

Germany

Plenaries and Keynote Papers of the CERAMICS / KERAMIK 2023 Conference

The CERAMICS / KERAMIK 2023 Conference, which was held 27–30 March 2023 as a face-to-face event in Jena and Hermsdorf, comprised 3 Plenaries and 35 Keynotes. The abstracts of these lectures are presented below.

1 Plenaries

Monica Ferraris (Politecnico di Torino/IT) spoke about **Joining and Integration Issues of Ceramics and CMC**. Innovation in processing and characterization of ceramic- and CMC-based joined components developed at the GLANCE-Glasses, Ceramics and Composites Research Group at Politecnico di Torino (www.composites.polito.it) was presented and discussed. Joined components for energy storage and transformation have been designed, fabricated and characterized in simulated working conditions: recent results were briefly reviewed. The combination of advanced design of interfaces and joining materials/technologies, selective matrix removal from the composite surface, laser structuring and mechanical machining of the composite/metal surfaces were discussed and compared to existing solutions. The work done with the aim of developing reliable and user-friendly international standard test to measure the shear strength of joined components was also reviewed. Finally, the Advanced Joining Technology Research Center at Politecnico di Torino was presented together with collaboration actions and opportunities for common research activity on joining.

Clive A. Randall (Materials Research Institute, Pennsylvania State University/US) reported about **Cold Sintering of Functional Materials: A Path to a Possible Sustainable Future**. Cold Sintering involves a transient phase that permits the densification of particulate materials at low temperatures of 300 °C and below. Sintering at such low temperature offers so many new opportunities. It permits the integration of metastable materials that would typically decompose at high temperatures. Cold sinter enables a platform for better unification

of material science. Now ceramics, metal and polymers can be processed under a common platform in one step processes. With controlling the forming process new nanocomposites can be fabricated. Polymers, gels and nanoparticulates can be dispersed, interconnected and sintered in the grain boundaries of a ceramic matrix phase. With the ability to sinter metal phases, multilayer devices can be co-sintered with electrodes made from metals such as Al, Ag, Fe and Cu. With appropriate binder selection, polypropylene carbonate and its debinding at 130 °C, one can remove organic binders and leave metals and other more stable polymers within the layers that then can be co-sintered under the cold sintering process and form unique combinations of materials in multilayers.

The talk covered some of the fundamentals of cold sintering, as well as some new examples of this technology across different material systems, ranging from ferroelectrics, semiconductors, and battery materials. Ulf-Steffen Bäumer (thyssenkrupp nucera AG & Co. KGaA/DE) discussed the topic **Green Hydrogen – Key to the Energy Transition**. The goals are set by the Paris Agreement for the fight against the climate change and the reduction of CO₂ emissions. These goals require not less than the de-fossilisation of all sectors of our traditionally carbon-based society.

Green hydrogen from electrolysis is considered to be the key in this de-fossilisation as it connects the renewable energy sector with a wide range of industrial applications and other sectors like transportation, power generation and building heat and power. Already today, hydrogen is produced in large amounts mainly as industrial feedstock.

Anyway, hydrogen produced today is “grey” as it comes from SMR and is accordingly re-

sponsible for emissions of around 900 Mt/a CO₂. Converting all of this grey hydrogen into green hydrogen will require around 1 TW of installed electrolysis capacity. As the demand for hydrogen will expand also to other areas as mentioned above, it is expected that the hydrogen market will grow sevenfold by 2050.

Following this demand, the challenges are tremendous in view of e.g. sector coupling, hydrogen infrastructure, supply chain topics, availability of material and of course for the required technologies and their ramp-up to world-scale. Among the various technologies for water electrolysis, Alkaline Water Electrolysis (AWE) is acknowledged to be the most mature right now. Hence AWE will play an important role in the energy transition on short and long term having its strength especially in central and large scale production of green hydrogen. Anyway, ramping-up productions to gigawatt-scale, be resourceful with metals and noble metals and reduce the TCO (Total Cost of Ownership) needs to be on the list for improvements of all water electrolysis technologies to enable the energy transition.

2 Keynotes

2.1 Raw Materials

W. A. Eranezhuth together with G. Motz and St. Schafföner (all University Bayreuth/DE) addressed the topic of **Porous Carbon-Rich Transition Metal Modified SiCN Ceramic Fibers for Electrochemical Water Splitting**. The global energy demand and environmental pollution drives the need for the augmentation of the existing sustainable energy devices. Electrocatalytic devices such as fuel cells have raised considerable interest due to their high energy and power density. On the other

hand, electrocatalytic water splitting offers an attractive route to produce high-purity hydrogen and platinum based electrocatalysts have proven to be the best in terms of its oxidation/reduction reactions. Currently, platinum on a carbon support is extensively used for water splitting reactions. However, the use of noble metals increases the overall cost of electrocatalytic devices and platinum based electrocatalysts are also known to be unstable in fuel cell working conditions. Hence, the development of efficient and durable catalysts is critical for the commercialization of fuel cells, as the catalysts' reactivity and durability dictate their ultimate activity and lifetime.

In this work, carbon-rich cobalt modified SiCN ceramic fibers were produced from a Precursor Derived Ceramics (PDC) approach. The role of the pyrolysis temperature on the structure of the ceramics and its electrocatalytic activity were investigated. The phase evolution, structural and textural properties of the developed catalytic supports were evaluated with the aid of X-ray diffraction, scanning electron microscopy and nitrogen adsorption analysis. The ceramic fibres synthesized with a combinatorial approach using PDC and electrospinning had mesoporous structure. The electrocatalytic performance was determined using rotating disk electrode method under alkaline conditions.

