SOLID-STATE BATTERIES V

FROM FUNDAMENTALS TO APPLICATION

An International Bunsen Discussion Meeting (IBDM)

NOVEMBER 22-24, 2022

House of Logistics & Mobility (HOLM)

FRANKFURT/MAIN

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CONFERENCE PROGRAMME

Tuesday, Nov 22, 2022			
11:30	Registration		
12:00	Lunch		
13:00	Opening Remarks		
	Session I: Thiophosphate and Sulfide Electrolytes and Cell Concepts		
13:15	KEYNOTE LECTURE Understanding the Interphasial Phenomena in All-Solid-State Batteries	**Y. Shirley Meng** (Chicago/US, San Diego/US)	O 01
14:00	INVITED LECTURE Characterization of Solid Electrolytes and All-Solid-State Batteries under Active Pressure Control	**Bernhard Roling** (Marburg/DE), N. Kaiser (Marburg/DE), M. Kroll (Marburg/DE), M. Duchardt (Marburg/DE), V. Miß (Marburg/DE), M. Cronau (Marburg/DE), C. König (Marburg/DE), A. Ramanayagam (Marburg/DE)	O 02
14:30	INVITED LECTURE Solid-state batteries at Umicore	**Shinichi Kumakura** (Olen/BE)	O 03
15:00	Recent development on components and processing for thiophosphate-based all-solid-state-batteries	**Felix Hippauf** (Dresden/DE), S. Cangaz (Dresden/DE), A. Dupuy (Dresden/DE), S. Poetke (Dresden/DE), M. Fiedler (Dresden/DE), B. Schumm (Dresden/DE), T. Abendroth (Dresden/DE), H. Althues (Dresden/DE), S. Kaskel (Dresden/DE)	O 04
15:20	Coffee Break		
15:50	Conformal Nanoparticle Coatings for Stabilizing Layered Ni-Rich Cathodes in All-Solid-State Battery Environments	**Yuan Ma** (Eggenstein-Leopoldshafen/DE), Jürgen Janek (Eggenstein-Leopoldshafen/DE), Aleksandr Kondrakov (Eggenstein-Leopoldshafen/DE), Torsten Brezesinski (Eggenstein-Leopoldshafen/DE)	O 05
16:10	Understanding the role of charge carrier transport in high performance silicon-based anode composite for solid state lithium-ion battery	**Moumita Rana** (Münster/DE), Wolfgang Zeier (Münster/DE)	O 06
16:30	Interface evolution of the $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2/Li_6PS_5Cl$ solid-state battery cathodes during cycling	**Barthélémy Lelotte** (Villigen/CH), C. A. F. Vaz (Villigen/CH), C. Borca (Villigen/CH), T. Huthwelker (Villigen/CH), V. Pelé (Bordeaux/FR), C. Jordy (Bordeaux/FR), L. Gubler (Villigen/CH), M. El Kazzi (Villigen/CH)	O 07
16:50	Implementation of conversion alloy active materials as anodes in solid-state batteries and their stability compared to liquid systems	**Julian J. A. Kreissl** (Gießen/DE), J. Janek (Gießen/DE)	O 08
17:10	Visualizing mechanical defects of sulfidic solid-state Li-ion batteries	**Robert S. Young** (London/GB), F. Iacoviello (London/GB), A. J.E. Rettie (London/UK), R. Jervis (London/GB)	O 09
17:30	Poster Speed Talks		
18:30	Poster Session and "Dinner@Poster"		

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09:15	INVITED LECTURE Beyond PEO with Hybrid Concepts: Caprolactone Oligomers as Key Strategy Towards Higher Energy Densities	**Gunther Brunklaus** (Münster/DE), Y.-H. Chen (Münster/DE), F. Kempe (Münster/DE), K. L. Liu (Münster/DE), A. Buchheit (Münster/DE), M. Winter (Münster/DE)	O 11

09:45	INVITED LECTURE The importance of interface chemistries to optimize ion dynamics in all solid-state batteries	E. Querel (London/UK), I. Seymour (London/UK), R. Brugge (London/UK), A. Cavallaro (London/UK), N. Nabi (London/UK), F. Pesci (London/UK), **Ainara Aguadero** (London/UK, Cantoblanco/ES)	O 12
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17:25	INVITED LECTURE Microstructure of Composite Cathodes for All-Solid-State Batteries: Origins, Influences and Consequences	**Anja Bielefeld** (Gießen/DE), J. Janek (Gießen/DE)	O 25
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Thursday, Nov 24, 2022

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11:20	Cost-efficient Na^+ halide solid electrolyte using earth-abundant metal elements for all-solid-state Na-ion batteries	**Juhyoun Park** (Seoul/KR), J. P. Son (Seoul/KR), H. Kwak (Seoul/KR), Y. Choi (Seoul/KR), Y. S. Jung (Seoul/KR)	O 31
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12:00	Elucidating the redox processes of lithium thiophosphate solid electrolytes by X-ray spectroscopic techniques	**Valerie Siller** (Villigen/CH), C. A. F. Vaz (Villigen/CH), C. Borca (Villigen/CH), T.Huthwelker (Villigen/CH), M. El Kazzi (Villigen/CH)	O 33
12:20	Concentration and Velocity Profiles in a Polymeric Lithium-ion Battery Electrolyte	**Hans-Georg Steinrück** (Paderborn/DE), C. J. Takacs (Stanford/US), H.-K. Kim (Lemont/US), D. M. Mackanic (Stanford/US), B. Holladay (San Diego/US), C. Cao (Upton/US), S. Narayanan (Lemont/US), E. M. Dufresne (Lemont/US), Y. Chushkin (Grenoble/FR), B. Ruta (Grenoble/FR), F. Zontone (Grenoble/FR), J. Will (Erlangen/DE), O. Borodin (Adelphi/US), S. K. Sinha (San Diego/US), V. Srinivasan (Lemont/US), M. F. Toney (Boulder/US)	O 34
12:40	Probing the interfacial dynamics of polymer electrolyte-based SSBs	**Yaolin Xu** (Berlin/DE), E. Kataev (Berlin/DE), R. Felix-Duarte (Berlin/DE), R. Garcia-Diez (Berlin/DE), K.V. Tran (Berlin/DE), Z. Kochovski (Berlin/DE), P. Feng (Berlin/DE), M. Bär (Berlin/DE), I. Manke (Berlin/DE), Y. Lu (Berlin/DE), P. Adelhelm (Berlin/DE)	O 35
13:00	Concluding Remarks		
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POSTER PROGRAMME

Advanced Characterization

P 01 **In-Situ Transmission Electron Microscopy Heating Experiments of $LiNiO_2$ Particles in O_2 Atmosphere**
Thomas Demuth (Marburg/DE), M. Malaki (Marburg/DE), S. Ahmed (Marburg/DE), P. Kurzhals (Giessen/DE), A. Beyer (Marburg/DE), J. Janek (Giessen/DE), K. Volz (Marburg/DE)

P 02 **In-situ TEM observation of Na-filament formation in oxide electrolyte**
Ziming Ding (Eggenstein-Leopoldshafen/DE), G. Melinte (Eggenstein-Leopoldshafen/DE, Ulm/DE), Y. Tang (Eggenstein-Leopoldshafen/DE), C. Kübel (Eggenstein-Leopoldshafen/DE, Ulm/DE, Darmstadt/DE)

P 03 **Methods from machine learning for the structural analysis of Li-ion electrode particles**
Orkun Furat (Ulm/DE), D.P. Finegan (Golden/US), Kandler Smith (Golden/US), Volker Schmidt (Ulm/DE)

P 04 **Monitoring of structural changes in sodium/sodium-ion cells by advanced in-situ and ex-situ solid-state NMR**
Thorsten Gutmann (Darmstadt/DE), E. Šić (Darmstadt/DE), M. Melzi d'Eril (Darmstadt/DE), K. Schutjajew (Jena/DE), M. J. Graczyk-Zajac (Darmstadt/DE), H. Breitzke (Darmstadt/DE), R. Riedel (Darmstadt/DE), M. Oschatz (Jena/DE), G. Buntkowsky (Darmstadt/DE)

P 05 **Revealing local ionic conductivity and chemical distribution in solid state electrolytes by Electrochemical Strain Microscopy**
Florian Hausen (Jülich/DE), P. Veelken (Jülich/DE), N. Schön (Jülich/DE)

P 06 **Comparative evaluation of degradation in thiophosphate based all solid-state batteries**
Jonas Hertle (Giessen/DE), F. Walther (Giessen/DE), J. Janek (Giessen/DE)

P 07 **Stability and surface modification of LLZTO thin film**
Maximilian Mellin (Darmstadt/DE), G. Cherkashinin (Darmstadt/DE), T. Ferber (Darmstadt/DE), J. P. Hofmann (Darmstadt/DE), M. Donzelli (Stuttgart/DE), O. Clemens (Stuttgart/DE)

P 08 **A method for visualizing Li distribution in solid-state batteries by Plasma FIB-SEM, EDS, and SIMS**
Yige Sun(Oxford/GB, Didcot/GB), G. M. Hughes (Oxford/GB), J. Bu(Oxford/GB), C. R. M. Grovenor(Oxford/GB), P. S. Grant (Oxford/GB, Didcot/GB)

SSB cell concepts: thin film and bulk ("thick film") SSB

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Jean Philippe Beaupain (Dresden/DE), K. Wätzig (Dresden/DE), C. Baumgärtner (Dresden/DE), M. Vinnichenko (Dresden/DE), A. Aurich (Dresden/DE), H. Auer (Dresden/DE), N. Zapp (Dresden/DE), K. Nikolowski (Dresden/DE), M. Partsch (Dresden/DE), M. Kusnezoff (Dresden/DE)

P 10 **Thin Polycaprolactone Separators for Polymer Solid State Batteries**
G. Brunklaus (Münster/DE), Yi-Hsuan Chen (Münster/DE), F. Kempe (Münster/DE), K.L. Liu (Münster/DE), A. Buchheit (Münster/DE)

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Joshua. H. Cruddos (London/GB)

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P. Odenwald (Jülich/DE, Duisburg/DE), Enkhtsetseg Dashjav (Jülich/DE), J. Gross (Jülich/DE), F. Tietz (Jülich/DE), D. Fattakhova-Rohlfing (Jülich/DE, Duisburg/DE)

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Industrial Processing of SSB

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ABSTRACTS (ORAL)

