filler concentration falls below a certain level, some of the filler becomes completely surrounded by the substrate and is unable to come into contact with the dissolution solution. This greatly restricts the use of the template method in the production of less porous films. In this study, we fabricated highly self-assembled 3D T-shaped NaCl microstructure composite films by controlling the location of NaCl in the polymer matrix through external AC electric field treatment. NaCl was arranged in chains along the direction of film thickness, and it self-assembled into a network structure on the surface. Even when the NaCl content was well below the percolation threshold, it could still be fully solubilized in water due to its aggregation on the surface, resulting in a porous film. The field of application of the sacrificial template method is extended by the electric field treatment method.

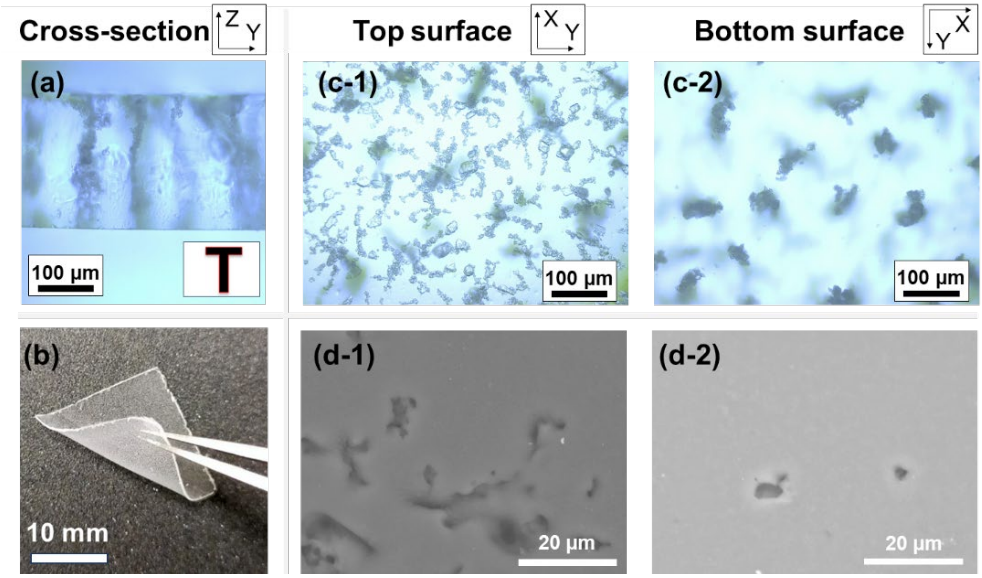

Fig. 1. T-shaped structure of 2 vol% NaCl/polymer composite film treated by AC 3 kV/mm electric field. Top and bottom surface (c) before and (d) after water treatment.

One-pot room temperature synthesis of $In_3Sn/\gamma\text{-}Ga_2O_3$ core-shell nanoparticles via two-step sonication to EGaInSn alloy

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Keywords: ultrasound, EGaInSn, core-shell, nanoparticles, room-temperature synthesis

Introduction: γ-gallium oxide (Ga_2O_3) is a wide-gap semiconductor showing catalytic activity, gas-sensing properties, and fluorescence. However, owing to its unstableness under high temperatures (>550 ºC), γ-Ga_2O_3 has been synthesized by a limited liquid phase method such as the hydrothermal method.

Our previous study has reported that metal-doped γ-Ga_2O_3 nanoparticles can be synthesized by two-step sonication to the liquefied Ga–aluminum (Al) alloy at room temperature [1]. This ultrasound method is an easy and ecological process for synthesizing γ-Ga_2O_3-based nanomaterials, and this previous study indicates the redox potential of metals consisting of Ga-based alloy affects the oxidation behavior of that. Herein, the ultrasound-assisted oxidation behavior of the eutectic alloy of Ga, indium (In), and tin (Sn) was investigated (denoted as EGaInSn alloy). Because In (-0.338 V_{SHE}) and Sn (-0.138 V_{SHE}) have more positive redox potential than Ga (-0.560 V_{SHE}), Al (-1.662 V_{SHE}), one-pot room temperature synthesizing the nanocomposite materials of metals and γ-Ga_2O_3 nanoparticles are expected by the ultrasound-assisted oxidation of EGaInSn alloy. From the perspective of a carbon-neutral society, non-thermal processing such as the ultrasound process for synthesizing inorganic nanomaterials is quite important because of its low energy loss, safety, and ease of handling.

Method: Ga, In, and Sn granules were mixed in a 300 mL flask heated at 100 ºC, and EGaInSn melt (1 g) was obtained. After the flask was cooled to room temperature, degassed ethanol (50 mL) was added into the flask. The flask was sonicated (45 kHz, 100 W) for 24 h (emulsification step). $N_2H_4{\bullet}H_2O$ was added into the flask, and the flask was sonicated (45 kHz, 100 W) for 24 h (oxidation step). The temperature of irradiated dispersion in the flask was maintained at 30 ºC during sonication.

Results and Discussion: Emulsification step – Emulsified EGaInSn particles sonicated in ethanol showed only broadened XRD patterns, indicating EGaInSn particles were a liquid state. FE-SEM images showed EGaInSn particles has sub-micron diameter. Compared with pure Ga, miniaturization of EGaInSn alloy by sonication did not proceed. It is considered that the difference in surface tension, viscosity, and redox potential between pure Ga and EGaInSn affected the emulsification behavior of the liquefied alloy.

Oxidation step – After sonication in $N_2H_4{\bullet}H_2O$, EGaInSn submicron particles were oxidized to γ-Ga_2O_3, and In_3Sn intermetallic compound was obtained (Fig.1). The results indicate only Ga of EGaInSn were preferentially oxidized to γ-Ga_2O_3 by sonication in $N_2H_4{\bullet}H_2O$. It is considered In_3Sn precipitated with the decrease of Ga owing to the oxidation from Ga to γ-Ga_2O_3. The contrast of brightness observed in TEM image indicates that the obtained submicron particles had a core-shell structure of metal and oxide. STEM–EDX mapping (Fig.2) revealed the core particles contain In and Sn a lot, and the shell contains Ga a lot, indicating In_3Sn/γ-Ga_2O_3 core-shell particles were synthesized by ultrasound-assisted oxidation of EGaInSn submicron droplets at room temperature. This ultrasound method can be a versatile method for synthesizing various γ-Ga_2O_3-based core-shell nanoparticles.

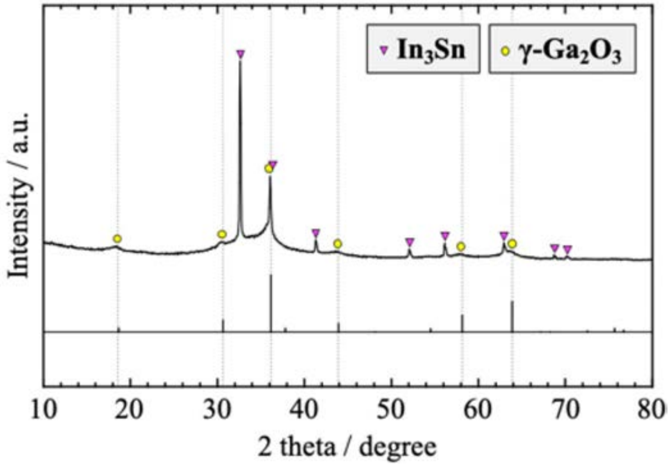

Fig.1 XRD patterns of γ-Ga_2O_3 core-shell particles obtained after ultrasound-assisted oxidation of EGaInSn droplets.

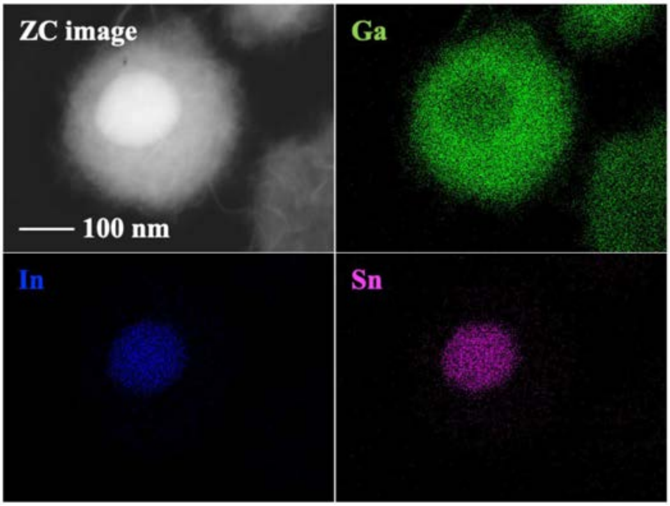

Fig.2 STEM–EDX mapping of γ-Ga_2O_3 core-shell particles obtained by oxidation of EGaInSn droplets.

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Concept and application of polycrystal Ag nanowire flexible transparent conductive film for sustainable development goals by organic precursor painting reduction method

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Keywords: silver nanowire, organic precursor, polycrystal silver, sustainable prosess

Ag nanowire transparent conductive film is one of alternatives to indium tin oxide films in the application of flexible touch panels. Ag nanowire transparent conductive composite film, which is prepared by depositing Ag nanowires onto a substrate, shows both high optical transparency and high electrical conductivity. The film can be easily prepared via liquid suspension, so it is said to have advantages as compared to Indium Tin Oxide transparent conductive film from the viewpoints of cost saving and applicability to large area substrate. Moreover, Ag nanowire transparent conductive film coated onto flexible polymer substrate shows good bending tolerance, it can be used in flexible devices, such as flexible display, lighting equipment, and so on. Generally, polyol method, which is performed in liquid phase, is used as a synthetic method of Ag nanowires. Although Ag nanowires with high aspect ratio and nanometer-sized diameter can be synthesized by this method, there are some problems on synthetic conditions, processes, cost and waste emission. Furthermore, Ag nanowires obtained by polyol method are single-crystalline solid wires. Although Ag nanowires with high aspect ratio and nanometer-sized diameter can be synthesized by this method, there are some problems on synthetic conditions, processes, and waste emission. Furthermore, Ag nanowires obtained by polyol method are single-crystalline solid wires. In general, it is necessary to apply Ag nanowires to complicated high temperature and high pressure annealing process to make connections among wires when transparent conductive film is prepared. Consequently, the overall process requires high cost and emits much waste.

To improve these problems, a novel method, painting and subsequent reduction of organic precursor, is proposed in this satud. In this method, needle-shaped organic precursor was fabricated by economy and ecology process (low cost, low environmental impact), and then Ag nanowire is simply obtained by splaying and reducing them to metallic Ag with retaining their needle-shaped morphology. By optimizing painting and reducing conditions of the precursor, preparation of highly transparent and conductive Ag nanowire transparent conductive film could be expected. Nanowire are not single crystal nanowire but polycrystal structure.

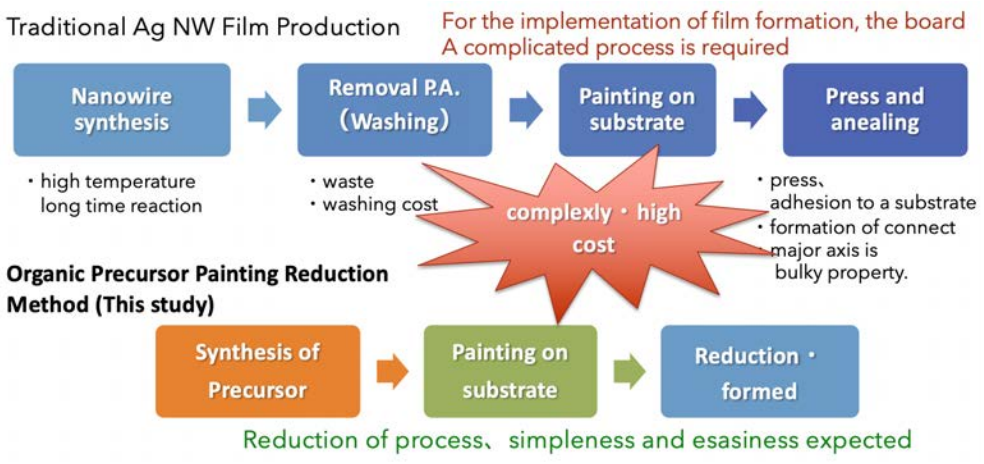

Figure. Comparison with conventional method in Ag TC film

This film can be easily prepared *via* liquid suspension, so it have advantages as compared to Indium Tin Oxide transparent conductive film from the viewpoints of cost saving and applicability to large area substrate. In addition, it doesn't require high temperature condition when reducing the precursor, that is, it can be applicable to low heat resistance materials, such as PET, PC, and so on. Anyone can easily make a flexible transparent conductive film by this process for SDGs.

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T4.11 Hybrid and Bio-inspired Materials

Effect of interfacial Fe_3O_4 nanoparticles on the microstructure and mechanical properties of textured alumina and utilizing the result to make hierarchical bioinspired ceramic composites

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Keywords: crystallographic texture, magnetically assisted slip casting, ultrafast high-temperature sintering, crystallographic defects, strength, fracture, toughness, bioinspired microstructures

The recent texturing process of alumina employs magnetic fields to align alumina microplatelets coated with a small amount of Fe_3O_4 [1,2]. After ultrafast high-temperature sintering (UHS), Fe atoms are found at the grain interfaces and within the grains, influencing the mechanical properties. Here, we compare the microstructure and mechanical properties of textured alumina prepared with and without Fe_3O_4 and sintered using UHS or conventional sintering (CS). Microstructural analysis using electron backscattering diffraction (EBSD) indicates that Fe_3O_4 induces crystallographic defects in the ceramic after UHS. Nanoindentation-induced fracture enlightens that the presence of Fe_3O_4 in the UHS samples leads to plastic flow that increases the energy dissipation by 122 % compared to pristine samples. Overall, these crystallographic defects increase the flexural strength and fracture toughness by 16.3 and 75 % compared to pristine samples, reaching values of 287 MPa and 7 MPa.m$^{0.5}$, respectively. This result is thus utilised to make hierarchical ceramic composites with bioinspired microstructures such as horizontal, periodic and graded, thus filling the design space for tuneable mechanical properties and saving the time and energy required for densification. These results could be leveraged to produce stronger, tougher ceramics with more complex designs in the future, with applications ranging from structural to biomedical.

Acknowledgments

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Electrospun piezoelectric patch enriched with smart drug nanocarriers for the functional regeneration of infarcted heart tissue

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Keywords: drug nanocarriers, organic-inorganic patch, heart regeneration, electrospinning

Cardiac diseases are the principal cause of death in the EU, and, among those, myocardial infarction (MI) impacts a significant portion of the total occurrences. After MI, a portion of the myocardium tissue is substituted by fibrous tissue showing very limited physiological functions, with consequent severe heart dysfunction [1]. The Horizon Europe REBORN project (*https://www.rebornproject.eu/project/*) aims to address this clinical need through the design of a novel implantable cardiac patch enabling the remodelling of functional heart tissue.

The overall idea relies on the development of a piezoelectric fibrous patch enabling the following multiple functions: *i)* provide electromechanical coupling to the myocardium *ii)* mimic the structure of the extracellular matrix for supporting myocytes, and *iii)* incorporate drug nanocarriers to provide *in situ* on-demand release of anti-inflammatory and anti-fibrotic agents in the most appropriate timeframe after the MI.

The present work aims at exploiting EPS coupled with a rotating drum collector for the fabrication of polyvinylidene fluoride (PVDF) piezoelectric membranes with well-defined aligned nanofibres. To provide drug release according to defined spatiotemporal specifications, ultrasound (US) responsive mesoporous nanoparticles (MSNs) have been prepared and loaded with ibuprofen. To this aim, amino-modified-MSNs were grafted with sodium alginate (SA) and cross-linked with $CaCl_2$ solution to exploit the reversibility of coordination bonds between Ca^{2+} and COO^- grupos of SA [2].

Morphology (FESEM) size and zeta potential (DLS) of drug@MSN-SA were analysed, while FT-IR and TGA analysis confirmed the successful surface functionalisation and drug loading.

An *ad hoc* US system has been used to investigate the drug release upon highly controlled US stimulation and explore a broad range of US parameters (i.e. frequency, intensity).

The optimised SA-coated MSNs were incorporated into the electrospun patch, which was proved to retain well-aligned PVDF fibres and appropriate mechanical properties.

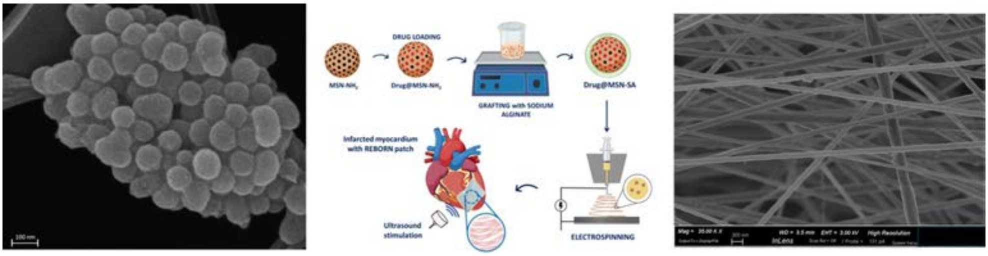

Figure 1: FESEM of drug@MSM-SA(left); methodology and rationale of REBOR project (center); electrospun PVDF containing (5%wt.) of drug@MSM-SA (right)

Acknowledgements

"Funded by the European Union. Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or the European Health and Digital Executive Agency (HADEA). Neither the European Union nor the granting authority can be held responsible for them."

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T4.12 GRAPHENE AND 2D MATERIALS

In-situ TEM study and fracture behavior characterization on 2D materials: from graphene to beyond

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Keywords: in-situ TEM, 2D materials, fracture behavior, mechanical property

Two-dimensional (2D) materials, epitomized by graphene, have captivated researchers worldwide with their extraordinary peroperties as promising materials in electronics/opto-electronics, energy storage/conversion, etc. [1] However, the full potential of these materials can only be realized through a comprehensive understanding of their structure-property relationships at the nanoscale. In-situ transmission electron microscopy (TEM) is a technique where a TEM tool is used to unravel the intricate microstructure and dynamic behavior of materials in real time. The fast development in the microscopy instrumentation advances in-situ TEM into a fast-growing, increasing important and fascinating technique in various fields ranging from materials science to chemistry, biology, etc. [2] It provides crucial kinetic information on a material that cannot be obtained by conventional ex-situ methods. [3]

In depth understanding the mechanical behavior of 2D materials at the nanoscale is crucial for optimizing their performance and engineering novel applications. However, this is a very challenging task considering their extremely small sizes and thicknesses. In-situ TEM shows great superiority in this respect due to very high spatial resolution, but it normally requires delicate sample preparation and methodology development. Here, we present in-situ mechanical testing inside a TEM tool to study several types of 2D materials including graphene, silicene and covalent organic framework (COF). The fracture behavior of studied 2D materials is oberserved in real time. Dedicated sample preparation and transfer methods are also provided.

Figures

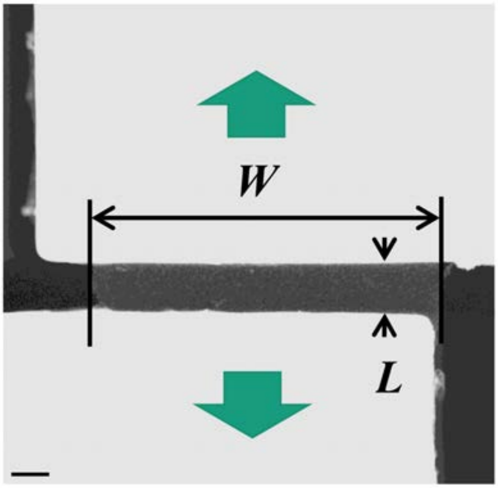

Figure 1. A suspended 2D COF testing sample on push-to-pull device (L, length; W, width).

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Gamma irradiation effects on the synthesis and properties of 2D-and graphene-based materials and their application in electromagnetic interference shielding

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Keywords: gamma radiation, EMI shielding, 2D materials, graphene-based materials

Electromagnetic interference (EMI) is a term representing such a phenomenon where one electromagnetic wave interferes with other waves, resulting in the degradation of electromagnetic signals. For the use in EMI shielding, the new material should be optical transparent, thin, elastic, durable, fexible, chemically stable, economically acceptable, produced by eco-friendly procedure, low-cost and resistive to moisture, in order to be applicable in the space and aircraft industry, motor vehicles, portable and wearable electronic devices. The unique and advantageou properties of graphene, such as large specific surface area, low density, aspect ratio and electrical conductivity, outstanding electrical conductivity, and ease of processability, make it as the best candidat from 2D-materials for application in various research areas of material science, chemistry and physics, condensed matter, nano-technology, chemical and electrical engineering and in medicine.