Ceramic and Glass Particles for Precision Drug Delivery was the title of the presentation made by S. Mathur (University Köln/DE). Chemical processing of functional ceramics and glasses has played a key role in converging disciplines, which is especially true for biomedical applications: For example, the development of biocompatible drug-carriers that can hold back the payloads and release the drugs or antibiotics at the specific diseased area is a materials processing challenge. The selective transport and retention of drugs in sufficiently high concentrations at the target site is inhibited by various physiological barriers, which reduces or even blocks the therapeutic efficiency of molecular drugs. Therefore, advanced drug-delivery systems designed to overcome biological barriers are needed to meet the specific traits of physiological and disease-related barriers. In this context, chemically functionalized SiO₂ nanoparticles act as efficient drug-carriers to transport

higher amounts of therapeutic payloads to diseased sites that also reduces the undesired off-site effects. Moreover, hollow nanocarriers can incorporate more than one drug enabling theranostic and theraregenerative approaches. Finally, silica nanoparticles can be modified with surface-bound target ligands to exploit the overexpression of receptors and promote cell specific attachment of the carriers for a localized high concentration of drug around disease sites. The talk discussed the potential benefits of silica nanoparticles towards precision drug delivery.

T. Khalil together with K. Wegner and M. Ommer (all IBU-tec Advanced materias AG/DE) reported about **Particle Synthesis of CuO-Fe₂O₃ Composites by Pulsation Reactor Technology and Study the Dispersing Character as Slurry for Metal Air Batteries.**

Composites of copper (II) oxide-iron (III) oxide are widely used materials for many different applications, such as pigment for paints, coating on magnetic tapes, catalysts or main component in metal air batteries. The precise control of the thermal treatment steps during particle synthesis is a beneficial method of tailoring the material characteristics to the required application. Due to that, fine particles of CuO-Fe₂O₃ with specific properties have been thermally synthesized by the Pulsation Reactor (PR). PR consists of a hot gas generator that produces a pulsating stream. That means: fast and unsteady-state periodic combustion of natural gas in a chamber, with a resonance tube and a separator. The particles produced using this technology are thus subjected to rapid thermal treatment as it advances in the hot gas stream. Therefore, the process is suitable for the production of powders with modified characteristics.

This work described the characteristic of the composite particles with the addition of carbon to improve conductivity. During synthesis in the PR, the effect of process parameters such as temperature, residence time and configuration on properties of the produced particles were studied applying different analytical methods. According to this work, it was concluded that the PR technology could reach a wide range of composite particles with tailored properties in a continuous process. The produced particles were successively dispersed using wet

milling process. Also, the effect of wet milling parameters on the dispersed particles were studied and optimized to select the best conditions for the production of stable non agglomerated suspension for the application as metal air battery slurry.

Green Synthesis of Anatase TiO₂-Based Powder Nanoparticles for Microplastic Photocatalytic Removal was analysed by E.I. Cedillo-Gonzalez, M.C. Ariza-Tarazona and C. Siligardi (all University of Modena and Reggio, Emilia Department of Engineering Enzo Ferrari/IT). Microplastics (MPs) are present in aquatic ecosystems and are consumed by their biota. Strategies to fight MPs pollution include photocatalysis using TiO₂ nanoparticles. Photocatalysis is based on the interaction of TiO₂ with photons with E higher than E_g, and the generation of hydroxyl and hydroperoxyl/superoxide anion radicals. Those species mineralise MPs into CO₂ and H₂O or degrade them into less toxic substances. Here, N-TiO₂; C, N-TiO₂ and C, N-TiO₂/SiO₂ nanoparticles obtained from 3 different renewable raw materials were prepared, characterized and tested for removing MPs. Two green syntheses were used: A bio-inspired route where proteins from *Mytilus Edulis* and *Mytilus Galloprovincialis* Mussels, respectively were used as renewable raw materials and a biomineralization route using *Pteria Sterna* Oysters. The structural, chemical, optical, and textural properties of the powders were investigated by XRD, XPS, DRS, FTIR, nitrogen adsorption, and FEG- SEM. Photocatalysis of MPs was monitored by gravimetry, FTIR, carbonyl index, MO and SEM-EDS. It was found that the mussel's derived nanoparticles have a better ability to degrade MPs than the biomineralized powders. The C, N-TiO₂ derived from *Mytilus Edulis* can degrade up to 70 % PE MPs and the C, N-TiO₂/SiO₂ derived from both mussels can degrade PET MPs. The photocatalytic degradation of MPs in an aqueous medium using TiO₂-based advanced ceramics is possible and can be used to fight MP marine litter.

2.2 Ceramic Processing

F. J. Clemens together with L. Gorjan and A.N. Conzelmann (all Empa/ETHZ/CH) presented their **Rheological Investigation on Thermoplastic Al₂O₃-Feedstocks.** Aluminum oxides are frequently used to investigate routes or analyze parameters for

ceramics processing methods. One reason is the cheap price in comparison to other ceramics like ZrO_2 .

In their studies, alumina thermoplastic feedstocks based on ethylene vinylacetate and stearic acid were prepared and shaped by a commercial 3D filament printer. In addition, the rheological properties of the feedstocks compositions were investigated using plateplate configuration. The effect of the stearic acid content on the rheological behavior was investigated in detail and compared with existing rheological models. The results showed that at a low amount of stearic acid, a viscosity plateau (cross model) could be observed. At higher stearic acid content, a yield point (Herschel-Bulkley model) occurred, as the stearic acid content surpassed the amount needed to cover the powder surface. Stearic acid also influenced the mechanical properties of the filament. A higher content resulted in a more brittle and less flexible behavior of the filaments.

Thin wall structures were printed, debonded and sintered to demonstrate the shape stability and fusion between the layers. Complex ceramic tetrahedron structures, which are challenging to produce by more conventional methods such as injection molding have been printed and the thermal debinding process was investigated in more details. Shrinkage of the parts was found to be anisotropic, depending on the orientation of the printing pattern. The alignment of the ceramic particle orientations introduced by FDM printing was identified as a potential cause of the anisotropy. This study further demonstrates that using a powder bed during the thermal debinding process yields sintered structures that can withstand twice the compressive force.

DMD-DLP-Based Additive Manufacturing of Ceramics – Inspired by Colloid Chemistry was discussed by Th. Graule, P. Zubrzycka, L. Conti and M. Stuer (all Empa) together with M. Borlaf (University Madrid/ES).

