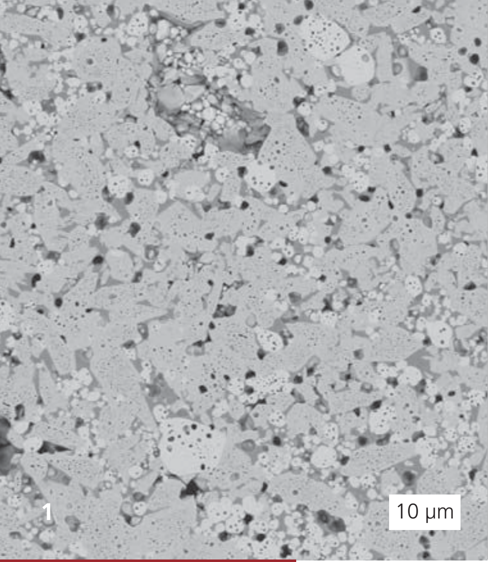

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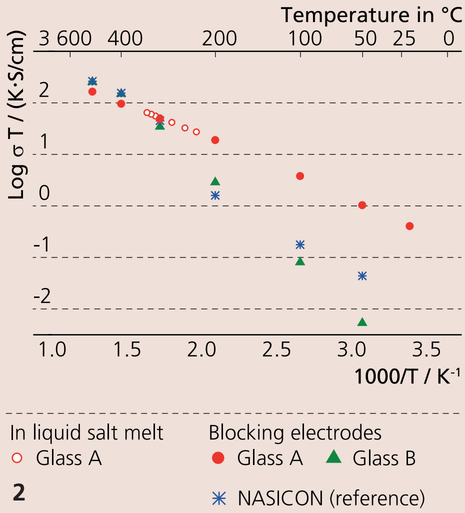

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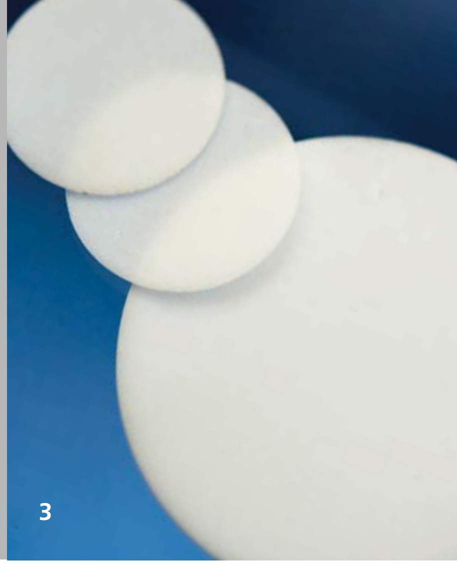

3

ENERGY

SOLID ELECTROLYTES FOR SODIUM-BASED BATTERIES

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Sodium-based batteries are especially suitable for stationary energy storage applications because all required raw materials are available cost-efficiently and cell concepts show high storage densities. While high-temperature batteries exist in an advanced stage of development, the low-temperature sodium-sulfur battery concepts are only available in the laboratory scale on an experimental level. With progressing development, it has turned out that in all known types of these battery concepts ceramic sodium-conducting separators can fulfill decisive functions in order to enable their operation in principle or to avoid degradation processes. Besides their function as separators, they also operate as solid-state electrolytes and, thus, have a major effect on the power density and the intrinsic safety of such batteries. Fraunhofer IKTS develops and characterizes materials and process technologies for ceramic components in sodium-based batteries.

Low-temperature Na/S battery concepts

In conjunction with liquid electrolytes, low-temperature sodium-sulfur battery concepts have been the subject of research activities for several years, as operation temperatures below 100 °C down to room temperature can be possible. The migration of dissolved sodium-polysulfides through porous polymer separator foils leading to an irreversible degradation represents, therefore, one major drawback of this cell concepts. This process can be prevented by the application of dense sodium-conducting separators with a solid-state electrolytic functionality. While Na-β-aluminate ceramics meet these requirements in the field of the high-temperature batteries, different prerequisites for the electrolytic materials result from lower operation temperatures. Here, it is necessary to realize hermetically dense and thin membranes with a high ionic conductivity and a good stability in liquid battery electrolytes. Promising materials are crystallizing glasses, which can be processed as powders at temperatures below 1000 °C. Suitable technologies include tape casting for producing monolithic planar substrates and screen printing for realizing conductive layers. In the basic system Na_2O-RE_2O_3-SiO_2 (RE = rare earth oxides), numerous different compositions can be molten as glasses and processed as powders for glass ceramics by using additives. Sintering and crystallization for the formation of the crystalline microstructure and the conductive phases can be performed below 1000 °C (Figure 1). Resulting conductivities of the glass ceramics are in the range of values known from literature for Na-β-aluminate and NASICON (Figure 2). Ionic conductivities up to 0.25 mS/cm at room temperature have been measured. Planar glass-ceramic substrates with ionic conductivity and thickness of 160 µm were produced by means of tape casting (Figure 3). Measurements of these substrates in low-temperature sodium-sulfur test cells in combination with liquid electrolytes yielded results comparable to NASICON- and Na-β-aluminate substrates. Possible applications for such separators and solid-state electrolytes are new concepts of low-temperature sodium-sulfur batteries.