In recent years, there has been a growing interest in the application of gamma irradiation as a tool for a simple, eco-friendly, clean and easy method for structural modification and turning the physicochemical properties of different (nano)materials, as well as 2D-and graphene-based materials. This established non-contact process is used to create a reductive medium which is deemed simpler, purer and less harmful than conventional chemical reduction. As a radioactive source, a ^{60}Co gamma source was used in the gamma sterilization facility at the Vinča Institute. In order to study the possibility to improve optical properties, a lower doses of gamma irradiation up to 15 kGy on GQDs were done and after gamma irradiation the increase of photoluminescence was noticed. Due to their chemical properties, AgNWs create complex easily with GO and highly improve electrical conductivity and electromagnetic interference shielding efficiency. An increasing of ξ-potential values of gamma-irradiated GQDs compared with p-GQDs was due to a change in the amount of negatively charged functional groups during gamma irradiation in the presence of ethylenediamine, probably due to the lower number of carboxyl functional groups. [1] Gamma irradiation could highly improve graphene electromagnetic interference shielding behavior. The shielding efficiency of around 6.5 dB was measured for the r-GO free-standing film, while gamma-irradiated graphene in two different solvent, isopropyl alcohol and water, as oxidation and reduction media, will be additionaly measured.

Acknowledgments

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T5 Technology, Society and Sustainability

T5.1 GLOBAL INNOVATIONS IN BIOMATERIALS, BIOMANUFACTURING, AND BIOTECHNOLOGIES

Ball-on-three-balls strength testing of hydroxyapatite ceramics depending on the powder origin

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Keywords: strength, hydroxyapatite, ball-on-three-balls, bioceramics, mechanical properties

Hydroxyapatite as the mineral occurring naturally in bones, it is an ideal replacement in situations where it is necessary to replace or supplement part of the bone. Although enormous scientific efforts have been made in recent decades to synthesize it by various methods and procedures, and many companies now produce pharmaceutical-grade hydroxyapatite or deficient hydroxyapatite powders for medical applications, they differ mainly in physical properties.

In this research, three different commercial hydroxyapatite powders were used to prepare the disk-shaped specimens sintered at 1300 °C for 1h, with parameters selected due to the best biocompatibility response during the cytotoxic testing. Specimens were used to determine mechanical properties under biaxial loading using B3B testing, which secures maximal stress distribution in the centre of the disk without edge effects. The strength of as-sintered bioceramic specimens was evaluated according to Weibull statistical fracture theory and showed variation not only depending on the bulk density but also on the origin of the powder. This effect shows the importance of powder characteristics such as grain size, grain size distribution, powder compressibility as well as flow functions.

Acknowledgments

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Development of antimicrobial composite coating incorporating AgNPs-decorated SiO_2 nanospheres in a polysilazane matrix

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Keywords: silver nanoparticles, coatings, polysilazane, antibacterial

Among global concerns about the spread of superbugs and viruses, new antimicrobial coatings have been explored to develop innovative solutions. One approach involves the synthesis of a composite coating comprising polymeric ceramic precursor and silica nanospheres decorated with silver nanoparticles (AgNPs-nSiO_2). The method consists in two phases. Firstly, AgNPs-nSiO_2 are produced through a sol-gel synthesis process followed by heat treatment at 700°C. Subsequently, the so-obtained AgNPs decorated nSiO_2 are incorporated into a polymeric matrix to introduce silver as the antibacterial agent. The resulting coating is deposited on sodalime substrates.

Morphological, compositional and structural analysis confirmed the synthesis of AgNPs onto nSiO_2 and quantified their concentration. The antibacterial properties of AgNPs decorated nSiO_2 was also demonstrated through the inhibition test towards *Staphylococcus epidermidis*.

The dispersion of the AgNPs decorated nSiO_2 into a polysilazane as a ceramic precursor (commercially known as Durazane 1800) successfully occurred and the so-obtained composite coating was characterized in terms of morphology, composition, structure and antibacterial properties. This research was made possible through the collaborative efforts of the MICS extended parnership within the Nanosustech project. The goal of this project is to innovate and create intelligent, eco-friendly nanostructured materials aimed at mitigating the impact of chemical pollutants and microbiological contaminants on indoor air quality.

Acknowledgments

This study was carried out within the MICS (Made in Italy – Circular and Sustainable) Extended Partnership and received funding from the European Union Next-GenerationEU (PIANO NAZIONALE DI RIPRESA E RESILIENZA (PNRR) – MISSIONE 4 COMPONENTE 2, INVESTIMENTO 1.3 – D.D. 1551.11-10-2022, PE00000004). This manuscript reflects only the authors' views and opinions, neither the European Union nor the European Commission can be considered responsible for them.

Morphological and structural evaluation of conventional prepared calcium silicate ceramics from eggshell and silica gel

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Keywords: bioceramics, calcium oxide, eggshell, silica gel

Calcium silicate-based materials (CS) have attracted a lot of attention as promising materials for bio-applications, including dental restoration, drug carrier, tissue engineering, and bone repairing and regeneration, owing to their remarkable biocompatibility, bioactivity, and biodegradability properties. In general, CS materials can promote apatite formation on the surface upon implantation when they are connected to biological fluids in the form of ceramics, powders, and ceramic coatings. Nonetheless, the biological activity of calcium silicates is determined by their structure, which can be manipulated by a variety of factors including the sintering temperature, precursors, composition, porosity, and manufacturing technique. An increase in demand for synthetic bioactive materials has been marked by the increase in clinical demands and the population. Therefore, a new approach has been recently trending that adopts the use of natural wastes, as raw materials for the preparation of bioactive materials to overcome the issues regarded the high-cost manufacturing and diminish the chemical residuals remaining from the production process.

In the present talk, calcium silicates were successfully prepared using eco-friendly natural sources namely chicken eggshells and silica gel from desiccators. Upon the heat treatment in the air at 900 °C for 7-12h, the reaction of the extraction of calcium oxide (CaO) will occur. Whereas the silica (SiO_2) has been prepared by ball milling. Different ratios have been produced, pressed in dry conditions, and then subjected to heat treatment in the air at 800 °C for 1h. An extensive set of analytical methods was used to determine the effect of the CaO/SiO_2 ratio on the evolution of the phase structures, morphology, and biological properties. Different phases and microstructures were observed for the variety compositions that resulted in high porous and melted composites.

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T5.2 GLOBAL YOUNG INVESTIGATOR FORUM

Elucidation of liberation mechanism of cathode active materials from lithium-ion battery cathode composite for direct recycling

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Keywords: lithium-ion battery, recycle, DEM

Cathode active materials in LiBs (lithium-ion batteries) contain rare metals such as lithium, nickel, cobalt, and manganese. Since these metals have high scarcity value, their recycling is important issue[1]. Currently, a combination process of pyrometallurgy and hydrometallurgy is used for recovering of these rare metals. This is a process with high environmental impact due to the lengthy processes and the large amount of chemicals used. In recent years, investigation of direct recycle has been conducted to recover cathode active materials from spent LiBs and/or manufacturing scraps in manufacturing of new Li-ion batteries[2]. This process is environmental-friendly to require fewer steps and less energy than existing processes. To realize the direct recycling process, it is inevitable to liberate cathode active materials from the cathode composite via grinding process. Since cathode active materials are bonded by PVdF binder, it is difficult to liberate cathode active materials from the cathode composite by simple grinding. In addition, deteriorating during the grinding process should be avoided for regeneration of active materials.

In this study, we tried to liberate and to recover the cathode active materials from the cathode composite by using a stirred media mill. A stirred media mill is a machine for fine grinding with grinding media. In order to liberate cathode active materials, it is necessary to detach the active materials from PVdF binder. It is considered that surface grinding by tangential forces such as friction and shear forces generated in a stirred media mill was suitable for liberation because PVdF binder is bonded around active materials. Therefore, grinding conditions for surface grinding with large tangential energy and a large number of grinding media collisions were determined from DEM (Discrete Element Method) simulations. The simulation results showed that the optimal grinding conditions could be achieved by using different diameters of the media. Based on these simulation results, we conducted grinding experiments. In this experiment, the liberation was evaluated by weight fraction under 32 μm. In case of using only ϕ10 grinding media, weight fraction under 32 μm was 53 wt%. In case of using ϕ10 and ϕ3 grinding media, the fraction increased to 62 wt%. We discussed the liberation mechanism of cathode active materials from simulation and experiment results. In addition, we verified that the recovered cathode active materials was not altered via grinding process and was suitable for direct recycling . We believe that this liberation process is applicable not only for cathode active materials but also for various ceramic powder materials.

Acknowledgments

We are grateful to AESC Japan LTD. for providing cathode samples.

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Antimicrobial/antiviral composite coatings via co-sputtering method

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Keywords: antibacterial, antiviral, coatings, silver nanoclusters

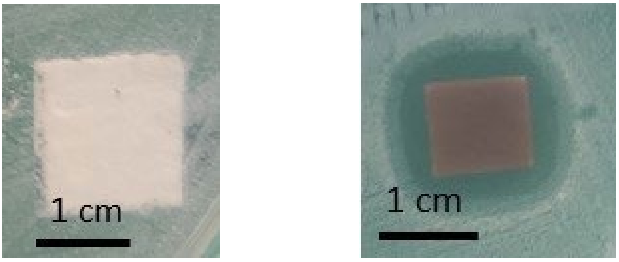
Recently, the rapid spread of the Coronavirus led to a drastic increase in respiratory illnesses; stringent lockdowns, and preventive measures were adopted worldwide to reduce the risks. This resulted in a global economic and health crisis, with numerous confirmed cases [1]. Studies demonstrated the ability of the SARS-CoV-2 virus to remain active on surfaces for varying periods of time, and its rapid transmission through contaminated surfaces, droplets, direct contact, and aerosols brought the attention of the scientific community to the use of antimicrobial and antiviral materials in everyday life [2].

In this scenario, the european NanoBloc project will provide reliable antimicrobial, antifungal, and antiviral coatings through environmentally friendly technologies, suitable for numerous textiles and surfaces. The main goals of the interdisciplinary consortium of Nanobloc project would develop and industrially upscale new nanocoatings, guaranteeing effectiveness and durability, and to be applied to several final products, including porous filter materials, and high-traffic solid surfaces, textiles.

Research at Polito has focused his attention on the study and development of thin, flexible composite coatings made of glass or ceramic matrices, exhibiting antibacterial and antiviral properties due to the presence of well-dispersed silver nanoclusters embedded within them. These coatings were deposited using the co-sputtering technique, which is an environmentally friendly method suitable for all types of materials [3]. The coatings demonstrated a slow and gradual release of silver ions, capable of slowing down and inhibiting the proliferation of bacteria, fungi, and viruses, including respiratory syncytial and influenza viruses. Their good thermal stability allowed for thermal regeneration processes and sterilization, without compromising their bactericidal and virucidal effectiveness.

The project involves other technologies, including UV cured lacquers, sol-gel, and electrophoretic deposition, building upon prior successful work.

Figures



(a) (b)

Figure1: Inhibition halo test of (a) unocated and (b) coated air filter

Acknowledgments

This project has received funding from the European Union’s Horizon Europe programme under grant agreement n. 101057597.

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T5.6 FunGlass

Enhanced shaping and functionalization of silicate bioceramics by the use of silicone precursors

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Keywords: biosilicate, akermanite, silicones, additive manufacturing

Silicone polymers emerge as very interesting precursors for silicate ceramics for bone tissue engineering applications. Being polymers, they may be shaped at nearly room temperature, by application of plastic-forming technologies, including modern additive manufacturing technologies. The specific chemistry allows for the obtainment of a relatively abundant ceramic residue, based on reactive amorphous silica. Finally, they are sensitive to the atmosphere, during heat treatment, so that pyrolysis in non-oxidative gasses (nitrogen, argon) may yield a SiOC residue, comprising nano-sized carbon domains embedded in silica-based matrix [1].

Silicate bioceramics derive from the interaction of silica with other oxides, such as Na_2O, CaO, MgO: precursors of these oxides, in form of various salts, can be easily incorporated, as fillers, in silicone matrices. The homogeneous mixing generally favours the obtaiment of phase-pure crystalline silicates, upon heat treament (at 900-1200 °C), but some difficulties may arise from the release of large amount of gasseous byproducts (from both ceramic transformation of matrices and decomposition of fillers), causing internal stresses and favouring extensive cracking, and from kinetically unfavoured reactions. These paper tackles the engineering of formulations with alkali borates and phosphates, having a multiform impact. These additives, in fact, offer, upon thermal treatment, some liquid phase, in turn providing some stress relaxation and promoting ionic interdiffusion. Hydrated variants of these salts are even more interesting, since they undergo dehydration at low temperature (300-350 °C) and determine the homogeneous foaming of silicone-based mixtures, later transformed into highly porous ceramic foams [1]. As an alternative, highly porous scaffolds with non-stochastic porosity, may be easily obtained by direct ink writing or stereolithography (the latter exploiting the easy addition, in silicone-based mixtures, of photocurable acrylates) [2].

Na_2O and CaO precursors, added with sodium phosphate, yield glass-ceramic products strictly resembling commercial Biosilicate® glass-ceramics [1]. CaO and MgO precursors, added with sodium phosphate or borate, yield akermanite ($Ca_2MgSi_2O_7$) ceramics with B- or P-containing intergranular glass phase [3]. In all cases, cell viability tests indicate a lack of cytotoxicity; this is coupled with acellular *in-vitro* bioactivity, upon immersion in SBF, as well as antibacterial activity against *S. aureus* and *E. coli*. Carbon nano-inclusions, present for silicate synthesis in nitrogen atmosphere, do not cause any cytotoxic effect; on the contrary, they accelerate the dissolution and the formation of apatite, reasonably due to the many silicate/carbon interfaces. The inclusions also determine an enhanced absorption of IR radiation, with remarkably fast heating above 60 °C, which could be exploited for disinfection of scaffolds [1].

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Phase Transition of High Entropy Oxides (HEOs) during Spark Plasma Sintering

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Keywords: phase transformation, functional ceramics, high-entropy ceramic, spark plasma sintering

High entropy ceramic oxides (HEOs) have emerged as a cutting-edge frontier of advanced research in the field of materials science and engineering. These materials have generated considerable research interest because of their novel intrinsic properties and significant potential for application in various fields. In this study, single-phase high-entropy oxides with the composition $(Y_{0.2}Ce_{0.2}RE_{0.2}Sm_{0.2}La_{0.2})\ O_{2-\delta}$, where RE= Dy, Pr, Gd was prepared by combustion synthesis. Through X-ray powder diffraction and scanning electron microscopy, both the phase composition and morphological characteristics of the powder and sintered ceramics were analyzed.

The synthesized powders were Spark plasma sintered (SPS) at temperatures ranging from 1200 °C to 1600 °C to achieve high density ceramics. Sintering above 1400°C under vacuum and reducing conditions induced phase transformation of the densified HEOs. A close correlation between the phase transformations, oxygen depletion, and the ionic radii of Ce^{3+} and Ce^{4+} was demonstrated. In the reducing environment and elevated temperatures characteristic of SPS, the reduction of Ce^{4+} to Ce^{3+} results in the increase of the Ce ionic radius resulting in the stabilization of the monoclinic B- Phase. An annealing of the samples at 1200 °C in air resulted in, the reversible transformation back to cubic structure. The change in the oxidation state of Ce was confirmed by X-ray Photoelectron Spectroscopy (XPS).

Acknowledgments

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Photochromic glass-ceramics embedded with $Gd_3Sc_2Ga_3O_{12}$:Cr^{3+}, Cr^{3+}/Pr^{3+} garnet crystals with modulated and persistent luminescence for high-security multi-mode optical storage and temperature sensing

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Keywords: glass-ceramic, photochromism, persistent luminescence, lanthanide, modulated luminescence, optical thermometry

There has been an increased attention on the development of smart materials with multifunctional photochromism (PC), luminescence modulation and persistent luminescence (PersL) due to their energy storage capability and great potential for data encryption[1]. Basically, in this kind of materials the information can be optically written-in and read out by stimulation of an external field such as thermal, optical, or mechanical stimulus, e.g. mechanoluminescence induced by ultrassound[2]. Among the suitable materials, optically activated glass-ceramics (GCs) have been widely recognised as promising candidates for optical thermometers, scintillators, and high-power solid-state lightning devices. However, most of GCs for optical applications have been based on crystallization of fluoride crystals in glasses, and the design and preparation of oxide GCs containing crystals that present persistent photoluminescence, mechanoluminescence, and photochromic properties remain challenging.

Novel optical materials with garnet structure represented by the formula $A_3[B_2](C_3)O_{12}$ exhibit both PC and PersL with readily tunable emission. However, garnet materials with micro-sized powders or single crystals limit the suitable applications due to difficulties in processing, especially where the use of bulk materials is essential.

Here, $Gd_3Sc_2Ga_3O_{12}$ garnet-based GCs were prepared by conventional melt-quenching and subsequent heat-treatment of the as-prepared gallogermanate glasses. Due to the high crystal volume fraction these GCs show long PersL and a high-contrast PC. A proper selection of dopants led to visible and near-infrared light emission covering the bio-window. As a proof of concept, a multi-modal optical information storage and read-out application was demonstrated with the simultaneous response of PersL and PC to temperature, optical, and ultrassound stimulation.

Acknowledgments

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Multifunctional biodegradable nanocomposite coatings for corrosion control of magnesium alloys

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Keywords: corrosion protection, self-healing coatings, corrosion inhibitors, adhesion strength, corrosion monitoring, stimuli-responsive release, nanocarriers

Magnesium (Mg) is considered the lightest engineering material of the 21st century. The similarity of the mechanical properties of Mg alloys to those of human bones, along with their biocompatibility and biodegradability in biological systems, have established their applicability as bone implants. However, a high degradation rate accompanied by a large volume of hydrogen evolution and an increment of the pH causes premature fractures and wound-healing complications, which limit the clinical effectiveness of Mg-based implants. Functional composite coatings have been thus of great interest for enhancing the performance of Mg-based implants[1,2]. In this work, we developed an optimized stimuli-responsive self-healing composite coating by adding polydopamine-coated chitosan-loaded mesoporous bioglass nanoparticles (PD@Chi@MBG) to a polyurethane (PU) matrix, which allows substantially slower degradation of Mg alloys upon coating damage due to the adsorption of PD and chitosan on a Mg substrate. The nanocomposite coatings were homogenously coated on a Mg AZ31 alloy using a simple dip coating method at a controlled withdrawal rate. Scanning electron microscopy–energy-dispersive X-ray analysis, Fourier-transform infrared spectroscopy, X-ray diffraction and thermogravimetric analysis were used to evaluate the surface morphology, composition and distribution of PD@Chi@MBG in the PU matrix. Electrochemical and immersion tests were performed to investigate the biodegradation performance of AZ31 alloy with and without different surface coatings in simulated body fluids (SBF) at 37 °C. The nanocomposite-coated AZ31 Mg alloys exhibited a significantly lower degradation rate than the uncoated AZ31. These results suggest that biodegradable composite coatings have great potential for application in orthopedic implants.

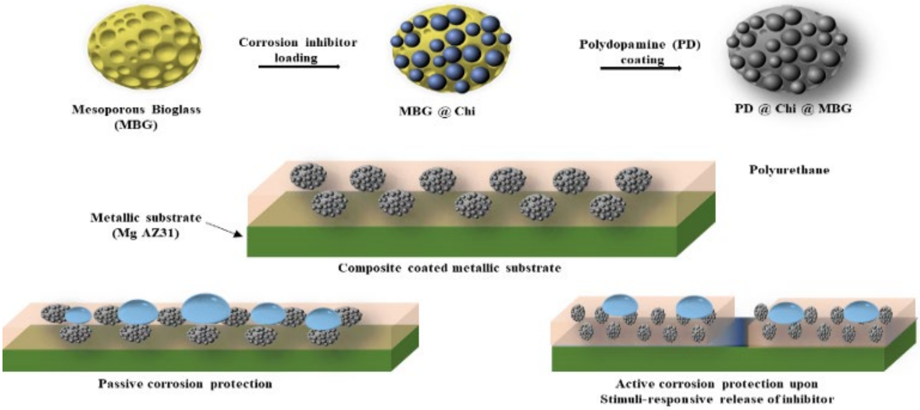

Figure: Multifunctional biodegradable composite coating system and its working principle.

