

Paving the Way for All-Solid-State Batteries: Ceramic Materials, Components and Cells for Electrochemical Storage

Energy storage is an essential element of the energy transition. Besides Li-ion, all-solid state lithium and sodium batteries attract a lot of attention due to their expected better performance. These electrochemical storage technologies rely on ceramic materials as active electrode materials, separator and electrolyte, that need to be processed and integrated into full cells.

1 Introduction

The global transition to a sustainable energy supply implies a broad diffusion of power generation technologies based on renewable energy, in large part provided by the sun and wind. However, the electricity produced by wind turbines and photovoltaic panels for example is intermittent in nature and most of the time does not correspond to the instantaneous energy demand.

Large-scale storage solutions are therefore required as buffer or for grid stabilisation. For these stationary applications, reversible (or secondary) batteries with long life-time and high efficiency are very attractive electrochemical storage devices. For a deep decarbonisation of the transport sector and the development of electromobility, batteries with both high capacity and safety are also required [1].

The most advanced and widespread rechargeable battery technology is based on the lithium ion, which travels from one electrode to the other through a liquid electrolyte. The development of this technology has been recently recognised by the Nobel prize in chemistry. Beyond lithium, there are other emerging chemistries, like sodium, working over a wide range of

Keywords

lithium, sodium, cathode active material, electrolyte, solid-state batteries

temperature. The replacement of toxic, organic liquid electrolytes of limited electrochemical and thermal stability by solid electrolytes is an important step towards higher safety and possibly higher energies if new electrode materials can be enabled. Especially on the anode side, metallic lithium or sodium have very high capacities but for the moment cannot be implemented because of instability.

Besides polymers and sulphides, oxide electrolytes are a promising class of solid electrolytes. Li-ion compounds comprise amorphous lithium phosphorous oxynitride (LiPON) and bulk polycrystalline materials as phosphates ($\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$) and garnet-type oxide ($\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$) with room-temperature ionic conductivities of about 1 mS/cm.

Their processability and properties can be further tuned by elemental substitution and optimised synthesis. Typical solid electrolytes for sodium ions are beta-alumina and the Na-superionic conductors NASICON ($\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ and derived compositions) [2]. $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (respectively $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$) are stable against Li- (respectively Na-) metal and thus attractive materials for separators enabling metal anodes. In all cases, advanced processing of ceramic powders plays a key role and requires fundamental know-how with respect to powder synthesis, powder

handling, powder characterisation, shaping technologies and sintering. In this context, the Institute of Energy and Climate Research: Materials Synthesis and Processing (IEK-1) of Forschungszentrum Jülich provides a broad portfolio of material synthesis and processing technologies for envisaged applications in the field of all-solid-state batteries, as detailed in this article.

2 Powder synthesis for solid electrolytes

Different methods are available, e.g. solid state reaction, Pechini or citrate complexation method, precipitation, solution assisted-solid state reaction, spray pyrolysis or spray drying followed by calcination. Most of them are scalable towards industrial production. Whereas the solid state reaction is the simplest method to

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Fig. 1
Photograph of a newly developed, high temperature fluidized bed coater for spray pyrolysis and coating of Li-containing compounds on battery materials

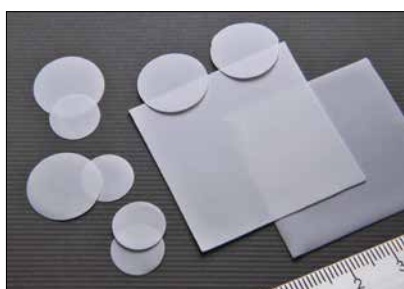


Fig. 2
Sintered $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ti}_{1.5}(\text{PO}_4)_3$ tapes

obtain a ceramic powder, it sometimes requires several calcination steps and thorough grinding to improve the homogeneity of the product. Nevertheless, for $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) solid-state reaction is an economic way to produce highly conductive ceramics materials in the mS/cm

range [3]. The substitution type and concentration can be easily modified, the oxidic-precursors are cheap and milling technology well established.