UNDERSTANDING THE INTERPHASIAL PHENOMENA IN ALL SOLID STATE BATTERIES

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Compared with their liquid-electrolyte analogues, Solid state electrolytes SSEs have drawn increased attention as they promote battery safety, exhibit a wide operational temperature window, and improve energy density by enabling Li metal as anode materials for next-generation lithium-ion batteries. Despite suitable mechanical properties to prevent Li dendrite penetration, relatively wide electrochemical stability windows, comparable ionic conductivities, and intrinsic safety, most SSEs are found to be thermodynamically unstable against Li metal, where SSE decomposition produces a complex interphase, analogous to the SEI formed in liquid electrolyte systems. An ideal passivation layer should consist of ionically conductive but electronically insulating components to prevent the SSE from being further reduced. The past four decades have witnessed intensive research efforts on the chemistry, structure, and morphology of the solid electrolyte interphase (SEI) in Li-metal and Li-ion batteries (LIBs) using liquid or polymer electrolytes, since the SEI is considered to predominantly influence the performance, safety and cycle life of batteries. Study of the buried interfaces in solid state electrolytes has been challenging. Originating from the structural biology field, cryogenic focused ion beam (cryo-FIB) and cryogenic electron microscopy (cryo-EM) have recently been introduced to battery research, and have proven the ability to preserve and probe Li metal for quantitative structural and chemical analysis. All-solid-state batteries (ASSBs) have been promoted as a highly promising energy storage technology due to the prospects of improved safety and a wider operating temperature range compared to their conventional liquid electrolyte-based counterparts. While solid electrolytes with ionic conductivities comparable to liquid electrolytes have been discovered, fabricating solid-state full cells with high areal capacities that can cycle at reasonable current densities remains a principal challenge. To overcome these challenges, a quantitative and in-depth understanding of the phenomena governing ionic and electronic transport limitations within the cathode composite, in addition to mechanical aspects arising from significant volume changes associated with Li metal anodes (including anode-less cell designs) are needed. Such understanding can be obtained from proper electrochemical measurements described herein. In this talk, we will highlight solutions to these existing challenges and several directions for future work are proposed.

Characterization of Solid Electrolytes and All-Solid-State Batteries under Active Pressure Control

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Lab-scale all-solid-state lithium batteries consist typically of a Li alloy anode, a solid electrolyte separator layer and a composite cathode. The composite cathode contains a mixture of active material particles, such as $LiNi_xMn_yCo_zO_2$, and solid electrolyte particles, such as thiophosphates or halides [1-3]. The performance of all-solid-state batteries depends crucially on the contacts between the solid particles and is thus strongly influenced by the fabrication pressure as well as by the applied pressure (stack pressure) during cycling. Consequently, characterization of solid electrolytes and of complete all-solid-state battery cells under pressure control is important for achieving a better understanding of pressure-dependent transport and charge transfer processes.

Here, we discuss recent results for (i) the pressure dependence of the ionic conductivity of amorphous, glass ceramic and microcrystalline solid electrolytes [4]; (ii) the influence of the cathode morphology on the ion transport tortuosity [4-6]; (iii) different contributions to the electrochemical impedance of complete all-solid-state battery cells [7] and (iv) the achievable exchange current densities at AM/SE interfaces [7].

Literature:

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Materials for All-Solid-State Batteries at Umicore

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Rechargeable lithium-ion batteries based on liquid electrolytes and graphite anodes is currently the dominant technology in many industries. However, their energy density, safety and power rate are no longer sufficient to meet the demands of large scale applications such as electromobility and power grids.

On the other hand, Solid-state batteries (SSBs) are enjoying a growing interest as the nextgeneration of battery systems enabling higher energy cell chemistries, improved safety, and simplified cells design.

Despite the vast research around solid-state batteries conducted in the past decade, technological demonstration of high quality SSB devices is not commonplace in the literature. 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.

Recent development on components and processing for thiophosphate-based all-solid-state-batteries

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All-solid-state lithium-ion batteries are promising candidates to overcome safety and energy limitations of common lithium-ion batteries. Excellent results have been reported for sulfide based electrolytes on a small scale. More and more companies announce their first pilot production lines. Therefore, scalable concepts for material and component development are of crucial need.

The so-called DRYtraec® process had been developed as a viable approach to replace slurry-based binders by fibrous PTFE and produce laminated electrodes with a low carbon footprint. It has been demonstrated to work for, both, liquid and solid electrolyte batteries. NMC cathodes can be produced in a wide range of loading. Now, we evaluate this process for the fabrication of thin argyrodite separator films and compare it with slurry-based separators.

To test new cell concepts and components under relevant conditions, it is important to manufacture prototype cells with thin separator layers and flexible housing. Therefore, we prepared slurry-free pouch cells based on Ni-rich NMC cathodes and PVD-synthesized Si anodes.

The columnar structure of the anode has a 1D breathing mechanism similar to lithium, which preserves the interface toward the electrolyte. Stable cycling is demonstrated for more than 200 cycles with a high coulombic efficiency (CE) of 99.7–99.9% in full cells with industrially relevant areal loadings of 4.5 mAh/cm². Symmetric charging and discharging with 3.6 C was demonstrated at room temperature and 50°C. A multi-layered prototype all-solid-state pouch cell was assembled paving the way for developing demonstrator cells in the Ah-class.

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Conformal Nanoparticle Coatings for Stabilizing Layered Ni-Rich Cathodes in All-Solid-State Battery Environments

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Abstract: Improving the interfacial stability between cathode active material (CAM) and solid electrolyte (SE) is a vital step toward the development of bulk-type all-solid-state batteries (ASSBs). One of the challenges is the preparation of conformal protective nanocoatings on the CAM particles. Here, we present a new coating strategy using preformed nanoparticles dispersed in solution. Non-agglomerated nanoparticles of the coating material (here, ZrO_2 or HfO_2) were prepared by solvothermal synthesis, and after surface functionalization, applied to a layered Ni-rich CAM, namely $LiNi_{0.85}Co_{0.10}Mn_{0.05}O_2$ (NCM851005), producing a uniform secondary particle coating. When used in argyrodite Li_6PS_5Cl-based ASSBs, the surface-modified NCM851005 was found to exhibit superior performance in terms of capacity, rate capability and stability over the bare reference CAM. The effectiveness of the protective coating in mitigating electro-chemo-mechanical degradation was probed using various techniques.

Understanding the role of charge carrier transport in high performance silicon-based anode composite for solid state lithium-ion battery

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Solid state lithium metal batteries are promising as the next-generation energy storage system due to their high energy density, thermal stability, and volumetric miniaturization.[1] However, the use of Li metal anode is detrimental in terms of dendrite formation and Li deposition in the solid electrolyte (SE) layer that causes short-circuit, thereby limits the battery cyclability. Besides, the mechanochemical instability of the Li-SE interface, and the low earth abundance of Li establish the need for alternative high-capacity anode development. In this regard, silicon is a potential alternative due to its high theoretical capacity of 4200 mAh/g and low lithiation potential. The realization of electrochemically stable and high-performance Si based anode is limited by low electronic and ionic conductivity of Si. [2] Despite appreciable advances in achieving stable Si based anode, the influence of the transport properties on the rate capability and long-term stability remain unclear.

In this study, we investigated the role of effective ionic and electronic conductivity in modulating the electrochemical performance of Si based anodes. First, we have developed Si-based composites with SE (Argyrodite) and carbon additive, which significantly improved the ionic and electronic conductivity of the electrode composite, respectively. By optimizing the ion/electron conducting phase ratio in the composite and relating corresponding cell performance with effective transport coefficients we have estimated the limiting conductivity values. The particle size of Si is also found to significantly influence the effective transport properties, which in turn modulate the rate performance as well as the long-term stability. This study provides a comprehensive understanding on the role of charge carrier transport in achieving high-performance silicon based anode for solid-state batteries.

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Interface evolution of the $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2/Li_6PS_5Cl$ solid-state battery cathodes during cycling

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All-solid-state Li-ion batteries (ASSBs) are closer than ever to wide-scale applications. They bring improved safety and increased energy density if the compact solid electrolyte (SE) can prevent the Li metal dendrite growth and interface degradation at high operating voltage. Due to the narrow electrochemical stability window of the SE, one of the current focus is to stabilize its interface with both cathode and anode materials. Understanding the degradation reaction mechanism taking place at these buried interfaces is extremely challenging: it requires the use of non-destructive surface sensitive techniques capable to provide fine chemical analysis with depth profile sensitivity combined with an excellent lateral resolution to discriminate signals originating from the surface and near surface of the different particles (active materials, SE and conductive carbon additive) composing the working electrode (WE).

In this contribution, we present a detailed study of the interface in the $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ (NCM_{622}) / Li_6PS_5Cl (LPSCl) / conductive carbon (C65) WE cycled up to 4.3 V vs. Li+/Li. First, galvanostatic cycling and electrochemical impedance spectroscopy demonstrate a low coulombic efficiency of 72% during the 1st cycle and a gradual increase of the impedance with the number of cycles, respectively. To explain the electrochemical performance, the chemical evolution of the interface is monitored *ex situ* by soft and tender-X-ray absorption spectroscopy (XAS) at the transition metals (TM) L-edges, P and S K-edges, as well as, at the C and O K-edges at the SIM and Phoenix beamlines of the Swiss Light Source. These techniques provide information on the oxidation states and local environment during cycling of both NCM_{622} and LPSCl. The XAS acquisition is performed by combining measurements with the (i) high lateral resolution and surface sensitivity of X-ray photoemission electron microscopy (XPEEM) and (ii) depth profile total electron yield (TEY) and total fluorescence yield (TFY).

Implementation of conversion alloy active materials as anodes in solid-state batteries and their stability compared to liquid systems

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The increasing demand for energy storage systems requires further development of commercial batteries. In particular, the need for high-energy and high-power batteries for electric vehicles requires the optimization of lithium-ion batteries (LIBs) or development of new battery systems like solid-state batteries (SSBs). Considering the charging rate, the anode material becomes the focus of research. Graphite anodes tend to lithium plating at elevated C-rates and low temperatures in LIBs.[1] Due to the high specific energy of lithium, it is the most desired anode material for LIBs and Li-SSBs. However, dendrite growth and the instability of the anode/electrolyte interface is a major challenge in both systems.[2]

Due to their high specific capacity (*e.g.* q_{ZnO} = 987 mAh g^{-1}), high lithium-ion diffusion and high-rate capability conversion/alloy active materials (CAAMs) are considered as one of the most promising candidates to replace graphite anodes in LIBs. Besides the positive aspects, the lithiation/delithiation of CAAMs is hampered by drastic volume changes, large voltage hysteresis, and the formation of unstable solid electrolyte interphases (SEIs).[3] To improve the CAAM/electrolyte interface degradation, composite anodes (CAAMs, conductive carbon, solid electrolyte) can be used in SSBs.[4]

Within this work, we compare different CAAMs – SnO_2, $Sn_{0.9}Fe_{0.1}O_2$, ZnO and $Zn_{0.9}Fe_{0.1}O$ – for their implementation in SSBs. Furthermore, we shed light on the interphase formation at the CAAM/electrolyte interface by FIB-SEM, EDX and ToF-SIMS analysis. Surprisingly, we observe a different performance and stability of the CAAMs in comparison to CAAMs in liquid based batteries.