Na-β-alumina for high-temperature batteries

Na-β-alumina ceramics are used for solid electrolytes in $Na/NiCl_2$ and Na/S high-temperature batteries. At operation temperatures of about 300 °C, ceramics provide an excellent sodium-ion conductivity. Furthermore, a good stability in the highly corrosive cell environment (molten sodium, sulfur and $NaAlCl_4$) is given. Generally, Na-β-alumina as well as the battery cells are made of cost-efficient and available raw materials, which are re-evaluated at IKTS by means of new approaches regarding a cost-efficient technology.

Materials development

In a raw materials screening, Na-β-alumina powder was synthesized in the lab scale. Aiming at optimized physical and electrochemical material properties, approaches were systematically varied. The powder synthesis resulted in a Na-β-alumina

with a desired β"-phase content of approximately 100 %. Sodium-stable high-temperature kiln furniture is used for sintering specimens (cups, sticks, discs – Figure 4) applied in electrochemical tests. Important material properties, such as density, phase and the sodium-ion conductivity were determined according to laboratory samples and, thus, an optimized raw material and treatment technology was developed. The sodium-ion conductivity of ceramic sample rods were measured by impedance spectroscopy in customized high-temperature test cells. The measured conductivities amounted to 0.24 S/cm at 300 °C and rank in the top range regarding the international comparison. Densities of about 98 % of the theoretical value and mechanical strength of about 200 MPa were reached. Final result of the lab-scale development is a process line for the production of Na-β"-alumina solid electrolytes from the raw material to the ready component.

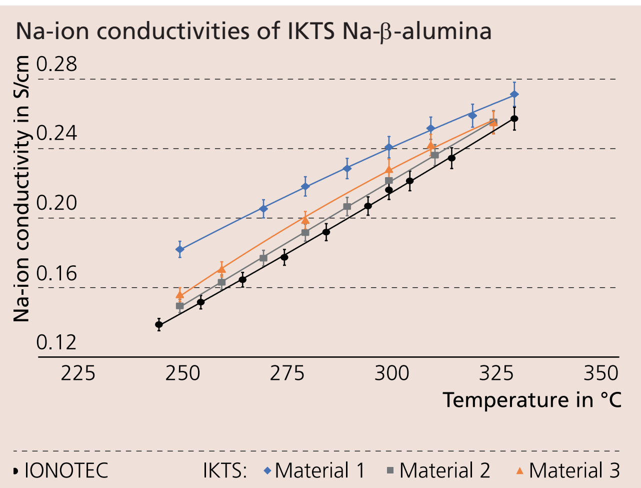
The R&D results were transferred from the lab scale to the pilot scale. Batches of 20 kg powder and granules were processed by using a scalable machinery. Based on the established power production, electrolyte tubes with a length of up to 300 mm and a diameter of 33 mm were manufactured by pressing (Figure 4). Using a laboratory extruder, a screening of different organic plasticizers and binders was carried out. After several optimization steps, electrolyte tubes with a diameter of 10 mm are currently extruded, resulting in densities about 95 % after the sintering.

Development of cells

At IKTS, several specific high-temperature test cells are available for the electrochemical characterization of the Na-β-alumina and the $Na/NiCl_2$ cathode materials (Figure 5). Starting with conductivity measurements on rod-shaped and cup-like samples up to full cell measurements in 5 Ah $Na/NiCl_2$ lab cells (Figure 6), in-house developments were constructed and tested. Currently, the gained experiences are transferred to a 40 Ah test cell. In CAD/FEM supported design studies, a cost-efficient, industrialized cell design including the sheet metal parts and the cell lid components was developed. The constructive realization of the first prototype is being prepared.

Services offered

- Materials development and manufacture of Na-β-alumina powders, granules and electrolytes
- Development of $Na/NiCl_2$ cathode materials and characterization
- Materials development of conductive glass ceramics
- Shaping and sintering methods for solid electrolyte components (pressing, tape casting, extrusion)
- Material-scientific and electrochemical characterization of materials and components
- Cell tests (cyclization, degradation)



1 Structure image of glass ceramics with a conductivity of 0.24 Scm^{-1} at room temperature.
2 Comparison of temperature-dependent conductivities of glass ceramics and NASICON.
3 Sintered glass-ceramic tapes.
4 Na-β-alumina electrolyte samples.
5 Granuled $Na/NiCl_2$ cathode material.
6 3D CAD of a 5 Ah $Na/NiCl_2$ test cell.

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