The efficient stabilisation of ceramics based nanopowders is a prerequisite for the achievement of highly reliable ceramic materials and for the development of three-dimensional printing technologies, recently known as Additive Manufacturing. The authors performed studies to stabilize alumina, magnesium-spinel and zirconia sub-micron/nanoparticles. Anion and cation type

comb copolymers were applied as a promising dispersants in case of titania stabilisation. Highly charged counterions were furthermore used to modify the electric-steric double layer of mixed oxides. These slurries were successfully applied to the stereolithographic shaping of ceramics using a digital light processing.

J. Günster, B. R. Pauw and J. Chr. Sängner (all BAM/University Clausthal/DE) reported on **Two-Photon-Polymerization for Ceramics Powder Processing**. Manipulating ceramic powder compacts and ceramic suspension (slurries) within their volume with light requires a minimum transparency of the materials. Compared to polymers and metals, ceramic materials are unique as they offer a wide electronic band gap and thus a wide optical window of transparency. The optical window typically ranges from below $0,3 \mu\text{m}$ up to $5 \mu\text{m}$ wavelength.

Hence, to penetrate with laser light into the volume of a ceramic powder compound, its light scattering properties need to be investigated and tailored. In the present study, the authors introduced the physical background and material development strategies to apply Two-Photon-Polymerization (2PP) for the additive manufacture of filigree structures within the volume of ceramic slurries.

P. Colombo and G. Franchin (both University Padova, Department of Industrial Engineering/IT) gave an overview on **Additive Manufacturing (AM) of Ceramics from Liquid Feedstocks**. AM of polymeric materials has reached a far greater maturity with respect to ceramics, the latter being 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. The research activities have therefore focused on AM of ceramics from liquid feedstocks. In particular, the authors investigated the use of preceramic polymers as well as geopolymer and 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, the strategies for producing high quality ceramic components using a variety of liquid feedstocks and different AM techniques, from direct ink writing, digital light processing and two-photon polymerization to robotic and volumetric AM were presented.

U. Scheithauer, L. Rebenkalu, J. Abel, E. Schwarzer-Fischer, S. Weingarten, and H. Barth (all Fraunhofer IKTS/DE) gave their presentation about **Hybridization of Materials and Technologies for the Manufacturing of Highly Functionalized and Reliable Ceramic Components**.

Three different manufacturing strategies for ceramic components were presented and discussed, in which different materials (sequential or simultaneous manufacturing of multi-material components) or shaping methods were hybridized. On the one hand, the resulting component properties and functionalities can be further increased. Possible combinations of properties that can thus be realized in a component are electrically or thermally conductive and insulating, magnetic and nonmagnetic, dense and porous or different optical properties (e.g. colors or transparency). On the other hand, the manufacturing costs can also be reduced, by combining the benefits of different shaping technologies.

Using different examples from the field of space applications (ceramic reactor for thermal decomposition of H_2O_2 , ceramic igniter, ceramic aerospike nozzle), processing (high-performance thermal cyclers, ceramic components with integrated heaters or sensors), and luxury (multi-colored ceramic components), not only the potentials and existing challenges of the different strategies were discussed, but also the potential of ceramic materials in general was shown.

Blacklight Sintering – a Disruptive Innovation in Ceramic Processing? was the title of the presentation made by L. Porz (University Darmstadt/DE).

Rapid sintering has attracted spotlight attention with multiple forms of energy transfer already demonstrated. Blacklight sintering, using intense illumination with UV-light to transfer power directly into the ceramics, now allows to process ceramics on-the-

spot without contact or container. Extraordinary practicability with minimal sample handling and process times in the seconds range, allow hundreds of iterations per day. Moreover, fabrication in quick succession immediately enables mass productions with tons-per-year capacity.

The minimal process time and the absence of any container minimize the energy needed so drastically, that efficiency competes with or even outperforms current industrial standards. Simultaneously, the efficiency gains of up to 80 % are independent of batch size. This talk foreshadowed the prospect of blacklight sintering by contrasting energy efficiency to industry standards reflecting on scalability and associated changes in the value chain.

2.3 Ceramics for Energy

W. Bauer together with M. Müller, N. Bohn, J. Binder, J. Klemens and P. Scharfer (all KIT/DE) presented **Hierarchically Structured Nano Porous Cathode Materials – Potential, Limits, Applications**. Typical cathode materials for batteries have micron sized particle diameters. In contrast, nanoscale cathode materials are able to achieve very high rate capability and significantly improved cycling stability due to short diffusion paths and high stress resistance. However, inefficient packing density and increased additive demand limit the achievable energy density.

Hierarchically structured cathode materials represent an approach to combine the advantages of both worlds and allow nanoparticles to gain access as electrode materials in batteries. For this purpose, the nanoparticles are aggregated into secondary particles in the microscale, for which a comparable processing can be applied as for established materials. Characteristic of the hierarchically structured particles is the high share of open intraparticle porosity. It leads to lower energy density, since a higher residual porosity remains in the electrode despite an untypical plastic deformation behavior of the secondary particles.

However, the ability to create favorable conditions for fast charge transport makes the hierarchically structured particles particularly attractive for electrode materials with low conductivity and for post-lithium systems, such as the sodium or magnesium ion batteries, where classical particle structures

only lead to electrodes with significantly limited performance.

The paper gave an overview of the state of development of hierarchically structured cathode materials with established electrode materials. It also addresses the potential of this particle morphology for future developments in the battery field.

Na-Beta"-Alumina – Novel Concepts for an Established Ceramic Electrolyte were shown by C. Dirksen together with M. Fertig, M. Hofacker, M. Schulz and M. Stelter (all Fraunhofer IKTS). Ceramic electrolytes made from Na-beta-alumina are commercially utilized in Na/NiCl₂ and Na/S-batteries since the 1990s. They offer a variety of benefits like a high ionic conductivity, a neglectable electronic conductivity, stability towards Na and a low toxicity. Fraunhofer IKTS worked for the last years on the next steps to pave the way towards novel fields of application and production methods for Na-beta"-alumina electrolytes. Highlights presented were the mechanical and electrochemical material properties of Na-beta"-alumina modified by transition metal doping.

