High-Performance Ceramics for Electrochemical Energy Technologies

Research and development at Forschungszentrum Jülich (Jülich Research Center) concentrates on three global challenges: Health, energy and environment, and information technology. Jülich is a member of the Helmholtz Association (HGF) of German Research Centers. The Institute of Energy and Climate Research (IEK) uses a holistic approach to scientifically and technologically accompany Germany's energy transition ("Energiewende"), evaluating its impact on the atmosphere and climate. The IEK was founded in 2010, consisting today of fourteen divisions. „Materials Synthesis and Processing" (IEK-1) focuses on an unique combination of materials science and the related processing technologies to manufacture structures, layers, multi-layered parts and components. The envisaged application fields are solid-state batteries, environmental-related membranes, solid oxide fuel and electrolyzer cells and materials for high-temperature applications. IEK-1 is headed by Prof. Olivier Guillon (see interview) and hosts nowadays more than 125 researchers, students, technicians and administrative supporting staff.

IEK-1 deals mostly with ceramic materials and metals prepared via powder technological routes. Besides the synthesis of powders and materials by diverse technologies (spray drying, solid-state reaction, sol-gel, etc.) relevant manufacturing techniques from the fields "ceramic processing", "physical thin-film" techniques and "thermal spraying" are available for all research areas. Typical layer and structure thicknesses range from nano-sized layers (applied by e.g. ALD-CVD or PVD) to thick-films in the sub-millimeter scale (e.g. by plasma spraying). R&D covers the materials, tailoring their chemistry and particle size/shape, the related transport media (e.g. pastes, slurries, targets…), shaping, drying and sintering, integration of functional layers into component fabrication on different size scales. Our activities cover besides the materials and the related manufacturing technologies also the influence of operation conditions on the microstructure (coarsening, inter-diffusion, formation of secondary phases) and intensive post-test analyses especially for mid- and long-term operated components.

Within the research areas ion-conductors play a crucial role. Solid-state batteries are based on e.g. Li- or Na-conducting separators. In fuel/electrolyzer cells oxygen ions or protons are transported through the gas-tight electrolyte and the electrons close the outer current path, thereby ensuring charge neutrality. However, mixed ionic-electronic conductors as electrodes of fuel and electrolysis cells are indispensable for the efficient operation of the system. Such materials are also required in ceramic membranes where either protons or oxygen ions, electrons, holes or more than one charge carrier are mobile.

Materials classes used are perovskites, spinels, fluorites, pyrochlores, apatites and modifications thereof like e.g. complex double perovskites, Ruddlesden-Popper phases, defective fluorites. Envisaged operation for batteries is at room temperature, while for the membranes and fuel/electrolyzer cells temperatures between 400 and 900 °C are required.

In the following paragraphs the three application fields „solid-state batteries", „membranes" and „solid oxide cells", all based on ion-conducting ceramics are presented more in detail.

Solid-state batteries

Lithium-ion batteries (LIBs) represent the most advanced electrochemical energy storage technology with energy and power densities superior to that of other rechargeable battery systems. Still, to satisfy the increasing demand in long range electromobility and high power portable electronics (smartphones, power tools, etc.), it is necessary to develop novel battery chemistries to further increase the energy and power density on cell level. Among the emerging concepts, solid state lithium and sodium batteries attract increasing attention. Among different inorganic ceramic solid electrolytes, oxide and phosphate-based lithium ionic conductors such as $Li_7La_3Zr_2O_{12}$ (LLZO) or $LiAl_xTi_{2-x}(PO_4)_3$ (LATP) and NASICON-type sodium ionic conductors show ionic conductivities in the range of 1 mS cm^{-1} at room temperature and a large electrochemical stability window. However, to fully utilize their potential, several challenges exist which are currently in the focus of international research. First, optimization and demonstration of large scale synthesis of solid ionic conductors is necessary to demonstrate their industrial relevance. Thereby, scalability needs to be shown while particle size, morphology and composition are simultaneously fine-tuned in order to meet price, quality, processing and performance targets for the desired application [1]. Second, processing of the obtained ceramic powders into components and cells needs to be demonstrated also using scalable techniques. Layers and coatings as well as their high temperature treatment are thus a crucial point of investigation. For example, tape casting is an established technique to produce multi-layered ceramic components using a roll-to-toll process, while the development of thin layer techniques such as physical vapor deposition (PVD) [2] or atomic layer deposition (ALD) to reduce the separator thickness will dramatically improve cell performance. Additionally, the interface resistance between solid electrolyte and active material needs to be reduced to obtain good performance at room temperature [3]. Third, the optimization of the full cell to meet the desired performance values (mainly energy and power density but also cycle life, fast charging, etc.) is necessary and requires adjustments on all levels, from materials over processes to cell designs and thus needs to be an integral part of the previous two areas of research.

