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Abstract Book

The 4th World Conference on
Solid Electrolytes for Advanced Applications:
Garnets and Competitors

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Host:

Prof. Daniel Rettenwander

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Invited Abstract

Multiscale Simulations of Interface Effects on Chemistry, Mechanics, and Transport within Garnet Solid Electrolytes

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When incorporated into real components and solid-state cells, garnet $Li_{7-x}La_3Zr_2O_{12}$ (LLZO) solid electrolytes and cathode-electrolyte composites introduce a variety of complex homogeneous and heterogeneous solid interfaces, including grain boundaries, phase boundaries, and interphase regions. These interfaces introduce structural disorder, strain, and compositional variations that can affect transport, mechanical response, and chemical reactivity. Moreover, many of these interfaces evolve during processing or operation, introducing additional sensitivity that can be difficult to probe. To better understand the underlying physics, we have been developing multiscale simulation frameworks based on ab initio molecular dynamics, machine learning-derived force fields, microstructure-aware continuum fields, and phase-field models. These frameworks have been applied to both grain boundaries within LLZO and interfaces between LLZO and model cathodes. We will present results of these studies, highlighting the role of interfacial structural and chemical disorder on the desired transport of Li through and across interfaces, as well as on the undesired transport of other cationic species that can lead to chemical changes and degradation. We will also show how our simulations can predict the mechanical response of LLZO during cycling, highlighting the significant effects of interfaces on stress distributions that would otherwise be neglected in simplified and homogenized models. Finally, we will show how cycling of a solid-state battery cathode can impact the chemo mechanical response of the electrolyte in a dynamical fashion, leading to continuous evolution of stress distributions and impedance as different charge states are accessed. The interplay among atomic-scale interactions, mesoscale microstructural effects, and operating conditions will be discussed, with general applicability to ceramic solid electrolyte materials. This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC5207NA27344.

Ab-Initio Equilibrium and Non-Equilibrium MD Studies on Ion Transport around Interfaces in Solid Electrolytes

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Development of solid electrolyte (SE) with high ionic conductivity has been a most important target for the realization of solid-state battery (SSB). Although several pristine SEs with high conductivities have been found so far, the grain boundary (GB) effect is still an open question. As SE usually has high ion concentration, understanding of ion-ion correlation is also indispensable to control the conductivity. However, the experimental observations of these microscopic phenomena have been still difficult. In this work, using density-functional-theory based *ab-initio* equilibrium molecular dynamics (EMD) and non-equilibrium molecular dynamics (NEMD), we have addressed the elucidation of the microscopic ion behaviors, especially around GBs or interfaces in the SEs.

First targets are the electronic states and the ionic conductivities around the GBs of the garnet-type $Li_7La_3Zr_2O_7$ SE as well as the dopant effects (Al, Ga, Nb, Ta) [1,2]. The present *ab-initio* EMD simulations provided the interesting results: (1) Some GBs do not lower the ionic conductivities, (2) certain Li-Li correlation contributes to the conductivity, (3) the dopants segregated to the GB regions may have positive effect on the GB ionic conductivity. Besides, the electronic states calculations indicated the probable dendrite growth mechanism through the GBs.

In most EMD studies including our previous works, self-diffusion is treated within the Nernst-Einstein approximation. Meanwhile, the conductivity diffusion with ion-ion distinct correlation is more substantial in practice. However, the corresponding correlated ionic conductivity is difficult to be calculated because of the slow convergence of sampling. To mitigate this problem, we developed a new type of NEMD and coupled with *ab-initio* method [3]. The method generally makes around one-order speed-up of the sampling, enabling the correlated ionic conductivity calculation with reasonable accuracy and cost. Applying to $Li_{10}GeP_2S_{12}$, we successfully reproduced the conductivity as well as the Haven ratio, a measure of the ion correlation. This NEMD has another advantage allowing to evaluate local conductivity. We have applied it to the $Li_7La_3Zr_2O_7$ GB models as well and evaluated the Haven ration. In the talk, I'll discuss more applications as well as the issues of this NEMD method.

These works were done in collaboration with my NIMS colleagues, Dr. Bo Gao now in Jilin University, and Dr. Ryoma Sasaki now in a company and Dr. Randy Jalem. The works were supported in part by MEXT (JPMXP1020200301, JPMXP1121467561), JST(JPMJCR2204), and JSPS (JP19H05815, JP21J12566).

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Beyond the Bulk: Modelling Interfaces and Ion Transport in Solid Electrolytes

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Ion transport is pivotal to the performance of energy technologies, particularly batteries, and therefore the journey to net-zero emissions. The materials that exhibit ion conduction in these technologies present stunning heterogeneity and a plethora of complicated ion diffusion mechanisms from which they often derive their functionality. This situation is further complicated when we begin to consider the nanostructures, microstructures and interfaces of these materials. Nevertheless, it is imperative to understand these mechanisms and interfaces, and their influence on the performance of ion conductors, in order to design next-generation materials and devices, as well as improving existing technologies. Here, I will discuss how atomistic simulations can help us in the understanding, design and improvement of next-generation solid electrolyte materials for solid-state batteries. In particular, I will present some of our recent work on the influence of grain boundaries on ion transport in different solid electrolyte families and how we can discriminate between the complex correlation factors that determine the characteristics of ion transport. The importance of the synergy between modelling and experiment in the development of solid electrolytes will also be disseminated.

Past, Present, and Future Perspectives of Garnet-Type Li ion Electrolytes

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2019 Nobel Prize in Chemistry was awarded jointly to John Goodenough, Stanley Whittingham, and Akira Yoshino for the development of lithium-ion batteries (LiBs) that are being used to power portable electronics, electric vehicles and drones. However, the development of LIBs is running into a bottleneck as their energy densities are reaching the theoretical values. The employment of flammable organic liquid electrolytes also poses a safety concern. Solid-state Li batteries using a non-flammable inorganic solid electrolyte have been received much attention due to their safety and reliability. In this talk, recent developments in garnet type solid electrolytes and advanced sulfur cathodes for hybrid and conventional electrolytes will be presented. Fabrication and characterizations of the composite electrolytes, interface engineering, and cathode structure design will be discussed.

Lithium chemical potential engineering for low-resistive electrode/solid electrolyte interface by sintering process

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One of the problems in developing oxide-based all-solid-state batteries is to form a low resistive electrode-solid electrolyte interface. Most of the high Li^+ conductive oxide-based solid electrolytes are hard and fragile ceramics. Therefore, sintering the electrode with solid electrolytes is a common way to develop well-bonded interfaces. However, undesirable side reactions proceed during sintering, which often generates highly resistive reaction phases.

In the case of $LiCoO_2$(LCO)/NASICON-structured crystalline-glass Li-Al-Ti-P-O (LATP) interface, the theoretical calculation has suggested that the difference in lithium chemical potential results in the formation of de-lithiated LCO coupled with Li-rich LATP [1]. TEM-EELS analysis has detected the Li-rich LATP region around the interface even though the LCO/LATP interface is formed at room temperature by aerosol deposition. Once such LCO/LATP stacks are annealed over 300 °C, Co_3O_4 is detected as a reaction phase by Raman spectroscopy, and its Raman peak increase with increasing the annealing temperature [2]. Interfacial resistivities (R_{int}) at LCO-type electrodes/LATP have been reported to be ca. 100,000-100 Ω cm^2 depending on the interface formation temperature, and the R_{int} reduces with the decreasing of the interface formation temperature. Both the species and proportion of the reaction phases vary depending on the sintering temperature, and the reaction phases appearing at the lowest sintering temperatures are reported to be Li_3PO_4 and Co_3O_4 [3]. These two reaction phases are formed probably because of the thermal decomposition of de-lithiated LCO coupled with the Li-rich LATP region triggered by the difference of Li chemical potential. The alignment of lithium chemical potential at the interface plays an important role [4] in suppressing the reaction phases, which will be discussed with other experimental data.

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Pyrochlore-to-Garnet: Effect of Synthesis Route on Microstructure, Ionic Conductivity, and Lithium Striping/Plating Behavior in Ta-doped Garnet Solid Electrolytes

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Garnet-type solid-state electrolytes such as Ta-doped $Li_7La_3Zr_2O_{12}$ (LLZTO) are promising ceramic electrolytes for all-solid-state batteries because of their high (electro)chemical stability and ionic conductivity. LLZTO is typically synthesized from oxide precursors via solid state reaction (SSR), but use of other precursors such as pyrochlores has also received recent interest. We have shown that Ta-doped pyrochlores prepared using molten salt [1] and non-aqueous sol-gel methods [2] can serve as precursors for LLZTO in a process we call "pyrochlore-to-garnet" (P2G). Dense LLZTO ceramic can be directly obtained via a reactive sintering method and display comparable ionic conductivity as LLZTO prepared by SSR, but with lower sintering time needed. The grain size of LLZTO prepared via P2G is less than 2 μm, indicating that fine-grained garnet ceramics are accessible with this approach. The microstructure, relative density, and ionic conductivity of LLZTO prepared using the P2G method are compared to LLZTO prepared using SSR. The synthetic conditions were controlled so that the two types of LLZTO have similar properties (*e.g.*, ionic conductivity, relative density, *etc.*) except for the smaller grain size in P2G LLZTO. Also, in this work, the electrochemical characteristics of LLZTO pellets during lithium stripping and plating were compared to see the influence of the different synthesis methods. We find that P2G LLZTO, which has smaller grain size than SSR LLZTO, shows similar or even longer cycling life under galvanostatic Li stripping/plating. Linear sweep voltammetry (LSV) experiments indicate that P2G LLZTO can sustain higher voltages before shorting compared with SSR LLZTO. Reflection electron energy loss spectroscopy (REELS) and X-ray photoelectron spectroscopy were used to confirm that both types of LLZTO have similar average band gaps and chemical states, while energy dispersive X-ray spectroscopy (EDS) suggests higher local compositional inhomogeneity in LLZTO prepared by SSR, consistent with our previous observations [3]. This work can shed more light on the role of grain size and compositional inhomogeneity on the properties of LLZTO ceramic electrolytes used in lithium metal solid-state batteries.

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Development of Nb/Ta containing solid state electrolytes for Li ion batteries

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In terms of solid-state electrolyte materials for Li ion batteries, oxide materials offer promise in terms of their stability. However, there remains a need to improve the room temperature conductivity, as well as the interfacial resistance with the electrode materials. One of the most promising oxide electrolyte systems is garnets, and in this talk, the flexibility of the garnet structure to doping will be discussed, using rare earth dopants as examples [1,2]. Another system attracting recent interest is $LiTa_2PO_8$, which has been reported to show high Li ion conductivity through Si doping [3]. Further doping strategies on this material will be discussed, with a view to improving Li ion conductivity and interfacial stability in contact with Li metal.

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Development of Complex Oxides from Crystal Chemistry to Solid State Batteries

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Solid state electrolytes for use in all solid-state batteries face demanding performance criteria. They must conduct Li^+ ions between electrodes during battery cycling and withstand the electrical and chemical potentials in the cell, all whilst maintaining stable interfaces as electrode materials (de-)swell during lithium (de-)intercalation and redox.

We have developed various fast ion conducting phases for this purpose from the garnet, NASICON and perovskite structural families. These materials are characterized using combinations of crystallographic and local structural probes, and lattice dynamics are measured by complementing impedance analysis with muon spin relaxation measurements. Deployment of these electrolytes in all solid-state batteries requires matching of electrolyte properties with cathode and anode materials.

Here we will show how we chemically tune the material's functionality to form electrolyte/electrode combinations from a common structure type. This can be achieved with minimal change in chemical composition such the $\mathrm{Li}M_2(\mathrm{PO}_4)_3$ phases that form electrolyte (M = Zr) and electrode (M = Ti) materials. We will present examples of lattice matching and interfacial chemistry for electrochemical performance from garnets [1, 2, 3], NASICONs [4], and perovskite families of materials where we aim to deliver drastically different materials performance with minimal change in materials composition and structure. A key example [5] comes from the electrolyte/electrode materials $\mathrm{Li}_{1.5}\mathrm{La}_{1.5}M\mathrm{O}_6$ where M = Te functions as an electrolyte and M = W delivers redox active electrode behavior.

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Challenges to manufacture solid state electrolyte separators for all solid-state batteries

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All- solid-state batteries (ASSBs) are a viable option for next generation batteries. Advanced features of ASSBs over the state-of-the-art Li-ion batteries include enhanced intrinsic battery safety and increased energy density by application of lithium metal or silicon anode and thick high voltage cathodes. However, there are still some challenges with the materials and their processing to produce working ASSBs. In particular, the electrolyte material must meet a variety of functional requirements, which include high ionic conductivity and electronic insulation, chemical and electrochemical stability, and good scalable manufacturability. Furthermore, economic, and ecological aspects, such as cost, and availability and environmental impact should be considered [1]. Currently, a vast number of ASSB related research focuses on the investigations of suitable ceramic, glassy and polymer-based solid state electrolyte materials and their interfaces as solid state alternatives for the liquid electrolyte. Due to the higher material density of the solid electrolytes, thin separators are necessary to obtain low internal battery-cell resistances, i.e., good battery-cell performances, and higher energy densities than the state of the art of lithium-ion batteries. Also, sodium based solid state batteries have attracted huge interest due to the possibility to create high performance batteries without scarce elements. Hydroborates have shown excellent ionic conductivities over 1 mS/cm at room temperature with a electrochemical stability window of 0 – 3 V vs Na/Na+ thus, making them perfect for the usage of metallic sodium [2]. In this presentation we will give some strategies and challenges for processing of sulfide-based electrolytes separators for lithium ion based ASSB and hydroborate based electrolytes separators for sodium ion based ASSB in view of electrochemical performance and manufacturing technologies of battery cells.

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The Lithium Metal Anode on Solid Electrolytes – SEI Formation and Morphological Instability

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The lithium metal anode is considered as key factor for the success of solid-state-batteries. Its kinetics and its stable and reversible operation depend on the properties of the lithium solid electrolyte interface, at which charge transfer is coupled to the generation of local defects (e.g. metal vacancies during stripping). Once these defects cannot relax fast enough, morphological instability results and the interface changes its local microstructure (voids, metal nuclei, dendrite, and filaments). All this is strongly influenced by the formation of an SEI (solid electrolyte interphase).[1]

In this lecture, three cases will be considered: In the first case, no detectable SEI formation takes place, and the charge transfer kinetics is not influence by SEI formation (i.e., in the case of LLZO).[2] In the second case of typical sulfide electrolytes, a stable SEI forms that allows reversible operation.[3] In the third case of advanced halide solid electrolytes, a stable SEI cannot form, and the electrolyte is degrading fast.[4]

Finally, the role of these kinetic phenomena for practical applications in solid-state batteries will be discussed.

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Mechano-electrochemical Phenomena at the Li/LLZO Interface

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There is tremendous interest in making the next super battery, however Li ion technology continues to improve and has inertia in several commercial markets. Recent material breakthroughs in solid-electrolytes (SE) could enable a new class of noncombustible solid-state batteries delivering twice the energy density (>1,300 Wh/L) compared to Li-ion [1]. However, technological and manufacturing challenges remain, creating the impetus for fundamental and applied research.

This discussion will consist of fundamental aspects such as the mechanoelectrochemical phenomena at solid interfaces as well as manufacturing challenges related to the integration of Li metal electrodes. Owing to its stability against Li metal and high conductivity (~1mS/cm), LLZO garnet is used as a model system in these studies. The underlying physics that controls the stability and kinetics of Li/SE interfaces are fundamentally different from interfaces in Li ion technology. Moreover, the mechano-electrochemical phenomena that occur during discharge and charge at the Li/SE interface are considerably different. For example, during charging at higher rates Li metal filaments can initiate defects and propagate through relatively hard ceramics [2]. During discharge, if the Li stripping rate is sufficiently high and the temperature is sufficiently low, voids form at the interface causing delamination at of the interface.

In another example, novel mechano-electrochemical phenomena are emerging when analyzing the formation of Li anodes in using the Li^0-free manufacturing approach. Using this approach for solid-state batteries, Li et al in interposed between a current collector and the SE. The mechanics at this interface will determine the feasibility of this approach by controlling the homogeneity of the *in situ* formed Li anode. While significant progress is advancing the technological maturity of solid-state batteries, there remain fundamental questions regarding the physics at interfaces and whether they exhibit sufficient stability and kinetics relevant to EVs.

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High-Rate Li-Metal Anodes in Solid-State Batteries by Tailored Materials, Structures, and Interfaces

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Oxide-based solid-state Li-batteries (SSLiBs) have the potential to be a transformational and intrinsically safe energy storage solution due to their non-flammable ceramic electrolyte that enables the use of high-capacity Li metal anodes and high voltage cathodes for higher energy density over a much wider operating temperature range. However, their progress has been limited due to electrode/electrolyte interfacial issues. In particular for Li-metal anodes concerns over dendrite formation/propagation and the requirement for elevated temperature and high stack pressure are still prevalent. To eliminate these concerns a rational design of tailored materials, structures, and interfaces in Li-metal anodes will be presented. In addition, demonstration of high-rate Li metal cycling, achieving 100 mA/cm^2 at room temperature with no applied pressure, and progress toward full cells using these tailored materials, structures, and interfaces will be presented.

Understanding the Evolution of High-Capacity Anode Materials in Solid-State Batteries

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Solid-state batteries offer the promise of improved energy density and safety compared to lithium-ion batteries, but electro-chemo-mechanical evolution and degradation of materials and interfaces can play an outsized role in limiting their performance. Here, I will present my group's recent work to understand structural evolution, interfacial dynamics, and chemo-mechanics in solid-state batteries with lithium metal and alloy anodes. *Operando* X-ray tomography is used to reveal interfacial dynamics in solid-state batteries with Li metal anodes and sulfide solid-state electrolyte. Segmentation and detailed image analysis enable correlation of interfacial contact loss to electrochemical behavior of symmetric cells, and the loss of interfacial contact area at the Li metal interface is found to cause current constriction and cell failure. I will next discuss the unique aspects of interfacial evolution in "anode-free" solid-state batteries associated with localized lithium depletion using sulfide-based cells, as revealed by X-ray tomography, cryo-FIB, and finite-element modeling. Based on these results, the beneficial influence of metallic interfacial layers on controlling lithium evolution and mitigating contact loss from localized lithium depletion will be introduced. Finally, chemo-mechanical evolution and mechanistic aspects of the use of alloy anodes in sulfide-based solid-state batteries will be discussed. Real-time measurements of stack pressure evolution show the importance of dynamic control over stack pressure when using such large-volume change anodes. In addition, dense alloy anodes with controlled microstructures are shown to yield promising cycling performance. Taken together, these findings show the importance of controlling chemo-mechanics and interfaces in solid-state batteries for improved energy storage capabilities.