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Visualizing mechanical defects of sulfidic solid-state Li-ion batteries

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The solid-state lithium-ion battery (SSB) has the potential to address concerns in energy density, safety, and fast charge/discharge rates [1]. Sulfidic solid electrolytes have advantages compared to other types of solid electrolytes, mainly their ease of machining and relatively high ionic conductivity [2]. SSBs also come with challenges such as mechanical degradation of the electrolyte; forming cracks, voids, and Li dendrites that ultimately limit their performance and lifetime.

In the field of SSBs, many experiments have taken advantage of the power of X-ray Computed Tomography (XCT). With XCT, researchers can track cracking, void development, and loss of interfacial contact during cycling [3,4]. The objective of this work is to enhance the utilization of XCT on SSBs, to give better insight into the formation and degradation of SSBs.

Here, the formation and operation of sulfidic SSBs is studied via XCT with the utilization of bespoke cell designs. In-situ pellet formation is made possible in an x-ray transparent apparatus that doubles as a cell fixture. Radiography and XCT can be performed during the formation of the solid electrolyte pellet, giving insight into pellet formation at various pressure and temperature conditions. Additionally, functional SSBs are manufactured within the apparatus which is optimized for lab based and synchrotron radiation sources. These cells are developed for high resolution imaging with minimal artifact production, providing key insight into the mechanical degradation of sulfidic SSBs.

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Mechano-electrochemical Phenomena at Li-Solid Electrolyte Interfaces

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ABSTRACT

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 non-combustible solid-state batteries delivering twice the energy density (>1,300 Wh/L) compared to Li-ion. However, technological and manufacturing challenges remain, creating the impetus for fundamental and applied research.

This discussion will consist of fundamental aspects such as the mechano-electrochemical phenomena at solid interfaces as well as manufacturing challenges related to the integration of Li metal electrodes. The underlying physics that control 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 and lower temperatures, Li metal filaments can initiate at defects and propagate through relatively hard ceramics. 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 metal 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 advance the technological maturity of solid-state batteries, there remain fundamental questions regarding the physics at interfaces and whether or not they exhibit sufficient stability and kinetics that are relevant to EVs.

Beyond PEO with Hybrid Concepts: Caprolactone Oligomers as Key Strategy Towards Higher Energy Densities

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The market demands for larger energy densities in battery applications necessitate polymer electrolytes that are compatible with Li metal anodes and operate at moderate temperatures. Polymers are inherently safer than typical liquid electrolytes due to their non-volatile properties and viscosity that prevent leakage even upon mechanical abuse of the cells. While commercially available batteries with PEO (Bollore) are operated at >60°C, tailor-made polycaprolactones provide reasonable electrochemical performance already at 40°C. In addition, PCL-based electrolytes are considered as biodegradable, affordable and are straightforward to produce. [1]

Increased discharge capacity was realized with suitable hybrid cell concepts employing composite cathodes, an approach that was particularly successful in case of flowable caprolactone oligomers, thereby enabling NMC622||Li cells with cathode mass loadings of up to 6 mg/cm² and discharge capacities of >150 mAh/g. In addition, the hybrid cell concept invoked an ultra-thin matrix-supported polymer electrolyte membrane. Since oligomers are viscoelastic fluids, they reflect a compromise among conflicting demands of low viscosity liquid electrolytes and high yield strength polymers, rendering this approach applicable to numerous other oligomers. Also, their rather low vapor pressure makes them safer candidate materials for achieving high energy density batteries.

The introduced hybrid cell concept based on oligomer infiltrated composite cathodes and thin polymer electrolytes constitutes a key strategy to facilitate benefits of polymer-based solid-state batteries that can be achieved for a variety of polymer chemistries.

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The importance of interface chemistries to optimize ion dynamics in all solid-state batteries

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The need to develop safer batteries with enhanced energy densities is promoting the development of non-flammable solid electrolytes and their integration with alkali metal negative electrodes. A major challenge is the optimization of the dynamic metal/solid electrolyte interfaces that lead to premature cell degradation specially at high current densities. Whereas some of these problems can be solved by the application of high pressures or temperatures during operation, the integration of these systems requires optimization of performance in unpressurised systems at room temperature. Two of the best solid state alkaline-ion conductors are derivatives of $Li_7La_3Zr_2O_{12}$ Garnet-type structures for Li and $Na_3Zr_2Si_2PO_{12}$ NaSICON type structures for Na able to reach values of 15-10^{-1} mS/cm at RT.[1,2] In this work, we focus on the study of Na/NaSICON and Li/Garnet interfaces paying particular attention to the effect that surface chemistry has on the charge transfer resistance and stability under high current densities. The study brings a combination of surface sensitive techniques including secondary ion mass spectrometry, low energy ion scattering and x-ray photoelectron spectroscopy with electrochemical and computational analysis. We prove that the surface chemistry of solid electrolytes has a dominant role on the design of stable, high-performance metal/solid electrolyte interfaces and that the tuning of the surface chemistry is a powerful tool to improve the performance of these devices at high current densities.[3,4]

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Understanding the Dendrite-Growth of NaSICON Electrolytes and Enhancing their Dendrite-Tolerance by Surface Engineering

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Compared to their lithium counterpart, solid-state sodium battery (SSNB) is regarded to have similar properties but is a much less mature technology because it has been much less addressed. Besides their well-known natural endowment like high element abundance, low price etc., in the present study, some technological advantages of SSNBs are discussed in comparison with solid-state lithium batteries (SSLBs). Recently, $Na_{3.4}Zr_2Si_{2.4}P_{0.6}O_{12}$ (NZSP) ceramics were reported to have total conductivity of 5×10^{-3} S cm^{-1} at 25 °C, higher than previously reported polycrystalline Na-ion conductors.[1] Inhibition of dendrite growth in SSLBs and SSNBs has long been a challenge to the field. In the present study, with simply sticking sodium metal to NZSP ceramic pellets and without external pressure applied during operation, the critical current density (CCD) of Na/NZSP/Na symmetric SSNBs reaches 9 mA cm^{-2} at 25°C. The cells can be stably operated at areal capacity of 5 mAh cm^{-2} (per half cycle, with 1.0 mA cm^{-2}) at 25°C for 300 h in a galvanostatic cycling measurement without any dendrite formation. This CCD is much higher than those of existing SSLBs operated at similar conditions. The influence of metal self-diffusion on the dendritic plating as well as a self-forming Na-P-O nano-layer on the surface of NZSP are the main explanations of the high dendrite tolerance of SSNBs.[2,3] Moreover, NZSP also shows interesting dendrite growth along the surface of NZSP rather than through the ceramic. *Operando* investigations and *in situ* SEM microelectrode experiments were conducted to reveal the Na plating mechanism. By blocking the surface from atmosphere access with a sodium-salt coating, surface-dendrite formation is prevented. The dendrite tolerance of Na | NZSP | Na symmetric cells is then increased to a CCD of 14 mA cm^{-2} and galvanostatic cycling of 1 mA cm^{-2} / 1 mAh cm^{-2} (half cycle) is demonstrated for more than 1000 h. Even if the current density is increased to 3 mA cm^{-2} or 5 mA cm^{-2}, symmetric cells can still be operated for 180 h or 12 h, respectively.[4] Since SSNBs have these special advantages, the future roadmap of the development of solid-state batteries may shift from SSLBs towards SSNBs despite the higher molar weight of the sodium compounds in comparison to the Li analogues.

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Grain Boundary Engineering to Control Chemistry and Transport for Safe Garnet-type Solid-state Electrolytes

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Lithium (Li) metal is regarded as the holy grail for the next generation Li batteries, but unstable Li plating in liquid electrolytes causes a formidable safety challenge. Instead, lithium lanthanum zirconium oxide (LLZO) solid electrolyte draws attention with superior material characteristics to control the Li growth. However, Li metal deposits still penetrate along various interfaces in polycrystalline LLZO. Recently, the grain boundary (GB) of LLZO was claimed to be a major Li nucleation site given its ionically-blocking and partially electronically-conducting nature. Till now, limited understandings, both theoretical and experimental exist on the origin of GB charge transport mismatch.

In this work, we apply the grain boundary core-space charge layer model to explain the observed transport at the GBs and critical current density (CCD) impact on a cell level. The excess negative charge at the GB core induces Li vacancy (V_{Li}') depletion and hole ($h^{\bullet}$) accumulation forming an adjacent space charge zone. The defect concentration changes then lead to locally reduced ionic conductivity and enhanced electronic conductivity at the GB regions.

This understanding enables design principles for practical engineering strategies to control Li metal penetration. First, oxygen-rich sintering was able to decrease the space charge potential by suppressing negative charge accumulation at the GB core.

Second, higher donor dopant Ta concentrations levels revealed more effective compensating the negative core charge with its net positive charge. Both approaches effectively impeded Li metal nucleation by lowering the local electronic conductivity. We successfully achieved CCD of ~ 1 mA cm^{-2}, more than two-fold increase within the same conventional processing. The GB core-space charge model and the two GB engineering strategies appear to aid in addressing an important source of Li metal penetration in LLZO and can be expected to point to design future safe all-solid-state Li metal batteries.

Handling the carbonates: an easy modification of the LLZO surface towards better interfaces

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After the discovery[1] of highly lithium-ion conductive Li7La3Zr2O12 inorganic solid-state electrolyte, significant efforts have been made to gain an understanding of its structure to improve both Li-ion conductivity and its interface properties when employed in electrochemical systems. The formation of a lithium carbonate-based layer on its surface[2] , hindering Li-ion conductivity at the interfaces, currently represents one of the main issues to address. Several approaches to tackle such a detrimental layer have been reported, in many cases not fully addressing the latter, but rather improving the contact of the pellet with the electrodes and simply accepting the carbonate-based layer[3] . In other works, however, the neutralisation of this non-conductive layer has been considered[4] , assuming that such a change might help enormously the performance of the resulting electrolyte. In our work, we immerse LLZO pellets in a solution of boric acid to handle two issues at the same time: first, the acid treatment might react with the carbonate species formed on the LLZO surface and either etch or substitute them. Secondly, a high enough amount of acid in suspension might also form a sediment on the surface, generating a very thin, conductive and mechanically plastic surface layer that might enhance the electrochemical performance in a realistic electrochemical system.

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Investigations on the ion transport of NASICON for sodium all-solid state battery electrolytes

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The ongoing search of novel battery systems have catalysed the innovation for solid state battery, where solid electrolytes hold the key for better performances. Hence, understanding how these electrolytes transport ion is essential for building a solid-state battery. $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$ or NASICON as a mixed polyanion showed some of the highest ionic conductivities among its peers [1]. Although it has been studied for decades [1-3], our recent findings [4-5] show potential NASICON species that could push its ionic conductivity values even higher. Through our kinetic Monte Carlo simulations, mapping the compositional space of NASICON species over temperature ranges, optimum ionic conductivity was reached for x=2.4. Experimental work was carried extensively on this basis, choosing different x values (x=1.5, 2.0, and 2.4) to further understanding the effect of varying Na content.