Among the necessary solid state battery components, the fabrication of cathodes with high loading of active material and optimized morphology (with respect to ionic and electronic conductivity) is a crucial step in technology development to obtain high specific energy densities. Oxide- and phosphate-based ceramic electrolytes face a great challenge due to the necessity of high temperature processing, raising the issues of materials compatibility and formation of possibly low conductive interphases. The latter increases the total cell resistance, leading to low rate capability or the necessity of high operating temperatures. In view of using rigid ceramic materials in cathode fabrication and the rather high sintering temperatures required for processing, parameters like the thermal expansion coefficients (TEC) and chemical stability of the materials up to/nearby the sintering temperatures need to be taken into account.

As we previously demonstrated [4], most of the cathode materials react with solid electrolytes such as LLZO and LATP at temperatures much below their own decomposition temperature, with 600 °C been shown a threshold for thermodynamic stability for the majority of investigated material compositions. A promising solution to overcome thermodynamic limitations is a careful choice of the materials to adjust the temperature stability window, as well as the kinetic control of the reaction process. Among investigated cathode materials, lithium cobalt oxide (LCO) features the highest temperature stability of 900 °C or even at 1085 °C in combination with Ta-substituted LLZO [3]. From the processing point of view, another advantage are the matching coefficients of thermal expansion (CTE) of LCO and LLZO (1.3×10^{-5} K^{-1} and 1.5×10^{-5} K^{-1}, respectively) minimizing the risk of crack formation during sintering process. The sluggish reaction between LLZO and LCO at temperatures lower than 1085 °C and their similar CTEs thus provide a processing window for free sintering of these two materials and thus enable manufacturing of LCO/LLZO based solid-state batteries. We demonstrated that it is possible to minimize the reaction between LCO and LLZO : Ta by optimizing powder morphology and processing conditions, resulting in a well-functioning battery with a low areal resistance [5]. As mentioned above, the scale-up of cell area as well as reduction of separator thickness are necessary to improve the energy density of the cells and demonstrate industrial feasibility and competitiveness of this or similar cell concepts to state-of-the-art battery technologies [3].

However, when considering other active materials in order to improve the energy density further, e.g. low Co and high capacity NMC or high voltage spinel based materials, the low decomposition temperatures pose serious challenges for conventional ceramic processing technologies. Here, advanced sintering techniques have great potential to reduce sintering temperature and minimize sintering time. Field Assisted Sintering Technique / Spark Plasma Sintering (FAST/SPS) was demonstrated as an effective way to achieve low-temperature consolidation of LCO/LLZO mixtures. Densities similar or even higher than the ones achieved by free sintering were obtained with sintering times as low as 10 minutes [6], opening the pathway to rapid, low energy ceramic processing, pushing these types of inorganic ceramic solid state batteries closer to market relevance.