Paddlewheel Dynamics: Past, Present, and Future

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Correlations between the migration of cations and the rotational dynamics of cluster anions have been reported in several solid electrolytes throughout the years. One of the earliest examples of this phenomena, which is commonly referred to as the paddlewheel effect, was reported in sulfates such as Li_2SO_4 and Na_2SO_4. In these systems the high conductivity of Li_2SO_4 has been attributed to rotations of SO_4^{-2} anions, whereas the poor conductivity of Na_2SO_4 has been explained by the absence of these rotations. Using *ab initio* molecular dynamics, the dynamics of these two systems are revisited. It is shown that an explanation for conductivity differences in the sulfates lies not with differences in rotational dynamics, but in the availability of vacant sites in Li_2SO_4 which mediate Li hopping. The rotational dynamics of both systems are observed to be similar, suggesting that these dynamics alone are insufficient to explain differences in ionic conductivity. Looking to the future, attempts to identify new solid electrolytes using the concept of free volume fraction are described for multivalent conductors based on anti-perovskites.

On the Local Structure, Ionic and Thermal Transport in Solid-State Electrolytes

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In this presentation we will first discuss the importance of understanding the local and average structure of solid ionic conductors and the influence on the ionic transport.

Second, we will show that it is not only important to find fast ionic conductors, but that fast ionic conduction is paramount within solid state battery composites. Measuring the effective ionic transport in cathode composites provides an avenue to explore transport and stability limitations that in turn provide better criteria for solid state battery performance.

Finally, we will discuss that it is not only important to find fast ionic conductors but that for an effective thermal battery management the thermal transport properties of solid ionic conductors need to be explored and understood. Here we will show the diffusive thermal transport nature of solid electrolytes and their different scaling relations that put in question the assumption of Bruggeman transport in solid state batteries.

Magnetic Resonance Insights into Solid-State Batteries: Transport and Interfaces

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Understanding charge transport mechanisms and interfacial phenomena in solid-state batteries is critical to achieving performance enhancement yet challenging. With a complement of advanced magnetic resonance techniques, including *ex/in situ* nuclear magnetic resonance spectroscopy (NMR), magnetic resonance imaging (MRI), and electron paramagnetic resonance (EPR), we can non-invasively track ion transport and examine interfacial processes with temporal and spatial resolution. Compositional, structural, and dynamical entropy on different length scales, from atomic to micron, is shown to have varied effects on ion transport. We have identified lattice dynamics conducive to fast ion transport *vs.* those with little or no effects on transport. We have shown ion dynamics within grains *vs.* at grain boundaries are distinctively different, which influence overall transport and metallic microstructure formation in solid electrolytes. We have demonstrated that modification of grain boundary conditions can significantly enhance ion transport. Ion transport across electrode-electrolyte interfaces can be facilitated with improved interfacial contact via elevated temperature or stack pressure. However, these different approaches lead to opposite outcomes regarding dendrite formation. Limiting electron transport across the electrode-electrolyte interface is key to minimizing dendrite formation in solid electrolytes. These new insights into transport have guided the synthesis and discoveries of new inexpensive solid electrolytes and electrode-electrolyte composites with improved transport properties. The fundamental understanding of the complex interfacial phenomena advises strategic measures to improve interfaces for enhanced ion transport, limited electron transport, and minimized dendrite formation in solid-state batteries.

Module & Battery Pack Integration of All-Solid-State Lithium Ion Cells in the Automotive Industry – Facing the Challenges

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All-Solid-state batteries (ASSBs) are a very promising technology for electric vehicles (EVs) as they are prone to offer a higher energy density and a much higher level of safety regarding a thermal runaway compared to liquid-based lithium-ion batteries (LIBs). Thus, the automotive industry is closely following the development and progress of ASSBs. However, for becoming a viable option for a widespread implementation in EVs, various non-trivial issues need to be tackled that had already forced different companies to delay their start of production (SOP) multiply times. Hence, this makes it inevitable for universities and industry to work closely together to realize EVs based on ASSBs.

To overcome said issues, manifold challenges could be identified that hamper the widespread implementation of ASSBs in the automotive industry to this date: One of the key challenges lies in the significant breathing behavior of the metal anodes of up to 20% leading to the need of integrating thicker compression pads or other compression methods. These changes, however, result in an overall decreased energy density and a higher risk of an inhomogeneous pressure distribution on cell level. As solid electrolytes are characterized by low mechanical stability, this inhomogeneous pressure distribution may lead to (micro)cracks, and the formation of lithium dendrites is likely, ultimately leading to fast battery capacity loss or even failure. Solid electrolytes are characterized by a lower ionic conductivity compared to their liquid counterparts. In addition, ASSBs are sensitive to temperature fluctuations. Temperatures in the range of ~40-80°C are needed for an optimal operation window and ~80-120 °C are targeted for fast charging, respectively. This higher operation temperatures lead to a major impact on the temperature control system level. In this talk, we are going to speak about the main challenges and changes on module and pack level that need to be integrated and the main battery concept points that need to be adapted. This adaption of the battery concept includes optional as well as mandatory changes compared to liquid-based battery cells, such as functional safety, thermal insulation, battery management system (BMS) or manufacturing and assembly.

In summary, the development of ASSBs holds great promise for the future of EVs. However, significant challenges remain that must be addressed before they can become a serious alternative for mainstream applications. The automotive industry is closely following the research and development of ASSBs and will continue to work with researchers to address these challenges and bring this promising technology to market.

Design Considerations for Batteries based on LLZO

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Variants of lithium lanthanum zirconium oxide or $Li_7La_3Zr_2O_{12}$ (LLZO) are attractive electrolytes for solid state lithium batteries based on characteristics such as high ionic conductivities and wide operating voltage windows. Difficulties in its processing has meant that development of devices based on this material has lagged behind those of other solid electrolytes such as sulfides or halides. Its high density also means that its content must be minimized in batteries so as not to adversely affect specific energy. We have focused on scalable processing techniques and cell designs using this material to overcome these challenges. Two types of designs have been considered, both of which utilize a secondary electrolyte (catholyte) to ensure good contact among cathode components. The first design combines a thin dense LLZO component with a composite cathode consisting of active material, the catholyte, electronically conductive additives, and, optionally, a polymer binder. Lithium metal is attached to the separator at the end opposite to the cathode. The advantages are simplicity of cell design and minimization of LLZO contents (maximizing specific energy). The performance of coin cells in our lab utilizing this design, operating at room temperature without external pressure, is encouraging. Understanding and improving mechanical properties of the LLZO separator become increasingly important for successful scale-up to larger devices and the goal of a separator 20 um thick or less. To this end, we are considering several approaches for improving fracture strength and toughness. Another design combines the thin dense separator with a porous LLZO scaffold into which cathode active material and other components are infiltrated, in a bilayer configuration. We have recently shown results on a proof-of-concept cell, using a porous layer prepared by a freeze tape casting procedure. The bilayers are intrinsically more robust and easier to handle than the thin dense layer alone but are more complicated to fabricate. The need to minimize LLZO content means that the porosity of the scaffold needs to be at least 70 vol.%, depending on the thickness of the cathode (thicker cathodes do not require as high a porosity as thinner ones, if they can be made to work). One more aspect of our work is optimization of the catholyte. Electrolytes based on succinonitrile with lithium salts (organic ionic plastic crystals) are promising because of their high conductivity and good oxidative stability. These are waxy solids at room temperature, which allow good contact among cathode components and obviate the need for a co-sintering step.

Cycle Performance of All Solid-State Battery with LLZO Solid Electrolyte, NMC Composite Cathode and Li Metal Anode

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All solid-state batteries with $Al_{0.25}Li_{6.25}La_3Zr_2O_{12}$ (Al-LLZO) solid electrolyte, composite cathode of $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ (NMC622) and Li_3BO_3 (LBO) or $Li_3BO_3Li_2CO_3$ (LBCO) and Li metal anode were prepared by using Aerosol Deposition (AD) process with a post heat treatment. [1] Firstly, the composite cathode powders were prepared from NMC622 and LBO or LBCO. LBO and LBCO have a Li^+ ion conductivity. The composite powders were deposited on a sintered Al-LLZO solid electrolyte pellet by AD method to prepare the composite cathode layers. After this deposition process, the Al-LLZO with composite cathode layer consisting of NCM622 and LBO was heated at 600^{o}C and that consisting of NCM622 and LBCO at 500^{o}C, respectively. During this annealing process, the density of the cathode layer was increased, leading to good connection between LBO or LBCO and NMC622. Li metal was used as anode. In order to realize good connection between Al-LLZO pellet and Li metal foil, a gold layer was prepared on the Al-LLZO pellet. The Li metal anode was put on the gold layer and then was heated at 80^{o}C for one night for alloying gold and Li. This procedure provides low interfacial resistance between the Li metal anode and the Al-LLZO pellet. The all-solid-state cells were discharged at 0.1 C. The charging process was conducted by a constant current-constant voltage mode. The cut-off voltages for discharge and charge were 2.7 V and 4.3 V, respectively. The initial discharge capacity for NMC622-LBO composite was 158 mA h g^{-1} and that for NMC622-LBCO composite was 132 mA h g^{-1}, respectively. After 100 discharge and charge cycles, the discharge capacity decreased to 77 mA h g^{-1} and 101 mA h g^{-1}, respectively. The discharge capacity retention after 100 cycles were 49 % for NCM622LBO and 76 % for NCM622-LBCO, respectively. In order to investigate the degradation mechanisms, an electrochemical impedance of these cells was measured before and after the discharge and charge cycles. The electrochemical impedance for both cells increased with increasing cycle number. The interfacial resistance for NCM622-LBO after the cycling was larger than that for NCM622-LBCO, indicating that the impedance of cathode layer depended on additional solid electrolyte (LBO or LBCO). The increase of the interfacial resistance may be due to poor contact between NCM622 powders and LBO or LBCO powder. The thickness of the cathode layers increased observed by SEM, and the density of the cathode layers decreased with the cycling. The density of the cathode layers after the cycling were 87 % and 93 % of the initial density for NCM622-LBO and NCM622-LBCO, respectively. These results were in good agreement with the increase in the electrochemical impedance. The volume expansion of the cathode layers was confirmed by the SEM observation. This may be due to the volume change of cathode powder during the cycling. In addition, the volume change of cathode layer depended on the kind of additional solid electrolyte (LBO or LBCO).

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Enabling LLZO Based All-Solid-State Batteries – Utilizing the Unique Advantages of Garnets to Re-Design the Cell Production

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Full cell fabrication of all-solid-state batteries using only a LLZO based electrolyte faces several challenges, both on materials and processing level. While great improvements in energy density and safety are expected, such full cells featuring Li-metal anodes and high capacity cathodes still need to be demonstrated on industrial scale. To that regard, the required sintering at elevated temperatures is most often seen as a drawback, but the extremely high chemical and thermal stability of LLZO can open-up new processing opportunities for full cells. Re-thinking the common approaches of electrode and full cell manufacturing, we were able to demonstrate Li-metal anodes with high critical current densities of over 5 mA/cm² and high plating/stripping capacities of over 27 mAh/cm² for the first time. On the cathode side, re-design of the conventional ceramic processing route also opens-up new possibilities for a facile manufacturing of high-capacity mixed cathodes. In combination with advanced sintering techniques like FAST/SPS purely inorganic LLZO/LCO based cathodes with a capacity of 5 mAh/cm² can be achieved. While capacity fading is still an issue, the thermal stability of the optimized materials composition can again be utilized to enable new recycling strategies, which take place at the component level. The clear advantage lies in circumventing almost all the time and energy consuming recycling steps necessary for other solid-state cells or Li-ion batteries. Recovery rates of over 80% of the lost capacity were demonstrated for our cells already. These examples show, that in case of garnet based all-solid-state batteries, the whole process chain needs to be re-thought and adapted to the unique properties of oxide ceramic material. Great gains can still be expected if proper materials and process design is used, making this type of battery still a prospective candidate for a future market introduction.

Materials for Solid-State Batteries

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Lithium-ion batteries (Li-ion) based on liquid electrolytes and graphite anodes are the current dominate technology for many applications. Incremental improvements to Li-ion will continue into the next decade but a practical upper limit for the performance and cost will be reached which is insufficient for some applications.

Replacement of the liquid electrolyte by a solid is well identified in the literature as a promising means (so called solid-state batteries, SSB) to enable higher energy cell chemistries, improve safety, and simplify the design requirements at the systems level. With these benefits, the practical upper limits can be moved into acceptable ranges for most applications.

However, technological demonstration of high quality SSB devices is not commonplace in the literature. For example, cells are often limited in capacity, have rapid cycle fading, must operate at elevated temperatures, amongst others. Often, the origin of these limitations is driven by needs for better materials and processing.

Umicore is a materials company supplying cathode active materials for the lithium-ion industry and is actively researching several advanced battery concepts. This talk will highlight some current activities around materials for solid-state batteries.

Garnet Competitors Enabling Room-Temperature Solid-State Sodium Batteries

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Compared to their lithium counterparts, solid-state sodium batteries (SSNBs) are regarded as less mature technology despite some clear advantages which are going to be detailed in this talk. Solid oxide electrolytes $Na_{3.4}Zr_2Si_{2.4}P_{0.6}O_{12}$ (NZSP) and $Na_5YSi_4O_{12}$ (NYS) have total conductivity of several mS cm^{-1} at 25°C, higher than reported values for polycrystalline Li-ion oxide conductors. In addition, their stability, convenience of handling and processability as layers are significantly better. For example, electrolyte powder can be suspended in an aqueous slurry, tape cast and freely sintered up to almost full density. On the negative electrode side, they are not reduced in presence of sodium metal. An interesting Na dendrite-growth behavior along the surface rather than through the ceramic was found for NZSP. The influence of metal self-diffusion and a self-forming Na-P-O surface layer are the main contribution to the high dendrite tolerance of SSNBs. By blocking the surface from atmosphere access with a sodium-salt coating, surface-dendrite formation is prevented, and the dendrite-tolerance of Na/NZSP/Na symmetric cells is further increased to an extremely high CCD of 14 mA cm^{-2}. On the positive electrode side, the use of sintering aids for the co-sintering of fully ceramic half-cells or hybrid concepts for Na-Sulphur batteries are promising.

High-Energy and Long-Lasting Quasi-All-Solid–State Lithium Batteries Employing Garnet Solid Electrolytes and Interlayers

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Lithium metal batteries (LMBs) are considered the most promising next-generation battery system because of their high energy density and safety. Significant research effort has been devoted to developing more stable and energy-dense LMBs than the state-ofthe-art Li-ion batteries. However, the LMB performance remains unsatisfactory for commercialization, primarily owing to the inability of the inorganic solid-state electrolytes to hinder lithium dendrite propagation.

Here, using an Ag-coated $Li_{6.4}La_3Zr_{1.7}Ta_{0.3}O_{12}$ (LLZTO) inorganic solid electrolyte (SE) in combination with a silver-carbon interlayer, we demonstrate the production of stable interfacially engineered lab-scale LMBs. Via experimental measurements and computational modelling, we prove that the interlayers strategy effectively regulates lithium stripping/plating and prevents dendrite penetration in the solid-state electrolyte pellet. By coupling the surface-engineered LLZTO with a lithium metal negative electrode, a high-voltage positive electrode with an ionic liquid-based liquid electrolyte solution in pouch cell configuration, we report 800 cycles at 1.6 mA/cm^2 and 25 °C without applying external pressure. This cell enables an initial discharge capacity of about 3 mAh/cm^2 and a discharge capacity retention of about 85%[1].

In addition, we report various doped cubic-phase LLZO SEs without vacancy formation (i.e., Li = 7.0 such as $Li_7La_3Zr_{0.5}Hf_{0.5}Sc_{0.5}Nb_{0.5}O_{12}$ and $Li_7La_3Zr_{0.4}Hf_{0.4}Sn_{0.4}Sc_{0.4}Ta_{0.4}O_{12}$) prepared via high entropy-driven synthesis. When a $Li_7La_3Zr_{0.4}Hf_{0.4}Sn_{0.4}Sc_{0.4}Ta_{0.4}O_{12}$ pellet is tested at 60 °C in coin cell configuration with a Li metal negative electrode, a $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$-based positive electrode and an ionic liquid-based electrolyte at the cathode|SE interface, discharge capacity retention of about 92% is delivered after 700 cycles at 0.8 mA/cm^2 and 60 °C[2].