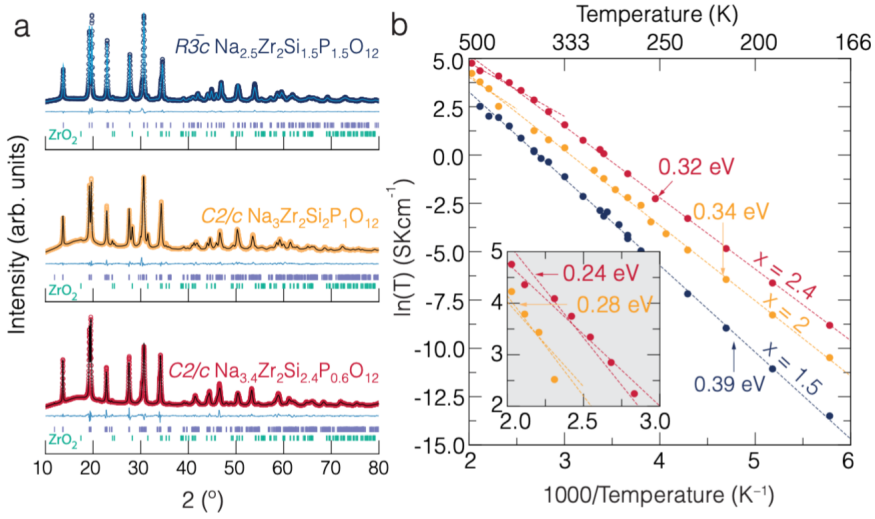

Figure 1. a) Powder X-ray diffraction of 3 different NASICON compounds and b) their electrochemical impedance measurements and different range of temperature.

Good purity and well-characterized NASICON samples (x=1.0, 2.0, and 2.4) were obtained at temperature higher than 1100°C. Electrochemical impedance measurements at elevated temperature were applied to further investigate the materials' activation energy and phase behaviour. Through high frequency impedance measurements, the separation of bulk and grain boundary resistance and their effect was well resolved, dependent on composition. Our reported experimental highest ionic conductivity reached at 473 K (about 0.165 S/cm) by x=2.4 is agreeing with our simulations (about 0.170 S/cm) [6].

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Beyond PEO: Sidechain Diester polymer electrolytes for all solid-state Lithium metal batteries

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A series of polymethacrylates and polyacrylates carrying diester sidechain moieties with varying alkyl spacer lengths are designed, synthesized, and evaluated as solid polymer electrolytes (SPEs) in lithium metal batteries (LMBs). These amorphous polymers with glass transition temperatures in the range of -58 to +32°C are tested as SPEs in combination with LiTFSI or LiFSI. At the optimum salt concentration of 25 wt.%, ionic conductivities up to 10^{-4} S cm^{-1} at 70°C are achieved. These SPEs reveal high lithium transport numbers (0.5-0.7) and high electrochemical stability (5.4 V vs. Li/Li^+) as determined by LSV. In combination with an ultrathin polyimide membrane and 10 wt.% TiO_2 nanoparticles, dendrite-free plating/stripping at 40 and 70 °C is realized in symmetrical Li|SPE|Li cells. Detailed Extended Distribution of Relaxation Times (eDRT) analysis of impedance measurements is employed for understanding the diverse cell processes. In solvent-free LMBs comprising a polyimide membrane soaked with nanocomposite polyester electrolyte, a lithium metal foil as anode and an optimized $LiFePO_4$ cathode, very high initial specific discharge capacities of 152 mAh g^{-1} (at 0.2C, 70°C), excellent capacity retention of 94 % after 100 cycles (at 1C, 70°C) and negligible capacity fading even at 2C (96% retention after 300 cycles) are demonstrated. These novel “beyond PEO” polyester-based SPEs exhibit high cycling stability at 40 °C, making them highly attractive for room temperature applications. [1],[2], [3].

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Towards Pilot-scale Production of Sulfide-based All-solid-state Batteries

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All-solid-state batteries are one of the most promising next generation energy storage technologies [1]. Among solid electrolytes, sulfide-based materials are particularly promising due to their high ionic conductivity and favorable properties regarding production [2]. The latter will likely enable production technologies for separators and composite cathodes that are already applied in the manufacturing of conventional lithium-ion batteries. However, from a production point of view, the industrialization of all-solid-state batteries depends on the development of cost-effective production technology [3]. To fabricate the thin-film components of ASSB cells, processing techniques have to be adapted to the properties of the sulfidic materials. Thereby, a fast scale-up and complex process interdependency handling must be enabled. This talk focuses on resulting challenges for production technology based on deepened knowledge about upscaling of sulfide-based composite cathodes and separators. Along the process chain, a detailed overview of the influence of introducing new materials on the design of machinery, production environments and process parameters is given.

The complexity thereof results from interlinked design parameters such as material choice, component composition, loading, and thickness influencing the energy density. To realize these design parameters, processes such as mixing, coating, drying, and densification are investigated in detail. Hereby, challenges to fabricate components, which are competitive concerning a high energy density are highlighted. Further, highly linked interdependencies such as a zero-porosity strategy to maximizes volumetric energy density are elaborated and discussed. With regard to full production lines, the high reactivity of the sulfide-based solid electrolyte with water and impact of this hydrolysis on the design of production environments is addressed. To maintain both occupational safety and a high material quality, a quantitative analysis of the formation of hydrogen sulfide is presented. The talk closes with an outlook on further required investigations and implications to set-up an industrial production for sulfide-based ASSBs.

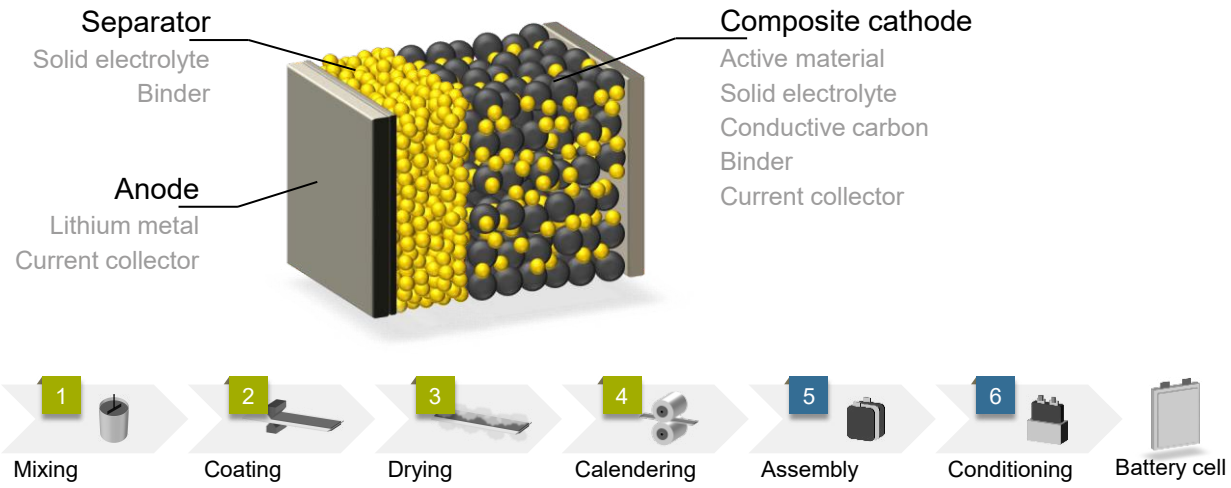

Figure 1: Left: Schematic image of an all-solid-state battery, which can be produced by the processes mixing, coating, drying and calendering and subsequent cell assembly.

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Technical, economic and ecological evaluation of production processes for Solid-State-Batteries

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Research within the field of energy storage aims to develop innovative battery technologies that are able to reach higher energy densities and capacities than Lithium-ion batteries (Li-ion), while meeting specifications in terms of stability and safety. All-Solid-State Batteries (ASSBs) are a promising technology to meet these objectives due to their high theoretical energy densities and improved safety aspects [1,2]. However, to be competitive on the market, ASSBs will need to meet several additional requirements, such as longer cycle life, low production cost and reduced environmental impact [1,2]. Furthermore, production processes for ASSBs will need to be highly automated and scalable to compete with current market production technologies [3]. To meet the above requirements, research on ASSBs has focused on the development of innovative materials, cell concepts and production processes. However, little is known regarding the environmental impacts of these innovations. Since ASSBs are still an emerging technology, with research being conducted on a laboratory scale, the assessment of the potential environmental impacts can help guide decision-making regarding the identification of scalable production routes.

Life cycle assessment (LCA) studies of ASSBs have previously applied defined scenarios for upscaling from laboratory scale to larger production scales [4], considering improvements in material efficiency, energy consumption and waste management. Expert knowledge regarding the processes and technical feasibility assessments can also be used to support the definition of scenarios for prospective environmental assessments. A technical feasibility assessment for defined production processes for ASSBs has previously been conducted, where specific criteria were defined and evaluated to determine the extent of which ASSB production can utilize the industrial-scale production processes of Li-ion batteries [3]. The ability to use processes that are already available at a large scale would ease the entrance of the technology into the market. The technical feasibility assessment was therefore conducted at a process-level in order to thoroughly assess the similarities and differences in the production processes. A technical feasibility assessment is therefore useful at a process-level to evaluate the scalability and optimization potential of specific processes.

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A solid state lithium-metal anode battery development at QuantumScape

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Metallic lithium is an attractive option of anode toward batteries of higher energy density. QuantumScape's approach to the metallic lithium is proprietary solid-state separator and anodeless architecture with metallic lithium plated during charge cycles. Its unique architecture is expected to offer high energy dense batteries combined with the improved cycle life. The QuantumScape cell's architecture and its performance will be presented in the meeting.

In addition to the high energy density and cycling capabilities, QuantumScape's cells show the potential to overcome things those often discussed as challenges of solid-state battery technologies yet quite important for applications. In the presentation, we are also going to show the performance of QuantumScape cells from these perspectives.