The observed effects were explained by changes of the microstructure. Shaping of green bodies is one of the critical processes of ceramic production. This process was mastered at Fraunhofer IKTS by several techniques. Besides the common production route of isostatic pressing, methods like extruding, slip casting, or tape casting were successfully investigated. Especially extrusion and tape casting were efficient ways to produce Na-beta"-alumina electrolytes. To utilize Na-beta"-alumina in room temperature cells, hybrid electrolytes of polymers and Na-beta"-alumina particles were prepared and tested. They unite the advantages of Na-beta"-alumina (ionic conductivity) with the advantages of polymers (flexibility).

The topic **Exploring Future Recycling Possibilities for Different Solid Oxide Cells** was presented by N. Menzler, St. Sarnier and O. Guillon (all Forschungszentrum Jülich/DE). Solid Oxide Cells (SOC) are able to operate in two modes: Either as electrolyzer, thereby converting electrical energy into valuable chemicals like hydrogen or a synthesis-gas (H₂ + CO), or by converting hydrogen or C_xH_y-gases into electricity. Additionally, a bifunctional mode, known

as reversible solid oxide cell, is possible. As the German and European future energy system will be largely based on renewables like wind and solar power systems, which are available only intermittent, electrolyzers will play a crucial role in "storing" the surplus energy at times of low consumption as direct fuel. Besides energy storage the produced gas can also be used as basis for e.g. e-fuels or carbon-based chemicals. Four types of electrolyzers exist: alkaline, polymer electrolyte membrane, alkaline proton-exchange membrane and solid oxide. The first three operate at low temperatures the latter at 600–900 °C. The materials used in an SOC are mostly high Cr-containing steels as interconnects, nickel as fuel-side contact, glass-ceramics as sealant and ceramics in the cell and air-side contacting.

Irrespective of the fact that all electrolyzers will play their individual role in the near or mid future, early thinking about the End-of-Life (EoL) or End-of-Use (EoU) stacks is relevant and necessary. Within the technology platform (H2Giga), funded by the BMBF/DE recycling capabilities for all electrolyzer types are characterized. In this presentation, the focus was on recycling strategies for three subtypes of planar cells, namely electrolyte-, metal- and fuel electrode-supported cells. Additionally, first results concerning the ceramic cell materials, aiming for either closed- or open-loop recycling, were presented.

R. Vassen together with S. Prajapati, St. Renz and F. Lohmann-Richters (all Forschungszentrum Jülich) spoke about **Manufacture of Diaphragms for Alkaline Electrolysis by Thermal Spray Techniques**. Alkaline electrolysis is a well-established technology and does not require noble metal catalysts. However, the current density is currently too low in comparison to alternative technologies like polymer electrolyte membrane electrolysis. An important factor for improvement is the ionic conductivity of the diaphragm and the performance of the electrodes. Higher operating temperature above 100 °C can improve both, ion conductivity and electrode performance, at the same time. On the other hand, degradation mechanisms as corrosion and dissolution reactions are accelerated by increased temperature.

As standard Zirfon diaphragms are not suitable in this temperature range, zirco-

nia-based stable diaphragms have been developed by thermal spray methods. The Atmospheric Thermal Spray (APS) technology allows the manufacture of mechanically stable layers with a certain porosity level. For the necessary mechanical stability of the diaphragms a low porosity level and a rather high thickness is needed, however, a good performance in the alkaline electrolysis requires good ionic conductivity, i.e. the opposite (high porosity and low thickness). The paper presented results on the optimization of the microstructure using different process conditions and also special pore forming additives. The performance of such diaphragms in alkaline electrolysis was shown and compared to standard Zirfon diaphragms.

3.4 Functional Ceramics

Structure-Property Relationships: A-Site Cations Redistribution in Complex Polar Perovskite Oxides were addressed by N. Khansur, H. Ursic, and G. Eyoun (all FAU Erlangen-Nürnberg/DE). Tailoring the electromechanical properties of a material without altering the original composition is an emerging phenomenon for the optimization of functional properties. Post-sintering annealing with varying maximum temperatures, cooling rates, and atmospheres can influence the crystallographic phases, domain structures, conductivity, mechanical properties, and the temperature stability of the electromechanical properties. However, the influence of post-sintering heat-treatment on crystal structure, domain structure, and functional properties is not well known. In this contribution, influence of annealing conditions on the functional properties, structure, and defect chemistry of A-site complex polar perovskite oxides $(A,A'')B_2O_6$ were highlighted.

U. Partsch (Fraunhofer IKTS), F. Bechtold (Via-Electronic GmbH/DE) and J. Müller (University Ilmenau/DE) discussed about **LTCC – Discontinued Model oder Enabling Technology for New Applications?**

LTCC technology (LTCC – Low Temperature Cofired Ceramics) has been established for many years for the production of highly integrated and reliable ceramic PCBs, components (filters, LNA), antenna modules and sensors. The intrinsic material properties

(CTE adaptation to Si, high thermal conductivity and operating temperatures, excellent dielectric properties) in combination with technical features (multilayer structure, integration of passive functions, non-electrical functions) make LTCC a perfect choice for the design and manufacturing of microsystems for harsh application conditions or high operating frequencies.

The energy transition and electrification of transport are changing the market requirements with regard to the electronic systems required. In the future, engine and transmission controls for combustion engines will lose importance, but systems for autonomous driving or real-time communication will gain in importance. New fields of application with high potential such as supercomputers and quantum sensors are on their way from research to industrial application. For this, the environment for electronics is changing significantly (high vacuum, ultra-low temperatures) and there are material and technological challenges that need to be solved.

The presentation gave an overview of the current performance of LTCC technology as well as some research topics addressed to fulfill the requirements in new applications. R. Moos, L. Hennerici, E. Kita, N. Leupold, M. Linz and D. Paulus (all University Bayreuth) reported on **Powder Aerosol Deposition (PAD): A Promising Coating Tool (not only) for Functional Ceramics**. Lithium ion conducting electrolytes and cathode active materials for all-solid-state batteries, sodium ion conducting membranes for future batteries, solar cells of organo-halide perovskites, materials for flexible thermoelectric materials, or even dense layers of Moon dust – such exciting applications can be manufactured with the Powder Aerosol Deposition (PAD), besides of course simple passivation films of alumina or zirconia. PAD is a novel technique to manufacture dense ceramic or ceramic-like coatings from a wide range of materials. The deposition occurs fully at room temperature, directly from the dry powder. Film thicknesses range from below 1 μm to over 100 μm . A high temperature step is not required, sometimes mild annealing improves the electrical properties. The field of PAD was presented and recent applications were overviewed. Some scientific problems were 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 concluded the presentation.