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Design Principles for Integrating Sulfide and Halide based Solid-Electrolytes in Solid-State Batteries

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Solid-state batteries (SSBs) are being sought as an ultimate replacement to conventional lithiumion batteries (LIBs) potentially increasing the cell energy density and safety. However, to achieve practical cell-level energy density in the range of 500 Wh/Kg and stable performance requires a multi-dimensional effort that includes, (i) robust materials and interfacial stability, (II) processing and compositional optimization and (III) effective integration and architectural design of SSB components. The talk will focus on the recent approaches to improve interfacial stability of sulfide based solid electrolytes (SEs) with Li-metal and NMC based cathodes for SSB's.[1-2] A comparative evaluation of SSB performance between Argyrodite (Li_6PS_5X, X= Cl, Br) and halide-based SE (Li_3ACl_6, A = In, Y) using them as a separator and catholyte will be presented. Overall, these results demonstrate that incorporating oxidatively stable SEs in composite cathodes does not necessarily ensure the formation of robust NMC/SE interfaces, and cumulative irreversible capacity losses in such cells can yield rapid performance decline. Rather than SE decomposition, the dominant cause for capacity fade in SSBs is due to active material isolation resulting from repeated volume changes during cycling. Further, additional understanding of the mechanics of solid-solid interfaces and their dynamical evolution during SSB operation will be critical to address key performance bottlenecks for Li metal SSBs. Finally, the talk will report our recent experimental approach where a combination of intermetallic alloys and compositions can serve the dual purpose of improving the interfacial reactivity of SE with Li and enhance wettability of the functional current collector for high-rate Li-deposition and dissolution.[3]

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Solid State Batteries with Ultrathin Composite Electrolytes

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Batteries relying exclusively on rigid solid-state electrolytes (SSE) are often challenged by large and quickly rising electrode/SSEs interfacial resistances that limit energy efficiency, rate capability and capacity retention over cycle life. To address this issue, we synthesize ultrathin SSEs (ca. 10 µm) by in situ UV-curing of ceramic-in-polymer composites consisting of LiTFSI-doped bisphenol A ethoxylate dimethacrylate, blended with plastic crystalline succinonitrile and the ceramic additive $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$. The heated precursor mixture is spin-coated directly onto the composite cathode and Li anode layers, respectively. The increasing viscosity in the quenched state helps to maintain an even distribution of the ceramic additive in the polymer phase. The resulting composite SSE features high ionic conductivity $>10^{-4}$ S·cm^{-1}, wide electrochemical window up to 5 V, and high thermal decomposition temperature (275°C). Temperature-dependent lithium-ion diffusion paths are analyzed to design the optimal composition and microstructure of the SSEs. Therefrom, it is seen that the evenly distributed ceramic component of the composite ensures a percolating network of high ionic conductivity interfacial paths for Li$^+$ ions even below the glass transition temperature of the bulk polymer. The electrochemical performance of our in-situ-cured SSEs and their interfaces with the Lithium anode was first evaluated in symmetric Li/SSE/Li cells. When cycled with a high current density of 2 mA·cm^{-2} over 500h, the overpotential remains stable and no dendrite growth is observed. In situ-curing a thin layer SSE on a porous lithium iron phosphate (LFP) composite cathode drastically reduces the SSE/cathode interfacial resistance. LFP/SSE/Li cells manufactured by combining the SSE-coated Li and LFP electrodes achieve a maximum specific discharge capacity of 148 mAh·g^{-1} and retain a specific capacity of 132 mAh·g^{-1} after 200 charge/discharge cycles.[1] Direct observation of the SSE/cathode interface layer demonstrates that the strong binding and three-dimensional architecture of in situformed interfaces brings about the high cycling stability. Stable room temperature cycling of solid-state batteries is also demonstrated for cells using a high cathode mass loading of 6 mg·cm^{-2}.

Viability and Transport Characterization of Hybrid Material Concepts for Sulfide-based Solid-State Batteries

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The renewed interest in further developing solid-state batteries (SSBs) is mostly due to the high room temperature conductivities (> 1 mS/cm) of sulfide-based solid electrolytes. However, such materials tend to have limited (electro)chemical stabilities against state-of-the-art oxide-based cathode materials and Li metal, both of which are likely necessary for the implementation of SSBs in electromobility applications. In this talk, we discuss how the combination of sulfide-based solid electrolytes with other materials can be exploited to tackle some of these electro-chemo-mechanical challenges. We present various classes of hybrid materials, namely solid electrolyte-liquid electrolyte; solid electrolyte-polymer electrolyte and solid electrolyte-conducting polymers:[1] how they are prepared, characterized electrochemically, and incorporated in solid state battery half-cells. Our approach is strongly focused on attaining a good understanding of the transport bottlenecks in these hybrid materials, in terms of both ionic and electronic transport, as well as interfacial (in)stabilities and monitoring the formation of new interphases. Therefore, a combination of various electrochemical methods beyond galvanostatic cycling is presented, namely electrochemical impedance spectroscopy. The talk concludes with a brief overview of potential future directions in this field.

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Interfaces and Ionic Transport in Solid-State Batteries

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Solid-state batteries have undergone significant progress in the recent years, mainly driven by the development of fast solid conductors. Fulfilling the ambitious promise of high gravimetric and volumetric energy density still represents several challenges, covering the processing of materials into components, cell integration and performance. Even fast ionic conductors such as oxides, sulfides or halides dare with resistive and dynamic solid-solid interfaces which are still the main bottleneck to develop high-performance devices.

Such interfaces appear naturally when processing the materials into components or even when stacking components during cell assembly. Some examples are the active material/solid electrolyte interface present at the positive electrode, the solid electrolyte/Li metal anode interface and even between electrolyte particles after densification. Such type of resistive interfaces can be minimized to a great extent from the careful choice of materials chemistry, optimization of microstructure and processing strategies.

Interfaces in SSBs can also be dynamic as a result of the different processes taking place during cell cycling. This leads to even more complex challenges, such as volume expansion and void formation at the anode during lithium electro-platting and dissolution, lithium dendrite propagation across the solid electrolyte, cracking of the positive material from continuous redox processes and resistive interfaces formed from poor electrochemical stability between solid electrolyte and electrodes. These complex interfaces may adversely affect the Li transport, often leading to a fast decrease on the cell performance.

In this talk we will analyze key solid-solid interfaces involving several chemistries present within the cell and how they affect to the performance and ionic transport: from redox processes at the positive electrode and electrochemical stability with Li metal electrodes to dendrite propagation. Besides, we will discuss on how the engineering of interfaces may improve cell performance and even pave the way towards the desired anode-less concept.

Stabilities of garnet-type Solid Electrolyte-Theoretical and Experimental Approaches

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Since sensational discovery of garnet-type solid electrolyte, $Li_7La_3Zr_2O_{12}$ (LLZO) is achieved by Prof. Weppner's group in 2007[1], the garnet-type solid electrolytes have been paid much attention for the application of all-solid-state Li batteries. The garnet-type electrolytes are featured by high ionic conductivity and chemical/electrochemical stabilities. Particularly, high stabilities of LLZO and $Li_5La_3Ta_2O_5$ (LLTaO) in contact with Li metal allows us to opt Li metal anode which can improve energy density of the all-solid-state battery drastically.[2] So far, enhancement of cathodic stability of solid electrolytes has been performed by elemental substitution. For example, cathodic stability of NASICON-type $LiTi_2(PO_4)_3$ can be improved by a replacement of Ti^{4+} with Ge^{4+} which has a more stable oxidation state. However, the influence of structure on cathodic stability of solid electrolyte is still unclear. Thus, in this study, both theoretical and experimental approaches are applied for a direct comparison of cathodic stability of garnet-type LLTaO with perovskite-type $La_{1/3}TaO_3$ (LTaO) to clarify origin of high stability of garnet-type solid-electrolyte. These two compounds are composed of the same elements. The difference in these two compounds is only structure, enabling to extract influence of structure on the cathodic stability[3].

The Li intercalation voltage of LLTaO and LTaO is -1.03 and +0.44 V, respectively, predicted by the first-principle density function theory, implying that garnet LLTaO is stable in contact with Li metal while perovskite LTaO are not. The result is also verified experimentally. No color change is observed in the garnet when contacting with molten Li metal for 24 h. Contrary, color of perovskite is changed from white to black only in 3 min. In the DOS analysis, LTaO possesses narrower band gap comparing to LLTaO (3 eV vs. 4 eV) caused by empty Ta 5d band in LTaO, resulting in the less stability of perovskite LTaO.

In the conference, our recent research on ceramic electrolytes is also presented.

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Garnet or NASICON: Materials and Processes for All-Solid-State Batteries

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All-solid-state batteries (ASSBs) are one of the next-generation batteries towards carbon neutral societies. While sulfide-based ASSBs are on the stage for their practical application, oxide-based ones are still under the feasibility studies, mainly because of their interfacial issues: interphases and/or contact areas that would limit the energy and the power of the ASSBs. These issues are more severe for the full-inorganic ASSBs without any organic electrolytes, although they would would extend the application fields of the next-generation batteries: high voltage batteries and batteries for severer environment (vacuum, high temperature, etc.). In this study, materials and processes of the garnet-type and NASICON-type solid electrolytes are developed to prepare the electrochemically active interfaces between the solid electrolytes and the active materials. The garnet ASSBs were prepared by using quick liquid phase sintering. LiOH was added to the cathode composites of $LiCoO_2$ (LCO) and $Li_{6.5}La_3Zr_{1.5}Ta_{0.5}O_{12}$ (LLZT) to promote the sintering. Quick infrared radiation selectively heated the LCO grains in the cathode layer and the garnet ASSBs with LCO-loading of 8.1 mg/cm^2 exhibited a capacity of 130 mAh/g (1 mAh/cm^2).

For the NASICON ASSBs, $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$ (LAGP) was prepared by a solution method using oxalic acid as a chelate. LAGP obtained by sintering the precursor at 600°C exhibited rather high total conductivity of 2×10^{-5} S/cm. The NASICON ASSBs fabricated with TiO_2 anode and $LiCoPO_4$ cathode exhibited an initial discharge capacity of 66 mAh/g (0.17 mAh/cm^2).

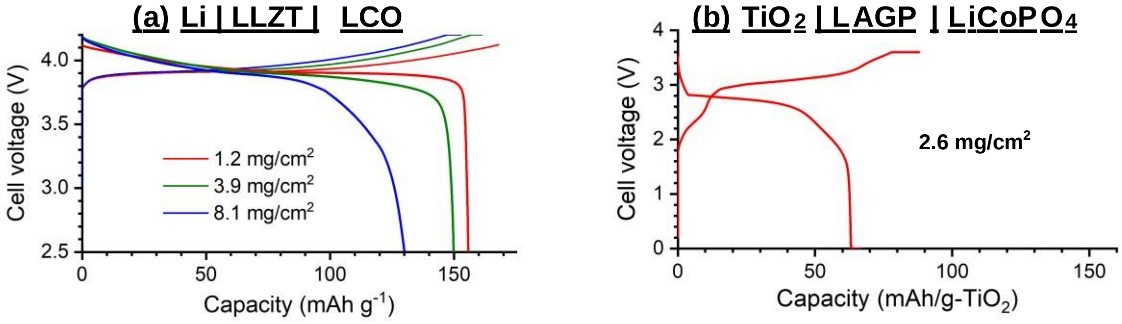

Figure 1. Charge/discharge curves of full-inorganic ASSBs in the (a) Li | LLZT | LCO and (b) TiO_2 | LAGP | $LiCoPO_4$ systems. The batteries were operated at 25 °C, 0.01 C.

Magnetron Sputtering of Amorphous LLZO and LiPON Thin Films as Li-ion Conducting Separators

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The talk will present our recent progress in developing thin films of amorphous oxides deposited by PVD methods with the intent of using them as electrically insulating yet Li-ion conducting separators in solid-state batteries. In contrast to solid electrolytes mixed into the composite cathodes, the essential property of a solid separator is its electronic insulation, which should be coupled with an acceptable Li-ion conductivity, mechanical endurance, and electrochemical stability of interfaces with cathode and anode. One of the popular thin-film separators employed over the last three decades in micro-batteries is glassy amorphous lithium phosphate oxynitride (LiPON), thanks to its stability against lithium metal and negligible electronic conductivity. The low ionic conductivity in the low 10^{-6} S cm^{-1} range and low deposition rates during RF magnetron sputtering restrict its scale-up. We follow several approaches to overcome these challenges by investigating amorphous LLZO and LiPON compositions with various dopants. Amorphous Ga-doped LLZO prepared by magnetron sputtering is an excellent insulator with electronic conductivity of ~ 10^{-14} S cm^{-1} that sustains plating-stripping of metallic lithium without signs of lithium penetration up to 3.2 mA cm^{-2}. A thin a-LLZO layer of only 70 nm is enough to cycle Li/a-LLZO/LCO thin-film battery for over 500 cycles at 10C. Next, a carbon-doped Li_3PO_4 target was used for DC sputtering of LiPON, increasing the deposition rate tenfold as compared to the RF mode yet still maintaining a comparable ionic and electronic conductivities in the order of 10^{-6} S cm^{-1} and 10^{-13} S cm^{-1}, respectively. Si-doped LiPON compositions known as LiSiPON were co-sputtered to push the ionic conductivity into the 10^{-5} S cm^{-1} range. Finally, hybrid cells consisting of selected composite cathodes, the sputtered thin-film separators (1…5 µm thick), and evaporated lithium metal anode were fabricated to verify the potential application of such separators in bulk solid-state batteries.

Synthesis of Highly Li-ion Conductive Garnet-Type Solid Ceramic Electrolytes by Solution-Process-Derived Sintering Additives

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The sintering of garnet-type solid ceramic electrolytes (e.g., $Li_7La_3Zr_2O_{12}$, LLZ) is rather challenging considering the easy volatilization of the lithium at high temperatures. Liquid-phase sintering using sintering aids such as Li_3BO_3 and Al_2O_3 has effectively used to sinter LLZ solid electrolyte at low temperatures. However, the presence of sintering additives strongly affects the total lithium-ion conductivity of the solid electrolyte. As the lithium-ion conductivity of Li_3BO_3 is approximately two orders of magnitude lower than LLZ, the addition of a large amount of the sintering additive increases the resistance of the composite solid electrolyte, while an insufficient amount leads to a poor densification and insufficient lithium pathway for the ionic conductivity.

In this study, we propose an alternative route to sinter garnet-type solid ceramic electrolytes using solution-process-derived sintering additives to overcome the limitations of current sintering additives. We utilized Li_3BO_3 and Al_2O_3 as well-known sintering additives for the Ta-doped LLZ solid electrolytes by varying the processing using the solution-derived sintering additives. This approach enables the significant reduction of the sintering additives and consequently, the enhancement of the lithium-ion transport properties achieving a high ionic conductivity of 0.8 mS cm^{-1} with low activation energy (9 kJ mol^{-1}) and almost negligible contribution of grain boundary resistance (10%) reported so far. Moreover, symetric cells with lithium metal demostrated that lithium borate in the solid electrolyte microstructure suppresses lithium dendrites up to 10 mA cm^{-2}. Finally, comparison with inorganic and hybrid interfacial materials for the preparation of all-solidstate batteries is also presented.

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Development of Glassy Sulfide Electrolyte for All-Solid-State Lithium Metal Batteries

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All-solid-state rechargeable lithium batteries attract much attention because they have several advantages of high safety and long cycle life. To increase the energy density of all-solid-state batteries, it is important to use lithium metal for the negative electrode. However, there is concern about short circuits in batteries due to the formation of Li dendrites. To solve this issue, it is important to form an appropriate interface between Li metal and solid electrolytes.

Sulfide solid electrolytes have several advantages of excellent electrical and mechanical properties suitable for all-solid-state batteries [1]. In particular, Li_2S-P_2S_5 sulfide glasses have high Li^+ conductivities from 10^{-4} to 10^{-3} S cm^{-1} and favorable formability. The sulfide powders can be easily compacted and densified without heat treatment, which facilitates the formation of close and extensive interfacial contact between electrode and electrolyte. Regarding elastic properties, the Li_2S-P_2S_5 glasses have a lower Young's modulus than oxide glasses [2,3].

The Li_2S-P_2S_5-LiI glasses exhibit higher conductivity, lower Young's modulus and better reduction tolerance to Li metal than the Li_2S-P_2S_5 glasses [4,5]. The structure and morphology of the interface between Li metal and sulfide electrolytes were analyzed by X-ray CT, SEM, and XPS techniques [6,7]. To improve the short-circuit tolerance of all-solid-state lithium metal batteries, the ionic conductivity of the interfacial phase near the lithium metal as well as the sulfide electrolyte itself is important [8,9]. The interface design by inserting an appropriate thin metal film is also effective in maintaining lithium stripping/plating performance [10].

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Copolymer Li-ion Electrolytes for New Generation Li-ion Batteries

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In the search for suitable dry solid polymer electrolytes (DSPE) for future (quasi-)solid state Li-ion batteries, we have investigated various copolymer-based systems to make the component integration into full battery cell more facile. We investigated four types of DSPEs. The first polymer family is an ABA triblock copolymer, poly(methyl methacrylate)-*b*-poly(poly(ethylene glycol) methacrylate)-*b*-poly(methyl methacrylate) (PMMA-*b*-PPEGMA-*b*-PMMA), with two hard PMMA outer segments and a comb-like rubbery PPEGMA inner segment. This triblock copolymer forms physical networks at ambient temperature with the hard glassy segments as crosslinkers, which improve the mechanical properties, while the PPEGMA inner segment is responsible for the ionic conductivity. According to our basic concept, using this type of copolymer results in better mechanical properties, due to the physical network, without considerable decrement of ionic conductivity. Additional advantage is the suppression of the crystallinity of the PEO-like domains. Factors such as side chain length, segment length, segment length ratio are the main set-points to fine-tune the polymer's performance. Moreover, wetting measurements show the changes of the surface characteristics as the function of the properties of the contact phase, which was expected to be advantageous in the composite formation. The second group of the investigated DSPE is the copolymer of 3,6-dioxa-octane-1,8-dithiol and poly(ethylene glycol) diacrylate, P(DODT-coPEGDA), in which the PEO-like structure is included, and it contains not only oxygen, but sulfur atoms as well in the polymer backbone. This type of polymer possesses low Tg and suppressed crystallinity. The third investigated polymer family, the synthesis of which was explored in our laboratories, are poly(di)thiophosphates, in which oligo(ethylene glycol) segments are between the acidic dithiophosphate groups. It was found that by changing the average length of the oligo(ethylene glycol) segments the mechanical properties of the polymer can be broadly varied. Since these materials have low Tg values, they are assumed to be promising candidates for polymer electrolytes. The lithium salt formation of the acidic groups in these polymers is expected to lead to the formation of single-ion conducting polymer electrolytes. The last family of the investigated polymers can be distinguished as random copolymers, such as random poly(PEGMA-*co*-(acrylic acid)). The developed copolymers belong also to the group of single ion conductive Li-ion polymer electrolytes.