Factorial Energy: Transformational Semi-Solid-State Battery Technology

Raimund Koerver, Munich

Factorial Energy, 19 Presidential Way, Woburn, MA 01801

As vehicle electrification advances, the need for high-energy, high-power energy storage solutions increases. Future lithium-ion batteries may not be able to meet these requirements, especially since their energy density is limited by the given electrode configuration, in particular by the graphite anode. On top of this, safety concerns arise for such high energy systems, as the liquid, organic electrolyte is potentially flammable. To counter such concerns, next generation batteries are intended to employ solid or semi-solid electrolytes (SEs). Those novel electrolytes possess higher thermal stability, thus increasing battery safety. At the same time, the use of lithium metal would significantly increase the cell energy density, while simultaneously allow for fast charging times. [1]

As the prerequisite technologies for the practical solid-state batteries (SSBs) are reported and developed at a quicker pace, their commercialization looks very promising. However, there are still problems to be solved when manufacturing at scale. In general, SSBs using inorganic SEs are more difficult for mass production rather than SSBs using polymer-based and/or semi-solid electrolytes. Factorial Energy is one of the frontrunners in the field of semi-solid electrolytes. Due to the semi-solid nature of the electrolyte, the cells have shown to perform well at ambient conditions unlike many other solid-state batteries which require elevated temperature operation. The successful demonstration of high performance semi-solid state batteries has allowed Factorial Energy to enter into joint development programs with three major OEMs, Mercedes Benz, Stellantis and Hyundai Motor Corporation. The deep collaboration is expected to help to accelerate the commercialization of next generation batteries.

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All-solid-state sodium-ion batteries based on hydroborates

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In the search of new electric storage technologies, sodium-ion batteries (SIBs) have attracted huge interest due to the possibility to create high performance batteries without scarce elements. However, the theoretical energy density of the liquid electrolyte system is only around half of that of a lithium-ion battery. One way to tackle this issue can be the application of a sodium metal anode. Similar to the lithium system this seems to be possible only with a solid electrolyte.

Beside the, for the lithium system commonly investigated, classes of oxides, sulfides and polymers another class of electrolytes have been identified. 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 [1]. Moreover, they can easily be processed by dissolution and precipitation, which allows for advanced processing techniques.

In this contribution, we are going to present the processing of all-solid-state SIBs based on hydrobrates via screen-printing. This technique is especially suited for producing customized cell sizes, while manufacturing the cells layer-by-layer. A glovebox system consisting of three interconnected boxes for paste preparation, material printing and cell assembly will be used to simulate an encapsulated process chain. We will show the printing process of electrodes as well as separators and first morphological and electrochemical results for these components.

[1] L. Duchêne, A. Remhof, H. Hagemann, C. Battaglia, Energy Storage Materials, 25, 2020, 782-794,

Towards water-processable catholytes for solid-state batteries

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All-solid-state batteries (SSBs) with a lithium metal anode are a promising candidate to surpass conventional lithium-ion batteries in numerous aspects.[1] NMC-based SSB cathodes suffer from electromechanochemical degradation due to the expansion/contraction of the cathode active material (CAM). Polymer binders are often used to mitigate interparticle contact loss. However, this necessitates conductive additives to maintain electronic conductivity increasing the volume of non-active components in the catholyte.[2] A direct substitution of the inactive binder and the conductive additive with a single polymer material, may result in catholytes that can accommodate volume changes during cycling and provide sufficient electronic conductivity.[3] Here, we demonstrate a novel, water-based synthesis of a composite containing an electronically conductive polymer binder and lithium indium chloride (Li_3InCl_6, LIC) as solid electrolyte. The developed synthesis provided homogeneous coverage of the high-purity LIC particles with the conductive polymer binder as was demonstrated by both SEM-EDX and Kelvin Probe Force Microscopy (KPFM) measurements. This composite is later mixed with an NMC-based CAM. The electrochemical performance of the catholyte composites was evaluated via partial electron conductivity measurements and cycling in sulfidic SSB half-cells. We observe that the partial electronic conductivity of the catholytes increases with increasing polymer content. We expect that the latter has a positive impact on the long-term cycling stability of the cells which showed promising initial performance (initial discharge capacities of ca. 140 mAh/g for unoptimized NMC622 cells).

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Structure-Performance Relations in Solid Electrolytes and Solid-State Batteries

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Due to their potentially higher energy densities and advantages in safety, all solid-state batteries (ASSBs) are being considered to replace conventional Li-ion batteries in a number of applications. Different material classes are discussed in literature. E.g. Oxide-type of materials promise higher stability and safety where thiophosphates exhibit excellent ionic conduction. But in addition to the material properties, structural features have a huge impact on the electrochemical performance. Internal interfaces between grain boundaries, formation of secondary phases in grain boundaries as well as structural properties of interfaces between electrolyte, active materials and current collector can limit the achievable energy density. Grain boundaries and structural defects within the solid electrolyte are obstacles for the flux of lithium ions and electrons and thereby affect the transient potential landscape and space charges at interfaces during the charging and discharging of the ASSB and may give rise to lithium dendrite formation in grain boundaries [1] or nucleation in the bulk phase of the solid electrolyte [2]. The complex interplay of microstructural features and performance are difficult to explore in operando. In our presentation we demonstrate how detailed microstructure resolved modeling and simulation may help to create a better understanding of local electrochemical processes and to identify correlations between macroscopic experimental results and the microscopic structural features of ASSBs [3,4]. This correlations in turn can be utilized to develop simulation based optimization strategies for all solid state batteries.

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Microstructure of Composite Cathodes for All-Solid-State Batteries: Origins, Influences and Consequences

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Imagine a composite electrode as interwoven mazes for electrons and ions; two mazes that interact with each other via lithium transfer. Sounds abstract?

In this talk, I want to invite you go on a trip into the microstructure of all-solid-state batteries. We will tackle a couple of basic questions:

- What makes and changes a microstructure?
- Why do we have to care about it?
- Where do we go from here?

In contrast to conventional liquid electrolytes, inorganic solid electrolytes possess a proper particle morphology, which implies that the latter cannot infiltrate pores and we have to consider an additional component in the composite: Pores or voids.

These voids are reported to take around 15% of the electrode volume in pressed cells [1,2], up to 40% [3] and down to 6% [4] for other manufacturing techniques. As it is not straightforward to assess the influence of microstructure effects in composite electrodes, we study the percolation of conduction paths [5], the efficacy of ion conduction [6] and the charge behavior [7] mainly from the model/simulation perspective. The microstructure models of different layouts feature cathode active material, solid electrolyte, void space and partly also binder. These allow us to develop a general understanding of the electrode design and identify trade-offs between energy and power layouts and/or electronic and ionic conduction.

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Materials Chemistry Spaces for Halide Superionic Conductors for All-Solid-State Batteries

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Owing to the potential of enhanced safety and energy density, all-solid-state batteries (ASSBs) employing inorganic solid electrolytes (SEs) considered as a promising alternative for lithium-ion batteries. Recently, halide SEs such as Li_3YCl_6 are newly emerging as the game changer because they are mechanically deformable, similarly to sulfide SEs, and exhibit excellent electrochemical oxidation stability, unlike sulfide SEs. However, most halide SEs developed thus far contain costly central metal elements, such as Y, Sc, and In, with the only exception of Zr. Elemental substitutions have been a common practice to tune the crystal structure and ionic conductivity of halide SEs. Meanwhile, a poor cathodic stability of halide SEs prohibits their use for anodes such as Li metal. In this regard, hybrid ASSBs using halide and sulfide SEs for cathodes and SE membranes, respectively, would be practically reasonable. However, their compatibility problem has been overlooked.
In this presentation, we report on our recent results of the designing new halide SEs with enhanced ionic conductivity, electrochemical stability, and sulfide compatibility. Also, results of ASSBs employing the developed SEs are discussed.

Literature:
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Electrode reactions with large volume expansion in solid-state batteries

Prof. Dr. Philipp Adelhelm, Humboldt-University Berlin and Helmholtz-Zentrum Berlin, Berlin/Germany

The use of electrode reactions with large volume expansion in solid-state batteries (SSBs) is believed to be very difficult as the unavoidable formation of stress and strain can cause mechanical failure of the cell. Large volume expansion is inherent for high capacity conversion reactions (typically > 300 mAh/g) which include also alloys such as Li-Si of Li-In, the latter being frequently used for research purposes. Here, we discuss examples on large volume expansion electrode reactions in SSBs. Examples will include Li-In, Li/Na-MoS_2, Li-Sn/Graphite and especially Li-CuS.

CuS shows some unique properties that make it an attractive cathode active material (CAM) for Li-SSBs. Next to a high intrinsic mixed conductivity, CuS reacts with Li via a unique conversion reaction mechanism that leads to macroscopic phase changes during cycling. Next to cycling studies, the storage mechanism and mechanical properties are discussed using 3D tomography. For the first time, a z-oriented displacement of CAM particles during cycling is shown as well as pressure dependent crack formation.

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Correlating electrochemistry, structure and morphology for a better understanding of sulfide-based electrolyte

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All-solid-state batteries have been presented as the ideal solution [1] but still many aspects regarding their chemical and mechanical issues remain unsolved especially during electrochemical activities [2]. As an example, sintering (even cold sintering) process is a key parameter that controls the lifetime of the batteries, the rate capability etc. If it is not properly performed, the Li-ion conduction will not be optimal which could create kinetics problem. If voids are present in the solid electrolyte pellet, then during stress/strain, the voids could lead to fracture, hindering the ionic conductivity and lowering the electrochemical performance during cycling.

In this work, we are proposing an in depth (operando and postmortem) multiscale investigation of the electrolyte “shaping” and its consequence on the electrochemical activity. As an example, in Figure 1, we can see the impact of 50 cycles on the morphological/structural activities of LPSCl solid electrolyte collected by X-ray diffraction coupled to computed tomography (XRD-CT) at synchrotron facilities.

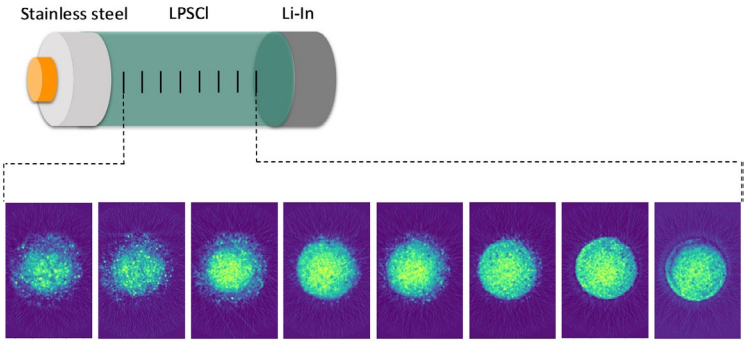

Figure 1: Morphological & structural evolution of LPSCl after 50 cycles collected by XRD-CT showing the extent of decomposition as a function of the electrode depth.

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Understanding inorganic/organic interfacial charge transfer by identifying the governing parameters of electrolyte/ceramic interface.