Acknowledgments

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Monitoring the stability of therapeutic ions in SBF

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Keywords: SBF solution, long-term ion stability, chemical analysis

The work focuses on the analytical determination of ions used as therapeutic dopants in bioactive glasses and their chemical stability in the simulated body fluid (SBF). The long-term stability of Al, B, Ce, Cu, Ga, Sr, Y, Zn in SBF solution was investigated. The selected elements were added to the SBF solution at the concentrations of 0.5, 2.5 and 10 mg/L to monitor stability of dissolved ions after 1 hour, 7, and 14 days.

For Al, Ce, Y and Zn, the measured concentration was found to be significantly lower than the nominal values. Simultaneously with the decrease in the concentration of these ions, phosphorus and calcium were depleted from the solution. Elements which disappear from the SBF solution are most probably incorporated into the hydroxyapatite along with another phosphate salts precipitated in the solution.

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Stabilization of cerium and neodymium in alkali-activated glass as a sustainable approach for nuclear waste management

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Keywords: cerium, neodymium, alkali activation, nuclear waste management

The growing demand for sustainable energy sources capable of minimizing the generation of greenhouse gases leads to the search for environmentally responsible technologies. This implies considering the technical challenges related to immobilizing waste from the nuclear industry.

Vitrification is a well-known technology for immobilizing high-level radioactive waste [1]. However, this process has drawbacks, such as the volatility of certain radionuclides at the glass melting temperature, requiring complex gas treatment systems. Additionally, some radionuclides, including actinides, exhibit low solubility in the glass matrix [2]. The immobilization of cerium and neodymium is particularly interesting as these elements are present in the nuclear waste composition and are also used as a uranium and minor actinide surrogate, respectively [3].

In this work, a sustaintable approach to stabilize cerium and neodymium was explored by alkali activation of pharmaceutical boro-alumino-silicate glass using diluted solutions of sodium and potassium hydroxide. The glass powders were mixed with these solutions and mechanically stirred for 150 minutes prior to final consolidation at 40 °C over 7 days.

The integration of waste surrogates was carried out by establishing similarities with the conventional vitrification process. Cerium and neodymium, which are the chemical species present in the waste solution, were used as nitrates and calcined to transform them into a solid and stable waste, CeO_2 and Nd_2O_3, respectively. Two different methods were used for incorporating each powder oxide. On one hand, CeO_2 was added to the glass powder before alkali activation, while Nd_2O_3 was included in the slurry during the final stages of the alkali activation process. The bridging of adjacent particles facilitated by condensation reactions yielding Si-OH, B-OH, and Al-OH in the hydrated surface layers promoted the solidification of the glass powders [4] and the fixation of cerium and neodymium. The binding phases that result from chemical reactions in the system exhibit a remarkable level of stability, withstanding boiling water, with the exception of carbonate phases. Further densification of the blocks was achieved through viscous flow sintering at 700 °C. The waste form integrity was confirmed by boiling test, which showed that no glass particles were released into the liquid. The use of non-radioactive substitutes with similar physicochemical behavior to their radioactive analogs, combined with alkaline activation as a stabilization method, constitutes an important tool for mitigating potential environmental risks in nuclear waste management.

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Robust visible light driven 3D α-Fe_2O_3/TiO_2 photocatalytic ceramic membrane from the utilization of brown mud waste for the degradation of Bisphenol derivatives in wastewater

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Keywords: brown mud, 3D photocatalytic membranes, wastewater treatment

During the production of alumina, brown mud (BM) is obtained as a waste material. This waste material contains a relatively high amount of Fe_2O_3 along with other components such as Al_2O_3, SiO_2, Na_2O, CaO, TiO_2, etc. For every 1 ton of alumina production, approximately 1-1.5 tons of BM are produced.

In this study, a stepwise leaching process was first carried out to separate and purify the valuable elements by using the HCl. Pre-leaching in optimized conditions using 3 M HCl at room temperature for 3 hours removed 89 % of the calcium and solid silica and resulted in the dissolution of iron and aluminum with up to 90% efficiency. After precipitation, the product was characterized by XRD, which confirmed that hematite (α-Fe_2O_3) was extracted successfully from the brown mud, and the formation of goethite (α-FeOOH) was suppressed. The α-Fe_2O_3 rich brow mud was dispersed in the mixture of TiO_2 with EtOH to synthesize α-Fe_2O_3/TiO_2 photocatalyst. The modification of TiO_2 had no effect on the band gap energy of BM in the α-Fe_2O_3/TiO_2 catalyst and the photocatalyst preserved the narrow band gap of 2.5eV due to the contribution of the BM base. The as-prepared catalyst was further explored to fabricate 3D photocatalytic ceramic membrane with variable porosity (70-90%) by Lithoz-DLP based additive manufacturing technique. The α-Fe_2O_3/TiO_2 membranes were tested for the degradation of Bisphenol in aqueous media. Due to a low electron transfer resistance and the enhanced carrier separation, the present membranes showed much better performance than brown mud or TiO_2. The photocatalytic membranes also exhibited high anti-interference ability, negligible leaching, and a long-term stability during the photocatalysis process.

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Novel microspheres YAG:Eu used for the preparation of phosphor in glass

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Keywords: PiG, viscous flow, YAG phosphor

White light-emitting diodes (WLEDs) are limited in high-power fields due to their poor thermal stability. To address this issue, spectral converters called phosphors-in-glass (PiG) are considered one of the most promising solutions. Among these, the $Y_3Al_5O_{12}$:$Eu^{3+/2+}$ phosphor embedded in a glass matrix was considered as one of the most efficient solutions. In this work, novel translucent YAG-PiGs are developed through preparation by viscous flow sintering at temperatures below 700°C.

The novel $Eu^{3+/2+}$ doped YAG partially crystallized glass microspheres were prepared using the sol-gel Pechini method and flame synthesis with subsequent treatment in the $10\%H_2/90\%N_2$ reducing atmosphere. The emission spectrum of the $Eu^{3+/2+}$ doped YAG microspheres exhibited a wavelength range spanning from 450 to 800 nm, which was ascribed to the broad emission bands of Eu^{2+} ions arising from $4f^65d^1 \rightarrow 4f^7(^8S_{7/2})$ transition.

To accommodate YAG:Eu phosphor, four different glass matrices with a refractive index similar to YAG (RI = 1.83) were employed: $11.4SiO_2$-$24.3B_2O_3$-$35ZnO$-$5.3Li_2O$-$12La_2O_3$-$12WO_3$ (M1, RI = 1.8), $20Bi_2O_3$-$20ZnO$-$60B_2O_3$ (M2, RI = 1.778), $20Bi_2O_3$-$30ZnO$-$50B_2O_3$ (M3, RI = 1.779), and $10Bi_2O_3$-$40ZnO$-$50B_2O_3$ (M4, RI = 1.73). TG/DTA analysis was used to determine the glass transition and crystallization temperatures as critical parameters for viscous flow sintering. The optical properties of all four types of PiGs after sintering were evaluated.

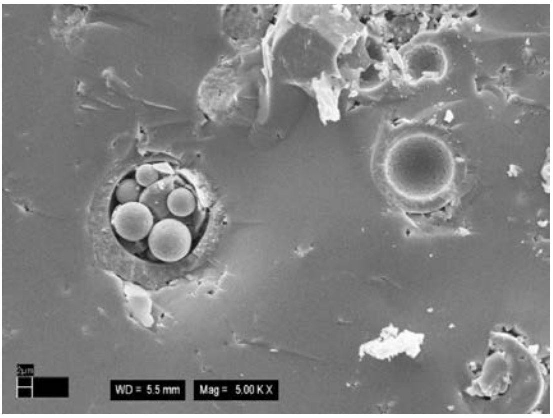

Figure 1.: SEM figure of $Eu^{3+/2+}$ doped YAG microspheres in Matrice 1 sintered in viscous flow.

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Effect of layered architecture and residual stress on contact damage of transparent ceramics

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Keywords: layered ceramics, contact damage, crack resistance

Transparent polycrystalline ceramics (TPCs) are potential alternatives to glasses and single crystals used for protective display covers in personal electronics such as smartphones. However, due to the brittle nature of ceramic materials, TPCs are prone to surface damage, which deteriorates both the mechanical performance and optical transparency of ceramic materials. In the present work, we propose a strategy to enhance the contact damage resistance of spinel ceramics through combination with alumina layers. Contact damage resistance of $MgAl_2O_4$ – Al_2O_3 laminates and their corresponding monoliths was investigated under Hertzian indentation using acoustic emission. The results showed that the generation of compressive in-plane residual stresses within the samples depends on the deposition of $MgAl_2O_4$ layers on the surface. While embedding Al_2O_3 between $MgAl_2O_4$ surface layers increased the load-bearing capability before crack initiation by ca. 70% compared to monolithic spinel, the laminar structure in which spinel was embedded between alumina layers exhibited a decrease in the crack initiation force, by ca. 25%, compared to monolithic alumina. The effects of elastic properties of the layers and non-linearities during loading were captured using finite element simulations and critically discussed.

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Structural analysis of magnesium aluminosilicate glass-ceramics by high-temperature raman and xrd studies

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Keywords: MAS glass, HT-Raman, HT-XRD, bio-active glasses

Owning to their high mechanical and thermal stability, high chemical stability, and, most importantly, osteogenesis properties, magnesium aluminosilicate glass ceramics are of particular interest to applications such as bone cement, bone grafts, implant coatings, tooth filling materials, and even toothpastes[1,2]. Glass composition, structure, and thermal history are critical parameters in modifying the properties of MAS glass ceramics[3]. For example, the mechanical performance and properties of dental crowns made from MAS glass ceramics are influenced by the heat treatment program used for sinter-crystallization. Understanding the effects of thermal history on the structural evolution of MAS glass is thus essential to developing products with the desired properties.

In the present study, we have studied the structural evolution of Magnesium Aluminosilicate Glasses (MAS) as a function of temperature by HT-Raman and HT-XRD in addition to other techniques such as SEM and XPS. Also, the impact of bulk and surface crystallization of the glasses was studied using glass powders with various particle sizes, that is, < 25 µm, 25-40 µm, 40-80 µm, and 80-100 µm). The results are beneficial in designing the sintering regime and tailoring the final properties of MAS glass-ceramics.

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ZIF-8 metal organic framework (MOF)/Ti$_3$C$_2$ MXene hybrid sheets for improvement of corrosion resistance of bio-based vanillin alcohol diglycidyl ether (DGEVA)-silica composite coatings

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Keywords: nano-carrier, Ti$_3$C$_2$ MXene, metal organic framework, smart self-healing, corrosion, biobased epoxy coating

Currently, 75% of global epoxy polymers rely on bisphenol A (BPA), a well-known reprotoxic substance. This not only represents environmental challenges but also hinders progress towards sustainable solutions. Our research focuses on changing this landscape by developing an environmentally benign alternative based on a green epoxy coating formulated with vanillin alcohol diglycidyl ether (DGEVA), a derivative of wood lignin. This innovative approach not only eliminates the reliance on BPA but also leverages the inherent properties of wood lignin to enhance barrier and adhesion properties, ultimately extending the lifespan of the coating through robust metal oxide-polymer bonds.

Based on this approach, the objective of the work focuses on further enhancing the performance of a composite coating prepared in our previous work. The incorporation of MXene nano-sheets as carriers for inhibitors would increase the overall efficacy of the coating. The critical aspect of our investigation lies in the functionalization of MXene surfaces through the in-situ growth of ZIF-8 (zeolitic imidazolate framework-8) nanoparticles. This intricate modification not only preserves the intrinsic properties of MXene nano-sheets but also adds additional functionalities, making it an ideal carrier for inhibitors in the composite coating. Electrochemical impedance spectroscopy (EIS) was applied to the reinforced intact coatings to evaluate their passive/active inhibition efficiency. The results obtained from the Nyquist diagrams indicated that the total resistance of the coating reinforced with ZIF8-modified MXene sheets was noticeably improved compared with the blank sample and the coatings containing only MXene or ZIF-8 nanoparticles.

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Fullerene (C-60) embedded MOF glass composite

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Keywords: MOF glass, fullerene, hybrid glass composite

The metal-organic-framework (MOF) glasses promise new horizons by easily extending the porosity limits of conventional porous glasses to microporous scale. There have been great effort to enhance the mechanical and chemical properties of melt-quenched ZIF glasses, the best MOF glass formers, by blending inorganic glass[1], ionic liquids[2], and polymers[3]. A similar strategy has been employed by embedding fullerene into ZIF-62 crystals to functionalize and improve the mechanical properties of ZIF-62 glass composites. Fullerene, a carbon allotrope with a diameter of approximately 7 Å, exhibits attractive characteristics due to its rich π electron nature[4,5]. Preliminary observations based on optical images (Fig. 1a), XRD data (Fig. 1b), FTIR, UV-Vis data of ZIF-62, C-60 and C-60@ZIF-62 crystals confirmed the presence of C-60 in ZIF-62. Differential Scanning Calorimetry (DSC) analysis (Fig. 1c) revealed a small reduction in the melting temperature by C-60 loading. To the best of our knowledge, the work resulted in preparation of a novel C-60@a_g(ZIF-62) hybrid glass composition.

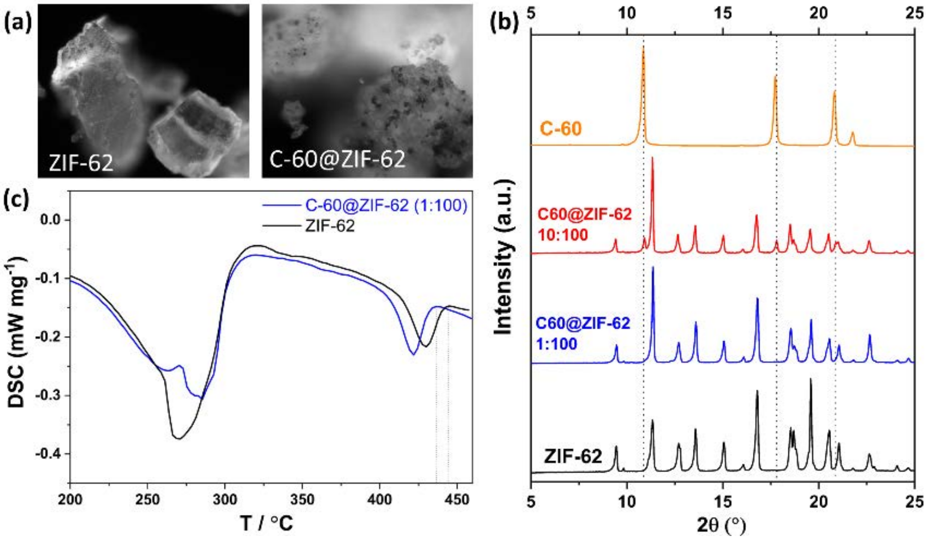

Figure 1.(a) Microscope images, **(b)** XRD profiles and **(c)** DSC profiles of ZIF-62 and C-60@ZIF-62.

Acknowledgments

This item is part of the dissemination activities of the FunGlass project, received funding from the European Union Horizon 2020 research and innovation programme under grant agreement No 739566.

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Chemical strengthening of borosilicate glass: challenges, applications, and opportunities

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Keywords: borosilicate glass, chemical strengthening, mechanical properties, wear

Specialty glass, and borosilicate glass in particular, plays a vital role in pharmaceutical packaging. The chemical stability of borosilicate glass enables the storage of medicines and drugs for a long time. However, glass is prone to surface damage at various stages of its lifetime, including production, packaging, transport, and shelf life, which dramatically reduces its mechanical durability. Therefore, developing glass products with improved resistance to surface damage and defects would be key to extending the use and shelf time of pharmaceutical packaging. In this presentation, the chemical strengthening of borosilicate glasses and its challenges and possibilities are reviewed. Different pharmaceutical glasses were subjected to conventional and electric field-assisted Na^+/K^+ ion exchange by immersion in molten KNO_3 salt baths containing various amounts of impurities such as sodium and calcium. The ion-exchanged glasses were characterized in terms of bending strength, hardness, resistance to indentation fracture, and wear behavior. The results show that the chemical composition of the salt bath greatly impacted the efficiency of chemical strengthening. Na^+/K^+ ion exchange doubled the bending strength of borosilicate glasses; the exchange of smaller Na^+ ions in glass with larger K^+ ions from the salt bath produces a compressive surface layer which increases the bending strength. In contrast, the results show that Na^+/K^+ ion exchange has a negative impact on wear behavior and scratch resistance; this is accounted for by the reduction of glass free-volume due to the stuffing of larger K^+ ions into the structure of glass.

Acknowledgments
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Multifunctional composite systems based on nanostructured magnetite anchored to SBA-15 as potential candidates for advanced materials technologies

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Keywords: multifunctional composite systems, SBA-15 mesoporous silica, magnetite nanoparticles, reusable magnetic catalyst

Nowadays there is a great demand for advanced multifunctional materials to provide effective solutions to several technological and scientific challenges associated with a variety of fields. Among the most in-demand fields are those related to biomedicine, environment, and energy. Therefore, the possibility of designing and developing a group of materials with the potential to be applied to a wide scope of problems related to those fields presents a significant advantage. Consequently, those composite systems that combine mesoporous silica particles with superparamagnetic iron oxide nanoparticles (SPIONs) are very promising candidates due to their versatility and tunability. Of particular interest are those based on SBA-15 rod-shaped particles and Fe_3O_4 nanoparticles, since both exhibit outstanding physicochemical and biological properties when studied separately. Combined, these components can serve as catalysts, sensors, adsorbents, scaffolds for tissue regeneration, theranostic platforms, and magnetic carriers. They offer protection to sensitive biological and technological molecules from degradation or harmful environmental conditions[1,2]. Accordingly, SBA-15 mesoporous silica has been shown to have exemplary chemical and hydrothermal stability, exhibiting 2D hexagonal symmetry with 3D pore connectivity constituted by a system of ordered cylindrical pore channels with diameter sizes in the mesoporous range interconnected by micropores. Furthermore, its surface reactivity due to the presence of a large number of silanol groups allows it to be modified with many different functional groups. For its part, the incorporation of SPIONs provides a new set of beneficial effects attributed to its nanoscale size and magnetic properties, creating a robust structure by reinforcing the mechanical properties of SBA-15. For environmental applications, its presence allows the composites to be used as recoverable Fenton and photo-Fenton catalysts to degrade pollutants in water bodies, which has become one of the main concerns of current societies[3,4].

This work describes the characteristics of different SBA-15@ Fe_3O_4 composites obtained from optimized synthesis procedures using various approaches and magnetic doping. The structural, textural, and magnetic characteristics, as well as the modification of the surface chemical composition, are discussed. The presentation also includes selected examples of their suitability as catalysts focused on the treatment and elimination of contaminants found in conventional wastewater.

Acknowledgments

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Robocasted Boron-doped S53P4 bioactive scaffolds for bone tissue regeneration

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Keywords: robocasting, scaffold, bioactive glass, bone tissue engineering

The incorporation of therapeutic ions, such as boron (B), into bioactive glass (BG), biologically enhances the performance of the system. This enables the fulfillment of specific requirements, including the stimulation of vascular endothelial growth factor (VEGF), which is essential for architectures that mimic natural bone structure. This study uses robocasting (direct-ink writing), an extrusion-based additive manufacturing (AM) technique, to craft three-dimensional (3D) scaffolds using a composite ink of B-doped S53P4-based BG and a gelatine-based binder. The B-doped S53P4 SiO_2-Na_2O-CaO-P_2O_5 BG system was fabricated through water quenching and ground to a particle size of less than 40 µm. X-ray diffraction (XRD) and inductively coupled plasma-optical emission spectroscopy (ICP-OES) were utilized to analyse the system's fidelity for scaffold fabrication. When thermal processes are conducted at temperatures surpassing the crystallization onset, the amorphous phases within the structure of BGs undergo an undesired transformation into crystalline forms. This structural change negatively impacts the efficacy of the ions released from the glass, thereby inhibiting their biological activity. Therefore, scaffolds were sintered at the crystallization onset obtained from differential scanning calorimetry/thermogravimetry (DSC/TG) analysis, resulting in a shrinkage of around 30% in volume. Both heat-treated and non-heat-treated scaffolds were subjected to *in-vitro* simulated body fluid (SBF) solution for various periods (24h, 72h, 1, and 2 weeks) to confirm the hydroxyapatite-like crystal formation. The scaffolds were examined after immersion to SBF using scanning electron microscopy (SEM), XRD, and fourier transform infrared spectroscopy (FTIR) for the *in-vitro* bioactivity. Evaluating further structural integrity and mechanical behaviour, significantly will contribute to advancing our understanding of their potential applications in tissue engineering.