Efficient Preparation of Moisture-Stable Lithium Garnet and its Lithiophilicity

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In recent years, lithium garnets ($Li_7La_3Zr_2O_{12}$, LLZO) have attracted extensive attention due to their high ionic conductivity and good stability towards lithium. LLZO is usually synthesized by solid-state reaction, which often requires the use of excessive lithium sources, organic solvents for wet milling, and long-time hightemperature sintering. LLZO also has problems such as instability to humid air. Moisture in the humid air will cause a Li^+-H^+ exchange reaction on the surface of LLZO, thus forming an insulating surface impurity layer [1]; meanwhile, LLZO has been reported lithiophobic, which leads to loose contact with the Li anode and may cause the nucleation and growth of Li filaments during electrochemical cycling. This talk will first introduce our recent work on the efficient preparation of

$Li_{6.5}La_3Zr_{1.5}Ta_{0.5}O_{12}$ (LLZTO). In this work, we systematically investigate the key factors affecting the stability of LLZTO, including synthesis process, microscopic morphology, second phase at grain boundaries, and lithium concentration in grains [2,3]. We design a dry process route and synthesize LLZTO with high moisture stability and a room-temperature ionic conductivity of 7.36×10^{-4} S cm^{-1}. This process route does not use solvents, does not require excessive lithium salts or mother powder, and the entire synthesis time is shortened to 24 hours. The as-synthesized LLZTO can maintain a high ion conductivity of 6.41×10^{-4} S cm^{-1} after being exposed to the air atmosphere for four months. Second, we prove the intrinsic lithiophilicity of LLZTO electrolyte and propose a "polishing-and-spreading" approach to obtain a tight Li/LLZTO interface [4,5]. By removing the surface impurities from both LLZTO and molten Li, the interfacial resistance between Li and LLZTO is only 17.5 Ω cm^2 without any interfacial modification. Meanwhile, we compare the wettability of different lithium-based alloy and composite anodes with LLZTO and find that they do not improve the wettability. The addition of alloying elements would actually hinder the ion transport on the Li/LLZTO interface.

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Garnet Solid Electrolytes for Ceramic-Based Solid-State Li Battery Applications

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Development of inorganic solid Li-ion conductive ceramics for the use as solid electrolytes is pivotal for the realization of next-generation all-solid-state batteries with high safety and reliability. The materials used as solid electrolytes must have not only high ionic conductivity well above 1 mS cm^{-1} at room temperature but also chemical stabilities against both cathode and anode materials, air and moisture. Although oxide-based solid electrolyte materials have lower ionic conductivity and poor deformability compared to sulfide-based ones, they have other advantages such as their chemical stability and ease for handling.

Among various oxide-based solid electrolyte materials, a garnet-type oxide with the formula of $Li_7La_3Zr_2O_{12}$ (LLZO) has been studied widely because of the high Li ion conductivity at room temperature, excellent thermal performance, and stability against Li metal anode with the lowest redox potential (= −3.045 V vs. SHE) and high gravimetric theoretical capacity (= 3,860 mAh g^{-1}). However, the formation of good solid-solid interface between LLZO and both cathode/anode active materials is still challenging to realize high performance solid-state batteries. Poor interfacial connection between LLZO and Li metal anode causes non-uniform Li plating and intergranular penetration of fibrous Li metal in polycrystalline LLZO when the cell is cycled at high current densities, resulting in internal short-circuit failure. In co-sintering process for fabricating solid-state batteries, high sintering temperature of LLZO (> 1000ºC) for its densification severely restricts the choice of cathode active materials that can be used for co-sintering.

In my presentation, our recent research works of LLZO-based garnet and other ceramic solid electrolyte for the application to ceramic-based solid-state Li batteries are presented, including the following two topics:

1. Effect of sintering additive on the microstructure, ionic conductivity, and tolerance for Li dendrite growth of Ta-doped LLZO.
2. Characterization of other ceramic electrolytes for cathode composite solidified on Ta-doped LLZO.

Oxide and Phosphate-based Ion Conductors: Synthesis and Low Temperature Densification Strategies

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Solid-state batteries (SSBs) have gained momentum in recent years thanks to striking advances at the material level, such as the discovery of new highly conducting solid-state electrolytes. However, the development of SSBs still faces formidable challenges, such as the integration of the various components, the functionality at full cell level, and the scalability of the fabrication processes.[1] Oxide and phosphate-based solid electrolytes stand out for their chemical and electrochemical stability but require temperature-assisted densification methods to suppress resistive interfaces that enable fast Li^+ transport. However, chemical reactivity among the different cathode components (which include a catholyte, the conducting additive, and the electroactive material) still represents a major challenge and processing parameters need thus to be carefully selected.[2]

In this talk we will discuss our recent work regarding oxide and phosphate-based ion conductors. It includes the synthesis and characterization of a new form of crystalline LiPON,[3] as well as the exploration of low-temperature densification strategies, such as the high-pressure low-temperature technique and cold sintering. Our results show that with these approaches a significant reduction of the processing temperature can be achieved, which would allow to overcome current densification constraints derived from the use of very high temperatures. Additionally, these approaches could help increase manufacturing yields and decrease energy consumption, overall being more environmentally friendly.

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Poster Abstract

P01. Increase In Critical Current Density Achieved in Li-Stuffed Garnet by Integrated Perovskite Secondary Phase

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Solid-state batteries have become a promising alternative to the conventional Li-ion battery as an energy source. However, challenges of Li dendritic growth are still much of a hinderance to the large-scale adoption of this technology.[1] Forming at critical current densities far below current commercialization targets Li metal dendrites are proving to be an obstacle to the wide scale implementation of the technology[2,3] One source of formation and propagation of Li dendrites has been identified by researchers as high electronic conductivity in solid electrolytes.[4] We have elected to introduce transition metals into the $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$ garnet systems to induce a change in electronic conduction. Changing the electronic conduction through the solid electrolyte allowed for controlled investigation into electrochemical properties and Li dendrite formation behaviour. Powder X-ray diffraction (PXRD) analysis was performed on Garnet $Li_{6.4}La_3Ta_{0.6}Zr_{1.4-x}Mn_xO_{12}$ (x = 0.035, 0.05, 0.07, 0.105) following synthesis, here the formation of a composite structure was observed, the target cubic phase $I\,a\,\bar{3}\,d$ was synthesised along with the presence of a perovskite-related $n = 1$ RuddlesdenPopper secondary phase La_3LiMnO_7. PXRD analysis following pelleting via plasma spark sintering found the predominant garnet phase to have been retained whilst the secondary phase was observed to undergo a phase transformation to $n = 2$, La_4LiMnO_8. Initial AC impedance and DC polarisation, undertaken to investigate the effect of the secondary phase on the electrochemical properties of the compound, revealed minor changes in electronic and ionic conductivity up x = 0.07. To further understand the role of Li metal in contact, and during cycling with the solid electrolyte, AC impedance and galvanostatic cycling were performed. Results revealed increasing amounts secondary phase reduced resistance in contact with Li, subsequently leading to an increase in critical current density (CCD). A natural solubility limit however appears to be reached at x = 0.07, whereupon the secondary phase counteracts the interfacial resistance, thereby reducing the CCD. This work provides an intriguing insight into the role of secondary phases within solid electrolytes, with different electrochemical properties they appear, even at low levels, to affect the electrochemical attributes of the whole system.

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P02. Tuning the ionic conductivity and electrochemical stability of Li_3InCl_6 analogues by the aliovalent substitution of In.

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Among the conventional and well stablished lithium-ion batteries (LIBs), all solid-state lithium batteries (ASSLiBs) are considered to be the more promising next generation technology for large-scale energy storage devices due to its safety and energy density outperformance allowing the use of a lithium metal negative electrode. Several inorganic materials have been studied as candidates to be used as solid electrolytes (SEs) in ASSLiBs such as sulphides, halides and oxides[1], however, none to date, meet simultaneously all the mechanical, stability and transport properties to develop scalable high performance ASSLiBs. Since the discovery of high Li^+ conductivity in Li_3YX_6 (X=Cl, Br),[2] this family of halides have received great attention as catholytes due to their high stability towards high voltage cathodes. However, there is still a lack of understanding of the relationship between structure, composition and ionic conductivity in these materials. Furthermore, the development of low-cost systems with scalable processing routes is still needed. In this work, a series of novel halide SEs with different stoichiometries ($Li_{2+x}M_xIn_{3-x}Cl_6$) have been prepared with the aim to optimize ionic conductivity and electrochemical stability by means of a simply and scalable eco-friendly synthetic route via the aliovalent substitution of the central metal of Li_3InCl_6 with noncritical raw materials like Fe(II), Mg(II) or Zr(IV). In addition, a number of solvents with different polarities have been tested proving that solution-like processing can aid to the scalability of these materials without compromising their performance. Neutron powder diffraction studies have been used in combination with electrochemical analysis to bring insight on the relationship between their crystal structure, stability and ionic conductivity.

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P03. Co-Diffusion-Initiated Interfacial Degradation Processes in SSBs and the Mitigation Strategies

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Interfacial instability of solid electrolytes with cathodes, e.g., LCO, during high temperature processing, resulting in a huge interface resistance, is one of the fundamental reasons for the failure of solid-state batteries based on garnet-type LLZO.[1-2] So far, the high interfacial impedance has been related to LLZO|LCO interface decomposition occurring due to diffusion of transition metals across the cathode-electrolyte interface.[3,4] Herein, we investigated the hypothesis that interfacial degradation originates from the incorporation of Co into the LLZO lattice.[5] The solubility limit of Co is determined to be 0.16 per formula unit, whilst the concentrations beyond promote phase transition (cubic LLZO-to-tetragonal LLZO). We investigated in detail the temperature-dependent Co diffusion into LLZO and proposed that detrimental cross diffusion could take place at any relevant process condition. Besides, the optimal protective Al_2O_3 coating thickness for relevant temperatures was studied, which allowed to create a process diagram to provide mitigation strategies toward enabling stable LCO|LLZO interface in all-solid-state batteries.

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P04. Effect of Operating Conditions on Li Stripping/Plating Performance in All-Solid-State Li Metal Cells Containing Sulfide Glass Electrolytes

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Li metal is considered an ideal negative electrode because of its high theoretical capacity (3860 mAh g^{-1}) and lowest electrochemical potential (−3.04 V vs. SHE). Sulfur also has a high theoretical capacity of 1672 mAh g^{-1}, and all-solid-state Li/S batteries combining these electrodes have attracted attention as next-generation batteries with high energy density. However, their practical application is limited by short-circuiting due to Li dendrite growth. One of the possible reasons for this phenomenon is the reduction of solid electrolytes (SEs). Sulfide glass electrolytes, such as Li_3PS_4, exhibit high ionic conductivity and excellent ductility [1]. Meanwhile, our group has reported that the volume changes caused by the decomposition of Li_3PS_4 induced short-circuiting in the all-solid-state Li metal cells [2]. We also reported that the addition of Li^I to Li_3PS_4 increased the reduction tolerance of the solid electrolyte resulting in the suppression of decomposition [3]. Another reason for short-circuiting is the contact failure caused by the void formation at the Li/SE interface during Li stripping [4]. Herein, we studied the operating conditions, such as stack pressure, operating temperature, and electrode composition, that could potentially suppress the formation of voids. We investigated the effects of these operating conditions on the Li stripping/plating performance of all-solid-state Li symmetric cells containing sulfide glass electrolytes with reduction tolerance. As a result, the all-solid-state Li symmetric cells exhibited good Li stripping/plating performance at stack pressures of 3 and 5 MPa, indicating that the Li/SE interfacial contact is maintained during Li stripping/plating by applying these stack pressures at room temperature. Meanwhile, Li metal penetrated the SE layer at stack pressures above 24 MPa owing to creep deformation, which resulted in poor Li stripping/plating performance. Symmetric cells with Li–Mg alloy electrodes instead of Li metal electrodes exhibited high cycling stability at current densities above 2.0 mA cm^{-2}, a temperature of 60 °C, and stack pressures of 3–10 MPa. In addition, an all-solid-state Li/S cell with a Li–Mg alloy negative electrode operated stably for 50 cycles at a current density of 2.0 mA cm^{-2}, stack pressure of 5 MPa, and temperature of 60 °C, with the large theoretical capacity of sulfur.

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P05. Defect Chemistry and Ion Transport in Low-Dimensional-Networked Li-Rich Anti-Perovskites as Solid Electrolytes for Solid-State Batteries

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Face the current climate emergency, solid-state batteries have been attracting significant attention due to a plethora of potential advantages, such as energy density gains, reduced costs, and safety enhancements.[1] In recent years, Li-rich anti-perovskites have stood out as promising solid electrolyte candidates as they combine high ionic conductivity, stability against Li metal anodes and structural versatility.[2] Here, defect simulations are used to explore the energetics of defect formation in a range of Li_xOX_y (X = Cl or Br; x = 3–6; y = 1–4) anti-perovskites with zero- to three-dimensional structures. Defect calculations are conducted utilising the Mott−Littleton approximation. Long molecular dynamics runs are carried to assess ion transport in these materials at a range of temperatures (200–800 K). The range of defects investigated includes full, Li-halide and Li-O Schottky defects and Li Frenkel defects. Our calculations predict that whereas almost all these materials present Li-halide Schottky defect pairs as dominant native defects, Cl interstitials are the dominant type of intrinsic disorder in Li_6OCl_4. We find that the formation of the great majority of defect types is energetically more favourable in the Li_xOCl_y series compared to the equivalent structures in the Li_xOBr_y set, potentially leading to enhanced Li-ion transport in these materials. We also report that the concentrations of halide Frenkel defects in the Li_xOBr_y set are lower than expected in the three and two-dimensional structures, based on the Li_xOCl_y series findings for their counterparts. Our molecular dynamics simulations reveal the strong connection between Li-ion dynamics and dimensionality in these anti-perovskite materials, where increased Li-ion diffusion and decreased activation energy can be seen as dimensionality is reduced. Density functional theory simulations and machine learning studies are currently ongoing to further assess ion transport and interfaces in these materials.

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P06. Hybrid Solid Electrolytes Based on $Li_{2.25}Zr_{0.75}Fe_{0.25}Cl_6$ for High-Energy Density Lithium Batteries

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In Europe, the battery demand is expected to be close to 1,000 GWh by 2025, passing 2,600 GWh by 2030.[1] Therefore, there is an according interest on the key parameters of these devices (i.e. energy density, cost, cycle life, safety and sustainability). The energy delivered by conventional Li-ion batteries has converged in its limit (200 Wh/kg) which restricts its usefulness for long autonomy electric vehicles (EVs). Todays' trend in the automotive sector passes through the increase of battery pack size at the expense of exponential increase of cost. Moreover, this generation of batteries still involves the use of liquid electrolytes with their respective main disadvantages (potential leakage and flammability). Battery community agrees in the use of thin lithium metal anodes to enlarge the energy of these devices (400 Wh/kg) and hence, compete against fuel-based vehicles in autonomy; like so the employment of solid-state electrolytes to prevent the commented liquid-state issues. In this regard, polymer electrolytes are still far from practical ionic conductivities at room temperature, remaining inorganic electrolytes as single operative candidate available. The use of lithium single-ion inorganic electrolytes with high mechanical resistance would indeed depress the heterogeneous lithium plating and parasitic reactions ("dead" Li) enabling its safe employment.

Oxides, sulfides and halides have emerged as promising candidates in this family. The first two present disadvantages in terms of temperature-pressure necessities for either its sintering or application and release of toxic H_2S in case of air-exposure. In contrast, halides exhibit a moderate temperature of synthesis (<300 ºC), air/humidity durability and electrochemical stability showing values of 1 mS cm^{-1} at 25 ºC.[2] Nevertheless, there is still a dependence with the pressure in terms of application and lack of flexibility. For this purpose, hybrid solid base electrolytes are presented as the combination of both inorganic and polymer materials in an attempt to overcome the drawbacks of each other. In this study, different hybrid electrolytes based on $Li_{2.25}Zr_{0.75}Fe_{0.25}Cl_6$ and different polymers (SEBS and biopolymers involving PEO, isosorbide and poly (1,4-cyclohexanedimethanol)) have been developed to provide flexible thin membranes (40 μm) with low pressure dependence. We have also studied the impact of the different polymers on the transport properties of the hybrid electrolytes. Finally, the processability of these hybrid electrolytes have also been investigated to form the inorganic conducting phase from its precursors in presence of the polymer. This process method is industrially relevant reducing the number of synthesis steps for a cost-effective line.

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P07. β-LiAl Anodes for All-Solid-State Lithium Batteries

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Lithium-indium (Li-In) alloys have been widely pursued as an anode in all-solid-state batteries thanks to its stability when paired with solid-state electrolytes [1]. However, In lacks abundancy in the Earth's crust, raising the risk of increased raw material cost and hindering its wide-scale utilization [2]. In this work, aluminum is electrochemically prelithiated[3] and β-LiAl is investigated as an anode material in all-solid-state batteries. This alloy can take advantage of the abundance of Al, the low operating potential range (<0.3 V versus Li/Li+), and high specific capacity (>1152 $mAh.g^{-1}$). Routes for prelithiation will be discussed in the context of solid-state battery designs. Furthermore, strategic utilization of the Li solubility range in β-LiAl, may result in an anode material that has no phase transformations and negligible volumetric expansion. These factors will be discussed, along with their implications for improving rate capability and enhancing Coulombic efficiency. As solid-state cells are compressed with a stacking pressure during operation, preliminary cell tests reported here will consider the importance of this pressure in the context of the anode-electrolyte interface.

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P08. Synthesis of Anion/Cation Doped Garnet Electrolyte Materials for Solid-State Batteries

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Garnet solid-state electrolytes have attracted great interest due to their high Li ion conductivity and good electrochemical stability[1]. To enable the production of All-Solid-State Batteries, several issues need to be addressed, such as to increase the Li^+ ion ionic conductivity, lower the interfacial resistance between electrolyte and electrode materials and prevent the dendrite growth of Li metal through electrolyte materials. There has been significant work investigating doping strategies to improve the conductivity of $Li_5La_3(Nb/Ta)_2O_{12}$ and $Li_7La_3Zr_2O_{12}$ systems[2, 3], with the key conclusions being that Li ion contents of the order of 6.4-6.6 are optimal. In this work, we report a combined experimental and modelling study of Ce^{4+} doping in $Li_7La_3Zr_2O_{12}$. We show for the first time that Ce^{4+} can be doped onto the Zr^{4+} site in this material. This doping strategy results in a reduction in the tetragonal distortion as well as a lowering of the temperature of the tetragonal−cubic phase transition, attributed to the increase in cell size reducing Li−Li interaction strain. Coupled with these changes, the conductivity shows a significant improvement. Furthermore, the Ce doping also reduces the interfacial resistance (388 Ω cm^2) in contact with Li metal, giving additional potential benefits to this doping strategy. The long-term cycling stability of a Li//garnet//Li symmetric cell over 190 h has been demonstrated[4]. Whilst multiple cation substitution studies of garnets have been undertaken to try and improve their overall performance, anion doping of garnets has rarely been attempted, owing to the synthetic challenges associated with this particular doping strategy. We present work on the halogenation (F, Cl) of the solid-state electrolyte $Li_7La_3Zr_2O_{12}$ (LLZO) via a low temperature solid state synthetic route using PTFE and PVC polymers for the first time. A reduction in tetragonal distortion (F incorporation) and a tetragonal to cubic phase transition (Cl incorporation) is observed in halogenated LLZO, suggesting the replacement of O^{2-} with F^- or Cl^- is associated with the creation of lithium vacancies. The effects of surface fluorination were also investigated for Al-doped LLZO ($Li_{6.4}Al_{0.2}La_3Zr_2O_{12}$, LLAZO) which suggest this strategy has the ability to prevent full dendrite penetration at high current densities[5,6].