Léa R. Mangani, Grenoble/33, James A. Isaac, Didier Devaux, Renaud Bouchet.
PhD Léa Rose Mangani, Laboratoire électrochimie et physicochimie des matériaux et des interfaces (LEPMI) 1130 Rue de la Piscine, 38402, Grenoble, France

Li-ion battery holds an everlasting role in energy storage for nomad devices, electric vehicles as well as for grid energy storage. To date, Li-ion batteries are the most advanced energy storage systems, but they are reaching their limitation in terms of energy density and safety. New technologies are currently under development, and among them, all-solid-state batteries should deliver better electrochemical performance and enhanced safety. Solid polymer electrolytes (SPEs) provide suitable mechanical properties, but suffer poor conductivity, whereas the ceramic electrolytes (CE) are providing the opposite features.[1] Hybrid electrolytes should then combine high ionic conductivity coupled to high mechanical stability. To date, this synergy is not yet reached due to the complexity of the Li-ion transport especially at the SPE/CE interface. Indeed, a decrease in the composite ionic conductivity is generally observed and ascribed to the blocking interfacial resistance at the SPE/CE interface [2]. Yet, there are no proper kinetic model to elucidate the parameters that could influence this interfacial barrier nor a deeper understanding of its behaviour.

Herein, we propose an electrochemical methodology relying on electrochemical impedance spectroscopy that allows to scrutinize electrolyte/ceramic interfaces. To identify the governing parameters of each organic/inorganic interface, we vary some parameters such as electrolyte chemistry, electrolyte concentration, lithium salt nature, etc... The results of this thorough screening provide valuable insights about Li-ion transport at the interfaces and thus, enable the design of an optimized hybrid electrolytes for all-solid-state batteries.

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Characterization of the interfacial chemistry and Li-ion exchange processes in ceramic–polymer composites by solid state NMR.

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Composite polymer electrolytes (CPEs) ideally benefit from the high ionic conductivity of the ceramic phase and the and processability and mechanical properties of polymer materials. A crucial question for the development of such composite membranes is the detection and quantification of the Li-ion exchange processes existing at the interface between the polymer and ceramic particles. We will show in this work how multidimensional solid-state NMR experiments conducted in our laboratory, can unequivocally determine the presence and quantify the rate of Li-ion exchange processes in a PEO:LiTFSI–LLZO composite material. [1] Furthermore, the results obtained provide an insight into the possible Li^+ migration pathways and the presence and influence of secondary phases present at the polymer-ceramic interphase.

The results obtained in this work illustrate the suitability of solid-state NMR for the characterization and rational design of interfacial Li-ion exchange properties in next generation polymer–ceramic composite materials.

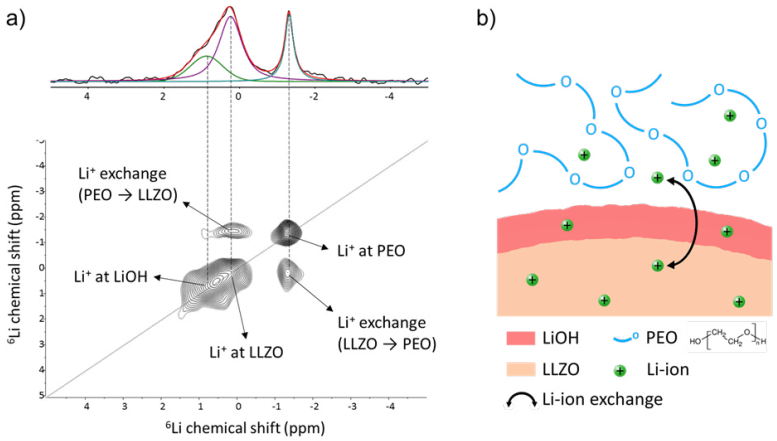

Figure: a) ^{6}Li-^{6}Li EXSY spectrum of a PEO:LiTFSI–LLZO composite, b) schematic representation of Li exchange [1]

Literature:

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Cost-efficient Na^+ halide solid electrolyte using earth-abundant metal elements for all-solid-state Na-ion batteries

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All-solid-state Na-ion batteries (ASNBs) using inorganic solid electrolytes (SEs) have attracted much interest owing to their combined potential advantages of improved safety and cost, compared to conventional lithium-ion batteries with flammable liquid electrolyte. Sulfide Na^+ SEs are highly attractive because they can be easily integrated into ASNB cells by simple cold-pressing-based fabrication. Thus far, several novel sulfide Na^+ SE materials, such as $Na_{3-x}Sb_{1-x}W_xS_4$, have been reported. However, sulfide SEs are defective in operating high-voltage batteries due to their electrochemical instability over 3 V region (*vs.* Na/Na^+), which thus hinders achieving high energy density of ASNBs. To alleviate this shortcoming, Na^+ halide SEs for high-voltage ASNB cells have been investigated. However, the number of the experimental reports is only a few: Na_2ZrCl_6, $Na_{3-x}Er_{1-x}Zr_xCl_6$, and $Na_{3-x}Y_{1-x}Zr_xCl_6$. In addition, the use of rare earth metal elements, such as Er and Y, offsets the advantage of the use of the low-cost Na in ASNBs.

In this presentation, our recent results on the development of new Na^+-conducting halide SEs with earth-abundant and cost-effective elements and their application to 3 V class all-solid-state batteries will be presented.

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Tuning halide solid electrolytes - synthesis, aliovalent doping and halogen substitution shed light into structure to property relationships

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Halide solid electrolytes with formula $Li_3M(III)X_6$ (M(III) = In, Sc, Y, Lanthanides, X = Cl, Br, U) are fast ionic conductors that can be used as solid electrolytes for all-solid state batteries (ASSB). Especially chlorides have demonstrated excellent performance in ASSB cycled with uncoated NCMs, demonstrating their compatibility against high voltage cathodes. Due to these promising results, it is interesting to learn about the structure to property relationship so that guidelines can be created for optimal material design.

We have found that for $Li_3M(III)Cl_6$ (M=Dy, Y, Ho, Er), small lithium deficiency during the synthesis leads to a trigonal to orthorhombic phase transition, improving the ionic conductivity by about one order of magnitude.

Investigating aliovalent substitution in monoclinic $Li_{3-x}In_{1-x}Zr_xCl_6$, the ionic conductivity is maximum at 30% Zr, indicating that the introduction of Li-vacancies aids diffusion. Structural analysis based on neutron diffraction only is tricky due to site co-occupancy of elements with opposite sign scattering length. Solid-state NMR measurements show multiple jump processes in the pristine material, which paired with the model of the crystal structure confirms anisotropy of the diffusion.

Halogen substitution in $Li_3YBr_xCl_{6-x}$ reveal a trade-off between ionic conductivity and electrochemical stability, as the larger Br opens up the Li-ion paths but is more prone to oxidize.

Finally, an Li_3YI_6 was synthesized and the structure characterized by neutron diffraction and single crystal x-ray diffraction. The Li-ion dynamics is characterized on multiple length scales using AC-impedance and a variety of NMR measurements.

Elucidating the redox processes of lithium thiophosphate solid electrolytes by X-ray spectroscopic techniques

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Besides the huge advantages all-solid-state batteries (ASSBs) potentially bear in terms of safety, energy and power density, shortcomings arise especially from their multitude of rigid/instable interfaces and internal resistances, known to be crucial bottlenecks for the cycling performance. Between the solid electrolyte (SE) and the high voltage cathode active material (CAM) or Li metal anode, the interface commonly suffers from (electro-) chemical instabilities, space charge layer formation and elemental inter-diffusion, in addition to volume changes inducing strain and contact loss.

Motivated by the high importance of understanding the redox-processes mechanism of the lithium thiophosphate SEs [e.g. Li_2S-P_2S_5 (LPS) and Li_6PS_5Cl (LPSCl)], we performed a systematic study using cyclic voltammetry, impedance spectroscopy, *ex-situ/operando* X-ray photoemission (XPS) and X-ray absorption spectroscopy (XAS). The SEs are mixed with conductive carbon to increase their interface surface area and cycled either in high or low voltage ranges to mimic the operating cycling voltages of the cathode and anode materials respectively.

We present the evolution during electrochemical cycling of the XPS S2p and P2p core levels, as well as XAS spectra at the S and P L- and K-edges. This combination of advanced surface and near surface analysis is capable of monitoring the dynamic changes in the chemical bonding and the electronic states, with additional depth-profiling for a multitude of redox reactions at the SE/conductive carbon interface.[1, 2]

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Concentration and Velocity Profiles in a Polymeric Li-ion Battery Electrolyte

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Jun.-Prof. Dr. H.-G. Steinrück, Paderborn Univ., Warburger Str. 100, 33098 Paderborn

Predictive understanding of charge and mass transport in electrolytes is at the heart of electrochemistry. The goal is to accurately simulate the performance of an electrochemical cell. For this purpose, the concentration-dependent transport coefficients of the electrolyte must be known. These include the transference number, which is an important metric to energy and power density of batteries. Nevertheless, researchers still argue about transference number values, even in baseline electrolytes.

We developed an alternative approach towards determining transport coefficients [1]. Specifically, we measured microscopic and macroscopic physical properties of electrolytes upon cell polarization in Li/electrolyte/Li cells, combined this with concentrated solution theory continuum modelling, and rationalized our findings with microscopic insight from MD simulations. We utilized a well-studied benchmark model system electrolyte consisting of LiTFSI and PEO. Under constant voltage polarization, we directly measured the velocity associated with electrolyte and ions via heterodyne synchrotron X-ray photon correlation spectroscopy (XPCS), and the TFSI-concentration gradient via X-ray absorption microscopy. The significance of our results lies in the unification of microscopic and macroscopic predictions from simulation with experimental measurements as well as the self-consistent determination of a concentration-independent transference numbers of approximately 0.2.

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Probing the interfacial dynamics of polymer electrolyte-based SSBs

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Understanding the underlying interplay at the electrode-electrolyte interface is crucial to improve the performance of batteries but has been challenging, especially for solid-state batteries (SSBs), whose interfaces are buried and inaccessible for many probes. [1] Here we highlight the importance of advanced characterization for probing the interfacial dynamics of SSBs. Specifically, (i) cryogenic electron microscopy, such as FIB/SEM & cryo-TEM [2-3], has emerged as a powerful tool to *ex situ* visualize sensitive Li and interfaces. (ii) *Operando & in situ* X-ray spectroscopy (e.g., XPS & XAS) and microscopy (e.g., XCT) are useful for monitoring the dynamic evolution of interfaces in SSBs during operation. We have been developing these methods to study the *real-time* evolution of interfacial chemistry between PEO-based polymer electrolytes and metal sulfide (MnS_2) cathode (Fig. 1a & 1b)) and the morphological evolution of Li metal anode in SSBs. [4]

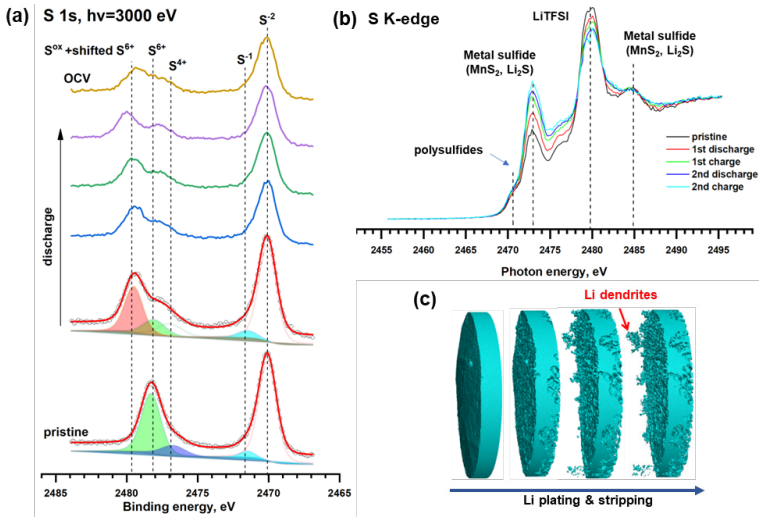

Fig. 1. (a-b) *Operando* XPS & XAS and (c) *in situ* XCT for interface monitoring of SSBs.