Acknowledgments

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Cold-sintering of phosphor in glass (PiG) for solid state lighting

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Keywords: solid state lighting, silicate glass, phosphor, cold sintering

The widely used white light-emitting diode consists of InGaN chip and YAG:Ce^{3+} phosphor dispersed in organic silicon. The silicone matrix is characteristic by a low thermal and chemical stability and is discolored after long-term exposure to high-power illumination [1, 2]. To solve this problem and meet the trend of high-power high-brightness wLED, multiple technical routes have been proposed. For example, the phosphor powder can be sintered on a ceramic plate, or a phosphor powder and silicate glass mixture can be sintered by viscous flow [3]. Both processes require sintering temperatures higher than 500 °C that can impair the phosphor properties and lead to photoluminescence quenching. Glass is considered a suitable substrate material to provide a chemically reliable and thermally stable environment for the phosphor. In previous studies, the possibilities of precipitating phosphor or rare earth doped crystals from glass were explored, but the luminescence properties were not satisfactory.

Cold sintering is an emerging technique that allows densification of ceramic powders under applied pressure and a comparably low temperature (< 350 °C). This technique also enables the sintering of silicate glass with random types and combinations of phosphors. In addition, with this technique, not only the selection of glass and phosphor, but also the color and device structure design can be flexible. In this presentation, as a first step of this research, we explore glass cold-sintering with low melting temperature flux, which, to the best of our knowledge, is used in the glass cold sintering for the first time. Starting from borosilicate glass, the influence of the glass formers and flux species / amount on cold sintering behavior was investigated. Preliminary results and lessons learned from the sintering process are presented.

Acknowledgments

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POSTER

T1 Ceramics for Energy Conversion, Storage, and Distribution Systems

T1.1 HIGH-TEMPERATURE FUEL CELLS AND ELECTROLYSIS

A study on recirculating hotbox design for a 10kW solid oxide electrolysis cell (SOEC) system

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Keywords: solid oxide electrolysis cell (SOEC), hydrogen production, hotbox, heat recovery, system efficiency

To enhance the efficiency of hydrogen production in Solid Oxide Electrolysis Cell (SOEC) systems operating at high temperatures, the development of hotbox systems with effective heat recovery functionalities is imperative. In this study, we analyzed the efficiency characteristics of a 10 kW SOEC system utilizing industrial waste steam as external heat sources and conducted the design of a hotbox maintaining stack temperatures within the SOEC system and featuring primary heat recovery for stack off-gas. To validate the stack model for system analysis, I-V tests were conducted on a stack with an active area of 100 cm^2. Evaluation of a 22-layer SOEC stack operating at 700°C indicated a stack efficiency of 34.7 kW/kgH_2 at 40A current, with a hydrogen production rate of 0.36 Nm^3/hr. Additionally, under high-current operating conditions, the same stack exhibited a stack efficiency of 43.6 kW/kgH_2 at 100A. Aspen HYSYS was used for the basic design of the SOEC system, and efficiency analysis was conducted based on the stack operating conditions, external steam supply temperature, and off-gas recirculating conditions. The design study shows that the system efficiency is influenced by the supply temperature of externally provided steam and the effectiveness of the heat exchanger, and that a stack off-gas recirculation system that receives 200°C steam can result in an SOEC system design with an efficiency of 81% or higher. In preparation for hotbox fabrication, a hotbox subsystem design was developed to supply steam through trim-heating from the off-gas of the stack after primary heat recovery. The study included the derivation of design specifications for the hot-BOP and an analysis of system efficiency. In order to design the insulation of the hotbox, incorporating steam supply piping, a thermal analysis model was developed. Analytical validation verified that insulation performance was effectively maintained, resulting in an average surface temperature of 47°C on five exterior insulation surfaces of the hotbox at a stack operating temperature of 700°C.

In conclusion, the hotbox design has been completed to ensure system efficiencies ranging from 56% to 78% during 10 kW stack operation, with external water supply temperature being a determining factor. Subsequent research will involve the integration of stack modules into the fabricated hotbox to validate hydrogen production efficiency within the hotbox system.

Acknowledgments

This work was conducted under the framework of Reseach and Development Program of the Korea Institute of Energy Research (C4-2402).

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"New design and performance evaluation of 1 kW-class reversible solid oxide electrolysis-fuel cell stack using flat-tubular cells" Y.S. Choi et al. J.of Power Sources, Vol.542 (2022).

Comprehensive investigation of LSCF degradation in varied aggressive atmospheric conditions for enhanced SOFC performance

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Keywords: SOFC, LSCF, degradation, aggressive atmosphere

Solid oxide fuel cells (SOFCs) epitomize a significant leap in clean energy conversion technologies, facilitating efficient and environmentally friendly electricity generation. The performance and durability of SOFCs crucially hinge on the electrode materials used. Among these, $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF), a perovskite material, is distinguished by its excellent electrical conductivity and operational stability, making it an ideal candidate for cathode applications. This study delves into the interactions of LSCF with a range of atmospheres containing HCl, CO_2, and H_2O over temperatures spanning 550 to 650 °C. The aim is to assess the material's resilience under conditions that simulate SOFC operation in poluted atmosphere.

The experimental results reveal that the full decomposition of LSCF, upon exposure to synthetic air containing 10% water vapor, 1% to 71% CO_2, and HCl, results in the formation of several compounds, including $SrCl_2(H_2O)_6$, LaOCl, Fe_3O_4, and Co_3O_4, indicating a complex degradation process. The experimental evidence underlines that CO_2 presence alongside HCl does not perceptibly alter the LSCF microstructure, with HCl solely dictating the degradation process. Additionally, atmospheres comprising synthetic air with CO_2 concentrations ranging from 5% to 100%, and those containing synthetic air, 10% water vapor, and CO_2 from 5% to 90% were meticulously tested. In experiments involving synthetic air, CO_2, with or without the presence of water vapor, the formation of strontium carbonate was observed. This is attributed to the reaction of strontium from LSCF with CO_2. The presence of water vapor in these atmospheres significantly increased the amount of strontium carbonate formed as a result of the perovskite's degradation.

For post-experimental characterization of the LSCF samples, scanning electron microscopy (SEM), Energy-dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD) were utilized. These methods provided in-depth insights into the microstructural changes and phase composition, shedding light on the degradation mechanisms. Significant physical transformations in the samples, such as pores emergence and surface whitening, were evident and validated through optical microscopy. The XRD analysis further supported the complete disintegration of LSCF after HCl exposure, while SEM and EDS showed perovskite degradation in CO_2 containing atmosphere.

Acknowledgments

This work was done in the framework of the WirLebenSOFC project, which is supported by the Federal Ministry of Education and Research, Germany (FKZ 03SF0622B).

Investigation of salt-material interaction in sea water electrolysis through solid oxide electrolyzer utilizing Ni-YSZ ceramic materials

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Keywords: solid oxide electrolyzer, Ni-YSZ, sea water, sea salt

The utilization of solid oxide electrolyzer (SOE) technology holds significant promise for sustainable hydrogen production, offering a pathway towards clean energy solutions. According to the current state of the art, technical water electrolysis processes rely on water that is at least of drinking water quality. For this reason, there is a conflict between the use of treated water in electrolysis and as drinking water. Accordingly, process water or seawater should ideally be used directly to produce hydrogen. Therefore, this research emphasis on a thorough investigation into the interaction dynamics between sea water salts and the constituent materials of the SOE cell, particularly focusing on Ni-YSZ (Nickel-Yttria Stabilized Zirconia) ceramic materials.

In a first step, thermodynamic calculations utilizing FactSage software were performed to investigate what proportion of the impurities contained in sea water from various origins reaches the electrolyzer cell and in what form they are present either as gas impurity or salt deposit. Different percentages of aerosols formed in the vaporizer were considered to determine their effect on the amount and composition of salts deposited in the cell.

Furthermore, computational modelling provided invaluable insights into the thermodynamic aspects of salt-material interaction within the SOE cell. The modelling results highlight the tendency of magnesia (MgO) and calcium oxide (CaO) to substitute yttria (Y_2O_3) within the yttria-stabilized zirconia (YSZ) lattice structure. This substitution phenomenon has most likely implications on the material's structural integrity and electrochemical performance.

In a second step, loosely pressed pellets consisting of a mixture of Ni-YSZ and the predicted salt composition as well as half cells (Ni-YSZ on YSZ) with salt deposit were annealed in a humid reducing atmosphere (52% H_2O in Ar/4%H_2) at 800 and 900 °C for 100 hours. Furthermore, salt-free pellets and half cell samples without deposit were annealed under the same conditions in an atmosphere saturated with respective salt vapours. The pellets were analysed by XRD and the half cells by optical microscopy and SEM.

Beside others, the experimental investigations reveal interesting results concerning the interaction between sulphur and nickel within the SOE cell. Such interactions are of great importance in understanding the operational behaviour and long-term stability of SOE systems.

Both, the experimental and modelling results will be presented and discussed. They contribute to a deeper understanding of the complex interactions between salt constituents and materials in SOE systems. By clarifying the mechanisms underlying salt-material interactions, this research paves the way for informed strategies aimed at enhancing the efficiency, durability, and overall performance of SOE technology in sea water electrolysis processes.

Acknowledgments

This work was done in the framework of the PRELUDE project, which is supported by the Federal Ministry of Education and Research of Germany (FKZ 03SF0650A).

Abbildung 3 Nickelsulfid nach dem Erstarren auf der Oberfläche der Elektrolysezelle.

T1.5 Nanostructured, and Hybrid Functional Materials for Energy and Sustainability

Is it possible for naphthalimides to be a future organic battery?

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Keywords: diselenolo-1,8-naphthalimides, cycling voltammetry, capacity testing, carbon-based electrolyte, ionic liquid-based electrolyte

Environmental pollution and the depletion of natural resources have always been essential problems that humanity strives to solve. With technological advancements and the rampant use of lithium-ion batteries in our daily lives, the need to look for more environmentally friendly and potentially cost-effective alternatives has come to the fore. Organic rechargeable batteries can be excellent successors to LIBs as next-generation energy storage systems due to organic design flexibility, environmental friendliness, etc.

This report presents the synthesis procedure of *peri*-substituted dichalcogen naphthalimides and their redox interaction with Li^+ ions. The compounds containing dithiolo- and diselenolo-bridge were investigated electrochemically by a cyclic voltammetry and galvanostatic method in carbon-based and ionic liquid-based electrolytes (Figure 1). The cycling-voltammetry indicates that the Se-substituted compounds participate in *n*- and *p*-type redox reactions at about 2.0 V and above 4.0 V vs. Li/Li^+, respectively. At lower potential, the Se-substituted compounds are able to uptake up to 6 Li^+ ions, depending on the kind of electrolyte used. The results for Se-substituted compounds are compared with previously reported data for S-substituted ones [1].

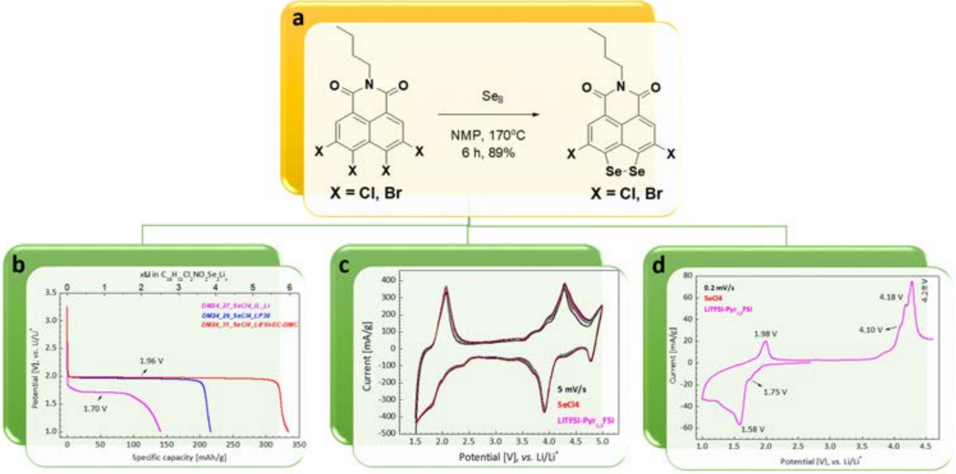

Fig.1 The synthesis scheme (**a**), the first discharge curve in different electrolytes (**b**), and CV curves at 5 mV/s (**c**) and 0.2 mV/s (**d**) of naphthalene monoimides with *peri*-annulated diselenide bridge in an ionic liquid-based electrolyte.

Acknowledgments

The financial support from the National Science Fund of Bulgaria (Project КП-06-Н69/1) is acknowledged. Part of the experiments was performed with equipment included in the National Center of Mechatronics and Clean Technologies, co-financed by the European Union through the European Regional Development Fund under grant agreement BG05M2OP001-1.001.

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Multiscale confinement synthesis of nitrogen-rich molybdenum carbide for efficient hydrogen evolution reaction

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Keywords: molybdenum carbide, hydrogen evolution reaction, multiscale confinement synthesis, valence band modulation, nitrogen doping

The molybdenum carbide (Mo_2C) has been regarded as one of the most cost-efficient and stable electrocatalyst for the hydrogen evolution reaction (HER) by the virtue of its Pt-like electronic structures [1-3]. However, the inherent limitation of high density of empty valence band significantly reduces its catalytic reactivity by reason of strong hydrogen desorption resistance [4-6]. Herein, we propose a multiscale confinement synthesis method (Figure 1) to design the nitrogen-rich Mo_2C for modulating the band structure via decomposing the pre-coordination bonded polymer in a pressure-tight tube sealing system. Pre-bonded C/N-Mo in the coordination precursor constructs a micro-confinement space, enabling the homogeneous nitrogenization in-situ happened during the formation of Mo_2C. Simultaneously, the evolved gases from the precursor decomposition in tube sealing system establish a macro-confinement environment, preventing the lattice N escape and further endowing a continuous nitridation. Combining the multiscale confinement effects, the nitrogen-rich Mo_2C displays as high as 25 % N-Mo concentration in carbide lattice, leading to a satisfactory band structure. Accordingly, the constructed nitrogen-rich Mo_2C reveals an adorable catalytic activity for HER in both alkaline and acid solution. It is anticipated that the multiscale confinement synthesis strategy presents guideline for the rational design of electrocatalysts and beyond.

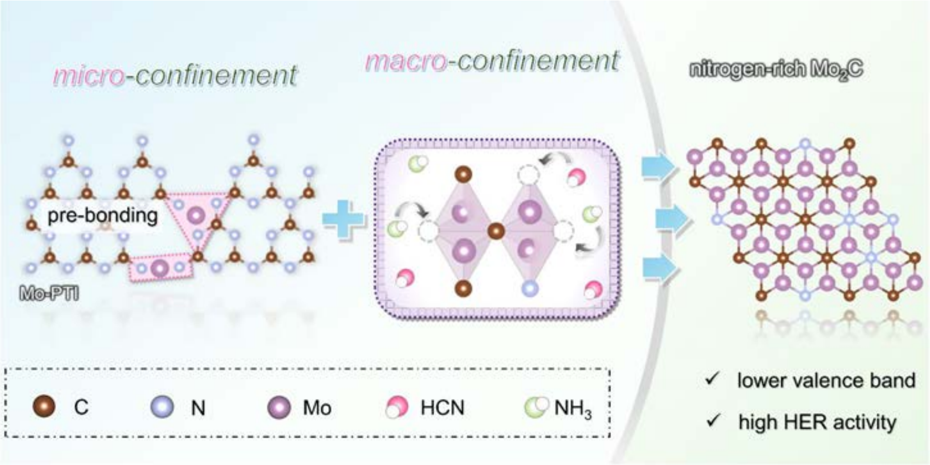

Figure 1. Schematic representation of multiscale confinement pyrolysis strategy to prepare the nitrogen-rich Mo_2C

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Unlocking mechanocatalysis: exploring nanocrystalline $BaTi_2O_5$ in a centrosymmetric phase with anti-directional dipole layers

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Keywords: mechanocatalysis, $BaTi_2O_5$, nanocrystalline

Innovative phase of nano materials which break the traditional structural constraints are highly desirable, particular in the field of mechanocatalysis, offering versatile applications ranging from energy, healthcare and medical diagnosis and treatment. In this work, we successfully synthesized a distinct layered barium dititanate ($BaTi_2O_5$) nanocrystals using a pH-modulated hydrothermal method. These nanocrystals exhibit outstanding hydrogen generation capability (1160 $\mu mol \cdot g^{-1}h^{-1}$ in pure water) and demonstrate remarkable performance in organic dye degradation using ultrasonication, as demonstrated in Figure 1. The crystal structure of this newly discovered $BaTi_2O_5$ phase, was determined by a combination of synchrotron Powder Diffraction refinement and X-ray adsorption techniques, including X-ray Absorption Near Edge Structure (XANES) and Extended X-ray Absorption Fine Structure (EXAFS). Density Functional Theory calculations revealed that the newly-discovered $BaTi_2O_5$ phase demonstrates dipole moments along the z-axis, distributed in an antiparallel direction within a single unit cell. These inherent dipoles induce a surface polarization and a ferroelectric-flexoelectric response under mechanical stimuli when the materials go to nano dimension. With a band alignment well-suitable for hydrogen and reactive oxygen species generation, this $BaTi_2O_5$ phase demonstrates promising potential for Mechanocatalysis. The discovery of this distinct phase not only enriches the material candidates for mechanocatalysis but also offers valuable insights that can guide the exploration of previously unexploited mechanocatalytic mechanisms with exceptional performance.

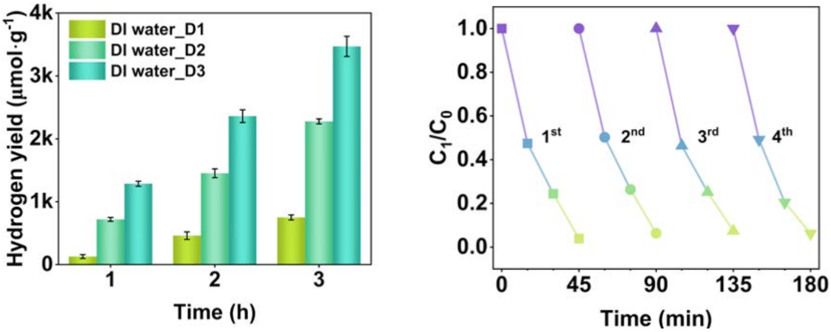

Figure 1. (left) Hydrogen evolution yield of $BaTi_2O_5$ catalysts in pure water under ultrasonic irradiation. D1, D2 and D3 represent for the catalytic procedure conducted over three consecutive days using the same catalysts. The error bar is determined by the maximum difference observed among multiple trials conducted under the same experimental conditions; (right) Rhodamine B (RhB) dye degradation stability test plotted in decrease of dye concentration. (C0: original RhB dye concentration, and C1: degraded RhB concentration after catalysis with different time intervals).

T1.6 ADVANCED BATTERIES AND SUPERCAPACITORS FOR ENERGY STORAGE APPLICATIONS

Unlocking the reaction mechanism of anode-protected Aqueous Organic Zinc Ion Battery

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Keywords: Aqueous Zinc Ion Batteries (AZIBs), redox-active organic cathode, anode protection

While non-aqueous Li-ion batteries are widely used in portable electronics and electric vehicles due to their high energy density and adaptability, the development of large-scale rechargeable Li-ion batteries will be constrained by cost and resource limitations. Aqueous rechargeable Zn-ion batteries (AZIBs) are emerging as promising alternatives to traditional Li-ion technology, offering higher safety, lower costs, and enhanced battery performance. AZIBs, particularly under ambient pH conditions, have the potential for large-scale applications due to natural abundance, low toxicity, low redox potential, and high specific capacity (~820.0 mAh g-1) of Zn. In contrast, conventional rechargeable batteries using inorganic electrode materials such as metal oxide and sulphides face operational challenges and are not environmentally friendly and cost-effective. Recently, there has been a growing interest in organic AZIBs due to their low cost, abundance, easily tunable redox chemistry, and structural flexibility. In this study, we have developed and synthesised novel n-type organic-based small redox active molecules, specifically 1,4,5,8-naphthalene diimide derivatives as cathodes for AZIBs. However, the challenges in AZIBs include adverse chemical side reactions leading to corrosion passivation, hydrogen evolution reaction (HER) at the anode side and dendrite formation. To address these challenges, we have modified the Zn-anode by appropriately coating it with Zn- phthalocyanine, which is highly conjugated metal porphyrin, effectively increasing the capacity and lifespan of cycling. In this work, we have investigated in detail the energy storage mechanisms and the coordination of solvated Zn-ion with redox motif (Carbonyl group). These studies will further aid in the comprehensive understanding of the function of organic AZIB and the design of efficient organic electrode materials.