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P09. Doping Implications for Garnet $Li_7La_3Zr_2O_{12}$ from First Principles

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The solid-state electrolyte, $Li_7La_3Zr_2O_{12}$ (LLZO), can facilitate a step towards safer, more energy dense and longer lasting batteries. However, there are still challenges concerning poor Li-ion conductivity and dendrite formation. Here we investigate the effect of Al, Ga, Nb, Ta, and Y doping in LLZO using hybrid density functional theory calculations. Our results show Li Frenkel defect as the major intrinsic defect and give clear indications of Al, Ga, Nb, and

Ta acting as donor defects, thus stabilising additional Li vacancies. The resulting increase in Li vacancy concentration leads to an increased disorder on the Li sublattice, thus predicting a stabilisation of the more ionic conducting cubic phase. Furthermore, our calculations indicate that the effect of dopants on the sintering process is their most important role after their ability to stabilise the cubic LLZO structure. In addition, we suggest a new possible explanation for the two orders of magnitude increase in ionic conductivity when stabilising the cubic phase.

P10. Processing and Sintering of Ceramic Powder with Nominal composition $Li_{6.25}Al_{0.25}La_3Zr_2O_{12}$ Produced by Spray Pyrolysis

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Due to its high Li-ion conductivity the garnet type $Li_7La_3Zr_2O_{12}$ (LLZO) has become one of the most promising candidates as electrolyte in solid-state Li-ion batteries (LiB). However, at room temperature (RT) tetragonal LLZO is the stable phase and conversion to the cubic phase is necessary to obtain a high Li-ion conductivity. There are several dopants that stabilize the cubic phase at RT and Al^{3+} is among the most studied. Al^{3+} enters the Li-sites, forms Li-vacancies and stabilizes the cubic structure. Here we will present results from sintering Al-doped LLZO powder precursors produced by spray pyrolysis (SP). Water based solutions were prepared with nitrate-based precursors according to the target stoichiometry $Li_{6.25}Al_{0.25}La_3Zr_2O_{12}$ (LALZO). However, due to loss of volatile Li-species during processing, solutions were prepared with Li-excess between 8 and 30 mol%. Two types of water-based solutions were prepared: With organic complexing agents (Solution 1) and without carbon containing species (Solution 2), respectively. The powder precursors produced by SP were spherical agglomerates composed of nanosized crystallites, and after wet milling and drying the powders were calcined at 750 °C. Solution 1 resulted in powders with significant amounts of Li_2CO_3 which allowed only small batches of powder to be calcined at a time to obtain a phase pure cubic LALZO. The amount of Li_2CO_3 was significantly reduced in powders obtained from Solution 2 and allowed calcination of larger powder batches. The optimal Li excess in both solutions was found to be around 20 mol%. Sintering of calcined powders in ambient air at 1150 °C for 2 hours resulted in densities above 90 %, however exhibiting abnormal grain growth (AGG). The presence of AGG is believed to originate from a liquid sintering mechanism due to the presence of eutectic liquids. The binary systems Al_2O_3-Li_2O and ZrO_2-Li_2O have eutectic liquid phases at 1064 °C and 1025 °C, respectively. Nevertheless, Li ionic conductivities measured by electrochemical impedance spectroscopy (EIS) at RT showed Li-ion conductivities around $3.0 \cdot 10^{-4}$ S$\cdot$ cm^{-1}, comparable to the best results reported in the literature. Ongoing work based on powder precursors produced by SP of Solution 2 will focus on suppressing AGG and produce high density LALZO with homogeneous microstructures and grain size in the range from 1 to 3 μm. Two different sintering procedures have been chosen for this purpose: 2 step sintering and spark plasma sintering (SPS) at temperatures well below the eutectic temperatures reported above. Microstructure, phase relations and Li-ion conductivity data will be presented.

P11. Na_2S–NaI Solid Solution as Positive Electrode in All-Solid-State Na/S Batteries

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All-solid-state sodium-sulfur (Na/S) batteries are promising next-generation batteries with high safety and high energy density. Sodium sulfide (Na_2S) is attractive as an active material in positive electrodes owing to its advantages such as low cost, low toxicity, and a large theoretical capacity. However, the electronic and sodium ionic conductivities of Na_2S are significantly low. Therefore, facilitating an electronic and ionic conduction path in the positive electrode is essential. In this study, Na_2S was reacted with sodium iodide (NaI) via a mechanochemical process and was used as an active material in an all-solid-state Na/S battery. As a result, a Na_2S–NaI solid solution was formed, and the ionic conductivity of Na_2S–NaI increased by five orders of magnitude compared to that of Na_2S. Na_2S–NaI showed large charge–discharge capacities and long cycle life for 100 cycles. In particular, $90Na_2S\cdot 10NaI$ (mol%) showed a large capacity and high cycle efficiency, and 94% of Na_2S acted as an active material. These results lead to the development of all-solid-state Na/S batteries with high performance.

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P12. Performance of NaSICON Electrolytes in Anode-Less Sodium Solid-State Batteries

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Sodium solid-state batteries (Na-SSBs) are gaining popularity due to the abundance of sodium, their low cost and their electrochemical properties being similar to lithium. Among the sodium solid-state electrolytes (SSE), those with NaSICON (Na^+ SuperIonic Conductors) type structure, in particular the composition $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$ ($0 \leq x \leq 3$) (NZSP) is a type of solid-state electrolyte that is receiving increasing attention in the field of Na-SSBs. It offers several advantages including improved safety, stability, and higher energy density. NZSP also exhibits elevated ionic conductivity (until $5*10^{-3}Scm^{1}$) and is highly resistant to moisture and air. These properties make it an excellent candidate for use in Na-SSBs, which have the potential to be more sustainable and cost effective. Furthermore, recently, NZSP has been reported to deliver fast charge transfer at the Na metal/NaSICON interface via stabilization of a conductive solid-electrolyte interface (SEI) layer through thermally activated surface decoration[1,2]. This work focuses on the development of anode-less Na-SSBs. This type of battery does not have an anode during assembly, the cell is assembled discharged with an "empty" negative electrode that is formed *in situ* during the first charge cycle. The aim of this study is the optimization of interfacial adhesion between $Na_3Zr_2Si_2PO_{12}$ solid electrolyte and the *in situ* formed Na metal so that full Na coverage of the solid electrolyte surface is achieved under subsequent charge-discharge cycles. We focus on the design of the current collector nature and morphology to improve cyclability and study the interplay of wettability of the current collector with the Na metal versus the wettability with the solid electrolyte. We use a variety of deposition methods with non-alloying (Cu, Al) and alloying current collectors (Au, Ag). The work provides important advance towards the design of stable anode-less all-solid-state-batteries.

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P13. Fabrication of Thin-Garnet Electrolytes Using Pulsed Laser Deposition for Solid-State Li-Metal Batteries

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Oxide-based electrolytes like lithium lanthanum zirconium oxide (LLZO) are promising material candidates for use in Li-metal batteries due to their high electrochemical and mechanical stability, as well as their high ionic conductivity. Despite their promise recent reports clearly show a lack in reducing the thickness in processing to similar ones of polymer-based electrolytes in the range of 10 microns. A shift from an electrolyte-supported to a cathode supported cell design with the solid electrolyte as the thin film is proposed to further improve energy density. Through this work, we investigate solid electrolytes $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$ in thin film form using pulsed laser deposition (PLD) and its integration on 80 µm-thick cathode composites. The latter cathode composites consist of a mixture and are graded in their content of $LiCoO_2$ and (Ta, Al)-doped LLZO phases to assure high energy density in performance. We demonstrate for the first time that rather thick 3.8 µm LLZTO films are directly deposited on cathode composite. The LLZO film reveals the desired high-conducting cubic phase without any secondary phase formation as determined by Raman and XRD techniques. Collectively, the first step toward cell fabrication is made by providing cathode composite tape/LLZO thick films maximizing the active electrode over the electrolyte volume. Compared to earlier efforts in the field it provides the opportunity to have combined solid/solid cathode/electrolyte architectures based on film/tape instead of tape/tape or other pellet approaches.

P14. Atomic-scale Investigation of Ion Conduction and Cation Doping in Halide and Oxyhalide Solid Electrolyte Materials

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In the search for novel solid electrolyte materials for solid-state batteries, a fundamental atomic scale understanding of ionic migration mechanisms, cation doping and local structural effects are important for optimising performance. Here, we employ atomistic simulation techniques to investigate two families of materials attracting growing interest as ionic conductors for battery electrolytes. For the anti-perovskite Na_3OCl, we explore the effects on Na-ion conductivity of doping with divalent (Mg, Ca, Sr and Ba) and trivalent cations (Al and Ga) to induce mobile Na vacancies and of possible dopantvacancy clustering.[1] For the ternary halide Li_3ScCl_6, we examine stacking faults and spinel-like Sc-ion disorder to open up three-dimensional networks available for fast Liion diffusion. Microscopic effects are considered, and the results are used to rationalise macroscopic observations to guide future work on optimising their solid electrolyte performance.

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P15. Upcycling Lithium Titanate (LTO) Anodes into NASICON Type Solid-state Electrolytes.

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The field of electrification has been increasing since the drive for 'net zero' was announced by numerous countries around the world. Lithium-ion batteries (LIB) is one way to keep up with this demand, however, this technology utilizes a liquid electrolyte which poses many health and safety issues along with unwanted side reactions. Introducing solid-state electrolytes into the next generation of batteries has the potential to increase the safety, and energy density of these batteries. One aspect that has not been considered much is the recycling of anode materials from Li ion batteries. While graphite is the dominant anode for conventional batteries, lithium titanate (LTO) is used in commercial high-power batteries and has recently been investigated as an alternative anode material to using Li metal for solid-state batteries (SSB) due to its' high stability, and the fact that it undergoes only the minor volume changes during the (de)lithiation processes [1, 2, 3]. LTO is currently used in approximately 4 % of current commercial batteries (standing at 235,000 tons) increasing the necessity to recycle to recover the critical Li salts and TiO_2 [4]. Given the fact that SSB are the next generation of battery materials and provide many advantages over the current LIB that contain aqueous electrolytes, we have been investigating the possibility to upcycle spent LTO anode material into NASICON type solid-state electrolytes. We illustrate a route to this, along with associated excess Li recovery.

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P16. Phase Evolution and Thermodynamics of Al-doped Cubic LLZO Studied by High-Temperature X-ray Diffraction

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$Li_7La_3Zr_2O_{12}$ (LLZO) is a promising solid-state electrolyte for advanced Li-ion batteries due to its high ionic conductivity, non-flammability and high electrochemical stability against Li anodes and high voltage cathodes. However, synthesis of phase pure LLZO is challenging due to easy formation of secondary phases, such as the pyrochlore $La_2Zr_2O_7$, that are detrimental to the performance of a LLZO electrolyte. Although many studies have been performed on the electrochemical performance of LLZO, the understanding of the thermodynamics of the synthesis of LLZO is still lacking. Here we report on high-temperature X-ray diffraction (HTXRD) following the crystallization of a gel of Al-doped LLZO. Gels with 0, 10 and 20 mol% excess Li were prepared and calcined at 500 °C to remove the volatile components before HTXRD. The powders calcined at 500 °C consisted primarily of $La_2Zr_2O_7$ with trace amounts of Li_2CO_3 and $La_2O_2CO_3$ and were used as starting materials to study the formation of the cubic LLZO phase. During HTXRD the samples were heated from 500 °C to 700 °C in steps of 20 °C, and further to 1000 °C in steps of 50 °C. Upon heating the pyrochlore phase gradually transforms to cubic LLZO. In all samples, cubic LLZO first appears around 600 °C and the pyrochlore phase disappears around 750 °C in the samples with 0 % and 20 % excess Li. We performed two analyses of the sample with 10 % excess Li by HTXRD, one with normal deposition thickness and another with thinner deposition thickness. In the thin sample, cubic LLZO appears at a lower temperature of 560 °C compared to the other experiments. The pyrochlore phase does not fully disappear but instead reappears and crystallizes at the highest temperatures investigated, indicating extensive Li loss from the thin sample. These observations suggest that atmospheric exposure and the relative surface area of powder are important factors for LLZO formation.

To understand the thermodynamics of LLZO formation, we propose the following reaction to take place based on the identified reactants and products:

$6.25\ Li_2CO_3 + 0.25\ Al_2O_3 + 2\ La_2Zr_2O7 + La_2O_2CO_3 \rightarrow 2\ Li_{6.25-x}Al_{0.25}La_3Zr_2O_{12-0.5x} + 7.25\ CO_2(g) + x\ Li_2O(g)$.

The enthalpy, entropy and Gibbs energy of the reaction were calculated from literature values and DFT calculations and agree with the experimental observations. Finally, we discuss the significance of the highly disordered Li sublattice for the entropy of cubic LLZO. We believe our findings will contribute to improved understanding of LLZO formation and facilitate the synthesis of high-performance phase pure LLZO electrolytes.

P17. Stripping Behavior of Li Foil and *In Situ* Plated Li Under Zero External Pressure in Solid-State Batteries

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One of the most critical hurdles to enabling Li metal solid-state batteries (SSBs) is understanding and preventing void formation in the Li anode during discharge (stripping). Previous studies of Li foil metal anodes paired with oxide or sulfide solid-state electrolytes (SSEs) have suggested that a critical stack pressure is required to suppress void formation during stripping of Li metal. It is believed that Li void formation is caused by a flux imbalance of Li metal at the Li/SSE interface, and that higher stack pressures alleviate this flux imbalance by encouraging creep of Li metal. While current Li-ion batteries are manufactured with stack pressures <1 MPa, it has been suggested that a critical stack pressure of at least 2 MPa is required for the oxide $Li_7La_3Zr_2O_{12}$ (LLZO) with a Li anode at the relatively low current density of 0.4 mA cm^{-2}. Studies of stripping Li metal foil below 1 MPa are rare due to the poor performance exhibited at low pressures, with only 1.2 mAh cm^{-2} Li stripping capacity accessible at the low current density of 0.1 mA cm^{-2} [1]. While these studies use thick (>150 µm) Li foils, to achieve commercially relevant performance it is necessary that the Li metal anode is thin (<25 µm). Manufacturing thin Li anodes is complicated by the reactivity of Li metal, which forms a thin passivation layer even in controlled environments. The "Li^0-free" cell manufacturing approach provides an alternative to these challenges. "Li^0-free" cells are manufactured with a bare anode current collector (CC) and the Li metal anode is plated *in situ* at the CC/SSE interface during the first charging step using the Li stored in the cathode active material [2]. The thickness of *in situ* plated Li can easily be controlled, unlike conventional Li foils. Further, *in situ* plated Li should have a higher purity than Li foil, as the LLZO SSE will only allow Li to pass through, while Li foil can contain impurities from the refinement process. Therefore, there is a need to understand the discharge behavior of *in situ* plated Li under commercially relevant stack pressure (< 1 MPa). Here, we studied the stripping behavior of both Li foils and *in situ* plated Li at zero externally applied pressure. During stripping of Li, *operando* galvanostatic electrochemical impedance spectroscopy (EIS) was conducted to measure and analyze the various transport phenomena that comprise the total cell resistance. *Operando* galvanostatic EIS measurements during stripping correlate the interfacial contact loss between Li and LLZO with the growth of the Li/LLZO interfacial resistance and shows how the contact loss process differs for *in situ* Li versus Li foils. After stripping, potentiostatic EIS is used to observe the recovery of the interface over time. Finally, mechanical testing of the Li/LLZO adhesion strength before and after stripping is used to analyze the changes in Li/LLZO bonding associated with Li/LLZO de-wetting during the stripping process. These studies highlight the importance of utilizing *in situ* plated Li in electrochemical tests as opposed to thick Li foils to produce data sets relevant to future commercial SSBs.

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P18. Investigating Aliovalent Sn(+IV) and Isovalent P(+V) Substitution Series in Li_3SbS_4

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The search for feasible solid electrolytes has led to discovery of lithium ion-conductors from different material classes, especially the halides and sulfides. However, an indepth understanding of the connection between Li^+ conduction and the structure has to be established in order to further improve the solid electrolytes. The thio-LISICON family contains three distinct structure types labelled as α-, β- and γ-Li_3PS_4, differing in the orientation of the $(PS_4)^{3-}$ tetrahedra. The β- and γ-polymorph can be stabilized at room-temperature, where the γ-polymorph is experimentally less investigated than the β-polymorph because of the lower inherent ionic conductivity. The aliovalent

$Li_{4-x}Sb_{1-x}Sn_xS_4$ ($0 \leq x \leq 0.2$) and isovalent $Li_3Sb_{1-x}P_xS_4$ ($0 \leq x \leq 0.5$) substitution series, crystallizing in the γ-polymorph, were performed to shed light on variables, e.g. number of Li^+, volume changes, which can affect the conductivity beneficially within this polymorph. The P(+V) substitution decreases the unit cell volume (~2.3%), while the Sn(+IV) substitution increases the unit cell volume slightly (~0.18%). The Li^+ conductivity in both cases improves from $9.2 \cdot 10^{-11}$ S·cm^{-1} for Li_3SbS_4 to

$2.9 \cdot 10^{-6}$ S·cm^{-1} and $4.9 \cdot 10^{-7}$ S·cm^{-1} for the highest substitution content for Sn(+IV) and P(+V), respectively. However, the Sn(+IV) substitution shows a threefold faster increase in conductivity compared to P(+V) substitution in the Li_3SbS_4 structure suggesting that more Li^+ ions in the structure might be favourable within the γpolymorph. Additionally, at these low conductivities the defect formation enthalpy might play a more predominant role in these ordered structures as it is not negligible anymore.