In the case of solution-based methods the homogenisation takes place in the solvent on the atomic level. For specific cations the methods were optimised to avoid segregation of elements during the drying stage, like the Pechini methods for earth alkaline elements [4].

A more simplified version of this method, the solution assisted-solid state reaction, has been developed at IEK-1 as a compromise between easy handling, less additional chemicals and less rigorous homogenisation.

With this method the solid electrolytes $\text{Na}_{3+x}\text{Sc}_x\text{Zr}_{2-x}(\text{SiO}_4)_2(\text{PO}_4)$ [5] and $\text{Na}_{1+x}\text{Zr}_2(\text{SiO}_4)_x(\text{PO}_4)_{3-x}$ [6, 7] for instance

were successfully synthesized resulting in ceramics with high ionic conductivities up to 5 mS/cm.

3 Development of cathode materials

For high energy density, cathodes require the capability to incorporate as many mobile ions (Li^+/Na^+ for lithium/sodium batteries) as possible along with a high chemical potential difference to the anode. Details of the composition and processing of cathode materials can have a large impact on the electrochemical performance. At IEK-1, sophisticated analysis techniques like Rietveld analysis of combined neutron and X-ray diffraction data as well as nuclear reaction analysis are applied to gain insight into the reaction mechanisms and allow large improvements in performance even at low doping levels [8].

However, not a single cathode or anode active material decides on the success of the battery, but the interplay with the electrolyte. Coatings are deposited in the event of a detrimental reaction between them. Besides the pure coating material, the processing plays again an important role for optimum electrochemical behaviour.

Low heat impact coating technologies are a current focal point of research, firstly in conjunction with liquid electrolyte [9], and with the potential to be expanded to solid-state batteries. Fluidized bed chemical reactors are used for particle synthesis and coating at a large scale (Fig. 1) as found in the industry.

4 Processing of solid-state batteries

4.1 Tape casting

For $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ti}_{1.5}(\text{PO}_4)_3$ (LTP), free-standing electrolyte sheets with a thickness of 50–150 μm were prepared by tape casting followed by sintering at 850–1000 $^\circ\text{C}$ in air (Fig. 2). Maximum relative density of 95 % was obtained at 920 $^\circ\text{C}$. At higher sintering temperatures, the microstructure changed with large grains (>10 μm), accompanied by a decrease in relative density due to the increasing appearance of microcracks.

The sintering behaviour was improved by adding 1,5 % of amorphous silica to the slurry. In this way, almost full densification (99,8 %) and an ionic conductivity of 0,2 mS/cm was achieved [10]. Densification and reduction of grain size improve the mechanical properties of the free-standing LTP tapes.

For LLZO, similar approaches require a more careful control of the ceramic powder pre-processing and an optimised casting route. For the first time, the intricate interplay of Li⁺/proton exchange during processing in air and in various solvents was elucidated and an optimised tape casting route was designed that enabled similar casting results compared to the more stable LATP [11]. Even more, the fundamental knowledge gained regarding the interactions with water enabled the water-based processing of LLZO using environment-friendly binders and additives, pushing the already fluorine free electrolyte further towards a “green” battery application [12].

4.2 Screen printing

Fully inorganic all-solid-state cells only comprising LLZO as electrolyte, LiCoO₂ as cathode active material and Li-metal as anode were demonstrated using screen printed composite cathodes, reaching application relevant capacities for the first time (Fig. 3 A–B) [13]. Screen-printing of thixotropic pastes is therefore adapted to the fabrication of battery components with a defined geometry based on thick pastes.

4.3 Sintering

Advanced techniques like Field-Assisted Sintering/Spark Plasma Sintering (FAST/ SPS), flash sintering, cold sintering or Ultrafast High-Temperature Sintering (UHS) are currently investigated to improve the performance of such cells and enable new materials combinations, boosting the density and the stability of the composite cathode (Fig. 3 C) [14]. A more detailed overview of the sintering technologies available at IEK-1 is given in [15].