Literature:

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ABSTRACTS (POSTER)

In-Situ Transmission Electron Microscopy Heating Experiments of $LiNiO_2$ Particles in O_2 Atmosphere

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Nickel rich layered transition metal oxides $Li(Ni_{1-x-y}Co_xMn_y)O_2$ (NCM) and $Li(Ni_{1-x-y}Co_xAl_y)O_2$ (NCA) are the state-of-the-art cathode active materials (CAMs) for lithium-ion batteries, which deliver specific capacities of more than 190 mAh g^{-1} [1]. Research suggests that an annealing step at elevated temperatures can optimize the surface morphology and structure of the Ni rich particles leading to an improved electrochemical performance of the CAM [2]. This annealing process is executed in an oxygen atmosphere to prevent oxygen loss from the grains [3]. Our goal is to investigate this annealing step on a structural level using transmission electron microscopy (TEM) techniques.

Here, we report on our investigation of $LiNiO_2$ (LNO) as a model system for transition metal layered oxides during annealing in an oxygen atmosphere. Firstly, we present the elaborate sample preparation procedure by focused ion beam (FIB) milling which is required to prepare an electron transparent specimen on the heating chip of the in-situ holder, as well as the custom-built oxygen set-up. Moreover, we show in-situ high angle annular darkfield (HAADF) scanning transmission electron microscopy (STEM) images recorded during as well as electron energy loss spectroscopy (EELS) and energy dispersive X-ray spectroscopy (EDX) data of the particles recorded after the heating process.

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In-situ TEM observation of Na-filament formation in oxide electrolyte

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All-solid-state batteries (ASSBs) based on solid-state electrolytes are projected to overcome the performance and the safety limitations of liquid electrolytes counterparts. Unlike the sulfide or polymer based solid electrolytes, it is widely accepted that the polycrystalline microstructure of Li oxide electrolytes plays an essential role on the Li-ion migration. For instance, the grain boundaries (GBs) are one of the non-negligible factors that decrease the overall ionic conductivity. As the commercialized electrolyte for high-temperature Na-S batteries, Na-beta''-alumina ceramic is still an excellent candidate for room temperature ASSBs. Differing from most Li oxide solid-state electrolytes, Na-beta''-alumina possessed 2D Na-ion transport path due to its layer structure. Therefore, by the microstructural impact on the Na-ion transport and potentially Na-filament growth within electrolyte the GBs should not be the only considered factor, but also the orientations of the grains play an essential role on the local current density. Moreover, it's still unclear how the anisotropic Na-ion transport suffers from the grain boundaries. Hence, the comprehensive understanding of the effect of the crystallographic structure on the Na-ion migration was explored in this work through in-situ biasing TEM characterization.

With the purpose of getting access to the GBs of Na-beta''-alumina ceramic electrolyte (from Ionotec Ltd) in TEM, focus ion beam (FIB) (FEI Strata 400 S) is used on the ceramic pellet. Afterwards, the FIB specimen was assembled into STM-TEM holder (from ZepTools™) with W tip for in-situ bias experiment in TEM column to pump the Na-ion migration.

Initial experiments focused on Na-beta''-alumina solid electrolyte under high *in-situ* biasing voltage up to ±15V. The initial high voltage helps overcome the diffusion barrier at GBs and promotes the mobility of Na ions. During the biasing, Na segregation around certain GB was visualized in real-time. Through 4D-STEM and automated crystal orientation map (ACOM) analysis, the orientations and the GBs information were obtained. It was found that Na filament always start growing at the GB of the two adjacent grains with special orientation relationship, which is in good agreement with the anisotropic 2D pathways for ion migration in Na-beta''-alumina.

Methods from machine learning for the structural analysis of Li-ion electrode particles

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Microscopy techniques like scanning electron microscopy (SEM) or X-ray computed tomography (CT) can provide detailed image data of electrode particle microstructures. Followed by a quantitative structural characterization such data allows for the investigation of structure-function relationships, e.g., the influence of an electrode particle's microstructure on its electrochemical behavior. However, for the structural characterization by means of image data nontrivial processing tasks are often necessary. In this talk several applications of machine learning methods and stochastic geometry are shown for the structural characterization of particles in lithium-ion battery electrodes imaged by SEM, CT and focused ion beam (FIB) - electron backscatter diffraction (EBSD). In the first application, a generative adversarial network (GAN) is deployed to perform super-resolution on SEM-images of cycled cathode particles such that fine features like cracks within particles can be more reliably characterized to investigate the state of degradation [1]. The second application shows how convolutional neural networks can be used to achieve a grain-wise segmentation of FIB-EBSD data of polycrystalline electrode particles [2]. The third application deals with the structural multi-scale modeling of cathode particles to overcome limitations of different imaging techniques [3]. Therefore, a stochastic geometry model is calibrated using CT data depicting the outer shell of cathode particles and FIB-EBSD data of the grain architecture of a cathode particle. Then, the model can be used to perform structural scenario analyses, i.e., to generate arbitrarily many digital twins with statistically similar shape and grain architecture as the particles observed in the image data. These digital twins are used as input for numerical charge simulations to investigate their degradation behavior [4].

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Monitoring of structural changes in sodium/sodium-ion cells by advanced in-situ and ex-situ solid-state NMR

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For the past few years, sodium/sodium-ion batteries have become more and more attractive as alternative to lithium-ion batteries. Due to the high abundance of sodium in earth crust, its better availability compared to lithium and thus lower costs, sodium/sodium-ion batteries have the potential to be suitable for environmentally friendly energy storage technology in future. [1,2] Although, at first glance sodium and lithium are similar, there are significant differences in their physico-chemical properties, necessitating different materials i.e. electrodes and electrolytes etc. whose interplay has to be understood to make sodium/sodium-ion batteries available for the market. This goes in hand with a deeper analysis of structural changes in electrochemical cells that have to be characterized preferable under in-situ conditions. The presentation will introduce the use of ^{23}Na in-situ solid-state NMR as powerful tool to investigate local structural changes occurring during charging and discharging processes in sodium/sodium-ion cells. As an example, the in-situ NMR characterization of an electrochemical cell consisting of polymer-derived silicon carbonitride ceramic (SiCN) as a working electrode and sodium metal as a counter electrode is presented. After disassembling the cell, the sodium storage in SiCN material is investigated by ^{23}Na ex-situ MAS NMR at high spinning frequencies and different magnetic fields to obtain higher resolution.[3]

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Revealing local ionic conductivity and chemical distribution in solid state electrolytes by Electrochemical Strain Microscopy

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Solid State Batteries require a detailed knowledge of surface and interfacial reactions at a process relevant scale as key for developing materials with advanced functionality. Atomic Force Microscopy (AFM) is an ideal tool for such investigations because of its ability to work in numerous environments with high spatial resolution. Lithium Aluminum Titanium Phosphate, $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$, is a typical representative of a solid state electrolyte with NASICON type structure, exhibiting superior lithium ion conductivity. The appearance of secondary phases of aluminum phosphate under certain manufacturing conditions demonstrate the need for understanding the correlation of lithium ion mobility and microstructure. Furthermore, new challenges arise in optimizing interfacial processes in hybrid electrolyte systems.

Electrochemical Strain Microscopy (ESM), an advanced Atomic Force Microscopy mode, is employed to investigate the influence of the microstructure in LATP. A clear contrast between LATP and the secondary phase is observed, exhibiting a significantly reduced Li-ion mobility in secondary phase areas. In order to correlate chemical information with the ESM signal, Energy-Dispersive X-ray Spectroscopy (EDX) is utilized in a correlative approach. [1] ESM has also been successfully applied to investigate the ionic conductivity at the interface between polymer and ceramic in a hybrid electrolyte. [2] Clear interfacial effects between polymer and ceramic particles are observed and critically discussed. In a short outlook, applications of ESM for investigating cathode materials for solid state batteries are introduced. [3]

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Comparative evaluation of degradation in thiophosphate based all solid-state batteries

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Solid-state batteries using thiophosphate solid electrolytes are a promising candidate for future lithium battery technologies. Thiophosphate solid electrolytes (SE) offer high ionic conductivities while at the same time providing good mechanical properties which facilitates manufacturing of these cells. These solid electrolytes, however, are thermodynamically unstable against commonly used cathode active materials (CAM) such as $Li_{1-x}Ni_aCo_bMn_{1-a-b}O_2$ (NCM). Oxidation of the solid electrolyte occurs forming various products detrimental to the cell's performance. However, detailed understanding and quantification of these processes and degradation products is challenging and remains unclear to many researchers in the field. Developing optimal combinations of CAM and SE combinations requires both good understanding of degradation processes and mechanisms as well as good analytical procedures to quantify them.

Here, we present a series of complementary analytical techniques suited for fast evaluation of CAM/SE combinations. By combining both state-of-the-art electrochemical methods and post-mortem analytical techniques helps quickly analysing different combinations of CAM and SE.

Electrochemical testing is done using a reference electrode (µ-RE) to only show cathode side contributions in impedance. Rate tests are performed with a µ-RE as well to evaluate the true rate capability of the system under investigation without detrimental influence from the anode. Post-mortem analysis quantifies the amount and kind of degradation present in the sample after cycling using time-of-flight secondary ion mass spectrometry (ToF-SIMS). To avoid the influence of the current collector and to avoid the need for sputtering a modified current collector was used for this purpose.