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Fe-MIL-101 metal organic framework enhanced solid polymer electrolytes for high-performance Solid-State Lithium Metal Batteries

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Keywords: Solid-State Lithium Metal Batteries, metal organic framework, X-ray absorption spectroscopy, X-ray diffraction

Solid polymer electrolytes (SPEs) show tremendous potential for solid-state lithium metal batteries; however, challenges like low ionic conductivity and poor mechanical strength hinder their progress. This study integrates Fe-MIL-101 metal organic framework into a poly(vinylidene fluoride-*co*-hexafluoro propylene) (PVdF-HFP)-based SPE system to address these limitations. The integration of Fe-MIL-101 offers two critical benefits: 1) Interaction of inorganic Fe^{3+} metal centers with PVdF-HFP enables fast Li^+ transport by increasing free Li^+ availability in the system through Lewis acid-base interactions. 2) Fe-MIL-101 significantly improves the mechanical strength of the SPE, boosting its structural integrity. Fe-MIL-101-integrated SPE enables excellent room temperature cycling stability in solid-state Li||$LiFePO_4$ (LFP) full cells, retaining ~91% capacity after 300 cycles and ~89% capacity after 400 cycles at 0.2 C. Advanced characteristic techniques like synchrotron-based *in-situ* X-ray diffraction, and X-ray absorption spectroscopy were employed to explore structural evolutions in the LFP cathode and the Fe-MIL-101-integrated SPE during cycling. Furthermore, improved room temperature electrochemical performance is demonstrated in solid-state Li||$LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ (NMC622) batteries with Fe-MIL-101-integrated SPE, retaining 91.4% capacity after 175 cycles at 0.1 C. This work highlights the effectiveness of Fe-MIL-101 in enhancing the SPE properties, paving the way for the advancement of high-performance solid-state lithium metal batteries.

Acknowledgments

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Biowaste for electrodes: converting the biomass waste into a sustainable host for sodium-ion storage

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Keywords: biowaste, hard carbon, sodium-ion batteries, sustainable energy storage

Conversion of biowastes, obtained by households and bio-processing industries, into valuable materials is among the main aims of the waste management. Due to the high carbon content, biowastes can serve as excellent precursors for synthesizing important carbon materials such as activated carbon, graphene, soft carbons, etc.

Herein, we compare the Na-storage properties of biowaste-derived hard caprbons (bio-HCs) from spent coffee grounds (SCGs) and walnut shell waste (WS). The SCGs-derived carbons were prepared by a classical pyrolysis at 750, 1100 and 1300 °C, while pyrolysis and hydropyrolysis techniqniques were applied for the synthesis of WS-derived carbons. The effect of the synthesis procedure on the carbon micrstructure and porosity were examined. The electrochemical properties of bio-HCs were analysed in model Na-ion cells with carbonate-based sodium electrolyte. To quantify the Na-storage performance of bio-HCs, we determined four parameters: reversible specific capacity, first irreversible capacity, cycling stability and rate capability. Based on the above results, it is established that WS -derived carbons outperforms SCGs -analogues. Furhtermore, the best performed bio-HCs were used as negative electrodes in full sodium-ion cells with sodium transition-metal oxides as positive electrodes. The full-cells testing demonstrates that biowaste-derived hard carbons are a valuable material with potential applications for energy storage in sodium-ion batteries.

Acknowledgments

The authors thank for the financial support of the project BionN (КП-06-ПН-69/7 from 15.12.2022) for researching biowaste-derived carbon materials, as well as to the project CARiM (NSP Vihren, КП-06-ДВ-6/16.12.2019) for full-cells experiments.

Functionalized interfacial cover design toward pure silicon anode for high power density lithium-ion capacitor

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Keywords: lithium-ion capacitor, silicon anode, functionalized carbon coating layer, electrode failure

The lithium-ion capacitor, comprising a capacitor-type positive electrode and a battery-type negative electrode, was proposed to achieve high power and energy density. Nevertheless, integrating different charge storage mechanisms into a single cell naturally leads to a kinetic mismatch between the two electrodes, which limits the potential for high power densities. To address this issue, there is an emerging need for high-capacity anode materials that can reduce the thickness of the negative electrode. Silicon (Si), known for its high specific capacity, is considered a promising anode material for enhancing both energy and power density. However, the rapid capacity fading and increase in internal resistance due to volume changes during cycling make it difficult to use a pure Si anode. In this study, functional layers, comprised of functionalized herringbone-type carbon nanofibers, are applied to both sides of the electrode to protect it from Si degradation. The polar functional groups on the cover weakly interact with both the native oxide layer of the Si surface and the carboxyl groups of the binder, ensuring stable contact through repeated cycles. Furthermore, the conductive functional layer promotes uniform fluxes of Li ions and electrons, aiding in the formation of a stable solid electrolyte interphase layer. This study investigates the effects of this strategy on pure Si electrodes through surface morphology analysis, assessment of chemical interactions, and electrochemical testing. The approach holds the potential to overcome the degradation issues of Si electrodes, significantly contributing to the improvement of the power and energy density of lithium-ion capacitors.

Acknowledgments

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Shuttle effect suppression in Lithium-Sulfur Batteries by simultaneous use of electrospun Nb_2O_5 nanofibers and bioderived carrageenan binder

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Keywords: nanofibers, needleless electrospinning, ceramic nanofibers, lithium-sulfur batteries, Nb_2O_5 nanofibers, carrageenan

This contribution describes the preparation along with the detailed characterization of Nb_2O_5 nanofibers and their application in lithium–sulfur batteries for the improvement of electrochemical performance. The utilization of reactive needle-less electrospinning allowed obtain, in a single step, pre-ceramic composite PAN/ Nb_2O_5 fibers, which were further transformed into porous ceramic Nb_2O_5 nanofibers via calcination. Thermogravimetric studies defined that calcination at 600 °C resulted in pure highly crystalline ceramic fibers without carbon residues. The fibrous morphology and mean diameter of the ceramic nanofibers were analyzed via scanning and electron microscopy. A surface area was determined through nitrogen adsorption measurements, while X-ray diffraction was utilized to confirm the crystallinity and phase composition of the calcined fibers – single T-phase Nb_2O_5. Its performance in the cathode of lithium–sulfur batteries bound with bioderived carrageenan was defined through electrochemical tests, and the obtained results were compared to similar blank electrodes – without the Nb_2O_5 and one with commonly used PVDF binder. The initial discharge capacity of 0.1 C reached values of about 1300 $mAh \cdot g^{-1}$ while showing the capacity retention of approx. 75% after 200 cycles. The presence of Nb_2O_5 nanofibers in the carbon cathode combined with the carrageenan binder inhibits the shuttle effect through polysulphide confinement, which originates from porosity and chemical trapping.

Acknowledgments

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T2 Ceramics for Energy Conservation and Efficiency

T2.1 ADVANCED FIBER REINFORCED COMPOSITES FOR TURBINE ENGINES

Novel Carbon fiber/PEEK-hybrid yarn based non-oxide ceramic matrix composite

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Keywords: hybrid yarn, PEEK, C/C-SiC, LSI-Process, ceramic matrix composites

Carbon fiber reinforced silicon carbide (C/C-SiC) is produced via the liquid silicon infiltration process. To maintain a C/C-SiC, three processing steps are necessary. Firstly, a carbon fiber reinforced polymer (CFRP) is manufactured, followed by a pyrolysis step under inert conditions at temperatures above 1000 °C. During pyrolysis, the matrix polymer is transformed into carbon, creating a porous carbon fiber reinforced carbon (C/C). Eventually, the C/C is siliconized under vacuum above 1420 °C, resulting in a C/C-SiC.

The properties of the C/C-SiC can be altered by the choice of polymer in the CFRP. Important factors to consider for a successful C/C-SiC fabrication are the fiber bundle infiltration with matrix polymer during CFRP manufacturing and the char yield of the polymer after pyrolysis. As state of the art, phenolic resins are used as CFRP matrix material, because of their high char yield above 60 %, their low viscosity, which results in a good fiber bundle infiltration, and their low cost. However, there are some drawbacks to using phenolic resin as polymer precursor material. Besides health issues and possible pore formation due to gas evolution, it is not possible to recycle phenolic resins and therefore use recycled resins as CFRP matrix polymer. The substitution of phenolic resins with thermoplastics such as PEEK can tackle these drawbacks. However, melt viscosity of PEEK is a lot higher than for phenolic resins, potentially resulting in a bad fiber bundle infiltration.

In this study, thermoplastic PEEK is used as CFRP precursor material. To ensure good fiber bundle infiltration, a short fiber hybrid yarn has been developed in cooperation with DITF Denkendorf. The fiber bundles of the yarn consist of C- and PEEK fibers. The yarn is warm pressed at about 400 °C to a CFRP. After that, it is pyrolyzed and infiltrated with silicon. Microstructural analyses prove a good fiber bundle infiltration in the CFRP, a low amount of silicon and a homogenous SiC-network in the C/C-SiC state. Additionally, the pore network of the C/C was studied, using µ-CT and Hg-porosity, showing a fine and homogeneous crack network with a median pore diameter of 11.9 µm. The low Si (11 vol. %) and high SiC content (26 vol. %) are confirmed using XRD for phase analyses. Additionally, three-point bending tests reveal a pseudo-ductile behavior with a Young's modulus of 28 ± 5 GPa, a

strain to failure of 0.4 ± 0.1 % and a flexural strength of 97 ± 13 MPa. Finally, SEM images from the fracture surface of the sample tested by bending tests were conducted. The images show pronounced fiber-pull out and crack deflection, explaining the high values of flexural strength and strain to failure due to energy dissipating effects. C/C-SiC ceramics produced via the hybrid-yarn LSI route therefore facilitate the C/C-SiC production in various aspects and display a promising candidate for future applications.

Acknowledgments

Special thanks to Jonas Riesner at Materials Engineering, University of Augsburg, for the µ-CT measurements.

T2.2 ADVANCED CERAMIC COATINGS FOR POWER SYSTEMS

Quaternary rare-earth oxide co-doped ZrO_2 as a promising thermal barrier coating for gas turbine engine

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Keywords: thermal barrier coatings, Co-doped ZrO_2, phase stability, mechanical properties, thermal conductivity

Thermal barrier coatings (TBCs) are crucial for improving the reliability and lifespan of gas turbine engine. This study presents a novel quaternary rare-earth oxide co-doped ZrO_2, termed 1La-xGd-2Yb-3.5YSZ, synthesized via solid-state reaction. A systematic study was conducted to investigate the effects of co-doping-induced lattice distortion on the composition of solid solution phases, high-temperature phase stability, sintering performance, as well as the mechanical and thermal properties. It has been found that the addition of Gd_2O_3 effectively increased lattice distortion, improved phase stability, sintering resistance, mechanical properties, and reduced thermal conductivity. The results demonstrate the potential of the 1La-xGd-2Yb-3.5YSZ solid solution as a candidate material for thermal barrier coatings in gas turbines.

T2.3 ENGINEERING CERAMICS: ADVANCED PROCESSING, PROPERTIES, AND APPLICATIONS

Correlating impedance phase angle variations to nanoparticle size changes in silicon dioxide colloids

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Keywords: nanoparticle size, phase angle, AD8302, four electrodes

In industrial applications, changes in the particle size of nanoparticles within a colloidal suspension can impact physical properties such as the thermal conductivity and solubility of the solution. In 2015, Zhao utilized electrochemical impedance spectroscopy (EIS) to measure the impedance properties of colloidal solutions with varying particle sizes and discovered a correlation between particle size and impedance phase angle(Zhao et al., 2015). This method of measurement using EIS provides a non-invasive alternative for nanoparticle sizing. The AD8302 is an integrated circuit for amplitude/phase measurement that can be applied to impedance measurements in the low-frequency range(Yihong et al., 2018). This experiment attempts to utilize the AD8302 and establish a miniature fluidic circulation measurement system based on the four-electrode method. Within this system, an ultrasonic oscillation rod is inserted into the colloidal solution to separate clusters of silicon dioxide nanoparticles at varying concentrations (0.1%wt-0.5%wt) through oscillation over a set duration, thereby inducing relative changes in particle size while ensuring that other physical properties of the solution remain unchanged. The AD8302 measurement system is responsible for inputting a sinusoidal signal with a frequency range of 1KHz-4MHz into the colloidal solution, thus measuring the relative changes in the phase angle/amplitude of the colloidal solution when the particle size of the silicon dioxide changes within the tested frequency range.

Additionally, a Zetasizer is used to measure the size of the silicon dioxide particles in the solution after each ultrasonic oscillation, in an effort to determine the relationship between particle size variation and relative changes in phase angle. This four-electrode measurement method based on the AD8302 system is non-invasive and cost-effective, and the establishment of a correlation between particle size changes and impedance phase angle variations will aid in the development of a new method for measuring particle size variations.

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A metal-polymer self-lubrication composite based on PTFE and its prototype

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Keywords: bearings, tribology, self-lubricating, polytetrafluoroethylene (PTFE)

In general, various bearings are mechanical elements which convert one motion into another motion and reduce friction between the moving machine elements. Among them, an oilless bearing widely used in various industrial applications provides its self-lubricating property, superior shock and impact load resistance as well. When developing prototypes of *PTFE/ porous bronze sinter/ steel backing*, it is necessary to examine the correlation such as the kinds of particle reinforcements, fillers, shapes and sizes in a polymer matrix.

Advances in tribology of metal-polymer self-lubrication composites based on PTFE are mainly discussed in this study. It reviews to analyze the advanced technology trends of lubricated/ non-lubricated commercial bearings on a dry film lubricant with polytetrafluoroethylene (PTFE) and metal-polymer based dry bush components. Furthermore, we focused on the steel-backed bushings with PTFE based composites filled with various ceramic fillers (such as MoS_2, BN, and Al_2O_3) and for this study developed an experimental apparatus (mainly under 3 MPa and up to 2,000 rpm) for analyzing the wear performance in dry sliding of the prototypes. All PTFE composite films coated on the metal have been carried out varying analysis of organic/ inorganic and microstructure by TGA, DSC, FT-IR, OM and FE-SEM/EDS. As a result, the coefficient of friction for solid PTFE bushings/ or bearings produced was slightly lower by maintaining the surface temperature of itself around 30°C, compared to the commercial products. Adding lubricants could improve the tribological performance of bearings and wear-resistant polymers. And lastly, emerging a few progressive techniques of solid lubricants composites are briefly reviewed and future research opportunities are discussed.

The development status of SiC heating elements in Korea

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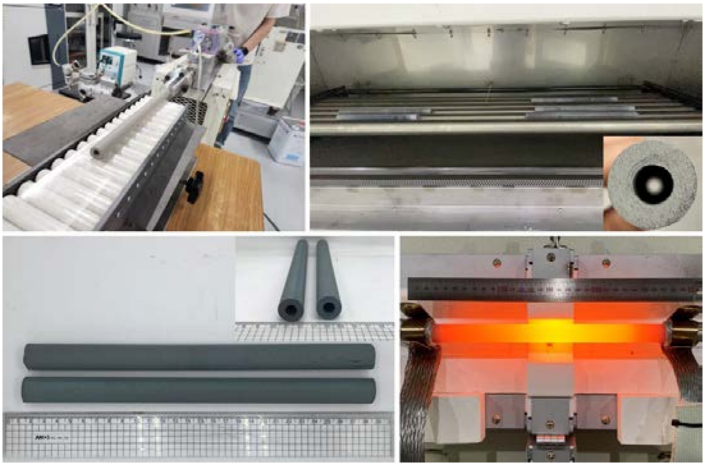
Keywords: silicon carbide, heating element, extrusion, sintering

The urgent demand to reduce greenhouse gas emissions necessitates a transition to electrification processes or the use of zero-carbon fuels as substitutes for fossil fuels. Especially for achieving carbon neutrality in key energy-intensive industries such as the steel and petrochemical sectors, it is essential to shift from combustion-based heating methods using hydrocarbon fuels to renewable energy-based electric heating methods, alongside increasing the availability of renewable energy. Silicon carbide (SiC) resistance heating elements, offering long-term durability at a maximum heating temperature of 1600°C, are currently widely used in Korea, both for laboratory and industrial electric furnaces. However, there are no research cases on SiC heating element development in Korea, and no production companies domestically. Consequently, Korea relies entirely on imported products mainly from abroad (Sweden, Japan, China, India, etc.). Therefore, the development of domestic SiC heating element technology in Korea is imperative. This study aims to first compare and analyze the status and characteristics of SiC heating elements, followed by introducing the process of domestic SiC heating element development in Korea."



Development Process of SiC Heating Element at Korea Institute of Energy Technology Research: Extrusion Forming Process - Non-Deformable Roll Drying Process - Recrystallization Annealing Process - Heating Test (1000 °C)

Acknowledgments

This work was supported by the Korea Institute of Energy Technology Evaluation and Planning(KETEP) and the Ministry of Trade, Industry & Energy(MOTIE) of the Republic of Korea(RS-2023-00234270).

T2.5 Advanced Polymer Derived Ceramics (PDCs) and Related Materials for Energy Applications

High-efficiency fabrication of SiC_f/SiC composites by Gradated Concentration Polymer Infiltration and Pyrolysis (GC-PIP) method

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Keywords: composite, fabrication, polymer-derived ceramics, processing

Silicon carbide fibre reinforced/silicon carbide matrix (SiC_f/SiC) composites are promising candidates for applications such as accident tolerant fuel cladding for nuclear power reactors and receivers for Gen3 molten-salt concentrating solar power plants, thanks to their excellent high-temperature stability, high mechanical strength, outstanding oxidation/corrosion resistance, and stability under irradiation. In this work, a novel Gradated Concentration Polymer Infiltration and Pyrolysis (GC-PIP) method has been developed to achieve high-efficiency fabrication of SiC_f/SiC composites with low porosity (<4% determined by X-ray μ-CT scanning). In this approach the polycarbosilane/xylene concentrations is systematically varied, whereby three progressively concentrated precursor solutions were used during each infiltration of every PIP cycle. The gradated concentrations of precursors have been designed and optimised based on the calculation of flow rate and investigation on the wetting angles, viscosities, surface tensions and retained weights at different concentrations. Gradated-Concentration Infiltration strategy avoids blocking of the near surface pores at the start of the process due to the first low concentration treatment while ensuring the most efficient delivery of material through the later higher concentrations, efficiently filling intra-bundle pores.

Combining a Gradated-Concentration Infiltration strategy with pressure-free pyrolysis using an optimised heating programme, such Gradated Concentration Polymer Infiltration and Pyrolysis (GC-PIP) method can rapidly produce SiC_f/SiC composites with densities higher than 94%. The resulting SiC matrix in composites was highly nano-crystalline, with a composition, crystallinity and Young's modulus similar to the 2nd Generation SiC fibres, surpassing other reported polycarbosilane-derived SiC matrices. No damage to the fibres or the interphase was observed after processing under pressure-free pyrolysis at 1300 °C. The resulting composite displayed enhanced mechanical properties under three-point bending, giving a tough fracture response with extensive crack deflection and long fibre pull-out. This novel method can be easily applied to other precursors and fibres, and is a promising approach to fabricating low porosity SiC_f/SiC composites of diverse shapes with excellent mechanical properties.

Acknowledgments
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T3 Ceramics for Environmental Systems

T3.1 PHOTOCATALYSTS FOR ENERGY AND ENVIRONMENTAL APPLICATIONS

Control of surface defects in ALD-TiOx thin films for an improved photoelectrochemical performance

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Keywords: amorphous titanium oxide, atomic layer deposition, defects

A proper control of defects in TiO_2 thin films is challenging work for enhancing the photoelectrochemical (PEC) efficiency in water splitting processes. Additionally, a deep understanding of how defects affect the PEC performance of TiO_2 thin films is of great interest for achieving better performance. Herein, therefore, an amorphous defective TiOx thin film was deposited on a Si wafer and a fluoride-doped tin oxide (FTO)–coated glass substrate via the ALD technique using TDMAT as a Ti precursor. The growth kinetics and crystal structures of ALD-TiOx thin films were carefully investigated. Then, the defect concentration was carefully evaluated using X-ray photoelectron spectroscopy (XPS) and electron spin resonance (ESR) spectroscopy. Moreover, the PEC parameters as well as PEC performance were systemically discussed according to the defect concentrations of TiOx thin films. Finally, a correlation between the defect concentration in TiOx films and their PEC activity was systematically determined.