4.4 Chemical infiltration

The infiltration of an active material into the scaffold of a solid electrolyte is a new method for electrode manufacturing of batteries, but it is long known for other electrochemical devices [16]. For solid-state batteries it is a very versatile method for integrating even temperature-sensitive electrode materials. Chemical infiltration is the combination of infiltration of a liquid and an in situ synthesis of the electrode material applying a heat treatment at which the active material is formed without significant interaction on the pore walls of the solid electrolyte. In this way, the interceramic contact problems are solved and has been demonstrated with model cells using Na₃V₂(PO₄)₃ (NVP) as cathode active material, Na_{3.4}Zr₂(SiO₄)_{2.4}(PO₄)_{0.6} (NZSP) as solid electrolyte and Na metal as the negative electrode material [17].

An optimised interface between NVP nanolayer and NZSP backbone was formed, providing effective ion transfer and minimising the stress caused by volume change of electrode active material during charging and discharging processes. The button cell delivered a highly stable battery performance at 25 °C.

4.5 Aerosol deposition

Aerosol Deposition (AD) is a spray process [18] using a gas carrier to generate an aerosol, which is ejected through a nozzle at low pressure to produce dense and nanocrystal-

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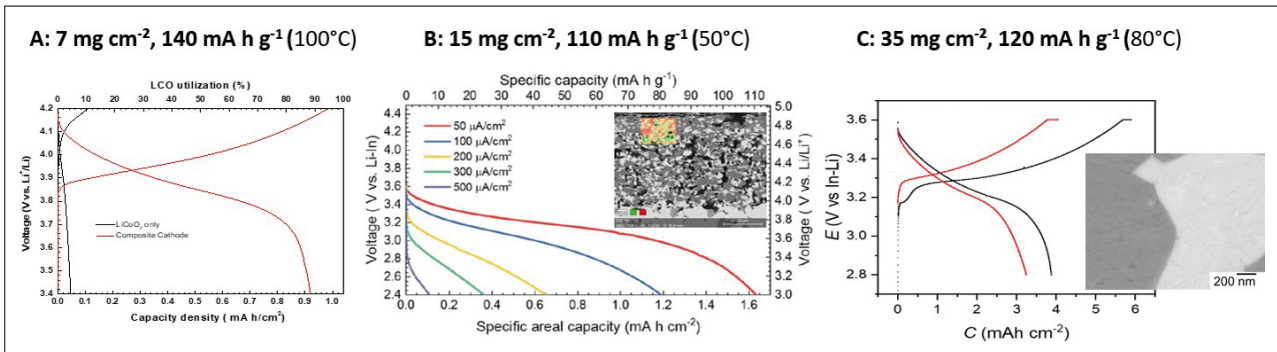


Fig. 3 A–C
Optimisation of the areal loading of cathode active materials [$\text{mg}\cdot\text{cm}^{-2}$], specific capacity [$\text{mA}\cdot\text{h}\cdot\text{g}^{-1}$], operating temperature and morphology of all-solid state cells with LCO-LLZO mixed cathodes sintered via conventional sintering (A, B) and FAST/SPS sintering (C)