M.W. Alkanj and J. Töpfer (both Ernst-Abbe-Hochschule Jena/DE) together with M. Töpfer, A. Kynast and F. Schubert (all PI Ceramic GmbH/DE) gave an overview about **Cofiring of Lead-Free Piezoceramic KNNLT Multilayer Actuators with Nickel Electrodes**. Potassium-sodium-niobate piezoceramics $(K_{1-x-z}Na_xLi_z)Nb_{1-y}Ta_yO_3$ (KNNLT) are considered a promising, environment-friendly alternative for lead-zirconate-titanate $Pb(Zr_{1-x}Ti_x)O_3$. For multilayer actuator fabrication, the use of inexpensive base metal alloys (nickel or copper) is desired. This requires firing in reducing atmosphere. For the fabrication of defect-free, high-performance piezoelectric components, a thorough understanding of the complex interplay between piezoceramic oxide and metal layers during debinding, sintering and reoxidation is necessary. Sintering protocols which avoid oxidation of the metal electrodes during sintering at low oxygen partial pressure and to tailor the oxygen vacancy concentration in the piezoceramic upon reoxidation have to be developed.

The KNNLT piezoceramic was successfully cofired with nickel electrodes. Manganese dopant segregation at the interface between the ceramic layer and the nickel electrode was observed. The effect of the firing parameters on the performance of the multilayer and on the distribution of manganese in the KNNLT multilayer was investigated. In addition, different reoxidation regimes were applied to enhance the properties of the multilayers.

Through optimizing the firing parameters, a multilayer actuator was obtained. However, further investigations are required to improve the performance of KNNLT multilayer actuators with nickel electrodes.

F. Kerbe (Verein für Regional- und Technikgeschichte Hermsdorf e.V./DE) together with U. Reichel and D. Grützmann (both Fraunhofer IKTS Hermsdorf) spoke about **100 Years Commercial Broadcasting in Germany – Challenges to Technical Ceramics**.

In October 1923 in Berlin, the first German commercial radio programme was broad-

casted via 400 m-band. Only 6 month later, its first programme hour "Berliner Funk Stunde" had 100 000 registered listeners. The prehistory of this important social event was characterised by some technical milestones, that were in parts connected to technical developments in ceramics. Isolation parts made from steatite showed excellent isolation properties even at high frequencies. Fired thick film metallization were the basis for reliable electrical connectors but also for vacuum save joining of metals and ceramics. Substantial experiences with glazing of ceramics were a good starting point for successful joining of ceramics and glasses. Ceramic materials became valuable and economic alternatives to natural dielectric materials like mica. Developments during the following decades lead to technical highlights like condensators with well-defined temperature coefficient and/or high dielectric permeability, high power condensators or fully ceramic amplifier tubes. Challenges from HF-technics were the origin for the development of a wide diversity of functional ceramic materials. In the beginning beside STEMAG and Rosenthal, the Hermsdorf Porcelain factory (later HESCHO GmbH) within Kahla AG was one of the important players in this field. In the thirties, HESCHO became the technology leader for high frequency components in civil and military applications. By means of original documents from the archive, examples for the vehement technical developments of that time were illustrated. With current developments made by companies at and around Hermsdorf, the bridging from the early 20th century to present age was given.

Processing and Investigation of Phosphors in Ceramic Light Converter Tapes were presented by Ch. Schmidt and J. Werner (both FGK – Forschungsinstitut Glas – Keramik GmbH/DE). A new system of near-UV emitting LEDs and radiation-converting ceramic tapes has been developed for durable and energy-efficient illuminated signage systems. Previous LED-based signage systems are usually very limited in terms of their colour, since either only single-colour LEDs or whitelight LEDs in combination with colour filters consisting of foils are used. In addition, these organic colour filters absorb a large part of the light and age as a result of ambient UV radiation, so that their endurance is limited to less than seven

years. Although the entire colour space can be displayed with RGB LEDs, but a very high level of technical effort is required to implement large format illuminated advertising in a visually attractive manner.

In a collaborative project with partners from industry and research, a new approach was therefore being pursued in which UV or blue radiation (365–465 nm) excites specially developed and synthesized phosphors in a ceramic converter film and red, green or blue light is emitted. For this purpose, phosphors in pure form and phosphor blends were used, integrated into a ceramic tape.

These tapes are manufactured by tape casting and formed into a variable shape by punching out in the green state. The thermal process is followed by debinding and sintering, which is individually adapted to the phosphors used.

The ceramics thus produced are used for radiation conversion, light scattering and to protect the LEDs from external influences. In this way, energy efficient, durable and large format displays should be designed, which can map the RGB colour space and its colour mixtures (CIE1931 colour space). An appropriate demonstrator was prepared within the project and its properties were characterised using various analysis methods.

3.5 Refractory Ceramics

Ch. Wöhrmeyer (Imerys Deutschland/DE) reported about **Raw Materials for 3D-Printing of Refractories**. Many industries have started to implement 3D printing technologies in their manufacturing processes. The ceramics industry is already printing high added value products, focussing on very complex shapes and high precision surface definition coupled with the need for dense ceramic bodies. The construction industry focuses on large scale projects like printing of whole buildings or bridges as they need to further scale up the productivity in this sector. While the ceramics industry first of all needs very fine powders as feedstock for Additive Manufacturing, the construction industry also needs to integrate coarser materials to achieve the required large scale structural integrity. Furthermore, 3D printing of building materials typically requires a cold setting cementitious binder system with precisely adjusted rheology stiffening and setting times, that is

able to develop the required strength without external heat treatment.

This paper discussed potential raw material options for the 3D printing of refractories. Both high-temperature resistant oxide powders and aggregates, but also potential binder concepts were highlighted. Since 3D printing of refractories is rather at its early stage, it allows to build on experience in other industries. But it can also build on existing refractory knowledge for example low cement castable technology, and castable self flowing/gelling technology as required for shotcreting.