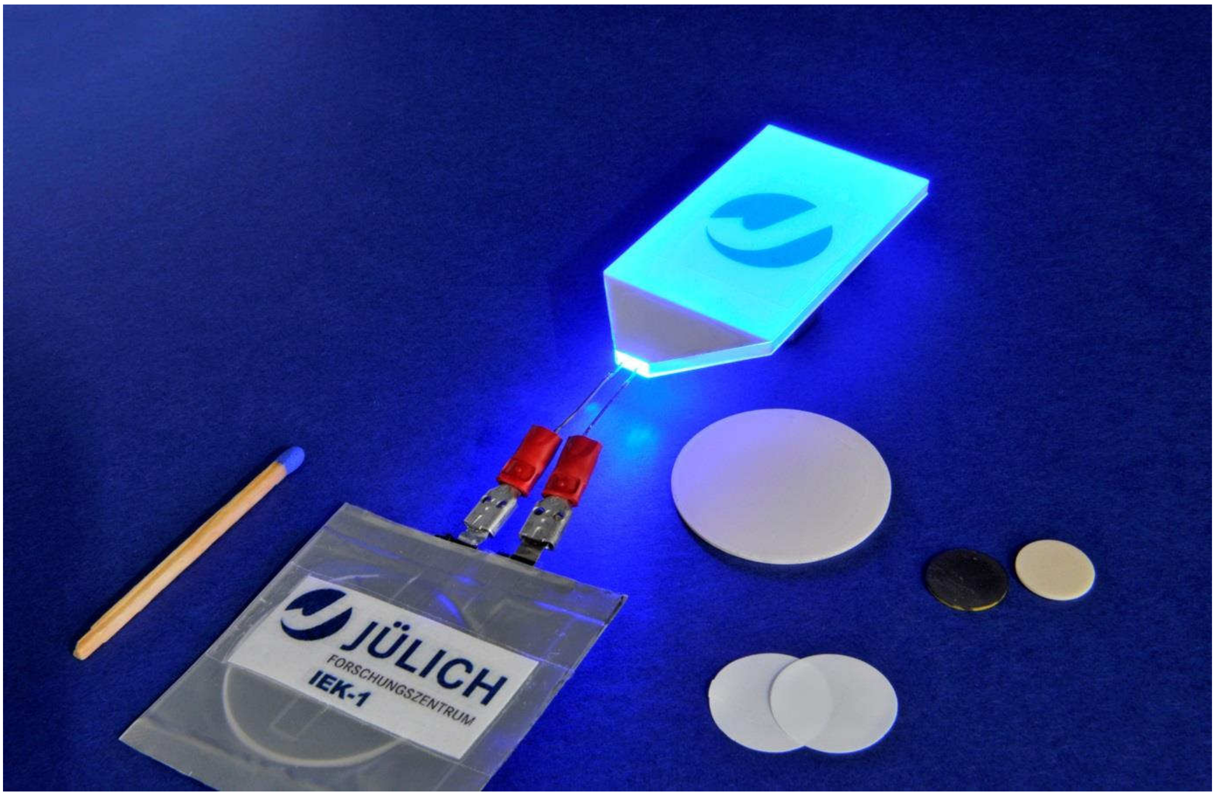

Figure 1: First Jülich's battery based on solid electrolyte

Membranes

Gas transport through dense ceramic membranes takes place via ion diffusion in the crystal lattice and simultaneous charge compensation through the electrical conductivity of these MIEC (mixed ionic-electronic conducting) materials. Therefore, membranes can be used to separate gases with infinitive selectivity from gas mixtures or to convert reactants into higher value products in a chemical reactor [7-9].

We develop at IEK-1 ion-conducting materials with desired conductivities and chemical-mechanical stability required during operation under harsh conditions. Two basic material options are available: single-phase ceramics and composites. Utilizing single-phase materials, a trade-off between performance and chemical stability must be accepted. For composites, the choice of materials and their ratios can be tailored to overcome this trade-off.

To realize the full potential of the membranes, the dense membrane layers are made thinner than 100 µm. As a result, a porous support is required for the mechanical rigidity, which affects the gas exchange as little as possible [10, 11]. The standard manufacturing technology we developed for those supported membranes is sequential tape casting. In this process, a ceramic slurry without pore former is cast for the membrane layer. After drying, a pore-forming agent containing slurry is cast on top of the membrane for the support (green-in-green). The pore former is burnt out during debinding and results in pores whose microstructure is consolidated during sintering. The use of pore formers, such as starch, cellulose, carbon black, as templates for the pores, leads to irregular pore networks. These pore structures include varying pore diameters, blind pores or non-tortuous pores, which have a negative effect on gas transport and thus for membrane performance [12]. A promising ceramic shaping technology capable of producing ideal microstructures with straight and uniform pores is ice templating.

The basic idea of ice templating is the solidification of a ceramic powder in a suspension by freezing a solvent. The growing solvent crystal repels the particles in the suspension and forms ceramic walls [13]. After freezing, the solvent is sublimated in order to retain the structure of ceramic walls. The formed pores are the resulting copy of the solvent crystal template. The green body is then sintered to solidify the microstructure, which is exemplarily shown in Figure 2.