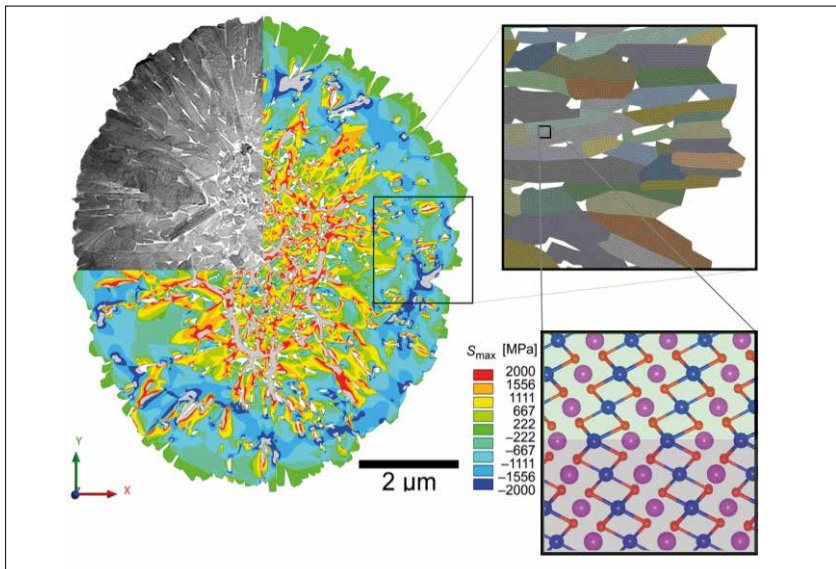


Fig. 4
Multiscale modelling of a Ni-rich cathode microstructure [27]

line ceramic films at room temperature directly from suitably sized powder particles (200 nm–2 µm) on various substrate materials. Large amounts of heat can be

produced upon impact, so that local temperature can increase by several hundred degrees Celsius. Nevertheless, a critical velocity range for successful AD must be

defined for each pair of materials (projected particles and substrate). Demonstrated at IEK-1 for fully dense zirconia layers [19], we are adapting the process to deposit dense electrolyte on free-standing composite cathodes as well as full cells as demonstrated recently [20].

4.6 Thin-film technologies

The key advantage of thin-film technology are dense layers with controlled composition and thickness that can be processed at lower temperature compared to conventional heat treatment for ceramics. While contamination of interfaces can be avoided to a large extent, well-defined multilayer set-ups can be analysed particularly with regard to interdiffusion or parasitic reactions [21, 22].

5 Contributions of multiscale simulations

Electronic, atomic, and microstructure of electrode and electrolyte materials can be tailored, for example, by doping or substitution and processing parameters



Fig. 5
Demonstration of an all-solid-state pouch cell with a sintered LLZO separator (l.), a composite LCO + LLZO cathode and a metal Li-anode operating at room temperature

to improve stability, capacity, and/or rate capability of all-solid-state batteries. Modeling and simulation can help finding the link between designing parameters and overall performance of energy storage devices. The authors used the Density Functional Theory (DFT) calculation to compute the effect of various dopants and/or substitutions on transition metal-oxygen bonds, band gap, mechanism of redox reactions, and phase transition in Ni-based Li-ion cathode materials [23–26].

Ab initio thermodynamics and Finite Element Methods (FEM) have been applied to study the effect of doping on the morphology and stress formation in the microstructures of cathode materials [26, 27, 28].

DFT calculation has also been used to investigate cation interchange and compatibility between solid electrolytes and electrodes [29]. In addition, by modeling the 3D-microstructures of LLZO/LCO composite cathodes followed by FEM analysis of the arising stresses during charge/discharge, we showed how the cell designing parameters can improve mechanical stability and thereby the performance of all-solid-state batteries [30].

6 Conclusion

The Institute of Energy and Climate Research (IEK-1: Materials Synthesis and Processing) of Forschungszentrum Jülich is one of the leading centres in the development of oxide/phosphate-based solid state batteries including the large scale synthesis of Li- and Na-solid ion conductors, the processing of ceramic battery components and full cells via a broad range of ceramic and thin layer deposition techniques.

This expertise is evidenced by the ability to fabricate working all-solid-state cells based on the ceramic LLZO electrolyte and Li metal anodes (Fig. 5) as well as NASICON-based all-solid state Na cells with high dendrite tolerance [31], whose performance is continuously improving via the understanding of key processes in solid electrolytes and solid interfaces as well as the development of advanced processing and sintering techniques.

As energy storage is one of the big challenges of this century, so is the necessary push towards a green and circular economy, especially in the field of batteries.

Investigating the environmental impact of new materials as well as processing and cell design of advanced Li- and Na-batteries need to be done in parallel to the performance optimisation. The authors thus already engage in life-cycle analysis and developing recycling strategies in addition to their core research activities [32, 33].

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