Refractory Masonries: Achievement of High Temperature Data and Modelling of Thermomechanical Behavior

was the title of the presentation made by Th. Tonnesen, W. Reichert, J. Gonzalez-Julian, M. Henze and G. Hirt (all RWTH Aachen University/DE). Refractory linings are, in addition to loads due to corrosion and creep processes, particularly affected by thermomechanical stresses caused by the restricted thermal expansion of the lining. These stresses can occur within individual components as well as in bricks and can lead to plastic deformation, cracks, and material failure. Thus, comprehensive knowledge about thermomechanical behavior is mandatory for an accurate prediction of occurring stresses to design load-optimized linings.

The paper presented a method for utilizing Refractoriness Under Load (RUL) tests to determine a temperature dependent static Young's modulus for refractories. In a first step, RUL tests with a negligible load were carried out in order to determine the materials temperature dependent thermal expansion coefficient. Afterwards, several RUL tests with higher loads were carried out. The measured data of change in temperature and length were then corrected by the thermal expansion and used to construct elastic lines for several temperatures, where the elastic slope was determined using the change in length and the respective load. Thus, Young's modulus for several temperatures could be determined. The obtained values for the Young's modulus were then compared to resonant frequency damping analysis measurements and validated using a finite element model of the RUL test.

Fracture Behaviour and Sub-Critical Crack Growth of Flame-Sprayed Ce-

ramics was shown in the paper made by M. Neumann, P. Gehre and Ch.G. Aneziris (all Institute of Ceramics, Refractories and Composite Materials, TU Bergakademie Freiberg/DE) together with H. Jelitto and G. Schneider (both Institute of Advanced Ceramics, TU Hamburg/DE).

The potential of flame-sprayed ceramic parts spans a wide field of applications, including high-temperature insulating linings (thermal barrier coatings) or protective coatings against wear and tear. For mechanical design purposes, fracture characteristics like crack resistance, behaviour under sub-critical loading, and the scattering of the flexural strength are crucial parameters. Therefore, the presented study aimed for an insight into the fracture processes in such flame-sprayed materials: Pure Al_2O_3 and an alumina-rich composition within the Al_2O_3 - ZrO_2 - TiO_2 system were employed for the preparation of self-supporting parts via rod flame-spraying.

Both materials were investigated by means of cyclic and biaxial flexure tests in order to derive the R-curve-potential, the sub-critical crack growth parameters, and the fracture statistics. It was revealed, that the addition of ZrO_2 and TiO_2 was beneficial in terms of the crack resistance and flexural strength and also allowed for better buffering of thermal shock.

3.6 Bioceramics

K. Hurler, R.E. Matta and R. Belli (all FAU Erlangen-Nürnberg) talked about **Rietveld Characterization of Graded 3–5 mol-% Y_2O_3 -Stabilized Zirconia for Dental Application**. Y_2O_3 -Stabilized Zirconia (YSZ) is applied in prosthetic and implant dentistry. In previous work, two tetragonal $\text{ZrO}_2(\text{Y})$ phases differing in their lattice parameters were identified and quantified by Rietveld refinement in commercial YSZ samples. The Y_2O_3 content of these phases, assigned as Y-lean t'' and Y-rich t''' , was derived from tetragonality c/a . The fracture toughness of the materials increased with increasing weight fraction of phase t .

In the recent study, the materials KATANA Zirconia YML (Kuraray/Noritake) and IPS e.max ZirCAD Prime (Ivoclar Vivadent) were characterized. According to the manufacturers, both materials show a gradient in Y_2O_3 content from 5–3 mol-% from surface to bottom to combine favourable optical ap-

pearance of Y-rich and better mechanical performance of Y-lean $\text{ZrO}_2(\text{Y})$.

In order to assess the gradient profile, 10 slices with thickness of 1 mm each were sawed from both samples. Each slice was analysed. All slices contained the phases t and t'' . In e.max ZirCAD Prime, constant decrease of t'' fraction occurred between depths of 2–5 mm, a plateau was reached thereafter. In KATANA Zirconia YML, the decrease in t'' started at 4 mm depth, reaching an intermediate level at 6–7 mm and then a constant plateau after 8 mm. The bulk Y_2O_3 content followed the same scheme. Hence, the proposed decrease of Y_2O_3 content from surface to bottom, resulting in decrease of Y-rich t'' , was confirmed for both samples, but in different profiles.

H. Elsayed and E. Bernardo (both Department of Industrial Engineering, University Padova), together with F.M. Stabile (CE-TMIC/ES), F. Dogrul and D. Galusek (both FunGlass – Centre for Functional and Surface Functionalized Glass, Alexander Dubcek University of Trenčín/SK) introduced the **Silicone-Assisted Advanced Additive Manufacturing of Glass-Ceramic Scaffolds**.

Silicone resins are attractive both as precursors of silicate bioceramics and as feedstock for Additive Manufacturing, including masked stereolithography. The two aspects may be successfully combined when engineered blends, as binders for ceramic powders, consisting of a silicone polymer are mixed with photocurable acrylates. The first case study concerned scaffolds with a composition resembling well-established Biosilicate® glass-ceramics, from the direct thermal transformation of silicone into silica, reacting with sodium and calcium salts (carbonates and phosphates). The technology enables the obtainment of novel composites, with the silicone yielding also pyrolytic carbon, by firing in nitrogen. The latter phase provides extra functionalities, such as intensive heating by absorption of IR light, useful for disinfection purposes. The second case study regarded wollastonite-diopside glass-ceramics, in which the final phase assemblage relied on the chemical interaction, upon firing, between binder-derived silica and softened glass. Compared to glass-ceramic scaffolds from stereolithography with fully sacrificial acrylate binders, with the same overall oxide formulation, the new

methodology enables a distinctive topological control.