Crystal growth and morphology of the solvent crystals can be controlled by the process parameters while freezing, additives in the suspension, solid particles used in the suspension, the viscosity or by the type of solvent itself. The porosity in such an ice templated ceramic is always determined by the ratio between solvent and ceramic in the suspension. The morphology of the solvent crystals is mainly controlled by the solvent itself leading to unique structures. Nevertheless the temperature gradient along the freezing direction offers a further degree of freedom to tailor size and direction of the growing crystals. Additives, such as dispersants prevent from particle sedimentation and in turn ensure a homogenous pore morphology across the full green body height. However, additives influence the phase diagram of the solvent, the viscosity, the inter-particle forces, the solid/liquid and particle/liquid interfacial energies as well as the degree of under-cooling ahead of the liquid front.

By enhancing gas exchange by ice templated supports, either significant increase in membrane performance can be achieved, or membranes from chemically more stable base materials without any loss in performance can be manufactured. The ice templating technology can be transferred to a variety of applications where a particularly high gas exchange rate (e.g. SOFC, SOEC) or good infiltration capability with a second phase (e.g. battery) is required.

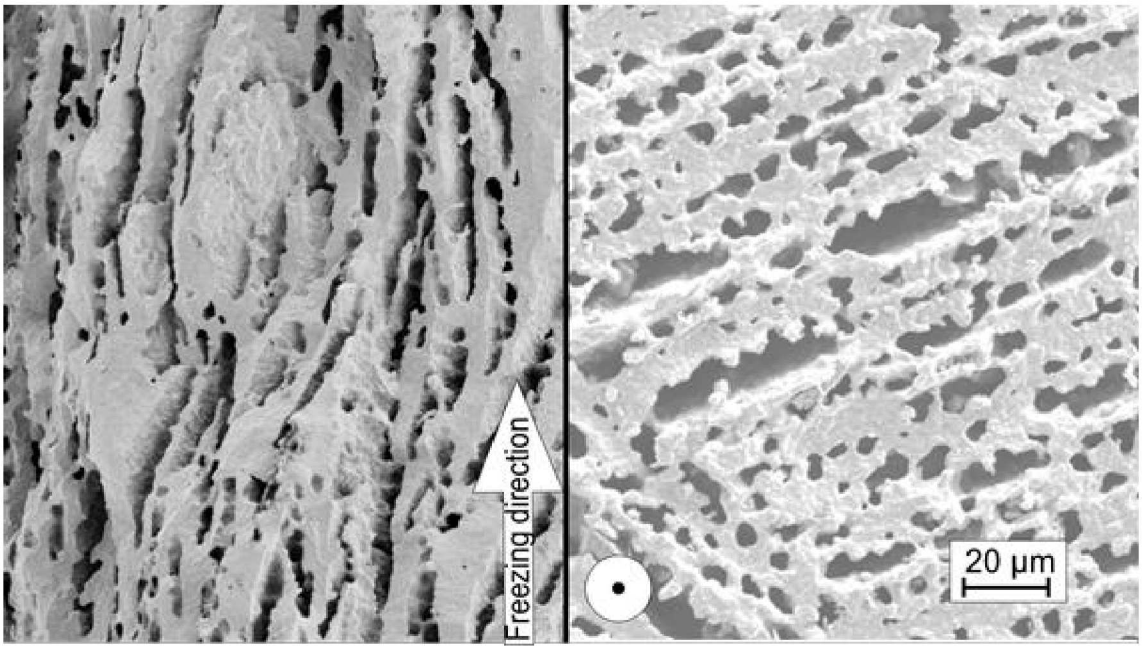

Figure 2: SEM images of ice templated and sintered ceramic for membrane support application: fractured cross section (left) and top view (right).

Solid oxide cells

Solid oxide cells (SOCs) are electrochemical energy conversion devices operating in the temperature ranges of 400 °C to 600 °C (Intermediate Temperature Solid Oxide Cells (IT-SOCs)) and 600 °C to 800 °C (High Temperature Solid Oxide Cells (HT-SOCs)), which convert chemical fuels to electricity (fuel cell mode) or generate hydrogen from water under surplus energy consumption (electrolysis mode). Such electrochemical devices are excellent systems for the generation of electricity due to their fuel flexibility (H_2, $C_x H_y$), and are a key element of electrical energy storage systems based on power-to-gas technology, laying the foundation for a H_2 based economy of the future.