P19. Powder Aerosol Deposition, a Novel Way for Processing Garnet Solid Electrolytes to fabricate All-Solid-State Batteries

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In recent years, much research work has been devoted to optimize garnet-like LLZO as a promising electrolyte material for ASSBs. Here, the focus was particularly on the adaptation of the material and its electrochemical properties with respect to application in an ASSB [1]. Since significant progress has been made in the above-mentioned fields, the next step is to find a processing method, which is suitable for mass production. The desired process should enable the fabrication of dense ceramic films utilizing economic processes that are suitable to manufacture film thicknesses in the range of 5 to 20 µm, in order to explore and to exploit the full potential of ASSB [2]. However, conventional ceramic processing methods such as tape casting require high temperature sintering steps that lead to prohibitively high processing costs [3].

The novel Powder Aerosol Deposition (PAD) is a suitable candidate with promising properties for processing LLZO. PAD enables the production of dense ceramic films at room temperature. In addition, the layer thickness can be arbitrarily adjusted in the range of a few µm up to 200 µm, depending on the respective application [4]. The so called “Room Temperature Impact Consolidation” (RTIC), the characteristic deposition mechanism of the PAD process, negatively affects the electrical properties of PAD films. Resulting stresses within the film and a distorted crystal lattice impede charge carrier transport in comparison to bulk materials [4,5].

First investigations show that for PAD-LLZO films only a thermal post-treatment at mild temperatures up to 400 °C after deposition is necessary to ensure a competitive ionic conductivity of the films [5]. Furthermore, it was already shown that PAD-LLZO films can be cycled in a Li | LLZO | Li symmetrical cell setup [3].

Based on these results, we aim at showing that PAD-LLZO films can be successfully applied to ASSBs. SEM images and EDX analyses show that a PAD multilayer film consisting of an NMC cathode, an NMC/LLZO composite cathode and an LLZO film with a dense and nanocrystalline structure can be obtained using PAD. In addition, polarization experiments confirm that an NMC | NMC/LLZO | LLZO | Li full cell can be cycled, which has not been shown before. Finally, we are identifying the remaining challenges for PAD-LLZO films or ASSBs before commercial use is feasible. Additionally, we show how a future PAD-based ASSB could be fabricated on a commercial scale and illustrate the potential of such an ASSB using a theoretical consideration of energy densities in respect to cathode layer thickness.

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P20. Cycling demonstration of Sequential Deposition Synthesized Lithium Garnet Films in Full Batteries

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Sequential deposition synthesis (SDS) is a recently discovered technique that allows a solid-state electrolyte layer to be fabricated directly from a liquid precursor which is then atomized onto a heated substrate where the solvent evaporates, and the precursor salts decompose to form a conformal layer. $Li_7La_3Zr_2O_{12}$ (LLZO) is a promising material that has seen much interest in the battery field but has challenges to synthesize this layer between 5-15 µm thick which SDS is capable of fabricating. LLZO films were fabricated directly onto a porous substrate that was infiltrated with a polymer gel electrolyte and the cycling performance was demonstrated in a full cell using Li metal anode and lithium cobalt oxide (LCO) cathode. The cycling performance is discussed in reference to state of-the-art performance in the battery field and post-mortem analysis on the cells is performed to elucidate failure mechanisms.

P21. Preparation of Ultrathin Sulfide Solid Electrolyte Membrane for High Energy-Density All-Solid-State Sodium Batteries

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All-solid-state sodium batteries (ASSLBs), utilizing sulfide solid electrolyte, are considered as the promising design on account of their superior safety and high room-temperature ionic conductivity; however, sulfide solid electrolytes are brittle after cold pressing and usually need to be prepared as thick solid electrolyte sheets, which will reduce the energy density of all-solid-state batteries. Herein, samples of $Na_{2.895}W_{0.3}Sb_{0.7}S_4$ is fabricated by a mechanochemical process and subsequent heat treatment. Three-dimensional ion diffusion structure promotes $Na_{2.895}W_{0.3}Sb_{0.7}S_4$ electrolyte to reveal ultra-high ionic conductivity (6.5 mS cm^{-1}).Furthermore, to realize the higher energy density of the battery, an ultrathin $Na_{2.895}W_{0.3}Sb_{0.7}S_4$ sulfide electrolyte membrane with superior ionic conductivity of 3.2 mS cm^{-1} is fabricated with the aid of dry-film technology. The assembled all-solid-state pouch cell can operate even under the severe conditions of bending and cutting, demonstrating the enormous potential of sulfide electrolyte membrane for all-solid-state sodium battery applications.

P22. Characterisation of Electrodes, Electrolyte and Electrode/Electrolyte Stacks Obtained by Powder Aerosol Deposition

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Powder aerosol deposition (PAD) is a relatively new technique for the manufacturing of dense nanocrystalline ceramic films. PAD can be used to manufacture ceramic electrodes and electrolytes for all-solid-state batteries. Among these ceramic electrolytes $Li_7La_3Zr_2O_{12}$ (LLZO) is one of the most promising materials due to its relatively high ionic conductivity and chemical stability against lithium metal. One of the main challenges implementing LLZO into solid-state batteries are the high temperatures required for processing (e.g., sintering of a composite cathode). Recent developments demonstrate that LLZO produced by PAD requires lower temperatures to achieve high ionic conductivity [1]. In our research within the German FestBatt Cluster we investigate how room-temperature PAD can be used for the production of solid-state batteries consisting of NMC-cathode and LLZO-electrolyte.

Here, we show how the microstructure of PAD LLZO films evolves during different heat treatments and how these procedures influence the electrochemical performance. Due to the nanocrystalline structure of the PAD films, determination of the grain sizes is challenging. Different methods for the determination of the average grain size have been explored. We select ion-channelling contrast as the most suitable method to analyze the microstructure with small grain size and high number of defects. We track the evolution of the microstructure at a selected region of a sample with increasing temperatures up to 500 °C. Of great interest is the interface between the LLZO layer and the copper current collector and, subsequently, the interface between the LLZO and the lithium metal. This interface is critical for the formation of voids and dendrites. For the imaging of interfaces before and after plating of lithium, we use intermittent helium-ion microscopy (HIM). For the preparation of cross sections, conventional mechanical polishing as well as a gallium FIB including neon ion polishing (no alloying reactions with lithium) are used. Mechanical stresses within a layered thin film system can be measured by the substrate curvature technique. Mechanical forces arising during cell operation lead to a curvature that can be measured by the deflection of laser beams [2]. We explore how this technique can be applied to thin film all-solid-state batteries und how the mechanical stress data can be used to infer fundamental electrochemical processes. Our results couple microstructure, mechanics, and electrochemistry in LLZO-based batteries and contribute to the optimization of the PAD technique towards the production of batteries with tailored microstructures.

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P23. The Effect of Site Disorder on The Li-Ion Diffusion Mechanism in the Argyrodites

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Lithium argyrodites (Li_6PS_5X with X = Cl, Br, I) employed as solid-state electrolytes show great promise to replace flammable liquid electrolytes in Li-ion batteries due to improved safety and Li-ion conductivity comparable to those of liquid electrolytes. Recent studies suggest that macroscopic Li-ion conductivity can be increased further by several approaches. Introducing halogens into the argyrodite structure ($Li_{6-x}PS_{5-x}$(Cl, Br, I)$_{1+x}$) increases the Li vacancies and leads to higher conductivity [1]. Additionally, Li-ion conductivity can be tailored by changing the rate of disorder in the anionic crystal sublattice of argyrodite S_2^{-}/ X^{-} (X =Cl, Br and I) caused by synthetic conditions. For Li_6PS_5Br, it has been experimentally shown that rapid cooling (i.e., quenching) of the sample during synthesis enables higher site disorder and leads to a higher ionic conductivity as shown by impedance spectroscopy in comparison to the sample cooled slowly [2]. A higher activation barrier for quenching samples has also been depicted by impedance spectroscopy and nuclear magnetic resonance (NMR). To investigate the mechanism of increasing Li-ion diffusivity and activation barrier correlated with site disorder between the anions S_2^{-} and Br^{-}, we perform ab-initio molecular dynamics (AIMD) on a range of Li_6PS_5Br argyrodite structures with different rates of site disorder and halide content. In the argyrodite structure, Li is distributed over the 48h Wyckoff positions; six pairs of 48h sites surround the 4c site introducing a cage-like structure. Three types of Li-ion jumps were identified by AIMD: doublet, intracage, and intercage, confirmed by published data [1]. Doublet jumps occur between 48h sites, intracage jumps take place between the 48h pairs with longer distances within the cage, and intercage jumps occur between the cages contributing to macroscopic diffusion of Li-ion. AIMD indicates that structures with a low rate of site disorder display only local mobility as high-Li-ion density regions reflect mostly doublet and intracage jumps; there is no connection between the individual Li^+ cages. With increasing site disorder, high-Li-ion density regions become more connected to neighboring cages explaining the higher rate of macroscopic Li-ion diffusion. The analysis of high-Li-ion density regions suggests the existence of an intermediate site located between the cages. Higher Li occupation on this site with increasing site disorder is considered to improve the macroscopic diffusion of Li. We measure jump diffusivity, quantifying the effective jumps contributing to macroscopic diffusion rather than local exchange. This is key in explaining NMR observation. Additionally, we discussed the effect of halide content increase ($Li_{6-x}PS_{5-x}Br_{1+x}$), providing more insights into the mechanism of Li diffusion in argyrodites with site disorder.

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P24. Domain-Limited Laminar Lithium Deposition Behavior Mediated by the Design of Hybrid Anode for Sulfide-Based All-Solid-State Batteries

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Notorious anode/electrolyte interface deteriorations including lithium dendrites hamper the commercialization of all-solid-state Li metal batteries (ASSLMBs). Herein, a three-dimensional hybrid anode (denoted as LiSnC) composed of LiC_6, $Li_{22}Sn_5$, and Li metal is proposed for sulfide-based solid-state batteries. LiC_6 particles construct a cross-linked skeleton inside the anode to ensure constant contact with sulfide electrolyte and lower local current density for uniform Li plating/stripping. Extensively dispersed $Li_{22}Sn_5$ inside the anode facilitates the facile diffusion of Li^+. The collaboration between LiC_6 and $Li_{22}Sn_5$ expands the electrochemical reaction area to the whole bulk, preventing interface deterioration due to sluggish Li^+ transport. Density functional theory (DFT) calculations and experimental tests also confirm the superiority of $Li_{22}Sn_5$ in guaranteeing the layerby-layer deposition of Li. Consequently, the LiSnC||Li_6PS_5Cl||LiSnC symmetric cell displays a long lifespan of 400 h at 0.5 mA cm^{-2}. And the

LiSnC||Li_6PS_5Cl||Li_2ZrF_6@$LiNi_{0.9}Co_{0.05}Mn_{0.05}O_2$ cell also achieves a high-capacity retention of 93.6% after 50 cycles at 0.1C, demonstrating the excellent compatibility of LiSnC anode towards Li_6PS_5Cl electrolyte. This work provides guidelines for designing composite metal anodes to establish a dynamically stable anode/electrolyte interface in ASSLMBs.

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P25. Designing a Li-N-H Based Solid Electrolyte

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All-solid-state-batteries (ASSBs) have long promised to be the next-generation of high-performance energy storage device, with a step-change in energy density, stability and cell safety touted as potential advantages compared to conventional Li-ion battery cells.[1] To realise commercially viable ASSBs, suitable solid electrolyte materials must first be found that adhere to a number of strict performance requirements. This includes possessing a high ionic conductivity (> 10^{-4} Scm^{-1}), wide electrochemical stability window (> 3 V), and the material forming low resistance interfaces in contact with lithium metal that are stable over long-term battery cycling conditions. [1,2] To date, numerous materials with different structure types have been proposed for this application, however significant challenges remain with the leading candidates. Complex metal hydrides, in particular BH_4^--derived materials, have gained recent attention due to their high Li-ion conductivities and wide voltage stability windows with respect to lithium metal.[3] Nitrogen-based complex hydrides, such as materials within the Li-N-H system, have largely been studied as solid-state hydrogen stores. However, a key characteristic that links the impressive properties of the Li-N-H system in this application is the high Frenkel defect-based Li-ion conductivity, which facilitates the formation of several anti-fluorite structured solid solutions. [4,5] We herein exhibit the first demonstration of an anti-fluorite structured Li-N-H material as a functioning solid electrolyte. Lithium imide (Li_2NH) and stoichiometries close to this compound, display high room temperature Li-ion conductivity (> 10^{-3} Scm^{-1}), wide electrochemical stability windows (> 5 V), conductive interface formation with lithium metal, and excellent stability under high current conditions. Through simple stoichiometric control we demonstrate the ability to tailor the conductivity of these materials between ionic insulator and superionic conductor. This highlights the exceptional tunability of these materials, with the capability to accommodate numerous anions (including but not limited to: Cl^-, Br^-, I^-, H^-, N^{3-}, NH^{2-}, NH_2^-) within the same anti-fluorite structure. Ultimately, these results identify disordered anti-fluorite Li-N-H materials as an exciting avenue of research for solid electrolyte application that is yet to be fully explored.

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P26. $Li_{0.3}La_{0.57}Ti_{1-x}V_xO_3$ vanadium doped to improve electrochemical performance as a solid electrolyte in lithium-ion batteries.

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All-solid-state Li-ion batteries (ASSB) are one of the future alternatives for electrochemical energy storage, because it improves energy density and safety. The solid electrolyte in the ASSB is a key element to improve the stability and reduce the flammability of lithium batteries [1-3]. Nevertheless, ASSBs industrial and commercial development have some challenges associated with the lower li-ion conductivity of solid electrolytes $1.0x10^{-4}$S cm^{-1} than liquid electrolytes $1.0x10^{-2}$S cm^{-1}, as well as high interfacial resistance due to the poor contact and interfacial reactions between the solid electrolyte and active materials. Although the $Li_{0.34}La_{0.51}TiO_{2.94}$ perovskite (ABO_3) shows high chemical stability, high bulk ionic conductivity ($1.0x10^{-3}$S cm^{-1}), the total ionic conductivity is lower ($1.96x10^{-3}$ S cm^{-1}) because of the grain boundary resistance, which reduces the Li^+ transport [4]. Doping the B site of the perovskite structure with cations of smaller ionic radius is an alternative to decrease the interatomic bonding forces and improve the lithium conductivity [5]. In this work, we present the synthesis of the material $Li_{0.3}La_{0.57}Ti_{1-x}V_xO_3$(x=0-0 .05) using the sol-gel method, thermal treated at 900 °C for 12 hours and sintered at high temperature (1200 °C) for 12 hours, for solid electrolyte of potential use in Li-ion batteries. The physicochemical characterization of the materials was performed by: TGA, DSC, Raman, XRD and SEM coupled to an EDS, while the electrochemical characterization was performed electrochemical impedance spectroscopy and chronoamperometry. The Raman spectra and XRD patterns indicate the perovskite structure formation in the orthorhombic crystal system of all compositions of materials $Li_{0.3}La_{0.57}Ti_{1-x}V_xO_3$(x=0-0 .05), showing lower lattice parameters with vanadium doping, which can be attributed to the V^{+5} substitution, which has an ionic radius (0.54 Å), lower than Ti^{+5} (0.605 Å) in B cation of perovskite structure. Vanadium-free $Li_{0.3}La_{0.57}TiO_3$ solid electrolyte exhibits the highest total ionic conductivity $4.54x10^{-3}$S cm^{-1}, and $Li_{0.3}La_{0.57}Ti_{0.98}V_{0.02}O_3$ exhibits the high grain conductivity ($7.43x10^{-4}$S cm^{-1}). All solid electrolytes exhibit electron conductivities with magnitude 10^{-8}S cm^{-1} required for the application of solid electrolytes in all-solid batteries.

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P27. Visualizing and Evaluating Microstructures of Composite Cathodes for All-Solid-State Batteries

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Recent advancements in the field of solid ion conductors have led to increased attention for all-solid-state batteries (ASSBs), which promise to have high energy and power densities. However, these batteries require efficient and short ionic and electronic transport pathways in the composite cathodes, as particles that are isolated electronically or ionically cannot contribute to the charging or discharging process. This presents a significant challenge for microstructures of ASSB cathodes, as they rely solely on solidto-solid contacts.

In this study, we aimed to optimize the microstructure of composite cathodes composed of an intercalation type active material and a thiophosphate based solid electrolyte. We varied the particle size distribution of the solid electrolyte to create different cathode microstructures and evaluated the effectiveness of the electronic and ionic conduction pathways using partial conductivities. We used both electronically and ionically blocking electrodes for electrochemical impedance spectroscopy measurements to quantify the respective partial conductivities. Our analysis revealed that the particle size of the solid electrolyte significantly influenced the charge transport and electrochemical performance of the cathodes. Additionally, we generated detailed 3D reconstructions of the cathode microstructure using FIB-SEM tomography and were able to correlate the obtained partial conductivities to microstructural descriptors such as tortuosity factors and determine possible kinetic bottlenecks. We found that residual porosity that blocks charge transport of ions and electrons must be minimized to optimize cathode microstructures and improve ASSB performance.

Our study highlights the importance of optimizing cathode microstructures for the improvement of all-solid-state batteries. By manipulating the particle size distribution of the solid electrolyte, we were able to achieve more efficient electronic and ionic transport pathways, leading to improved battery performance.

P28. Development, Manufacturing and Advanced Characterization of Solid Electrolytes for Polymer-Based Lithium Solid-State Batteries

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In the presented study, solid electrolytes are developed, manufactured and investigated regarding the use as component for polymer-based solid-state batteries. In general, depending on the specific chosen polymer, polymer electrolytes show lower electrochemical stability and insufficient ionic conductivity at room temperature, compared to other solid electrolytes. These properties can be significantly improved by modifying the polymer or the addition of ceramic particles. Both the mechanical stability and flexibility as well as their good and scalable production are benefits for their use in solid-state batteries.

As a passive cell component, the solid-state electrolyte is designed to electrically separate the two electrodes and prevent short circuits while allowing the exchange of ions. For reducing the inactive battery components weight and the interfacial resistance, as well as enhancing the cell's energy density, the thickness of this separator layer should be as thin as possible. Manufacturing solid-state electrolytes by using DIW ensures thin layers with a well-defined structure and homogenous distribution of materials. The process-property relationships are then comprehensively characterized.

The properties of the polymer electrolytes are further characterized by electrochemical methods such as impedance spectroscopy and galvanic cycling but also by advanced operando techniques. The modification of the polymer electrolyte, e.g. cross-linking of the polymer to enhance the mechanical stability at operation temperature, and process dependent parameters like thickness and homogeneity of the electrolyte show impact on their properties and behavior. during battery cycling. Furthermore, mechanical modifications or harmful side reactions are undesirable aging effects that can occur during cycling. These phenomena negatively influence the safety properties and cell performance and consequently limit cycling stability. The analytical operando method enables a deep insight into aging effects that occur.