Progressive photocatalytic nanocomposites based on electrospun TiO_2 nanofibers modified with AgNPs obtained by green approach

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Keywords: nanofibers, needleless electrospinning, ceramic materials, photocatalytic activity, Ag/TiO_2 nanofibers

This work describes the preparation and detailed characterization followed by the testing of the photocatalytic activity or ceramic TiO_2 nanofibers modified with AgNPs prepared by the green synthesis approach. Precursor TiO_2 preceramic fibers with different concentrations of AgNPs were prepared using reactive needle-less electrospinning. The obtained as-spun precursor fibers were subjected to heat treatment at two different temperatures 450 and 600°C and held for 60 minutes. For the electrospinning solution preparation, the polymer polyvinylpyrrolidone, titanium tetraisopropoxide, and acetic acid were used. Absolute ethanol served as the solvent for the system. Silver nanoparticles AgNPs were added from the pre-prepared concentrated solution at three different concentrations: undiluted – 100 %, maximum load, diluted by half – 50% of the maximum load, and diluted by a quarter – 25% of the maximum load. The presence of AgNPs in the final ceramic TiO_2 nanofibers was confirmed through a combination of scanning and transmission electron microscopy. For the testing of the photocatalytic activity, the materials were crushed, and the prepared powder was dispersed in a solution of a model pollutant with a sufficient concentration to ensure reliable detection accuracy. Model pollutants were dyes of various chemical natures: cationic – Methylene Blue, anionic – Methyl Orange, and molecular – Reactive Black 5. Degradation of the model dyes was observed under 365 nm UV light irradiation.

Acknowledgement

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T3.2 Ceramics for Carbon Capture and Storage Technologies

Complete combustion of methane using CeO_2–SiO_2 based catalysts

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Keywords: catalyst, methane combustion, CeO_2-SiO_2, OSC, acid–base property

CH_4 possesses a high warming potential over 20 times that of CO_2, and as a result, it currently accounts for ~18.6% of the total warming gas share [1]. Therefore, to achieve net-zero emissions, research is ongoing to suppress the emission of CH_4 and CO_2. The catalytic combustion method has also been considered as an ideal technology to decompose CH_4 gas because it achieves the combustion of CH_4 gas to yield only water vapor and carbon dioxide, thereby avoiding the discharge of noxious NO_x, CO, and hydrocarbons [2]. It has been reported that the complete oxidation of CH_4 could be achieved at 550 °C using systems wherein noble metals are supported on CeO_2–ZrO_2 (e.g., PdO/CeO_2–ZrO_2) [3]; this temperature is significantly lower than that required by the Pd/Al2O_3 system (i.e., 800 °C). However, it should be noted that the combustion of methane should be possible at more lowered operating temperature.

We have found that the introduction of SiO_2 into the CeO_2 promoter to enhance the acid–base properties and specific surface area of the catalyst. In addition, Bi2O_3 is introduced into the CeO_2–SiO_2 promoter to improve the oxygen release and storage capacities, while γ-Al_2O_3 is used as a support to increase the catalyst durability, and PdO is applied as an active species due to its high oxidation ability toward methane.

Figure 1 shows the temperature dependencies of methane combustion over PdO/$CS_{(0.08)}$ $Bi_{(0.07)}$/Al_2O_3 catalysts (PdO/CSB/Al_2O_3). Here, the methane combustion test was carried out in a fixed-bed quartz reactor. The mixed gas was composed of 2.5 vol% CH_4 in air with a total flow rate of 200 mL/min (mass hourly space velocity = 120,000 $L\cdot kg^{-1}\cdot h^{-1}$) was supplied to the catalyst bed by using a mass flow controller. The outlet gas composition was analyzed using a gas chromatograph (GC, GC-8AIT, Shimadzu) with a TCD. The reaction temperature was increased from 150 to 500 °C in 50 °C intervals, and the methane conversion at each point was obtained after stabilization for 15 min. The introduction of SiO_2 and Bi_2O_3 improved the catalytic activity owing to the increase of the oxygen storage capacity and acid-base property. By using PdO/ CSB/Al_2O_3, the complete methane combustion was achieved at 350°C, which is lower than the previous catalyst case (PdO/CeO_2–ZrO_2: 550 °C).

Acknowledgments

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Investigation of the effect of magnetic field on CO_2 absorption using $LiFeO_2$ nanoparticles

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Keywords: CO_2 absorption, nanoparticles, thermogravimetric analysis, saturation magnetization

The global climate change caused by the increase in greenhouse gas (CO_2) emissions is due to the combustion of fossil fuels, mainly from automobiles and coal burning power plants. For high temperatures CO_2 capture, the use of solid sorbents is being explored [1]. In this work, the $LiFeO_2$ nanoparticles (NPs) are used a catalyst during the absorption process.

The $LiFeO_2$ NPs were prepared by the combustion method. X-Ray diffraction (XRD) patterns of $LiFeO_2$ NPs show that the linewidth of the as-prepared samples is different than that of samples absorbed CO_2 gas, and the characteristic peaks shift to lower 2θ which means the mean crystallite size of as-prepared sample is bigger than the sample after absorbed CO_2 gas. The structure of these NPs is indexed to the cubic phase (JCPDS 70-2711). Thermogravimetric analysis (TGA) indicates that the absorption temperature of CO_2 is range from T_1=250 to T_2=500 ºC. Vibrating sample magnetometer (VSM) measurements shows that the saturation magnetization and remanence of the $LiFeO_2$ NPs showed an increase in behavior when subjected to the CO_2 flow at 450 ºC. The magnetism is due to the $LiFeO_2$ samples after CO_2 absorption produces the Li-doped spinel iron oxide or γ-Fe_2O_3 phases. Magnetization isothermal experiments [inset of Fig.1(c)] for different crystallite size of $LiFeO_2$ NPs performed at different temperatures before T_1 and choice of some specific temperatures. Time-dependent data were processed taking one exponential model $M(t) = A\exp(-k_1 t) + M_0$. In addition to exponential model fit, rate constants were obtained under Eyring model to calculate the active-state enthalpy (ΔH^*_1), and Arrhenius equation to obtain the activation energy (E_{a1}). It is suggested that a magnetic CO_2 gas detected sensor could be developed using this material. To clarify the impurity phases existed in the samples and their magnetic contributions, further studies of their electronic structure and micromagnetic structure by the X-ray photoelectron spectroscopy (XPS) and Mössbauer spectroscopy are underway.

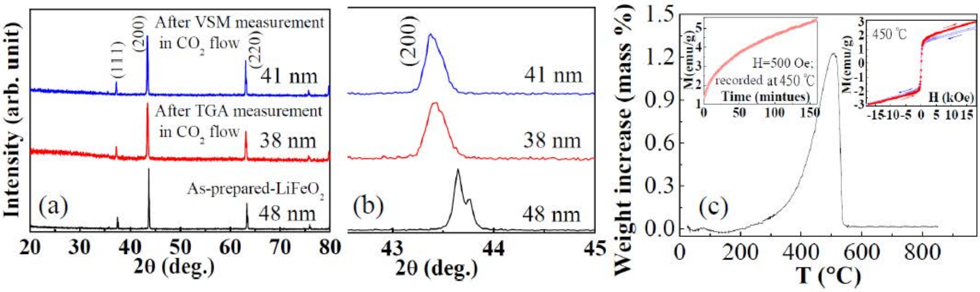

Fig. 1 (a) X-Ray diffraction (XRD) patterns of $LiFeO_2$ NPs before and after CO_2 absorption for VSM and TGA measurements; (b) enlarged scale of (a); (c) TGA curve for the CO_2 absorption measurement of as-prepared $LiFeO_2$ NPs, Inset: time-dependent magnetization and hysteresis curve recorded at 450 °C under CO_2 flow.

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Synthesis and morphology control of spherical silica by sustainable reprecipitation method using ultrasound

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Keywords: silica nanoparticle, sustainable process, ultrasound, reprecipitation method

Introduction: In this study, we developed a new method for colloidal silica synthesis which is called "reprecipitation method". In ordinary method for colloidal silica synthesis, alkoxide such as TEOS and TMOS or sodium silicate are used as raw materials. However, these raw materials have some disadvantages such as cost or removal process of impurities, so sustainable synthesis processes for colloidal silica are required. Then, we focused on hydrazine monohydrate and silicon metal as new raw materials. Hydrazine monohydrate is basic solution and solute silicon metal as silicic acid. We have found that ultrasound irradiation accelerates the dissolution of silicon into hydrazine monohydrate, resulting in a highly concentrated silicate solution. In this study, we tried to synthesize colloidal silica by adding poor solvent into this solution and decreasing solubility of silicic acid. In addition, to improve the monodispersity of the synthesized particles, the influence of ultrasound stirring was also investigated.

Method: Highly concentrated silicate solution was prepared by adding 0.15 g of silicon powder to 100 mL hydrazine monohydrate and dissolving it under ultrasound irradiation (50 kHz, 200 W at 20 ˚C). Then, to precipitate silica particles 50-70 vol.% methanol was added as a poor solvent into the precursor solution under ultrasound irradiation (100 kHz, 200W, 10 min. at 20 ˚C). Synthesized particles were analyzed using Field Emission-Scanning Electron Microscope (FE-SEM), Fourier Transform Infrared Spectroscopy (FT-IR) and X-ray diffraction (XRD).

Results and Discussion: From the results of XRD and FT-IR analysis, it was confirmed that amorphous silica was obtained through this procedure and 20-100 nm of spherical silica nanoparticles were observed in the FE-SEM analysis. Silica particles were expected to be produced by the decrease of the solubility of silicic acid associated with the addition of poor solvent into precursor solution. In the case of 50 vol.% methanol was added without ultrasound irradiation, non-uniform silica particles with average size of 63.3 nm and coefficient of variation (C_V) of 44% were obtained. On the other hand, in the case of 100 kHz ultrasound was irradiated, uniform silica particles with average size of 22.6 nm and C_V value of 23 % were obtained. This shows that ultrasound irradiation contributes to particle homogenization and refinement. In this method, it is expected that the homogeneous decrease in solubility is an important factor to obtain uniform particles, so ultrasound stirring caused the production of more uniform particles by efficiently promoting mixing of the solution than no-irradiation condition. In addition, when 70 vol.% methanol was added under 100 kHz ultrasound irradiation, particles with an average diameter of 74.1 nm and a C_V value of 15 % were obtained, indicating that the particle sizes can be controlled by the amount of poor solvent (Fig.1).

This reprecipitation method is expected to be a sustainable synthesis method because shape-controlled and high-purity silica particles can be easily obtained at room temperature from ordinary silicon powder.

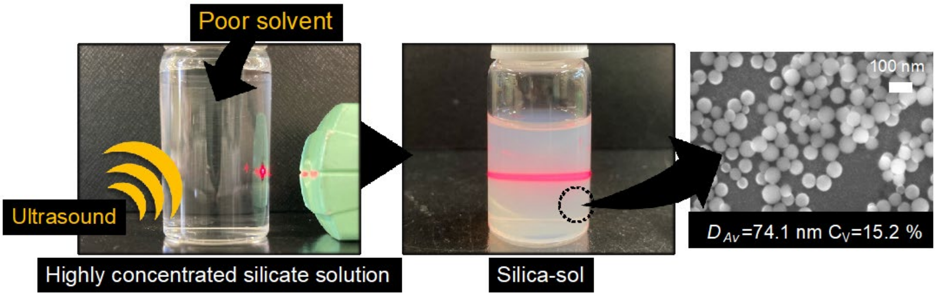

Fig.1 Overview of reprecipitation method and the SEM image of the synthesized particles (MeOH 70 vol.%)

T3.3 GEOPOLYMERS, INORGANIC POLYMER CERAMICS AND SUSTAINABLE COMPOSITES

Zinc Ion exchanged geopolymer derived from sodium geopolymer and comparison of their thermal behavior

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Keywords: geopolymer, sodium, zinc, ion-exchanged, sintering

In this study, sodium based geopolymer with about 1:1:2 NaO:Al_2O_3:SiO_2 molar ratio was synthesized by using metakaolin and sodium hydroxide solution. The synthesized geopolymer was subjected to an ion exchange process in an aqueous solution containing zinc ions. Almost complete ion exchange took place between Na^{2+} and Zn^{2+}. Thermal behavior of the sodium geopolymer and the Zn-exchanged geopolymer was followed by optical dilatometer and TG-DTA analysis. The sodium geopolymer crystallizes to nepheline at the early stages of sintering, which precludes further densification. On the other hand, the Zn-exchanged geopolymer starts sintering at about 50 °C lower temperature and sinters to a nearly full density before gahnite crystallization takes place. The dense Zn-exchanged geopolymer body contains extensive gahnite crystallization with sizes finer than 30 nm embedded in an amorphous matrix.

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Refractory ceramics for the aluminium foundries: Novel perspectives for greater process and product sustainability

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Keywords: ceramic, refractory, aluminium, sustainability, chemistry, analysis

Since the beginning of time creativity, intelligence, and consciousness have helped mankind developing a more convenient World. The mastery of metallurgy was a transformative leap for humanity which promoted the production of revolutionized tools and weapons. In the simplest terms, humans developed the first metallurgical techniques around 6000 B.C. by putting a start on the timeline of metallurgical advancements which spans several millennia. One of the metals that has the potential to change the global metallurgical industry is aluminium (Al). The exponential evolution of aluminium production over the past decades reflects its increasing importance, and future projections anticipate an 80% increase in demand by the year 2050[1]. Indeed, infinite recyclability, reduction of production costs, and eco-compatibility combined with extreme versatility of the metal make aluminium foundries sustainability-conscious and cutting-edge.

Castable refractory ceramics play a crucial role in the aluminium production process, allowing the transportation of molten Al from the furnace to the casting station. The key aspects of this ceramics involve high-temperature, thermal shock, chemical, and mechanical resistance as well as shape adaptability, durability and insulating properties. In order to test the materials, several analysis techniques are usually employed. Thermal Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) allow the study of the thermal profile of materials which is a key element because of the contact between the ceramic and molten Al. Strength testing are also crucial as ceramics are subjected to high mechanical stresses. Finally, extensive studies of both surface and bulk chemical composition allow the determination of erosion/corrosion resistance.

In this work, BN-doped ternary SiO_2-Al_2O_3-CaO ceramics were synthetized and characterized to evaluate the physicochemical properties of the materials. SiO_2-Al_2O_3-CaO composite is a well-known system which is able to meet many demands[2]. Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) analysis allowed an insight into the chemical composition confirming the theoretical values of the major elements derived from calculations on raw materials, *i.e.*, 33.4 ± 0.5 % Si (*vs* theoretical 35.0%), 7.2 ± 1.8 % Al (*vs* theoretical 9.0%) and 5.0 ± 1.2 % Ca (*vs* theoretical 5.1%). Scanning Electron Microscopy (SEM) analysis provided morphological and structural information of the samples showing the heterogeneity of the synthetized ceramics which consisted of a calcium aluminosilicate matrix in which fragments of silica and BN were dispersed. Moreover, porosity of materials as a function of calcination was highlighted. X-Ray Diffraction (XRD) technique revealed the presence of both amorphous and crystalline phases. Interestingly, XRD analyses before and after a heat treatment were similar, although the calcinated material showed a loss of water-related phases, *i.e.*, aluminium hydroxide (*nordstrandite*) and calcium aluminium hydroxide hydrate. This phenomenon has already been observed[3] and ascribed to water loss which changes crystalline lattice.

Finally, a MatLab project for calculating heat losses during the effective utilization of the ceramics was created to meet the need for improved product sustainability combined with the possibility of creating uniqueness, whose purpose is to lead to products and processes customization.

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Development of nanocomposite material synthesis and fatigue life evaluation method

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Keywords: nanocomposite, environment friendly material, naoclay, mechanical property, fatigue life

Rubber components have been widely used in industry as anti-vibration components for many years. These subjected to fluctuating loads, often fail due to the nucleation and growth of defects or cracks. To prevent such failures, it is necessary to understand the fatigue failure mechanism and evaluate the fatigue life for rubber components. For these reasons, not only the rubber component manufacturers but also their customers like automotive makers perform a series of strict fatigue test on the components such as component fatigue tests and driving fatigue tests. The fatigue lifetime prediction on the rubber components was increasing according to the extension of warranty period of the automotive components. A design of rubber components against fatigue failure is one of the critical issues to prevent the failures during the operation. Therefore, fatigue lifetime prediction and evaluation are the key technologies to assure the safety and reliability of rubber components.

In this study, we developed rubber material that is environment-friendly and superior in mechanical property using rubber-clay nanocomposites. Acrylonitrile butadiene rubber (NBR) was used as rubber in combination; ZnO and stearic acid were used as vulcanization activators; and 3C was used as an additive; sulfur of purity 99.9% was used as a vulcanizing agent; TT and CZ were used as vulcanization accelerators; and carbon black, clay, and nanoclay were used as reinforced compound. Polymer layered silicate was made by the melted intercalation method in which polymers in the melted state were inserted between silicate layers. We performed static and dynamic tests of rubber-clay nanocomposite synthesized by inserting nano-filler between silicate layers at the high temperature of +70 ~+100°C, and verified that their mechanical properties were superior to the existing rubber material. In addition, a new method was developed to estimate fatigue lifetime of rubber parts in a short period in the initial stage of design, assuming that the fatigue damage parameter was Green-Lagrange strain generated at the weak points of parts. As results of estimation of fatigue durability, it was verified that the fatigue lifetime obtained by fatigue tests on actual engine mounts and the expected lifetime relatively match. With the results of finite element analysis of rubber parts using the fatigue lifetime estimation method suggested in this study, the lifetime can be estimated without fatigue tests on rubber components. Therefore, we can save development time and expense and achieve good quality and reliability of rubber components.

Acknowledgments

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T3.5 Advanced Sensors for Energy, Environment and Health Applications

Electrochemical aptasensors for SARS-CoV-2 spike protein detection

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Keywords: COVID-19, electrochemical detection, aptasensor, screen-printed carbon electrode

Sensitive diagnostics of various pathogens represent a key tool, especially in the case of a pandemic like COVID-19. The development of fast, sensitive, portable, and selective sensors is important for the prevention of the spread of such diseases. That is why special attention is paid to electrochemical sensors, which represent a quick, simple, and portable solution [1]. Currently, there are 3 diagnostic techniques used in the clinical diagnosis of COVID-19 infection: 1) antibody testing, 2) nucleic acid detection, and 3) aptamer testing. Mentioned tests are based on fluorescence polymerase chain reaction or isothermal nucleic acid and display several disadvantages such as complicated sample preparation, necessary presence of trained personnel, and time-consuming detection [2]. For the fabrication of electrochemical sensors screen-printed carbon electrodes are used. These electrodes are usually modified by various nanomaterials or biomolecules to enhance their sensitivity and selectivity [3].

In this work, the electrochemical aptasensor for SARS-CoV-2 detection was developed. Screen-printed carbon electrodes modified by streptavidin (SPCE-str) molecules were obtained from Metrohm DropSens company. Thereafter, SPCE-str electrodes were modified by a specific aptamer with sequence - [Btn]TATCCAGAGTACGCAGCACCGACCTTGT-GCTTTGGGAGTGCTGGTCCAAGGGCGTTAATGGACA, obtained from Sigma Aldrich.

Modified electrodes were studied via electrochemical impedance spectroscopy (EIS), and differential pulse voltammetry (DPV). After the aptamer addition, the shape of Nyquist diagrams changed, the second semicircle could be observed. The change indicates the second phase interface creation, which confirms aptamer attachment on the electrode surface. After the addition of spike protein, the semicircle diameter increases, which indicates the increase in charge transfer resistance. The increase in charge transfer resistance is related to spike protein bonding to the aptamer molecule. If spike presence is related to the increase in the charge transfer resistance, it could be assumed that the current will decrease with the increasing concentration of the spike protein. The current response decreases with increasing concentration. The linear range window was between 2 µM to 20 nM, with a sensitivity of 0.011 µA/µM. For interference study, the bovine serum albumin is usually used for interference influence consideration. The current response was several times lower in comparison to spike like protein current response. So, the studied electrochemical aptasensor represents very promising candidate for SARS-CoV-2 spike protein detection.