The global effort for reaching highly efficient CO_2-neutral energy supply requires innovative technological solutions based on high performance materials [14]. Proton- and oxygen ion-conducting ceramics are both viable choices for achieving the IT-SOC target performance at decreased operation temperature, while exhibiting reasonable stability and durability under steam conditions. Proton conducting fuel cells (PCFCs) are based on proton-conducting ceramic materials, which structurally incorporate protons from moisture and/or H_2 containing atmosphere and transport them from the fuel to the air side of the fuel cell. Hence, proton conductors perform particularly well at lower temperatures, while at increased temperatures dehydration takes place and their conductivity diminishes. Our research focuses on the scale-up of fuel-electrode supported cells and their integration with high-performance air electrodes to achieve reasonable cell performance [15].

IT-SOCs based on oxygen ion conductors require microstructural adaptation compared to their high-temperature counterparts, since LT-operation necessitates an adapted balance of electrochemical activity and stability. We focus on the development of thin, highly conductive electrolytes and high-performance electrodes to offset the decreasing performance at low temperature [16 - 18]. Furthermore, we investigate the integration of IT-SOCs into the Jülich stacks and the resulting additional losses, as well as degradation mechanisms at low operation temperature.

Our R&D activities aim at systematic research and development of SOC in order to increase the readiness of this technology for the market. For that, we focus on improving the overall performance, long-term stability, durability and scalability of these electrochemical devices. As the SOC is a multi-layered ceramic system, we develop ceramic materials with tailored properties required for their specific function in the cell (solid electrolyte, cathode, anode, interconnect, contact and protective coating), and combine these materials into cell components with high compatibility and designed interfaces. Finally, we fabricate cells with tailored microstructure and scalable geometries by means of leading processing technologies [19]. Two of the core processing techniques used for micrometer scale layer formation in the field of SOCs are screen printing and tape casting, both comprising the preparation of a ceramic paste (for the screen printing process) or a ceramic slurry (for the tape casting process) with the aid of organic additives and their application onto a suitable supporting layer through a sieving screen or on the rolling bench of a specially designed equipment. As an example, Figure 3 highlights the tailored microstructure of a high-performance so-called anode-supported solid oxide cell (the anode in fuel cell operation is the mechanical bearing part of the whole cell).