Synthesis and Characterization of Molybdenum-Containing Mesoporous Bioactive Glass Nanoparticles for Biomedical Applications were described by M. Ospina (FAU Erlangen-Nürnberg), together with A.R. Boccaccini (Institute of Biomaterials, FAU Erlangen-Nürnberg) and F. Westhauser (Center of Orthopedics, Traumatology, and Spinal Cord Injury, Heidelberg University Hospital/DE). Mesoporous Bioactive Glass Nanoparticles (MBGNs) based in the system SiO_2 - CaO - MoO_3 were synthesized using a microemulsion-assisted sol-gel process. The synthesized MBGNs were characterized in terms of morphology, composition, in vitro bioactivity, and in vitro cytocompatibility. Scanning electron microscopy confirmed that the particles had spherical morphology with a disordered mesoporous structure. Energy dispersive X-ray spectroscopy confirmed the presence of Ca, Si, and Mo in the synthesized MBGNs. Preliminary results indicated that molybdenum-doped MBGNs form apatite crystals upon immersion in simulated body fluid. The effect of the release of molybdenum ions on cellular osteogenic differentiation of MC3T3-E1 cells (pre-osteoblast-like cells) were measured using an enzyme alkaline phosphatase marker.

3.7 Ceramics for Environment

Ch. Goebbert and M. Shaw (both Nanostone Water/DE) together with J. Quiros (Nanostone Water/US) analysed **Advantages of Ceramic Ultrafiltration Membranes for Pretreatment of SWRO and Wastewater Streams**.

Reverse Osmosis (RO) is the current preferred technology for seawater desalination. When provided water free of suspended solids and low in Dissolved Organic Carbon (DOC) RO membranes can last for 1–2 years between cleans and a lifetime up to 10 years. Conventional RO pretreatment has struggled when faced with challenging influent water quality resulting in: capacity loss, high cost of RO cleaning, Frequent RO element replacement. UF membrane pretreatment is expected to address these issues. Another topic was the treatment of municipal waste water as the 4th cleaning step to reduce the intake of critical chemicals like PFAS/PFOS, micro- and nano-plas-

tic as well as pharmaceuticals to natural waterways upstream. Results of several pilot trials under realistic raw water conditions for both topics were presented.

Carbon Molecular Sieving Membranes for H₂ Separation were introduced by T. Van Gestel, D. Sebold and W. Meulenber (all Forschungszentrum Jülich). Many extraordinary properties have been reported for graphene, a 2D carbon nanostructure. It has been demonstrated that thin films made of graphene, and its oxygenated derivative graphene oxide, show unique permeation properties for the smallest molecules (He, H₂, H₂O), which is attributed to the formation of a graphite-like structure. However, before such membranes can be practically used, there are several subjects that remain to be addressed, such as making large areas of membranes on regular porous ceramic supports, the stability of the material, and also the adhesion on the support.

The novel membranes reported are fabricated on a specially designed 8YSZ mesoporous support, which has been recently commercialized. The latter consists of two 8YSZ membrane layers with a pore size of ~5 nm and ~3 nm on top of a porous α -Al₂O₃ support disc or tube. This support is stable in all the harsh conditions tested so far (e.g. hydrothermal conditions, strong acids and bases).

In addition, the 8YSZ support was modified with a strongly bonded carbon layer, to provide the required adhesion. The developed 8YSZ/carbon membranes are highly stable and show the same transport performance for the smallest gases as the initial graphene-based membrane.

Development of Tubular One-Side Closed Porous Ni-Cermet Anode Support for Thin Film Based Membrane Electrode Assemblies was emphasized by O. Ravkina, R. Hoffmann and R. Kriegel (all Fraunhofer IKTS), together with A.-E. Surkus (Leibniz Institute for Catalysis e.V./DE), J. Wartmann (The Hydrogen and Fuel Cell Center ZBT GmbH/DE), and A. Kruth (Leibniz Institute for Plasma Science and Technology e.V./DE).

One of the big challenges of transition to emission-free economy is the development of a carbon-free processes for ammonia production. At present, up to 3 % of world fossil energy fuels are demanded for the Haber-Bosch process. A decentralized am-

monia production could be an essential part of the solution for this problem. One of the main objectives of the CAMPFIRE Alliance is a decentralized ammonia production using renewable energies as an innovative energy source for emission-free maritime mobility. The subproject CAMPFIRE 04 deals with the development of a tubular membrane reactor for Solid-State Ammonia Synthesis (SSAS). The combination of water electrolysis and ammonia synthesis in a single device intensifies the ammonia production process and avoids the individual steps for hydrogen generation and purification. Besides, it eliminates the CO₂ emissions of the conventional Haber-Bosch process utilizing natural gas. SSAS is based on proton conducting ceramic thin-film electrolyte consisting of a doped barium zirconate.

3.8 Structural Ceramics

Complex Nitride Ceramic Components for Various Applications Made by Modern Shaping was the topic of the presentation made by E. Schwarzer-Fischer, E. Zschippang, U. Scheithauer and A. Michaelis (all Fraunhofer IKTS).

Non-oxide ceramics such as nitrides still have an unrivalled combination of excellent properties, such as hardness, high mechanical strength, wear and corrosion resistance even at high temperatures. Especially silicon nitride is for high temperature applications up to 1450 °C, but also for medical applications. Aluminium nitride shows a unique combination of high thermal conductivity and electrical insulation with potential for disruptive innovations in the field of high-power electronics.

However, high-performance ceramic products of these materials are mainly processed with high effort by using conventional shaping method, sufficient for many various applications (e.g. cutting tools, bearings, prostheses or as substrates in electronic applications).

Nevertheless, the degrees of freedom in components design are limited by the used shaping methods, especially under the aspect of constantly increasing requirements for complexity and function. With the help of Additive Manufacturing (AM), there is the possibility of significantly expanding these limits for completely new fields of applications. However, the AM processes for high-quality nitride components as well as

the material portfolio are still limited and under progress.

The authors provided an insight into the development status of silicon nitride and aluminium nitride components at Fraunhofer IKTS using the so-called CerAM VPP process (Lithoz LCM technology/AT), based on three interesting applications: a finger implant and an aerospike nozzle, both based on different silicon nitrides (density >99 %) as well as a heating-cooling element based on aluminium nitride (thermal conductivity >170 W/mK).