Furthermore, lowering the interfacial resistance is targeted by optimizing the cell configuration. Therefore, different methods are applied to combine the cell components, electrodes and electrolyte, in an improved way to enhance both cycle stability and aging behavior.

P29. Solid State Battery using LISICON and Garnet electrolytes with Greensheet Technique

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One of the important issue for all solid state battery is interface construction having electrochemical compatibility between solid electrolyte (oxide) and cathode/anode materials. From the previous studies [1, 2], it was found that the layered rock-salt oxides (cathode) has good compatibility to LISICON compound, $Li_{3.5}Ge_{0.5}V_{0.5}O_4$. Green sheet process is proposed in this study, where the cathode/electrolyte stacking layers were prepared by tape casting, stacking and sintering. And the laminated cathode/electrolyte composites were evaluated with half-cell configuration using polymer electrolyte on Li anode side.

In the experiment at 333K and 0.01C current density, the laminated cathode/electrolyte composites exhibit the show the charge-discharge profiles, which were almost same as those of the cathodes in the ordinary liquid electrolyte battery. The areal capacity almost linearly increased with the cathode particle loading and reached about ~1.2mAhcm^{-2}. However, the capacity fading was observed in case of high-Ni compound cathode. It was thought to be attributed to large lattice contraction/expansion during the Li-extraction/insertion, which was also analyzed with use of operand XRD method.

Li ionic conductivity of the LISICON electrolyte is less than ~10^{-4}Scm, which is lower than that of the ordinary liquid electrolyte. For the advancement, solid electrolyte having much higher ionic conductivity, such as garnet, should be introduced. Considering thermal compatibility of garnet and cathode materials, solid electrolyte particles, garnet core and LISICON shell, were specially designed and utilized as the electrolyte in the laminated composites. Their charge-discharge experiments are being carried out, and the results will be presented at the conference.

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P30. Standardized Processing, Measuring and automated Evaluation of Solid Electrolyte Impedance Data for Reliable Characterization of Solid Electrolytes

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Lithium-ion batteries predominantly employ liquid electrolytes with disadvantages in terms of flammability and toxicity. Currently, great efforts focus on the development of inorganic and polymeric solid electrolytes, potentially all-solid-state batteries are also the target technology of new and established players on the battery market. However, commercial viability has still not been achieved. The further development and optimisation of solid electrolytes has a fundamental issue at the electrochemical characterisation level. Namely, the absence of standardized protocols in sample preparation (e.g. processing pressures and electrode contacting), test cells, measuring and evaluation procedures. As one consequence, the determination of the ionic conductivity is prone to large experimental uncertainty, even for nominally identical samples. This has recently been shown in an extensive round-robin study using inorganic halide argyrodite solid electrolyte samples.[1] On the other hand, it has also been shown in a case-study using ceramic oxide-based electrolytes, that harmonized procedures can lead to more reproducible results.[2] Sample fabrication procedures and the applied pressure during the measurement were also identified as playing a major role in the resulting ionic conductivities of the samples.[3] A survey of recent literature conducted in this project yields intriguing insights into the current situation: Publications on solid electrolyte characterization in many cases fall short on reporting experimental conditions like pressure during the measurement, sample thickness and temperature. Further, there is a broad range of contacting methods, cell designs and impedance procedures. In order to improve the reliability of ionic conductivity determination, there is a need for standardized sample preparation methods, measuring procedures, specialized hardware and evaluation software. Within the STAMPF project, we aim to identify optimized measuring and preparation conditions for sulfide, oxide, and polymer electrolytes as major material classes. Screening conditions include pre-processing pressure, contact materials, pressure during measurement, temperature, and AC amplitude as well as different cell designs. The experimental work is complemented by software development for automatic impedance analysis for the determination of the ionic conductivity of the samples. We would like to acknowledge the funding by the German Federal Ministry for Research and Education (BMBF) under reference numbers 03ET6155A and 13XP0497B.

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P31. Integrating *In Situ* X-Ray Tomography and Computational Analysis to Investigate Buried Electrode/Electrolyte Interfaces in Solid-State Lithium Batteries

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As the need for a clean and viable environment is growing, the development of energy storage systems is becoming increasingly important. Among the various energy storage systems, solid-state batteries using lithium metal has become an attractive option due to its potential to improve safety and energy density. Therefore, this technology can essentially be used in electric vehicles, consumer electronics, and other applications where reliable, long-lasting energy storage is needed [1,2]. However, the potential of lithium metal batteries is still not fully explored due to their intrinsic complexity: the structure, components, and chemistry of lithium metal batteries are highly correlated, making it difficult to gain in-depth understanding. Moreover, the interfaces, which are critical to the performance of solid-state lithium batteries, are buried throughout the battery stack and therefore inaccessible to conventional analysis techniques. The recent development of advanced 3D X-ray computed tomography (XCT) holds the promise to offer unprecedented insight into the internal operation of lithium metal batteries, as the technique enables non-invasive *in situ* and *operando* studies [3]. XCT is not only helpful in extracting hidden microstructural features of the battery but also can be utilised in combination with numerical modelling. The present research employs *in situ* XCT to investigate the buried lithium/solid polymer electrolyte interface while performing a galvanostatic test at different current densities in a purpose-built cell setup with optimized cell stack pressure. The dedicated cell setup, which is highly compatible with the microXCT imaging and electrochemical testing, successfully provides highly resolved and high signal-to-noise ratio 3D tomographic datasets at different stages of cycling. The datasets were filtered and subsequently segmented into morphologically distinct phases. In parallel, a digital twin of the cell was subjected to the same galvanostatic cycling protocol. By fusing the data from model and experiment, we obtain a unique view on the microstructural changes along the buried interfaces during cycling, the locally produced heat by the electrochemical reactions, the volume changes of each phase, and the local stress state induced by differential volumetric changes. These results are also supported by post-cycling examination with techniques as XPS to get detailed chemical information. We believe that the proposed approach will help to gain in-depth understanding of interfacial changes over prolonged cell cycling. By gaining deep understanding of the structure and chemistry aging of these lithium metal batteries, we believe it is possible to improve them and thus to make a significant contribution towards sustainable energy solutions.

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P32. CO_2 Reactive Laser Sintering of Garnet-type Li-ion Conductors

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In contrast to currently commercialized Li-ion batteries (LIBs), the most promising all-solid-state Li-ion battery (ASSLB) technology, with the integration of solid-state electrolytes (SSEs), has the potential to provide higher energy density, better safety, and longer cycle life. Over the decades, significant progress has been made for ASSBs by the development and optimization of SSEs that can provide efficient Li-ion conduction while mitigating the problems of leakage and high flammability associated with organic liquid electrolytes. The replacement of liquid electrolytes with safer, more reliable SSEs simplifies the battery design, alleviates safety concerns, and improves battery performance. Among the different developed chemistries of inorganic SSEs, e.g., sulfides and halides, oxides are considered promising SSE candidates for ASSLBs due to their chemical stability and ionic transport properties. Particularly, the garnet-like Li-ion conductive oxide $Li_{6.4}La_3Z_{1.4}Ta_{0.6}O_{12}$ (LLZTO) is one of the most promising SSEs due to its excellent chemical stability against lithium metal, high lithium ion conductivity (10^{-3} S/cm at 25°C) and wide electrochemical window (5.6 V vs. Li^+/Li). ASSLBs are difficult to process by traditional manufacturing strategies due to the brittleness of SSE ceramic materials, poor solid-solid contact (SSE/electrodes), and electrolyte-electrode stability issues; as a result, battery performance is far from ideal. Currently used SSEs manufacturing processes such as high temperature sintering and mechanical milling have a number of limitations including being time intensive, energy consuming, and difficult to scale up. In contrast, reactive laser sintering, an additive manufacturing (3D printing) technique that uses a laser as the power source, has drawn increasing attention due to its speed, cost, simplicity, and capability of achieving one-step manufacturing of materials with desirable properties that are difficult to achieve by conventional processes. Herein, we utilized the promising reactive CO_2 laser sintering technology to synthesize the LLZTO SSE in one-step process. The CO_2 laser sintering approach has been previously used for fuel cell applications; however, this is the first time that this technology is used to manufacture solid-state lithium-ion conductors. During the reactive laser synthesis of LLZTO SSE, the precursor mixture absorbs the laser energy directly, which leads to a rapid increase in temperature that accelerates the reaction and densification while reducing Li loss. A benefit of the inherent nature of ultrafast heating/cooling rates of reactive laser technology is the formation of non-stoichiometric materials with high concentration of defects. Allowing the development of highly disordered superionic conductive SSEs to enable high discharge/charge rate capabilities in ASSLBs. Our work successfully demonstrates that the cubic LLZTO phase, which has a high ionic conductivity (10^{-4} S/cm), can be formed using the CO_2 laser reactive sintering approach. The simplified processing steps dramatically reduce the processing cost and the production time of the promising LLZTO SSE, making it an ideal synthesis technique for large-scale battery manufacturing market.

P33. Impedance Analysis of Hybrid Polymer-Ceramic Solid-State Electrolytes for Sodium Batteries

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Sodium-ion batteries are extensively explored as an alternative or complementary option to lithium-ion batteries (LIB). Analogous to its lithium counterpart solid-state sodium batteries are researched as next-generation batteries because they could offer some advantages. These advantages may include an increased safety due to the absence of easily flammable liquid compounds and an increased thermal stability window of the electrolyte. In addition, the usage of a sodium-metal anode offers an increased specific energy and energy density, respectively. Different classes of solid-state electrolytes exist, i. e. solid polymer electrolytes (SPE) or inorganic solid electrolytes (ISE), each with their own advantages and disadvantages. While the flexible SPE offer a good contact to the electrode materials and are quite cost-effective (facile production, inexpensive raw materials), they severely lack in ionic conductivities at ambient temperatures. Additionally, their low tensile strength enables dendritic sodium-metal to penetrate the electrolyte and as a result cause an internal short circuit. [1] ISE on the other hand offer good ionic conductivities even at ambient temperatures and a very high tensile strength. However, their rigidity makes it difficult to achieve a good contact with the electrodes without a high stack-pressure. The high temperatures that are needed to manufacture them into dense pellets is another drawback concerning their large-scale production. [2] To overcome the disadvantages of each class of solid-state electrolyte research has been conducted into hybrid concepts comprising both inorganic and polymeric phases. [1, 2] One approach is to disperse the ISE as fine particles inside the polymer matrix, i.e. to increase the ionic conductivity and mechanical strength of the

SPE. A topic of interest in these hybrid electrolytes is the interface between ISE and SPE and its effect on the charge transport inside the electrolyte. In this work we introduced fine particles of a NASICON-ceramic inside a crosslinked PEO-based SPE and evaluated the electrolyte properties depending on the amount of ceramic filler material and particle size. Via EIS we measured the temperature dependent ionic conductivity, paying special attention to charge transport inside the electrolyte.

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P34. Spatially-Resolved Operando Stress Mapping in Solid-State Batteries Using Synchrotron X-Ray Diffraction

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Solid-state batteries[1] (SSBs) have the potential to become the next generation of high-power density batteries for electromobility. Since electron and ion transport pathways must be maintained throughout battery life, sustained mechanical pressure must be applied to the battery stack to ensure intimate contact with all active materials. However, during battery cycling, volumetric changes in the cathode and anode materials result in localized "hot spots" of increased stress concentrations that, if not properly managed, can lead to irreversible changes in the physical contact between the active materials and ultimately to premature battery failure. To address these shortcomings, a tailored battery engineering approach based on knowledge and design of the local stress distribution after battery assembly and during cycling must be applied. Electrochemical dilatometry is the most widely used method for tracking averaged stress variations. However, this technique cannot capture the local stress changes at the micrometer scale. Here we present spatially resolved stress mapping using high-energy wide-angle X-ray diffraction. This technique allows real-time observation of the spatial stress distribution across the individual layers of SSBs during cycling. To validate this method, we present stress measurements in an SSB model based on NCA as the cathode material, LSPS as the solid-state electrolyte, and Li-metal as the anode.

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P35. Ga_2S_3 as Redox-Active Material in Solid-State Batteries

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Current Li-ion batteries offer volume and mass energy densities of up to 770 Wh/l and 265 Wh/g, respectively. These parameters do not currently meet the demand for storing large amounts of electric energy. For this reason, new battery concepts are being developed intensively in order to increase energy density. One candidate for realistic advancements is the solid-state battery (SSB) concept, offering higher energy and power density. Solid electrolytes are more stable at higher temperatures, do not dissolve active materials, allow very fast charging without electrolyte polarization as well as can be used with metal lithium [1]. Charging and discharging of Li-ion batteries is accompanied by severe volume changes of redox-active materials. While for batteries with liquid electrolytes this appears to be less critical, for SSBs it is even more detrimental when using metal lithium. The relatively large volume changes lead to solid electrolyte interphase damage and active lithium loss, resulting in irreversible capacity fading [2, 3]. Gallium-based materials, including gallium sulfide, gallium oxide, gallium selenide, pure gallium, and its alloys, are redox-active materials suitable for Li-ion and Na-ion storage. Dual charge storage mechanism consists of conversion reaction and alloying, which lead to high theoretical capacity. Elemental Ga as an intermediate has a melting point close to ambient temperature, which leads to specific behavior of the battery during charging and discharging. Liquid gallium promotes enhanced ion diffusion, alleviates volume changes, and can recover contacts between electrode components during cycling, thereby guaranteeing superior cycling stability [4].

In our research, we focused on the fundamental electrochemical characterization of Ga_2S_3 as redox-active materials in SSB at 25 °C and 35 °C. Also, we examined different strategies to utilize stack pressure with the goal of reducing capacity fading. We present here a pioneering work in the field of using gallium sulfide as an active material in SSB.

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P36. In-Situ XRD Measurement for $LiCoO_2$ Under High-Voltage Charging

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$LiCoO_2$ is the first cathode material employed in lithium-ion batteries. Although it has been used in lithium-ion batteries since their birth, efforts to improve its performance are still in progress. For example, complete use of lithium in $LiCoO_2$ provides a theoretical capacity as high as 274 mAh g^{-1}; however, charge-discharge cycling with such a high capacity leads to rapid capacity fading, and thus the practical capacity has been limited to ca. 160 mAh g^{-1}. The capacity fading mechanism has been intensively studied for increasing the practical capacity. Phase transitions taking place in high-voltage charging have been considered to affect the cycling performance; however, influence of the phase transitions on the cycling performance has not been clarified, because side reactions induced by the high-voltage charging always overlap to blur the influence of phase transitions on the electrode properties.

This study aims at unveiling the relation between the phase transition and electrode properties by employing a solid electrolyte to eliminate the effects of side reactions. Electrochemical impedance spectroscopy is combined with in-situ X-ray diffraction to reveal the correlation between phase transition and electrode properties. The electrode resistance starts to increase rapidly, when diffractions from H1-3 phase [1] appears with those from the original O3 phase in the diffraction pattern, which suggests that formation of narrow interlayers with gallery height of 4.2 Å in the H1-3 phase impedes lithium-ion diffusion to increase the electrode resistance. In addition, the electrode resistance does not come back to the initial value, even when the electrode is discharged completely. The large change in the gallery height in the transformation between the O3 and H13 phases during the high-voltage charging is considered to destroy the diffusion paths in solids and limit reversible capacity of $LiCoO_2$ [2].

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P37. Understanding of the Liquid-Phase Syntheses of $Li_7P_3S_{11}$ Sulfide Electrolyte

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All solid-state lithium-ion batteries have recently gained significant importance due to the high energy density and safer operating conditions that they offer, as compared to liquid electrolyte batteries. $Li_7P_3S_{11}$ is a promising solid-state electrolyte (SSE) with high conductivity (upwards of 1.5 mS cm^{-1} [1]) and a lower production cost than that of other SSEs. While $Li_7P_3S_{11}$ may be synthesized via solid-phase or liquid-phase process, the latter is preferential due to low processing temperatures, shorter processing times, and the increased controllability of particle size and morphology. Even though the liquid-phase process of $Li_7P_3S_{11}$ is advantageous over the solid-phase process, the understanding of the reaction mechanism is still uncertain under various conditions. It has been shown that by combining precursors in various stoichiometric ratios and various solvents, distinct products will be formed [1]. A liquid-phase process using Li_2S and P_2S_5 with a 74:26 molar stoichiometry, respectively, in acetonitrile was reported to generate $Li_7P_3S_{11}$ with an ionic conductivity of 1.0×10^{-3} S cm^{-1} at 22 ºC [2]. The same precursors in a 50:50 molar stoichiometric ratio in acetonitrile lead to a $Li_2P_2S_7$ phase, identified as an intermedium product for the further preparation of Li_3PS_4 or $Li_7P_3S_{11}$[3]. The reaction mechanism of the liquid-phase process is strongly influenced by involved solvents and their precursor interactions. Here, we summarize the mechanism involved in the liquid-phase synthesis of $Li_7P_3S_{11}$ and compare it with different organic solvents and lithium precursors in terms of crystal phase, structure, morphology and ionic conduction properties.

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P38. Co-Sintered Solid-State Batteries based on Li-Stuffed Garnet Electrolytes

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The Li-stuffed garnet-typed $Li_7La_3Zr_2O_{12}$ (LLZ)[1] is a promising candidate for the solid electrolyte of solid-state battery. Since LLZ exhibits a high Li-ion conductivity of ~10^{-3} S/cm at 25 °C and high chemical stability against Li metal anode, which has a high capacity, LLZ has high potential as the electrolyte for Li-metal battery. Therefore, many LLZ series were actively researched last decade.

The most challenging issue for realizing the co-sintered solid-state Li-metal battery is lowering the sintering temperature of LLZ. Recently, we reported the self-formed liquid phase sintering based on Bi-substitution for the 16a site[2] and the deviation from the ideal chemical composition[3]. We have demonstrated that the self-formed Bi-related liquid phase promotes the sintering of $Li_6La_3ZrTa_{0.8}Bi_{0.2}O_{12}$ (LLZTB), resulting in the densification of LLZ at the temperature range from 775 °C to 950 °C without applying the pressure. Moreover, we have successfully demonstrated the co-sintering LLZTB and $LiCoO_2$ with low interfacial resistance. However, LLZTB was easily reduced by Li metal. Thus, in this paper, we aimed to develop LLZTB with both high sinterability and high stability against Li. We investigated the effect of Ta content in $Li_6La_3Zr_{1.8-x}Ta_xBi_{0.2}O_{12}$ on the conductivity, sinterability, and stability against Li metal. We especially focused on the grain boundary phase to enhance the stability against Li metal. In addition, we also demonstrated the co-sintered solid-state battery, which can operate at room temperature.