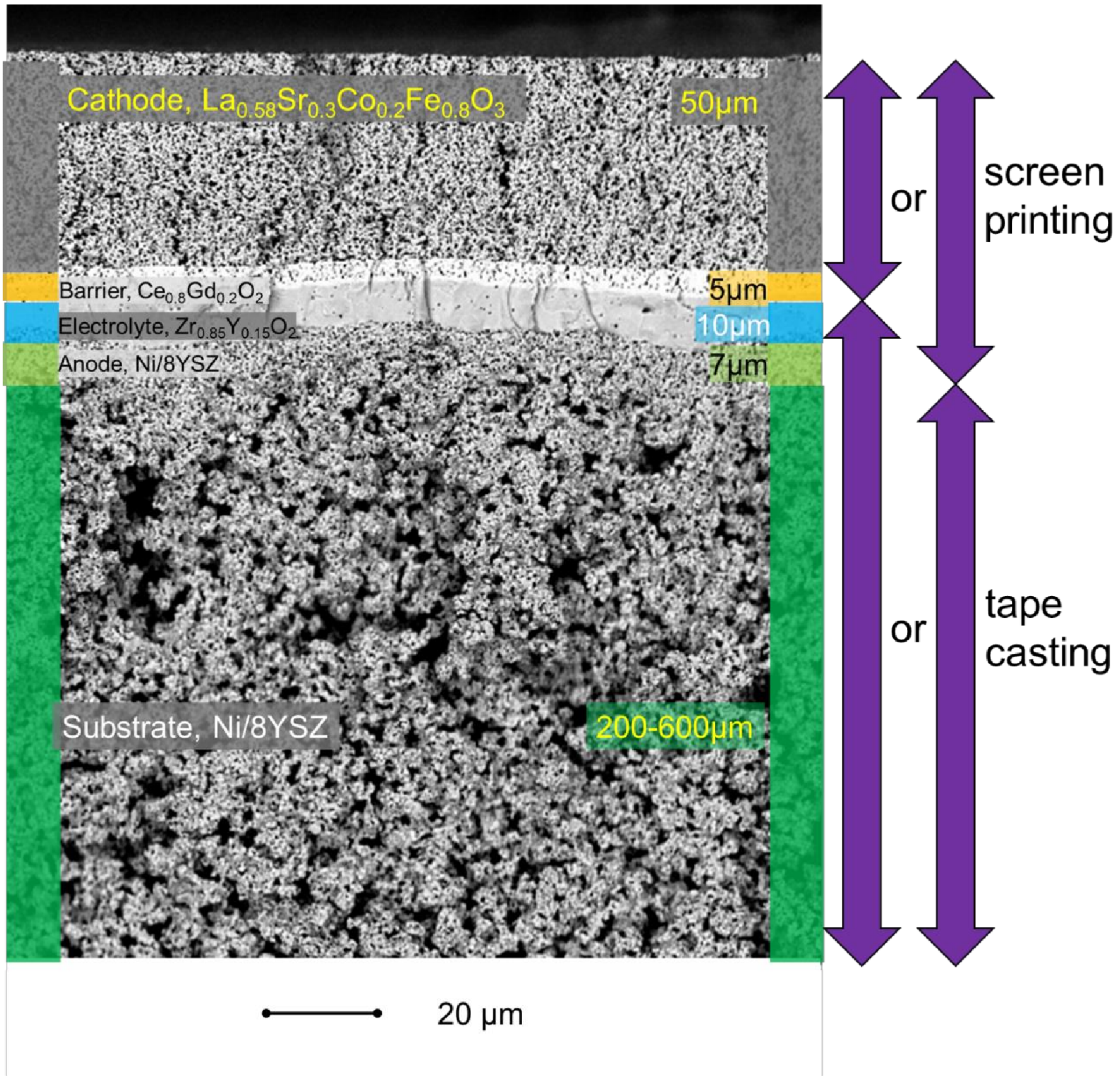

Figure 3: Cross section of an anode-supported SOC with state-of-the-art materials, layer thicknesses and manufacturing technologies applied

Conclusion

The Institute of Energy and Climate Research, Materials Synthesis and Processing (IEK-1) at Forschungszentrum Jülich GmbH offers a unique combination of expertise and infrastructure for materials development and the related processing technologies to manufacture layers and layered components for energy-related applications. Ceramics and to some extent metal powders play in areas like solid state batteries, membranes, solid oxide cells and high-temperature applications a crucial role for reaching Germany's future energy goals. The core funding by the Helmholtz Association (Federal Ministry of Education and Research, BMBF and local state of North-Rhine Westphalia) and the additional third party projects (industry, BMBF, BMWi, EU, DFG and other funding agencies) help us to maintain long-term theoretical and practical know how and to solve current problems of our partners. Close link to universities is secured by professorships at RWTH Aachen University, Ruhr-University Bochum, University Twente (NLD), University of Duisburg-Essen and others. In that way, knowledge can be both transferred to industry and to the next generation of ceramicists.

References

[1] Q. Ma, M. Guin, S. Naquash, C.L. Tsai, F. Tietz, O. Guillon; "Scandium-substituted $Na_3Zr_2(SiO_4)_2(PO_4)$ prepared by a solution-assisted solid-state reaction method as sodium-ion conductors". Chemistry of Materials 28/13 (2016), 4821-4828

[2] S. Lobe, C. Dellen, M. Finsterbusch, H.G. Gehrke, D. Sebold, C.L. Tsai, S. Uhlenbruck, O. Guillon; "Radio frequency magnetron sputtering of $Li_7La_3Zr_2O_{12}$ thin films for solid-state batteries". Journal of Power Sources 307 (2016), 684-689.

[3] M. Finsterbusch, T. Danner, C.-L. Tsai, S. Uhlenbruck, A. Latz, O. Guillon; "High capacity garnet-based all-solid-state lithium batteries: Fabrication and 3D-microstructure resolved modeling". ACS Applied Materials Interfaces 10/26 (2018), 22329-22339

[4] L. Miara, A. Windmüller, C.L. Tsai, W.D. Richards, Q. Ma, S. Uhlenbruck, O. Guillon, G. Ceder; "About the compatibility between high voltage spinel cathode materials and solid oxide electrolytes as a function of temperature". ACS Applied Materials Interfaces 8/40 (2016), 26842-26850

[5] C.L. Tsai, Q. Ma, C. Dellen, S. Lobe, F. Vondahlen, A. Windmüller, D. Grüner, H. Zheng, S. Uhlenbruck, M. Finsterbusch, F. Tietz, D. Fattakhova-Rohlfing, H.P. Buchkremer, O. Guillon; "A garnet structure-based all-solid-state Li battery without interface modifications: Resolving incompatibility issues on positive electrodes". Sustainable Energy & Fuels 3 (2019), 280-291