Acknowledgments

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T4 Cross-Cutting Materials Technologies

T4.1 COMPUTATIONAL DESIGN AND MODELING

Bandstructure modulation and molecular adsorption properties of Zirconia nanoparticles: A large-scale electronic structure study

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Keywords: nanoparticle, adsorption, computation

Zirconia-based materials find wide utilization in solid oxide fuel cells.[1] Interactions between Zirconia surfaces and molecules play a crucial role in these applications. Nanomaterials provide promising candidates to modulate electronic structures and enhance electrode surface properties. However, current understanding of small molecule adsorption behavior on Zirconia nanoparticles in function of particle size remains limited. We will present a comparative analysis based on first principles and semiempirical calculations of CO adsorption properties of ZrO_2 nanoparticles ranging in size from a few tens to a thousand atoms, to understand nanosizing effects of their surface adsorption properties at electronic structure-based level. The order(N) density functional theory (DFT)[2] and semi-empirical density functional-based tight-binding (DFTB)[3] computational methods are combined to strike a balance between computational cost and accuracy. The band structure of the nanoparticles, which proves sensitive to stoichiometry, exerts a significant influence on molecular adsorption behavior. Notably, nanoparticles can exhibit intrinsic as well as p- and n-doped characteristics corresponding to O-rich or O-poor conditions. The n-type particles display heightened reactivity for the adsorption of CO molecules with pronounced electron transfer from Zirconia to the adsorbed molecules. Additionally, a diminishing trend in surface adsorption activity as the nanoparticle size increases has been identified, which suggests a good potential of optimizing and adjusting the surface properties of Zirconia nanoparticles.

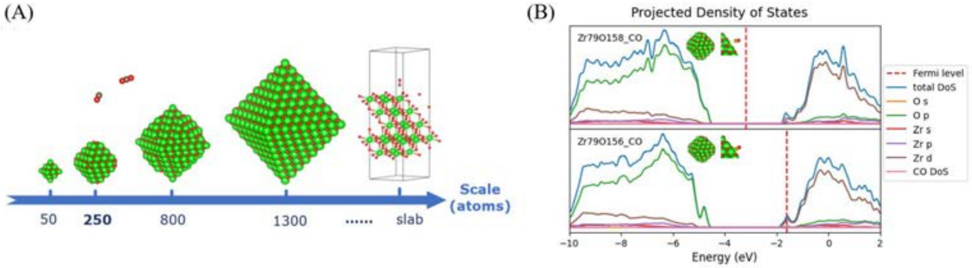

Figure (A). Schematic illustration of Zirconia nanoparticle models; (B). Modulation of band structures and adsorption performance by oxygen deficiencies.

Acknowledgments

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Develop of PVB laminated glass model for Head Injury Criterion-based collision safety analysis

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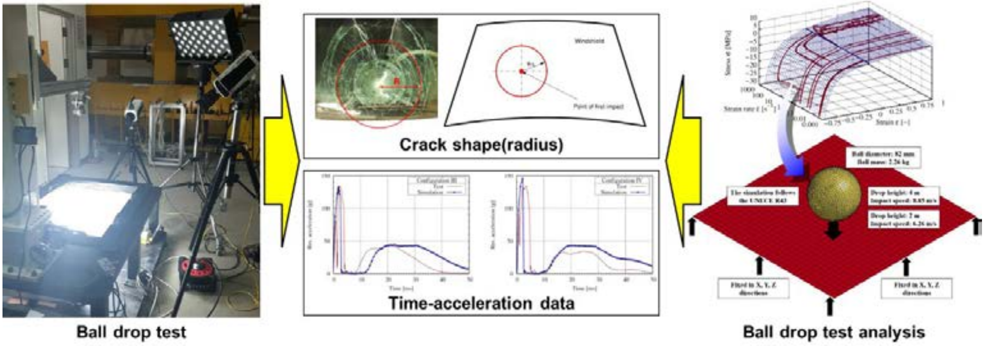
Keywords: PVB laminated glass, analysis model, Head Injury Criterion, ball drop test

The laminaged glass consists of a structure in which glass-synthetic resin film-glass is bonded, and in the event of a collision with the laminated glass, the synthetic resin film is bonded to the glass, preventing debris from being scattered and preventing secondary damage. Due to these characteristics, PVB laminated glass is mostly used for the front of the car and the front of the railway. Most of the front glass uses PVB laminated glass to prevent glass fragments from splashing and reduce impact during a collision between pedestrians and the front of the railway vehicle, and unlike cars with a bonnet part, the railway vehicle has the characteristic of a direct collision with the front glass. In the case of automobiles, leg models, head models, and human piles are used to evaluate the speed of collision and pedestrian safety through the amount of change in the hood in front of the vehicle, and various scenarios are used to promote pedestrian safety and legislate related laws. Also, the collision with metal parts other than bonded glass, such as bumper and hood on the front of the vehicle, will occur first, and the collision with PVB bonded glass will occur later, so it is expected to show a different trend from the collision scenario of road mixed driving railways. In this paper, the PVB laminated glass model is proposed which includes the experimental material properties and ball drop test results. The mechanical tests of PVB film with respect to the various strain rates were performed to get precise material model of PVB layer in laminated glass. The experimental tests to measure Head Injury Criterion was conducted, which is called ball drop test, in different impact speed. The time-acceleration results in different impac speed was extracted from the experimental tests and it was compared with the analysis data which has same boundary conditions with real expermental conditions. A numerical material model in LS-DYNA was used to match the impact acceleration and Head Injury Criterion. Numerical fitting model for high-strain rate mechanical properties of PVB film was calculated and applied in the analysis model.

Figures



Analysis model of ball drop test and verification proecess

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Computational models of grain structures of titania with nature-like grain distritbutions

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Keywords: grain boundary, molecular dynamics, microstructure, titanium dioxide

Microstructures of ceramics have significant effects on their mechanical, electronic and transport properties. Computational studies of microstructural elements, in particular grain boundaries (GB), are typically limited to individual postulated grain boundaries. Moreover, experimental studies of GB often use the bicrystal approach which effectively does the same. There is need for models that account for the natural distribution of grain sizes, GB types, and other features such as amorphous interlayers, in order to achive a more realistic understanding of effects of microstructural features on mechanical properties including plasticity, on ion transport, and on banstructure changes induced by the presence of GB – properties important for applications in batteries, fuel cells, solar cells, and precision optics.

We produce models of grainy structures of titania by large-scale molecular dynamics (TiO_2) with up to 4 million atoms. Computational heat treatment is adjusted to obtain different average grain sizes. While even in such large-scale, by the standards of atomistic simulations, the grains are nano- rather than micrometer sized (the obtained grains are on the order of 10 nm), the procedure is ‘nature-like’ and obtains a distribution of key microstructural features including grain sizes and of grain boundaries that can be used for a more realistic modeling of effects of microstructure on material properties.

We demonstrate how the obtained structures can be used to study the effects of grain boundaries on mechanical properties including plasticity and fracture, ion insertion, and electronic proprties. While mechanical properties are computabel with force field MD, DFTB (density functional tight binding) is used to compute the effects of GB on the electronic structure in several thousand-atom scaled models (Fig. 1).The grainy models we produced are available from the authors upon request.

Figures

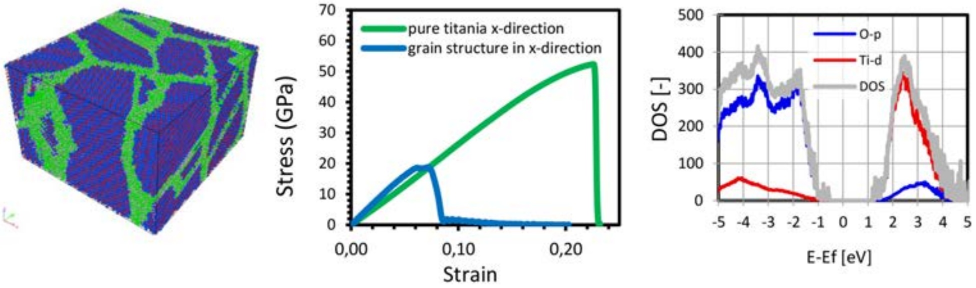

Fig .1. Left to right: an example of a grainy structure with about 500,000 atoms, An example of a stress strain curve comparing plastic response of ideal crystalline rutile TiO_2 and a grainy structure with an average grain size on the order of 10 nm. The PDOS of grain boundary with an amorphous interlayer.

Acknowledgments

This work is supported by the JST Mirai Program, Fugaku Small Scale Project program, Singapore A*STAR, and Singapore Ministry of Education Academic Research Funds.

Effects of Interfacial Segregation on Solubility and Morphology in Doped ZnO

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Keywords: thermoelectric ZnO, grain boundary engineering, codoping, complexions, nominal solubility

Grain boundary (GB) segregation of dopants in polycrystalline ZnO is a pivotal factor, in reducing its thermal conductivity while preserving its electrical prowess [1,2]. Employing a Multiobjective Genetic Algorithm-driven force-field-based atomistic modeling approach, the study delves into the role of GB dopant concentration on complexion transitions across five special twin GBs of ZnO. However, to establish the correlation between GB structure and macroscopic properties, a pivotal bridge between GB segregation and nominal dopant concentration must be established. Thus, a sophisticated phenomenological model steps in, seamlessly weaving the link between GB concentration and the nominal dopant concentration [3].

This model intricately calculates the nominal solubility of dopants, delicately tracing its evolution with the grain size of polycrystalline ZnO, validated with the experimental data available in the literature. Furthermore, the nominal concentration limit for achieving the single-layer GB complexions, which is most effective in suppressing grain growth during sintering, was also calculated.

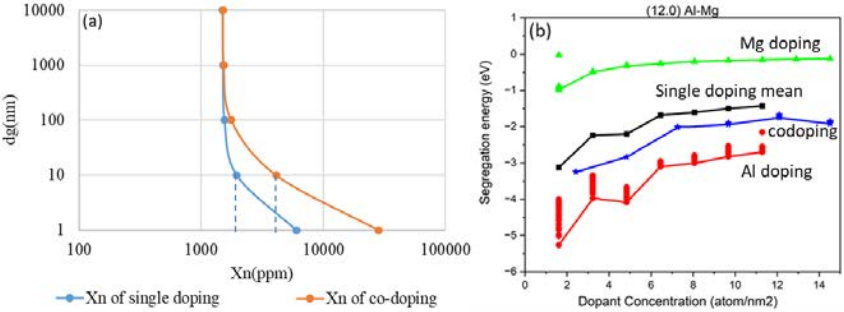

Figure: (a) Nominal Solubility of single and codoped systems for different grain sizes, (b) Segregation energy v/s dopant concentration plots of Al-Mg codoped for 50 configurations.

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T4.2 ADDITIVE MANUFACTURING & 3D PRINTING TECHNOLOGIES

Additive manufacturing of advanced ceramic filter structures

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Keywords: additive manufacturing, microwave hybrid sintering, robocasting, advanced ceramics, filters

Advanced ceramics with designed porosity have a multitude of applications into the realm of customized filters in the automotive, aerospace, and space industries. Complex porous structures face consistency of pore sizes and their design inaccuracy issues in conventional methods of manufacturing and this could be overcome by additive manufacturing (AM) techniques. Also AM methods result in less wastage of materials compared to conventional subtractive manufacturing. While AM techniques like direct ink writing (DIW) and stereolithography (SLA) ensure the required dimensional accuracy of the printed component, critical aspects like the structural and mechanical properties of the 3D printed ceramics are determined by its sintering process, which is also considered as the most energy intensive step in the production stages.

In this study, we have attempted to compare the processing and properties of 3D printed Alumina and Yttria stabilized Zirconia (YSZ) ceramics with designed porosity using direct ink writing (DIW), fused filament fabrication (FFF) and Digital Light Projection (DLP) methods, sintered using conventional (radiant power heating) and microwave assisted sintering methodologies. The sintered samples were analysed for density, microstructure, surface roughness, shrinkage, hardness, and toughness. Industrial standard testing of filtration efficiency was performed on the 3D printed filters and the results compared with conventionally manufactured components.

Acknowledgments

The authors acknowledge the funding support from United Kingdom Research and Innovation (UKRI) Strength in Places Fund (SIPF).

T4.3 NOVEL, GREEN, AND STRATEGIC PROCESSING AND MANUFACTURING TECHNOLOGIES

Improvement in powder injection molding process with addition of cellulose nanofibers

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Keywords: powder injection molding, cellulose nanofiber, debinding, sintering

We intended to suppress the deformation during debinding and sintering of the part with addition of cellulose nanofibers (CNF) to the binder. The materials used were SUS316L powder with average powder diameter 6 mm. The CNF contents are selected as 0, 0.5 and 1 mass%.

Figure 1 shows the results of bending test of green and solvent-debound compacts. The addition of CNF improves the bending strength of the debound compacts and is effective in improving handling.

Figure 2 shows the results of in situ deflection tests during sintering. The addition of CNF suppressed the deformation of the sintered compact. All sintered compacts show densities of more than 95%. The carbon content of the sintered compact was less than 0.03%, satisfying the SUS316L standard.

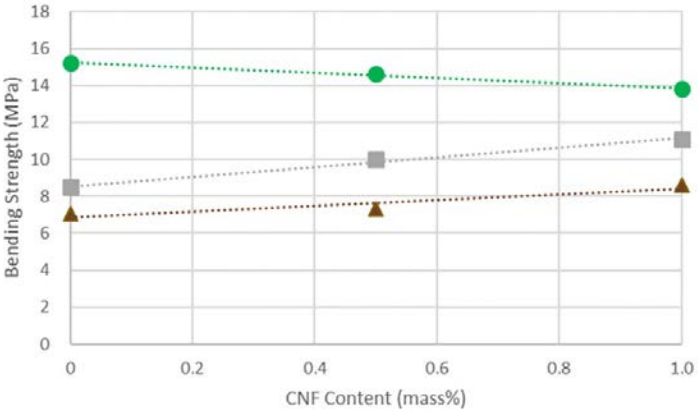

Figure 1 Bending tests results of green and solvent-debound compacts.

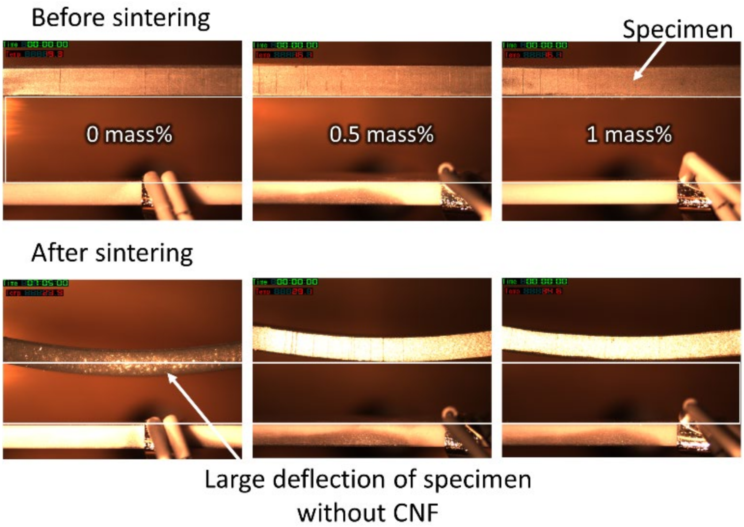

Figure 2 Deflection of the specimens during sintering.

T4.4 POWDER PROCESSING TECHNOLOGY FOR ADVANCED CERAMICS

Improvement of fracture toughness of B_4C-based ceramics reinforced by carbon nanotubes, nanofibres and graphene nanoplatelets

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Keywords: spark plasma sintering, carbon nanotubes, fibers, graphite nanoplates

In the present work, different high hardness nanocomposite materials have been synthesized using B_4C ceramics as a matrix with the aim to develop materials for next generation bulletproof vests. For this application, B_4C is one of the most promising candidates due to its excellent physical properties such as high thermal stability and high hardness. Despite these attractive properties, B_4C has a low fracture toughness, which is needed to be improved. In the present work, B_4C-based nanocomposites reinforced with carbon nanotubes (CNTs), nanofibers (CNFs) and graphene nanoplatelets (GNPs) were designed and sintered by spark plasma sintering technique. The fracture toughness of the samples was investigated by both indentation method and 3-point bending test. The obtained fracture toughness values exhibited a significant improvement compared to monolithic B_4C ceramics.

Acknowledgements
This research was supported by the Slovak Grant Agency for Science via the project(s) APVV-22-0493, and by the Slovak Academy of Sciences via the project(s): IMPULZ IM-2022-67.

Preparation of zinc oxide/silica composite hollow spherical particles by spray drying

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Keywords: spray-drying, zinc oxide, silica, composite powder, microcapsule, UV absorption

Zinc oxide (ZnO) powder is used as a UV absorber in cosmetics, and its form changes the sensation of the product. Recently, hollow spherical particles have attracted attention as a cosmetic materials. Spray drying is an industrial process used to produce spherical particles. Spray drying is a method for obtaining hollow spherical particles by spraying an aqueous solution containing a dissolved component into a dryer at approximately 100°C, while maintaining the shape of the sprayed droplets. However, these compounds is insoluble in water. In our previous study, we found that ZnO dissolved as soluble $Zn(HCO_3)_2$ when CO_2 was blown into the suspension. Furthermore, we have found that spray-drying this $Zn(HCO_3)_2$ solution can produce spherical hollow particles of basic zinc carbonate ($2ZnCO_3 \cdot 3Zn(OH)_2 \cdot H_2O$, BZC). However, when the BZC was heated to form ZnO, it broke down because of the volume change caused by dehydration and decarboxylation, and hollow spherical particles could not be obtained. In this study, we investigated the conditions for preparing ZnO/SiO_2 composite hollow spherical particles by adding silica, which reinforced the hollow spherical structure of the spraying solution.

Tetraethoxysilane (TEOS) was added to 1 dm^3 of deionized water with 0–5 cm^3 of TEOS, and CO_2 gas was blown in for 1 h to hydrolyze the TEOS to form a silica solution. Next, ZnO was suspended in the resulting silica solution (0.1 mass%), dissolved by blowing with CO_2 gas for 2 h, and filtered to obtain an aqueous $Zn(HCO_3)_2/H_4SiO_4$ solution. The resulting solution was spray-dried at a spray-drying temperature of 100°C and an atmozing pressure of 200 kPa to obtain hollow spherical particles of the precursor BZC. The precursor hollow spherical particles were calcined up to 400°C to obtain ZnO/SiO_2 composite spherical hollow particles.

Spherical hollow particles of 1–3 μm in diameter could be obtained by spray-drying from solutions with or without TEOS. When the precursor particles were heated, the particles without TEOS broke down, and hollow spherical particles were not obtained. However, adding TEOS resulted in ZnO/SiO_2 composite hollow spherical particles that maintained their shape. Figure 1 shows the average compressive strength of a single hollow spherical particle obtained by changing the amount of TEOS added using a microhardness tester that can test the compressive strength of one particle under a microscope to evaluate the strength of the particles. Without TEOS, the hollow spherical particles would not exist because of breakdown, but the addition of TEOS increased the compressive strength of the particles to a maximum of 20 MPa when 3 cm^3 of TEOS was added. The UV absorption capacity of the hollow spherical particles obtained by changing the TEOS content was investigated by UV-Vis measurements. The ZnO reagent used for comparison did not absorb light in the visible light range but was observed to absorb ultraviolet light below 390 nm. By contrast, the ZnO/ SiO_2 composite particles with TEOS showed the same UV absorption capacity as the ZnO reagent, but the UV absorption capacity tended to decrease as the TEOS addition increased.

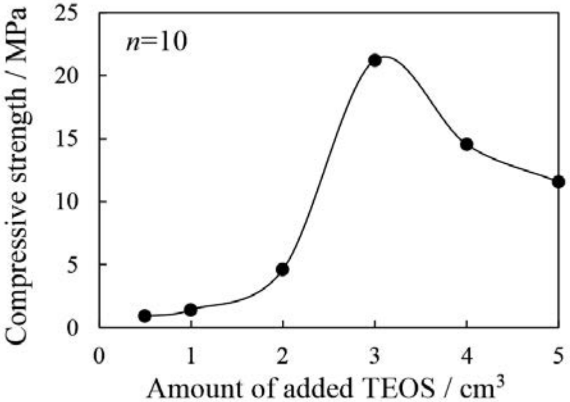

Figure 1 Compression strength of one hollow spherical particle obtained by changing the amount of added TEOS.

Acknowledgments

This study was supported by JSPS KAKENHI (grant number: JP21K04680).

Optimization of iron ore grinding method to secure high-grade iron ore as raw material for hydrogen ironmaking

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Keywords: hydrogen ironmaking, iron ore, crushing, mineral liberation

Carbon dioxide emissions from steelmaking account for 14% of Japan's total emissions. Therefore, it is inevitable to reduce the amount of carbon dioxide emission toward carbon nuetral society in steel making industry. Now hydrogen steelmaking, in which hydrogen is used for reducing agent of iron ore, has been attracting attention because this method does not release carbon dioxide during the reduction process. In the reduction process with hydrogen, shaft furnace will be used. After reducing, ore is melted in an electric arc furnace and impurities are removed as slag. Since an electric arc furnace has a lower impurity removal potential than a blast furnace, to secure the ore with low impurity for hydrogen ironmaking is important. In addition, because the reduction reaction with hydrogen is endothermic, there are concerns that a shaft furnace may experience powdering (the phenomenon in which iron pellets are broken into small pieces and become powdery) and product sticking (the phenomenon in which pellets become lumpy and clogged) due to temperature decrease. To prevent these problems, it is necessary to prepare the raw ores with high Fe-grade (over 67 wt%) and with low impurity amount.