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P39. Understanding The Evolution of Lithium Dendrites in $Li_{6.25}Al_{0.25}La_3Zr_2O_{12}$ by Interpreting Operando kpfm Measurements

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Lithium dendrite growth is a major drawback hindering the development of reliable all-solid-state lithium metal batteries based on inorganic solid electrolytes. These dendrites are often found at the grain boundaries of the solid electrolyte, as observed by ex situ postmortem measurements of battery components.[1] However, it is not fully understood how grain boundaries facilitate lithium dendrite growth in the first place. [2,3] To understand the origin of dendrite growth, we performed operando Kelvin Probe Force Microscopy (KPFM) measurements on a $Li_{6.25}Al_{0.25}La_3Zr_2O_{12}$ garnet-type solid electrolyte during cycling of a symmetric cell. We show that KPFM maps the Galvani potential (inner electrostatic potential) of the solid electrolyte during operation. We measured a drop in the Galvani potential at the grain boundaries close to the lithium metal electrode during plating, and we attribute the Galvani potential drop to a preferential accumulation of electrons at the grain boundaries. The results of time resolved electrostatic force microscopy measurements and electron injection experiments by electron beam irradiation support this finding. Based on these results, we explain how the conductivity properties of grain boundaries compared to the bulk [4] lead to the preferential growth of lithium dendrites at grain boundaries.[5]

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P40. Manufacturing and Co-Sintering of Li-Garnet-Electrolyte Tapes for Li Metal Batteries

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Garnet-type $Li_7La_3Zr_2O_{12}$ (LLZO) with its competitive ionic conductivity (~ 1 mS/cm), wide electrochemical stability (above 5.0 V vs. Li/Li^+), and compatibility with Li-metal, is a promising electrolyte for solid-state Li-metal batteries.[1] However, fabricating a full battery cell with a high energy density remains a challenge mainly due to the processing difficulties with the co-sintering of composite solid-solid cathode/electrolyte while maintaining thin electrolyte thicknesses of the tape around 20 µm. In this project, we investigate the scalable fabrication from powders towards a cathode/electrolyte half- and full-cell with $LiCoO_2$ as the active material and LLZO as the ion conducting electrolyte phase, combined with a Li-metal anode. Gradient composite cathodes can dramatically improve the battery performance due to high cathode active material loadings and good ionic and electronic conductivity through the cathode.[2] To manufacture a cell with low interfacial resistance, it is important to prevent secondary phase formation between $LiCoO_2$ and LLZO during conventional high temperature co-sintering. We find that minor addition of Al- and Ta- oxide co-doping of 0.05 and 0.4 stoichiometric amounts to LLZO chemistry stops Co interface-diffusion at high temperatures of 1050 ^{o}C. Additionally, synergistic effects of the co-doping and tailoring of the LLZO characteristics lead to high ionic conductivities up to 0.85 mS/cm and high theoretical densities of up to 97% in pellets, enabling the comparison of properties between pellets and tapes. Furthermore, we demonstrate the fabrication of a co-sintered half-cells with a 100 µm gradient composite cathode and a 30 µm electrolyte via free-standing tapes. To accomplish such a cell-design, we reveal the importance of controlling various synthesis parameters such as initial particle size distributions, mixing specifications, and co-sinter conditions. Our findings are important steps towards the ceramic manufacturing strategies for energy-dense, high-quality tape-based all-solid-state batteries, which have so far, the highest potential for upscaling and also in terms of area width an important aspect when considering integration of solid-state battery ceramic components to automotive applications.

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P41. Fe-S Conversion Electrodes in Sulfide-Based Solid-State Batteries

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Sulfide-based conversion cathodes provide a promising path towards realizing high energy density batteries. In particular, there is growing interest in rechargeable solid-state FeS_2 batteries due its high specific capacity (894 mAh g^{-1}), earth abundance, and versatility as a rechargeable cathode (Li^+, Na^+, K^+).[1-3] While transitioning to a solid-state system circumvents the key issue of polysulfide shuttling observed in the liquid electrolyte counterpart, solid-state FeS_2 batteries still undergoes capacity fade highlighting the need to better understand the different degradation mechanisms that arise when introducing solid electrolytes. Moreover, the formation of multiple products with drastically different electronic properties upon lithiation (Fe^0 and Li_2S) and de-lithiation (S_8 and FeS_x $1 \leq x \leq 2$) points toward the critical role of the electrochemically formed microstructure in maintaining the reversible redox activity of FeS_2. Lastly, understanding how the interface between the various redox active products and solid electrolyte evolve upon cycling is critical to developing strategies to improve the electrochemical performance of solid-state FeS_2 batteries.

The work presented seeks to provide an in-depth analysis of the influence of the starting microstructure formed during the irreversible initial lithiation on the electrochemical performance of argyrodite-based solid state FeS_2 batteries.

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P42. Computational Analysis of a Promising Earth Abundant, Stable, Lithium Solid Electrolyte

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Solid state electrolytes offer the potential to drastically increase the overall stability of rechargeable lithium batteries as well as provide the means to realise the use of Li-metal anodes maximising the charge capacity of a device. At present, batteries use liquid electrolytes such as $[LiPF_6]^-$ which although they possess high ionic conductivities of $1x10^{-2}$ S cm^{-1} limit the safe temperature ranges a battery can be operated at as well as forbidding the use of Li-metal anodes due to dendrite formation leading to short circuiting and "thermal runaway". Solid electrolytes such as the Li-rich garnet materials, LLZO, or anti-perovskites, Li_3OCl, have demonstrated low migration barriers (<0.3 eV), however issues arise regarding stability or a competing lower conductivity phase. In this work, we have identified a promising Earth-abundant, nontoxic, stable Li-solid electrolyte. Using a combination of density functional theory and experiment, we show that this material possesses thermodynamic, dynamic and electrochemical stability, ideal defect chemistry and low migration barriers leading to undoped conductivities of $\sim 10^{-5}$ S cm^{-1} which are expected to rise to at least 10^{-3} S cm^1 with minimal doping.

P43. Processing and Characterization of Li_6PS_5Cl Tapes for Solid-State Batteries

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In the field of energy storage, all-solid-state batteries (ASSBs) arise as an attractive substitute for traditional liquid electrolyte lithium-ion batteries, offering improved safety along with higher power and energy densities.[1-3] Yet, the exploration of ASSBs has primarily focused on dry blending methods, which are impeded by issues of scalability and the tendency of active particles to aggregate within composite electrodes, ultimately impacting overall efficiency. This highlights limitations in achieving mass production and uniform component distribution in ASSBs through dry mixing processes.[1-2] This research presents a structured exploration of ASSBs , produced using a solution-based slurry casting technique involving Li_6PS_5Cl as the solid electrolyte and a high-voltage cathode, $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ (NMC811). The optimized ratio of binder to solid electrolyte was achieved by systematically assessing various binder compositions ranging from 2.5 wt.% to 10 wt.%. The influence of binder weight proportion on ionic conductivity of solid electrolyte and cycling performance of SSBs was investigated using electrochemical impedance spectroscopy measurements. The subsequent step involves creating monolayer pouch cells using solid electrolyte tapes, lithium-indium or $Li_4Ti_5O_{12}$ as the anode, while NMC811 as cathode. X-ray tomography images of these tapes show higher binder volume, irregular particle size distribution, and lower active material in the tape indicating potential tape quality improvement. The research optimizes active material ratio from 50% to 70%, reduces binder content from 2.5% to 1%, and achieves optimal particle size distribution between cathode and solid electrolyte particles for achieving best performance. Cells further undergo comprehensive electrochemical assessments via galvanostatic cycling under varying environmental conditions.

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P44. Li_3InCl_6-Coated High-Voltage Cathodes for Thiophosphate-Based Solid-State Li Batteries

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Solid-state Li batteries are pursued as potentially safe and stable high-energy storage systems. However, key issues remain unsolved, impeding the practical realization.[1] One of the fundamental reasons for the failure of these batteries is likely the instability of solid-state electrolytes, such as Li_6PS_5Cl, towards high voltage cathodes. To mitigate the interface instability issues coating materials that prevent the decomposition of the solid-state electrolytes without limiting the ionic transport across them are thus urgently warranted.[2,3] Halides have been shown to have excellent high voltage stability up to 4.2 V in combination with moderate Li-ion conductivities of the order of magnitude ~10^{-3} S cm^{-1}.[4] Combining the properties of halides with sulfides, hence, could be a promising strategy to enable room temperature solid-state Li batteries. Therefore, we synthesized nano-sized Li_3InCl_6 powder by mechanochemistry achieving a phase purity of about 95 %. Thereafter, Li_3InCl_6 was coated onto micrometer-sized $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (LIC@NCA) cathode particles using mechanofusion technique. The thickness and uniformity of the coating were investigated using FIB-SEM and TEM. The coating thickness has been found to be as thin as several nanometers fully covering the NCA particles. Finally, LIC@NCA particles have been tested in a solid-state Li battery using Li:In-alloy as anode and Li_6PS_5Cl as SSE. Cells with LIC@NCA show a significant improvement in respect of the initial capacity loss and capacity fading compared to the pristine NCA. Protection effect has been studied using operando synchrotron XRD and XPS.

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P45. All Solid-State Sodium Sulfur Batteries: An Insight Analysis on Chemomechanical Behavior of Cathode During Cycling

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Sodium-sulfur batteries are promising for grid energy storage applications thanks to their high theoretical capacity, their abundance in the Earth's crust and raw materials being cost effective. Unfortunately, their practical application is limited by several technical challenges, especially polysulfide shuttling phenomenon and accompanied volume expansion, which can lead to serious capacity degradation.[1] In this case, solid-state sodium-sulfur battery (S4B) can effectively suppress the shuttle phenomenon.[2] However, the poor triple-phase contact among active material, solid electrolytes and electroconductive agent limits the battery performance. During cycling, the complete conversion of one mole S_8 into eight mole Na_2S expands its volume by 260 %, and contracts upon dissociation [1]. This phenomenon causes the chemo-mechanical failure, results in contact lost within the cathode composite and decreases the reversible capacity. In contrast to solid-state Li-S batteries [3,4], the understanding in case of S4B is lacking. In this study, we employed Na_3PS_4 as solid electrolyte due to its acceptable ionic conductivity as well as viable synthesis route. $Na_{15}Sn_4$ is used as anode instead of sodium metal because of higher compatibility of the alloy with sulfide electrolyte. The battery using composite cathode preparing by ball milling achieved the first discharge capacity of 1640 mAh/g and 50 mA/g current density which is close to the theoretical capacity of sulfur. This is owing to the homogeneous distribution of sulfur within the electrode and intimate contact of sulfur, solid electrolyte, and conductive carbon. Upon cycling the chemo-mechanical behavior of S4B has been studied using operando XRD, SAXS, WAXS, and electrochemical dilatometry.

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P46. A Wet-Li_2ZrO_3-Coating Process for $LiNi_{0.8}Co_{0.1}O_2$ for Solid-State Batteries

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All-solid-state batteries have emerged as a promising energy storage technology for the future. They offer the potential for higher energy and power densities, along with enhanced reliability and safety compared to traditional lithium-ion batteries that use liquid electrolytes. However, certain technical hurdles need to be overcome to achieve stable interfaces between the cathode active material and the solid electrolyte, such as Li_6PS_5Cl. In this study, we present a simple wet coating process to address this challenge and enhance the performance of thio-sulfide-based all-solid-state batteries. The process involves applying a uniform and conformal Li_2ZrO_3 coating on $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ cathode particles. To achieve this, zirconium and lithium precursors were added to an ethanol-cathode dispersion, leading to the adsorption of ZrO^{2+} and Li^+ species onto the $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ particles. After solvent evaporation, the resulting precipitate was calcinated. We investigated the effects of different precursor weight percentages, types of precursors, solvent evaporation conditions, and calcination temperatures on the distribution, uniformity, and crystallinity of the coating layers. A range of characterization techniques was employed to analyse the phases, structure, and microstructure of the coated cathode particles. To determine the optimal coating thickness, we tested the coated cathodes in pellet-type all-solid-state batteries. These batteries consisted of a composite cathode (composed of $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$, Li_6PS_5Cl, and conductive carbon in a ratio of 11:16:1), a Li-In alloy anode, and Li_6PS_5Cl as the separator. We evaluated the electrochemical performance of the batteries in terms of initial discharge capacity, capacity retention after 200 cycles, C-rate performance, and cycling stability. Our results revealed that all-solid-state batteries incorporating $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ cathodes with an optimized Li_2ZrO_3 coating thickness of 10 nm exhibited significant improvements. These batteries demonstrated increased specific capacity during the initial discharge (from 125 mAh/g to 149 mAh/g) and enhanced capacity retention from 83% to 98% after 200 cycles. These findings highlight the potential of the proposed coating process to enhance the performance of thio-sulfide-based all-solid-state batteries.

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P47. Free-Standing Composite Polymer Electrolyte for All-Solid-State Lithium Sulfur Battery

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Solid polymer electrolytes (SPE) have attracted much attention in recent times due to their reasonable ionic conductivity (>10^{-5} Scm^{-1} at RT) and wide electrochemical window. The characteristic properties such as Li-ion conductivity and mechanical stability of these electrolytes can be further improved by incorporating active inorganic ceramic fillers such as perovskite, garnets, sulfide electrolytes etc.[1] Garnet–type electrolyte e.g., $Li_7La_3Zr_2O_{12}$ (LLZO) in particular has attained more attention due its high lithium-ion conductivity (~ 10^{-3} Scm^{-1} at RT), wide electrochemical window and high electrochemical stability against metallic lithium.[2] However, contact loss between the individual components in the composite cathode caused by the significant volume changes of the cathode leads to fast capacity fade, which hinders the development of all solid-state batteries. LLZO solid electrolytes can physically block the polysulfide shuttling whilst volume expansion can be accommodated by using highly porous host materials with spatial constrictions such as meso-micro-porous carbons, mwCNT etc. for sulfur cathode.[3] However, to maintain proper electrode-electrolyte contact between the rigid materials during cathode breathing, elastic, highly flexible and Li-ion conducting polymeric materials are highly desirable. Therefore, the combination of polymer and LLZO as a composite solid electrolyte integrated with engineered sulfur cathodes could improve the performance of Li-S battery. In this work we developed a flexible and free–standing composite polymer membrane via tape casting method using PVDF polymer.[4] The as prepared membranes were investigated using a wide range of characterization techniques such as XRD, SEM, TGA-DSC etc. The Li-ion conductivity of the membranes from impedance spectroscopy measurement was calculated to be 3.6×10^{-4} Scm^{-1} and when integrated with sulfur cathode in half cell configuration, exhibited improved cycling performance.

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P48. Dendrites in Solid-State Batteries: Where They Come from and How to Mitigate Them

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To boost the current transformation to low-emission transport and a sustainable energy economy, new electrochemical energy storage solutions are needed for future electrical vehicles and other emerging technologies. Among these solutions, solid-state Li batteries are the most promising concepts due to their high energy and power density. However, to reach the required performance, solid-state Li batteries must reversibly plate a large amount of Li at a high current rate (>5 mA/cm^2) for at least 1000 cycles.[1]

Today, under such conditions, solid-state Li batteries invariably fail due to the formation of Li dendrites that penetrate the solid-state electrolyte and cause a short circuit, which poses major safety and performance concerns.[2] The formation and growth of these dendrites is believed to be driven by stress accumulation stemming from the deposited Li itself. Upon reaching a critical pressure, the solid-state electrolyte starts to crack, which propagates until the cell short-circuits.

On this poster it will be shown that pulsed current waveforms and ion implantation are promising strategies to mitigate the initiation and propagation of Li dendrites. Pulsed current waveforms can be used to increase the current density by a factor of six, reaching values as high as 6.6 mA/cm^2 before forming Li dendrites.[3] Moreover, ion implantation is introduced as a tool to tune the surface-near mechanical properties of $Li_7La_3Zr_2O_{12}$ (LLZO) with the aim to stop Li dendrites by taking away their driving force. This is achieved by generating high compressive residual stresses in the near-surface region of LLZO, up to -750 MPa, which allows the deflection of cracks, with potentially large implications on the ability of LLZO to withstand Li dendrites.[4] Finally, the current mechanism of dendrite propagation should be rethought to consider dislocations which are created by the extremely high pressures at the cracktip during failure.

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P49. Studying Li Anode Formation via Solid-State Hull Cell Architecture

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Understanding solid-state battery technology has become crucial in addressing the growing energy demands. An innovative approach involves anode-less design, where Li metal anodes are formed in situ during the initial charging phase.[1] This approach overcomes production challenges and reduces manufacturing costs, but also demonstrates heightened safety levels, amplified energy density, and prolonged cycle life. However, the anode-less configuration faces challenges due to non-uniform Li metal formation, leading to capacity loss during cycling. To address this, we conduct a study employing a solid-state hull cell with $Li_{6.5}La_3Zr_{1.5}Ta_{0.5}O_{12}$ as the solid electrolyte (SE) where Li morphology is plated over a range of current densities in a single galvanostatic experiment to assess the kinetics of the Cu current collector (CC). An Al interlayer is introduced to promote uniform Li plating and is deposited between the CC and SE.[2] Optical microscopy and PFIB-SEM analysis are performed to probe failure mechanisms causing non-uniform current distribution. Results revealed Li whiskers, islands, and extrusions on the CC surface, leading to heterogeneous interfaces. The inclusion of an Al interlayer reveal varying outcomes based on the deposited thickness, and a diminishing effect on the cycling efficiency is observed caused by the loss of solid-solid contact due to the Al-Li reaction-induced volume expansion. Nevertheless, despite the capacity loss, the Li plating uniformity is seen to increase proportionally with higher Al content after the initial galvanostatic plating procedure, emphasizing the importance of applying external pressure during cycling. ToF-SIMS analysis unveils Li migration through the interlayer and into the Cu CC, highlighting the confinement of Li-ions within Cu grain boundaries despite room temperature limitation for alloy formation.

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