3.9 Silicate Ceramics

C. Molinari, C. Zanelli, D. Giordano, and M. Dondi (all CNR – ISSMC/IT) reported about **Viscosity Measurement of Silicate Melts by Hot Stage Microscopy**.

The viscosity of silicate melts represents a key parameter to control the ceramic and glass manufacturing processes and to understand nature phenomena (e.g., volcanic eruptions). The techniques generally used are time wasting, requiring equilibrium conditions and limited to small viscosity ranges. The reduction of testing time represents a challenge for both academic and industrial aims. For this purpose, Hot Stage Microscope (HSM) technique was selected as alternative for a rapid viscosity determination and an experimental methodology was set up. Glasses with a measured viscosity-temperature dependence (Vogel-Fulcher-Tammann, VFT) were selected. Specimens (pressed powders) were heated at 10°C/min till melting and characteristic temperatures (CT) (start sintering, end sintering, softening, sphere, hemisphere and melting) were found.

Each CT viscosity was calculated based on the experimental VFT parameters. Viscosity was calibrated introducing correction factors based on glass chemistry to introduce the effect of surface tension on CT definition. Two independent data sets could be obtained – CT (by HSM) and the corresponding characteristic viscosity (from the glass composition) – to be used to calculate the VFT parameters. The comparison between the calculated and the experimental viscosity showed a good correspondence, significantly improved with respect to previous attempts in the literature disclosing a promising prospect of this noncontact technique.

3.10 Composites

The topic **Improving the properties of SiC/SiC CMC Manufactured by LSI Process and Development of Three-Dimensional Components** was presented by F. Suess, M. Friess, F. Vogel, L. Friedrich and L. Klopsch (all Deutsches Zentrum für Luft- und Raumfahrt/DE).

Increasing performance and efficiency of aero engines is mandatory for more environmentally friendly air transport. Rising temperatures, especially for combustion section and turbine structures, as well as lower weight of the components are key requirements for new materials. Together with adapted environmental coating systems and cooling features ceramic composites are good candidates for aircraft applications. They are capable of withstanding high temperatures in an aggressive environment while the density is 2/3 lower than conventional nickel-based alloys.

The Liquid Silicon Infiltration process (LSI) for the manufacture of silicon carbide fiber reinforced silicon carbide composites (SiC/SiC CMC) has recently been optimized. By using a novel phenolic resin, the remaining unconverted carbon in the matrix could be eliminated and the silicon proportion was reduced by ~60 %. This resulted in a higher Young's modulus and improved proportional limit stress. Furthermore, the Institute of Structure and Design is investigating turbine vanes made from SiC/SiC material together with several other DLR institutes in the DLR's project 3DCeraTurb. One goal of 3DCeraTurb is to design and manufacture ceramic stator guide vanes for a high-pressure turbine, to experimentally investigate the blade performance in a wind tunnel and to evaluate performance, damage and lifetime for the later application in an aircraft engine. The focus is the enhancement of the manufacturing process from plate dimensions to more complex three-dimensional components.

Size Effect of Strength for Ceramic Matrix Composites was the title of the presentation made by St. Flauder, N. Langhof, W. Krenkel and St. Schafföner (all University Bayreuth).

Ceramic Matrix Composites (CMCs) exhibit a peculiar combination of damage tolerance combined with typical properties of ceramics like thermal stability, wear resistance, and low density. CMCs overcome espe-

cially the brittleness of monolithic ceramics. Even so, CMCs also show a dependency of strength as a function of the tested size or volume of the sample. Up to now, the mechanisms, models, and even existence of a size effect of strength for CMCs are still unclear. This study analyzed the influence of the sample size and testing method on the strength of carbon fiber-reinforced silicon carbide (C/C-SiC). Hence, C/C-SiC samples with varying sample geometries were tested under bending and tensile loads.

A testing device was developed to ensure minimally biased tensile testing due to a self-alignment and centering of samples. It was found that a size effect of strength exists for C/C-SiC. It was further shown that the Weibull modulus was not a material constant for C/C-SiC and the classical probabilistic aspects of brittle fracture with the application of Weibull statistics is unsuitable to describe the size effect of strength. The size effect of C/C-SiC was discussed regarding the concepts of load sharing, the weakest link approach, and the energetic size effect of quasi-brittle materials.

3.11 Characterization

T. Fey (FAU Erlangen-Nürnberg) introduced **Characterization and Simulation of Porous Ceramics**. 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.

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 carried out at certain processing steps can be used as model for FEM-calculations. In this context, the Representative Volume of Interest (REVOI) in particular plays a decisive role in order to be able to determine the global and not

only local characteristics. By combining Minkowski and structural parameters, the REVOI can be determined as a function of the cellular structure. 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.

T. Lube and M. Staudacher (both Montanuniversität Leoben/AT) together with U. Scheithauer and M. Reichel (both Fraunhofer IKTS), D Brouczek (Lithoz GmbH/AT) and H. Schmid (Gramm GmbH/DE) report on **Strength Testing of AM Ceramics**.

The strength of ceramic AM components may depend on the orientation in which tensile stresses act with respect to the build direction. This is due to various aspects of the manufacturing method, i.e. insufficient layer bonding, delaminations or AM method characteristic surface structures. For Digital Light Processing (DLP)-based photolithography, such structures may stem from overpolymerization but also from the voxel effect. In order to provide reliable material data for design of components, the strength characteristics have to be assessed routinely for various processing conditions and/or as means for quality control.

Such investigations are laborious and costly if standardized strength specimens and methods for ceramics are used. Thus, an innovative test body was presented which allows to manufacture a specimen set of sufficient size for statistical evaluation to be printed as one part by vat photopolymerization (VPP) using Lithography-Based Ceramic Manufacturing (LCM).

Moreover, this design also allows the evaluation of the influence of surface structures. Conditions for a successful test execution and stress evaluation were discussed. In order to assess the practical applicability of the method and its meaningfulness, a round-robin test has been carried out. Several participants provided test bodies manufactured in different orientations from the same material. Tests were conducted in one lab and compared to tests performed on an alternative test infrastructure. The results on strength, strength-build direction relationship and also practical aspects of the method were presented.