Since high-grade iron ore that meets these requirements is scarce, and the average grade of iron ore that Japan mainly imports (Australia, Brazil) is much lower than 67 wt%. Therefore, we need to develop an beneficiation process to remove impurities (gangue minerals such as quartz) and low-grade iron mineral (goethite) for utilizing low grade iron ores in hydrogen ironmaking.

In order to improve the grade of iron ore through the beneficiation process, it is necessary to grind iron ore to the appropriate size and to liberate hematite (recovery target) efficiently. In this study, we tried to establish an appropriate grinding method in which grinding at the mineral boundary of hematite, goethite, and gangue minerals proceeds selectively with low energy. We conducted the grinding experiment of iron ores with ball mills, roll crushers, and jaw crushers, and calculated the degree of liberation of hematite and goethite for each grain size fraction of the ground samples. In addition, modeling breakage experiments with single ore grain were also conducted to investigate the detailed mechanism of mineral liberation proceed. Based on the experimental results, an optimal combination of grinding methods was determined based on the energy efficiency and achieved degree of liberation. As a result, the degree of liberation of hematite ground by ball mill exceeded that by roll crusher and jaw crusher. The results of modeling experiments showed that impact force has an advantage over compressive force for promoting the degree of liberation. Finally we concluded that coarse grinding to an average particle diameter of 3 mm using a roll crusher followed by secondary grinding using a ball mill is the optimum grinding method of iron ore for promoting the liberation of hematite.

Acknowledgments

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T4.5 Advanced Materials, Technologies, and Devices for Electrooptical and Biomedical Applications

Development of a saliva cortisol biosensor with an interdigitated electrode platform with barium titanate nanoparticles

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Keywords: biomedical application, cortisol, titanium nanoparticles, mesoporous

This research is focused on measuring cortisol levels in saliva samples through the use of mesoporous titanium oxide and complex impedance spectroscopy. A gold interdigitated electrode (IDE) platform, composed of semiconducting mesoporous barium titanate oxide nanoparticles (TiBaO3), was created. Albumin was linked to the mesoporous surface particles as a surface anti-binder agent to enhance the specificity of cortisol binding in complex samples. In the assembly of the electrochemical cell, the IDE served as a base for the TiBaO3 power deposits. Various standard cortisol analytical samples were prepared and evaluated at a steady voltage of 5 mV, producing a nominal current of 40 nA at 1 kHz. The complex impedance was recorded using a sinusoidal input voltage within the frequency range of 1000 Hz to 10 kHz. Data processing was carried out using Principal Component Analysis (PCA). The method was able to detect cortisol levels as low as 40 nanograms per milliliter. Ongoing research aims to apply this technique to quantify cortisol in complex human saliva samples.

Figures

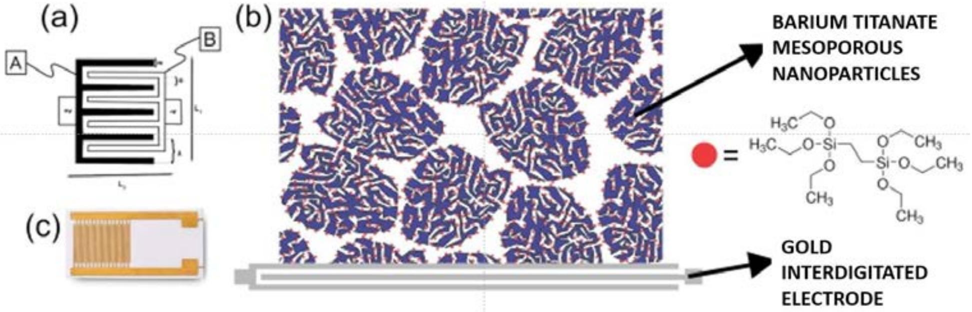

Figure 1. Schematic diagram of the biosensor system. (a) comb-like lines of the micro-electrode, (b) cross-sectional view of the schematic diagram of the IDE-TiBaO3 mesoporous nanoparticles, and (c) photograph of the biosensor.

Acknowledgments

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Laser and optical properties of Nd-doped fluorapatite ceramics with fine microstructure

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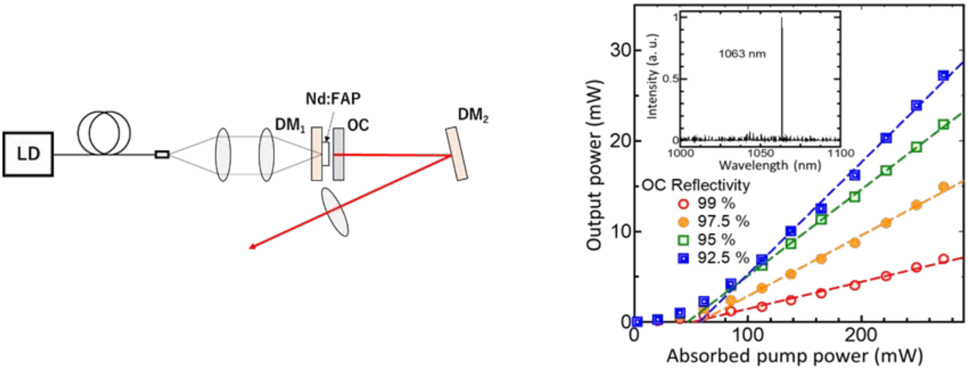
Keywords: ceramics, optical materials, fluorapatite

Advantages of transparent ceramics such as excellent thermal properties comparative to those of single crystals, ease of size enlargement and composites, are promising for high-power solid-state laser materials. Since there are many laser materials with non-cubic crystal structure for single crystal, it is fascinating to achieve transparent non-cubic ceramics.

The magnitude of grain boundary scattering due to birefringence is proportional to the difference in refractive index at the grain boundary Δn, the size of the crystal grains d, and is also inversely proportional to the square of the wavelength of light λ [1]. The first laser operation of non-cubic ceramics was achieved by reducing Δn from Nd-doped fluorapatite ($Ca_{10}(PO_4)_6F_2$: FAP) [2]. In contrast, we have tried to achieve non-cubic laser ceramics by reducing d, and Nd-doped FAP and S-FAP ($Sr_{10}(PO_4)_6F_2$) showed lasing at 1.0 mm wavelength range [3,4]. However, their efficiency is less than 10%, thus there is still needs to be improved.

In this study, we conducted a study to improve the efficiency in the 1.0 mm wavelength range by varying the output coupler reflectivity. Figure 1 shows an experimental setup and the laser output characteristics of the Nd:FAP ceramics. The cavity length was approximately 1 mm by a flat dichroic mirror (DM) and a flat output coupler (OC). A continuous wave (CW) 60 W fiber-coupled laser-diode (LD) was used as a pump source. As a result, we confirmed laser oscillation at a wavelength of 1063 nm for the Nd:FAP, with a maximum slope efficiency for the absorbed pump power exceeding 10% when the OC reflectance was 92.5%.



(a) (b)

Figure 1. (a)An experimental setup and (b) laser output power of Nd:FAP ceramics as a function of the absorbed pump power. Inset shows the typical lasing spectrum.

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T4.6 Multifunctional Coatings for Energy and Environmental Applications Applications

Microstucture and mechanical properties of carbon containing high entropy alloy films

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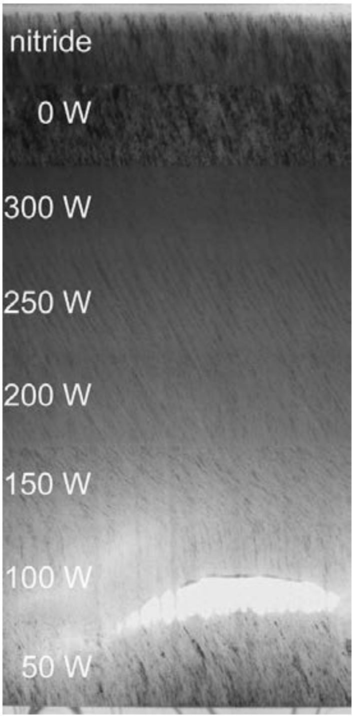
Keywords: high-entropy alloy composites, transmission electron microscopy, nanoindentation

High-entropy alloy (HEA) carbon composites exhibit improved mechanical properties compared to HEAs. The structure and properties of HEA-C films change significantly with carbon content. At low carbon content, a solid solution is formed, then, as carbon content increases, carbide precipitates appear, and finally, with a further increase in carbon content, a pure carbon phase also appears (graphite or amorphous carbon) [1]. Carbide formation strongly depends on the composition of the alloy, whether strong carbide forming elements are present. In this study, we investigate the mechanism of carbon incorporation into the CoCrCuFeNi alloy as a function of the carbon content. Furthermore, we correlate the growth and microstructure of the layers with mechanical properties. We deposited HEA-C films by DC magnetron sputtering. The power of the HEA target was kept at a fixed value (150 W), while the power of the carbon target changed from 0-300 W. For comparison we deposited a HEA nitride film by adding nitrogen to the sputtering gas.

HEA nitride and pure HEA films (top two layers) have columnar structure. Both are single-phase films, made up of non-stoichiometric HEA nitride and fcc metallic HEA phase, respectively. In contrast, all films containing carbon have two-phase structure. The grains do not extend from the substrate to the top of the layer showing that a minority phase hindered their growth. With increasing carbon deposition rate the grains become smaller indicating the increase of the ratio of the minority phase. Electron diffraction patterns revealed the crystalline phase is fcc metallic HEA and the minority phase does not add reflections to the diffraction patterns. This implies it is an amorphous phase, persumably amorphous carbon. Nanoindentation measurements showed the changes of hardness with carbon content. The hardness of all carbon containing films are approximately one and a half times higher (~14-16 GPa) than the hardness of pure HEA film (10.5 GPa), while the HEA nitride film was almost twice as hard (~19 GPa) as the pure HEA one.

Figures



Structure of HEA nitride film and HEA-C films with varying carbon content on cross-sectional TEM image.

Acknowledgments

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Oxidation resistance of AlTiSiN/TiSiN medium entropy ceramic coatings

Marián Palcut[1*], *Patrik Šulhánek*[1], *Libor Ďuriška*[1], *Paulína Babincová*[1], *Martin Sahul*[1], *Ľubomír Čaplovič*[1], *Martin Kusý*[1], *Ľubomír Orovčík*[2], *Štefan Nagy*[2], *Leonid Satrapinskyy*[3], *Marián Haršáni*[4], *Ivona Černičková*[1]

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Keywords: corrosion, oxidation, nitride, PVD

Cutting tools are often exposed to significant thermal and mechanical stresses during operation. The stresses may lead to a considerable underperformance and decrease of lifetime. The cutting tools, however, can be protected by depositing a hard surface layer on the metallic substrate [1]. The coating can improve the mechanical properties of the tool, including hardness, wear, and friction resistance. Furthermore, it can also improve the thermal stability and oxidation resistance, thereby prolonging the service lifetime. In the present work, medium entropy ceramic AlTiSiN/TiSiN coatings were deposited on a high-speed steel substrate using physical vapor deposition (PVD, [2]). The layers were deposited onto a high-speed steel substrate using PLATIT π80 + DLC with LARC® (lateral rotating cathode) technology. The ceramic coatings were prepared by cathodic arc evaporation of Al and Ti-Si alloy sources. The PVD was performed in a flowing nitrogen atmosphere. The as-deposited coatings consisted of three layers: the TiSiN adhesive layer with the thickness of about 50 nm, the middle AlTiSiN layer (~3µm) and the top TiSiN layer (~1.5 µm). The coatings were subsequently oxidized at 700–1000 °C in air. TiO_2 and SiO_2 were the main oxidation products identified at all annealing temperatures. At 1000 °C, however, Al_2O_3 was additionally observed. It was found that Al diffused from the AlTiSiN layer to the surface, where it reacted with oxygen and formed Al_2O_3. The corrosion mechanism is discussed and implications for the high temperature oxidation resistance of ceramic nitride coatings are provided.

Acknowledgments

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T4.7 Materials for Extreme Environments: Ultrahigh Temperature Ceramics (UHTCs) and Nano-laminated Ternary Carbides and Nitrides (MAX Phases) Applications

Microstructure, hardness and indentation fracture resistance of dual-phase high-entropy ultrahigh temperature ceramics

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Keywords: dual-phase high-entropy ceramics, microstructure, nanoindentation, mechanical properties

Dual-phase high-entropy ultrahigh temperature ceramics were prepared using a two-step spark plasma sintering (SPS) process at a maximum temperature of 2100°C, with a sintering time of 5 minutes and an applied pressure of 70 MPa. The resulting material consists of a hexagonal high-entropy boride (HEB) phase and a cubic high-entropy carbide (HEC) phase. The microstructure, deformation, and fracture characteristics of the material were studied using scanning electron microscopy (SEM), EBSD, and EDX analyses.

To measure the hardness of the individual phases, nanoindentation was applied using a Berkovich diamond tip and continuous stiffness measuring (CSM) mode with a maximum depth of 150 nm. Indents were arranged in 10×10 arrays with a distance of 6 μm between them. Vickers hardness testing was also performed with indentation loads of 9.8 N and 49 N for microhardness and indentation fracture toughness measurement.

The average grain size of the HEC and HEB phases were measured to be cca. 2 μm and 3 μm, respectively. The nanohardness of the HEC and HEB phases were found to have mean values of 40.4 GPa and 43.1 GPa, respectively. The microhardness of the material was measured to be 21.73±1.36 GPa and the indentation fracture toughness was 6.04±0.93 MPam$^{0.5}$.

Ablation resistance of titanium diborate based composites derived from Ti-Si or Ti-Al intermatallic systems

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Presented results of studies concern ablation resistance of TiB_2-TiC-SiC composites made of B_4C, C and intermetallic compounds via reactive sintering by the means of SPS technique. Intermetallics from two systems were used Ti-Si (TiSi, $TiSi_2$, or Ti_5Si_3) and Ti-Al (Ti_3Al, TiAl, and $TiAl_3$). Composites were sintered at the temp. range of 1000-1700°C. Density was determined using Archimedes' method. Phase compositions were studied utilizing Panalytical/Philips X'Pert Pro MD XRD diffractometer. X-ray absorption spectroscopy (XAS) measurements were performed at PIRX beamline of the Solaris National Synchrotron Radiation Centre, Krakow, Poland. Ablation resistance was tested using an oxyacetylene flame at 1800°C. Material was exposed for flame during 60 s. Ablated surfaces were examined using a confocal microscope (Lext OLS 3100, Olympus) to determine the depth of the ablation zone. The linear ablation rate of the material was determined. Microstructure and chemical composition of ablated surfaces were examined by the means of SEM/EDS method (Thermo Scientific Scios 2). Generally, investigated composites showed good resistance for ablation. In individual cases this resistance significantly exceeded values of commercially available materials.

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T4.8 Design, Processing, and Applications of Nanolaminated Ternary Transition Metal Carbides/Nitrides/Borides and MXenes and Mbenes

On the journey towards complex MAX phase solid-solutions

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Keywords: MAX phases, solid-solutions, non-conventional synthesis approaches, medium entropy alloys, X-ray diffraction

In the last years, the family of MAX phases has been growing rapidly to more than 300 different compounds. Roughly half of those are represented by solid-solution phases, which increase the compositional diversity and adjustability of the resulting properties tremendously. In this development, phases with solid-solutions on the X-site are considerably underrepresented and only few phases possess solid-solutions on more than one crystal site at a time.[1]

By introducing additional elements in solid-solutions on all three crystal sites, a novel triple-solid-solution MAX phase following the type $(M_{1-x}M'_x)_2(A_{1-y}A'_y)(X_{1-z}X'_z)$ can be synthesized. While carbides can be readily synthesized from the respective elements, the synthesis of nitrides and carbonitrides requires the use of precursors due to the gaseous nature and high stability of elemental nitrogen. To incorporate nitrogen into the structure, binary nitride precursors have been synthesized via non-conventional microwave-assisted synthesis approaches. The subsequent synthesis of complex MAX phases is finalized by conventional heat treatment but can be substituted by microwave heating.

First experiments in the system V-Ti-Ga-Ge-C-N proof the existence of those phases and refined lattice parameters show how the atom size of the implemented elements distort the crystal structure. Based on recent work of our group highlighting the potential of compounds in the system V-Cr-Ga-Ge-C-N,[2] I will also discuss preliminary results of complex solid-solution MAX phases in this system. These indicate interesting developments on the journey towards long-range magnetic ordered MAX phases.

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T4.9 Ceramic Integration Technologies for Energy and Environmental Applications

Comprehensive analysis of telluroborate glasses doped with Nd^{3+} rare earth ions: Exploring the thermal, structural, optical and physical characteristics

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Keywords: DSC, FTIR, Raman, optical properties and radiative properties

In the present study, Nd^{3+} rare earth ion-doped telluroborate glass samples were synthesized using melt quenching techniques. The glass compositions were $(50–x)\ B_2O_3{\cdot}20TeO_2{\cdot}15Mg_2CO_3{\cdot}15K_2CO_3{\cdot}xNd_2O_3$ (where x = 0, 0.5, 1, 1.5, 2 and 2.5 mol %). The samples were characterized through various techniques, including XRD, DSC, FTIR, Raman, Optical absorption, photoluminescence, and decay curve analysis. All samples exhibited an amorphous nature in the XRD spectra. The DSC thermograms revealed the thermal behavior, while FTIR and Raman spectroscopy confirmed the coexistence of trigonal BO_3 and tetrahedral BO_4 units. The optical absorption spectra were recorded at room temperature in wavelength range 180 nm to 1000 nm. The near infrared emission spectra recorded with 808nm laser diode excitation for different concentrations of Nd^{3+} ions and the emission for the $^4F_{3/2}\rightarrow{}^4I_{11/2}$ transition at 1060 nm found to be high intense. Optical absorption spectra indicated an increase in band gap energy with dopant concentration. Judd-Ofelt Ω_λ ($\lambda = 2,4,6$) intensity parameters were determined and spectroscopic parameters like spontaneous radiative transition probability, fluorescence branching ratio and emission cross-section were calculated. The study investigated the impact of Nd_2O_3 concentration on physical parameters such as optical dielectric constant, polaron radius, interatomic separation, molar refraction, and metallization criterion. Results showed an increase in density, molar volume, and refractive index with higher Nd_2O_3 concentration, leading to more non-bridging oxygen in the glass matrix. In conclusion, this study provides insights into the potential applications of Nd^{3+} doped telluroborate glass in advanced optical and photonic devices, contributing to the field of glass science and materials engineering.

T4.10 Environmental Friendly and Energy Efficient Manufacturing Routes for the Production Root Technology Applications

Insights into metal-oxide interactions for enhanced water electrolysis catalyst design via computational approaches

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Keywords: computational design, density functional theory, water electrolysis, electrocatalysts

As global efforts intensify to replace fossil fuels with sustainable energy technologies such as next-generation photovoltaics, wind energy, energy storage systems, electric vehicles, and hydrogen-based solutions including production, storage, and fuel cells, renewable energy technologies, particularly water electrolysis and fuel cells, are of paramount importance in this energy transition. Despite extensive research, the development of more active and durable water electrolysis catalysts remains a key challenge. The primary strategies for improving electrocatalyst performance are either to increase the intrinsic activity of known materials or to discover new materials. However, the dynamic nature of structural changes during electrocatalytic reactions complicates the understanding of structure-property relationships. Computational materials science has become an indispensable tool to explore and establish these relationships, thereby contributing to the development of materials with improved or new functions. This trend is evident in the increasing number of new energy materials innovations resulting from computational research, highlighting its critical role in renewable energy research.

In my presentation, I will discuss our recent findings on the improved catalytic performance of hybrid catalysts consisting of metal nanoparticles on metal oxide supports. Using a combination of density functional theory calculations, comprehensive electrochemical analyses, and operando X-ray absorption spectroscopy, we have found that the presence of oxygen vacancies in the oxide support plays a critical role in lowering the charge transfer energy. This allows for improved charge transfer both between the metal nanoparticles and the oxide support, and between the hybrid catalyst and the electrolyte. Our research highlights the importance of understanding the interactions between metal nanoparticles and metal oxide supports, and provides an innovative direction for the design of highly efficient electrocatalysts.

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