[6] A.M. Laptev, H. Zheng, M. Bram, M. Finsterbusch; O. Guillon; "High-pressure field assisted sintering of half-cell for all-solid-state battery". Materials Letters 247 (2019); 155-158

[7] J. Garcia-Fayos, J. M. Serra, M. W. J. Luiten-Olieman, W. A. Meulenberg; "Gas separation ceramic membranes" in O. Guillon (Ed.): Advanced Ceramics for Energy Conversion and Storage. Elsevier, Amsterdam, The Netherlands, ISBN 978-0-08-102726-4 (2019), 321-386

[8] W. Deibert, M.E. Ivanova, S. Baumann, O. Guillon, W.A. Meulenberg; "Ion-conducting ceramic membrane reactors for high-temperature applications". Journal of Membrane Science 543 (2017), 79-97

[9] W. A. Meulenberg, F.Schulze Küppers, W. Deibert, T. Van Gestel, Stefan Baumann; „Keramische Membranen – Materialien - Bauteile - potentielle Anwendungen“. *Chemie, Ingenieur, Technik* 91 (8) (2019), 1091-1100

[10] S. Baumann, W.A. Meulenberg, H.P. Buchkremer; “Manufacturing strategies for asymmetric ceramic membranes for efficient separation of oxygen from air”. Journal of the European Ceramic Society 33, (2013), 1251-1261

[11] N. H. Menzler, F. Han, T. van Gestel, W. Schafbauer, F. Schulze-Küppers, S. Baumann, S. Uhlenbruck, W. A. Meulenberg, L. Blum, H. P. Buchkremer; “Application of thin-film manufacturing technologies to solid oxide fuel cells and gas separation membranes”. International Journal of Applied Ceramic Technology 10 [3], (2013), 421-427

[12] F. Schulze-Küppers, F. Drago, L. Ferravante, S. Herzog, S. Baumann, P. Pinacci, W. A. Meulenberg ; “Design and fabrication of large-sized planar oxygen transport membrane components for direct integration in oxy-combustion processes”. *Separation and Purification Technologies* 220 (2019), 89-101

[13] E. Munch, E. Saiz, A. P. Tomsia, S. Deville; “Architectural control of freeze-cast ceramics through additives and templating”. Journal of the American Ceramic Society 92 [7] (2009), 1534-1539

[14] N.H. Menzler, F. Tietz, S. Uhlenbruck, H.P. Buchkremer, D. Stöver; “Materials and manufacturing technologies for solid oxide fuel cells”. Journal of Materials Science 45 (2010), 3109-3135

[15] C. Lenser, D. Udomsilp, N.H. Menzler, P. Holtappels, T. Fujisaki, K. Leonard, H. Matsumoto, A.G. Sabato, F. Smeacetto, A. Chrysanthou, S. Molin; “Solid oxide fuel and electrolysis cells”. in O. Guillon (Ed.): Advanced Ceramics for Energy Conversion and Storage. Elsevier, Amsterdam, The Netherlands, ISBN 978-0-08-102726-4 (2019), 387-547

[16] J. Zhang, C. Lenser, N.H. Menzler, O. Guillon; “ Comparison of solid oxide fuel cell (SOFC) electrolyte materials for operation at 500°C”. Solid State Ionics 344 (2020), 115138

[17] F. Han, R. Mücke, T. van Gestel, A. Leonide, N.H. Menzler, H.P. Buchkremer, D. Stöver; “Novel high-performance solid oxide fuel cells with bulk ionic conductance dominated thin-film electrolytes”. Journal of Power Sources 218 (2012), 157-162

[18] C. Lenser, N.H. Menzler; “Impedance characterization of supported oxygen ion conducting electrolytes”. Solid State Ionics 334 (2019), 70-81

[19] N.H. Menzler, J. Malzbender, P. Schoderböck, R. Kauert, H.P. Buchkremer; “Sequential tape casting of anode-supported solid oxide fuel cells”. Fuel Cells 14 No. 1 (2014), 96-106

N.H. Menzler, D. Fattakhova, W.A. Meulenberg

Forschungszentrum Jülich GmbH

Institut für Energie- und Klimaforschung

IEK-1: Werkstoffsynthese und Herstellungsverfahren

52425 Jülich