Stability and surface modification of LLZTO thin film

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Since the commercialization of rechargeable lithium-ion batteries, it was desired to boost the battery capacity by using a lithium metal anode. It was quickly realized that dendrites are formed through the liquid electrolytes, leading to a short circuit. Murugan et al. proposed a garnet-type $Li_7La_3Zr_2O_{12}$ (LLZO) solid electrolyte with stability against lithium to circumvent dendrite formation [1]. By using the novel CO_2-laser assisted CVD technique with highly controlled thin film growth, superior phase stability and ionic conductivity of garnet-type $Li_5La_3Ta_2O_{12}$ (LLTaO) compared to LA-CVD grown LLZO, was obtained [2]. Additionally, with surface science experiments performed in our group, it has been demonstrated that LLTaO shows high stability against lithium under equilibrium conditions [3].

One of the intrinsic problems of LLZO and $Li_{7-x}La_3Zr_{2-x}Ta_xO_{12}$ (LLZTO) is a high reactivity towards traces of water and CO_2 resulting in the formation of Li_2CO_3 and the surface passivation. In this work, LiF film as a protective layer is deposited onto LLZTO by using RF-magnetron sputtering technique. The LiF layer prevents the formation of Li_2CO_3 on the LLZTO surface under ambient air [4]. In upcoming research, it is envisaged to increase the ionic conductivity via aluminum and gallium doping. An anode-free all-solid-state thin-film battery can be prepared via the deposition of cathode materials on top of the solid electrolyte by using RF-sputtering. The chemical composition and electronic properties of the components of the battery cell as well as the interfacial properties can be studied by in situ photoelectron spectroscopy.

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A method for visualizing Li distribution in solid-state batteries by Plasma FIB-SEM, EDS, and SIMS

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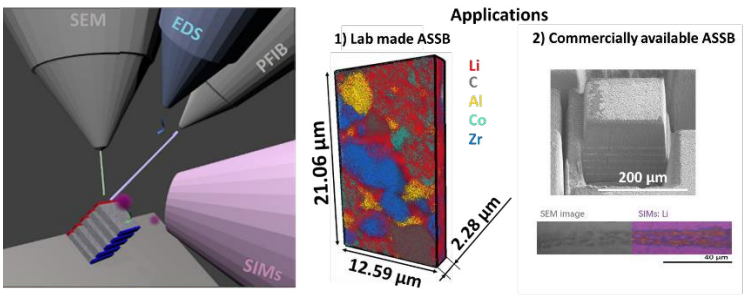
The all-solid-state battery (ASSB) is a strong candidate for solving safety concerns and surpassing lithium-ion battery performance in various applications. However, there is a key challenge of slow transport of Li-ions in the solid phase. Direct visualisation of the Li-ions dynamic provides new insight for understanding Li-ions transportation. But this presents a daunting problem.

In this talk, we report a method to directly map all elements, including Li, on an ASSB electrode cross-sectional face (~ 20 µm area of interest, AoI). As a validation, we then applied this technology on a commercially available ASSB over a large area (~ 200 µm AoI). A Dual-Beam Xe^+ plasma-focused ion beam (PFIB/SEM) with an inert atmosphere sample transfer capability was used for sectioning and polishing up to a sub-millimetre scale. Energy Dispersive X-ray Spectroscopy (EDS) was for mapping non-lithium elements at a high resolution. Secondary-Ion Mass Spectrometry (SIMS) was used for direct detection and mapping of Li at a similar spatial resolution. We have generated new correlative workflow protocols to combine milling and data capture from both EDS and SIMS detectors. New algorithms and image manipulation protocols were developed to merge and correlate SIMS and EDS datasets. We then reconstructed the structures of sample electrodes at multiscale through the use of these 2D and 3D correlative tomography protocols.

This method could be key to answering unsolved questions in lithium-related electrochemistry in ASSB. Progress to date, advantages, restrictions, possible future uses, and likely next developments of this analytical strategy will also be described.



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Comparison of Conventional Co- and Cold-Sintered All-Phosphate Based Composite Cathodes for Solid-State Batteries

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Oxide solid-state batteries (ox-SSB) are characterized by high safety and extended temperature range compared to conventional batteries. Oxide solid electrolytes (SE) achieve high ionic conductivities by sintering at high temperature T > 1000 °C. In composite cathodes, the SE must form a percolating, ion-conducting network around the cathode active material (CAM). High sintering temperatures of conventional sintering cause undesirable reactions between the materials [1,2], which limits the ionic conductivity of the SE and Li^+ intercalation of the CAM. This results in both potential lower energy density and rate capability of ox-SSB.

Cold sintering is an emerging method of ox-SSB materials preparation. Using high pressure (p ~ 500-600 MPa), liquid additives and reduced sintering temperature T < 200 °C enable SEs with ionic conductivities of 10^{-5} S/cm [3]. Post-annealing is required to obtain the same values as in case of conventionally sintered materials. In composite cathodes the lower temperature is expected to result in less decomposition reactions between CAM und SE.

In the presented study, the sintering behavior of all-phosphate composite cathodes based on $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ and $LiFePO_4$ is investigated. Comparative analyses of conventional co- and cold-sintered composite cathodes are made. The decomposition during sintering and thermal post-treatment is characterized by X-ray powder diffraction and the microstructure of the composite cathodes is analyzed with secondary electron microscopy. The electrochemical properties are investigated in half cells by infiltration the sintered cathodes by liquid electrolyte or polyethylene oxide.

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Thin Polycaprolactone Separators for Polymer Solid State Batteries

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Polymer electrolytes are inherently safer than classical liquid electrolytes due to their non-volatile properties and high viscosity that prevents leakage upon mechanical abuse. While commercial battery designs based on PEO have operating temperatures above 60 °C, this work demonstrated operating temperatures of 40 °C based on tailor-made polycaprolactone electrolytes. These electrolytes are considered biodegradable, affordable and are straightforward to produce. [1]

Cells with thin polycaprolactone separators yield decreased internal resistances and improved energy density, where higher cathode capacities were realized upon addition of flowable components. This approach was particularly successful in case of capro-lactone oligomers, realizing NMC622||Li cells with cathode mass loadings of 6 mg/cm² (coated NMC622) with discharge capacities >150 mAh/g.

Aspects of manufacture and processing including the thin matrix-supported electrolytes and composite cathodes as well as opportunities of the introduced cell designs are highlighted.

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Development of a zero excess Li-S battery containing an inorganic solid electrolyte

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To prevent the catastrophic effects of climate change, there is a large demand to produce batteries and energy storage devices offering both improved volumetric and gravimetric energy densities. One promising candidate is the lithium-sulfur (Li-S) chemistry due to the high theoretical capacity and abundance of sulfur. However, current designs require a 1000% excess of Li metal which impedes their commercialisation. An area gaining momentum is the development of “anode-free” or zero excess lithium (ZEL) cells which minimise inactive materials and mitigate the challenges of handling Li metal foils during fabrication. However, there are limited systematic studies concerning ZEL Li-S cell fabrication and optimisation.

Here, we present the development of a ZEL cell comprised of a Li_2S composite positive electrode, metallic foil current collector and non-aqueous electrolyte. We investigate the effects of electrolyte$_{volume}$:sulfur$_{mg}$ (ES) ratio, various current collector materials and positive electrode substrates. The optimised cell achieves good capacity retention with a Coulombic efficiency of over 98% after 50 cycles, and a final capacity of 360 mAh g^{-1}. Significant capacity decay is observed in the first five cycles and is attributed to Li loss during plating/stripping at the negative current collector. Initial work applying an ion-conductive protective layer to metal current collectors with the aim to improve capacity retention will be shown. Furthermore, directions towards ZEL Li-metal and all-solid-state cells will be discussed.

Surface optimization of phosphate-based composite cathodes for lithium batteries

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Tape casting is a promising technique not only for scalable and low-cost production of ceramic sheets, but also for optimizing their properties such as microstructure, ionic conductivity and stability [1]. Recently we achieved an excellent area-specific storage capacity above 3 mAh cm^{-2} over 30 cycles in a Li battery cell based on a tape-cast composite cathode $LiFePO_4/Li_{1.5}Al_{0.5}Ti_{1.5}(PO_4)_3$ (LFP-LATP) with approximately 100 µm thickness in combination with polymer electrolyte [2]. It is also shown that densification, ionic conductivity and sintering temperature of LATP could be optimized with a sintering aid of Li_2WO_4 (LWO) [3].

Here we present a tape-cast LFP-LATP composite cathode on the one hand with optimized surface by addition of 5 wt% LWO and on the other hand optimized percolation of components with higher conductivity by changing the ratio of the solid phases. Tape-cast and co-sintered composite cathodes LFP-LATP with mass ratio of 40:60, 50:50 and 60:40 were fabricated with approx. 100 µm thickness. By adding 5 wt% LWO, the sintering temperature of the composite could be lowered from 800°C down to 700°C. The sintered materials were characterized by XRD, TEM, and XPS. Electrochemical cell tests were performed using both liquid and PEO-polymer electrolytes. The electronic conductivity of this composite cathode is achieved by conducting carbon, which formed in-situ during the sintering process. The degree of carbonization was analyzed by Raman spectroscopy.

Acknowledgement

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Development of all-solid-state lithium sulfur battery cathodes with low binder content

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The concept of Lithium-sulfur (Li-S) batteries is considered as next-generation battery technology beyond lithium-ion batteries due to the high specific capacity of sulfur and low production cost. Despite years of research and improvement, LiS batteries with liquid electrolytes still suffer from low cycle life and continuous loss of capacity due to the polysulfide shuttle. The concept of all-solid-state batteries demonstrate a promising alternative to overcome the fundamental problems caused by soluble sulfur species.

In this study, we focused on the investigation of carbon composite cathodes and the transfer to prototype cell concepts. The results to date show, that the interfaces between carbon material, sulfur and solid electrolyte depend very strongly on the carbon morphology (porosity, particle size) and on the processing (type of sulfur infiltration or processing of the cathode composite). A specific capacity of >1600 mAh/g (sulfur mass) has already been achieved at different cathode compositions and loadings in small scale prototype cells. The high sulfur utilization above 95 % is very promising. Hence, the investigation of the cathodes in large-scale prototype cells under realistic conditions is crucial.

In order to assemble free standing cathodes, the approach of sulfur/carbon solid electrolyte dry films with low binder content was successfully demonstrated, showing the same performance as a powder cathode without binder. In further steps, the free standing cathodes have to be combined with the other cell components (e.g. thin separator layers) into realistic pouch cell concepts. By combining these materials and process innovations in multi-layer demonstrator cells, this cell technology is to be transferred from basic research to the first application-oriented prototypes.

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Fabrication of thin-garnet electrolytes using pulse 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 $Li_{6.5}La_3Zr_2Ta_{0.5}O_{12}$ 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 2.5 µm LLZO 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.

Investigations of negative electrode alternatives towards efficient anode-free solid-state batteries

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In recent times, anode-free batteries (AFB) have attracted increasing interest due to the elimination of a conventional negative electrode material from the cell, exploiting lithium inventory from a lithiated cathode. Such configuration implies a much simpler, cost-effective, and more sustainable approach, helping to overcome the main weak points of the solid state battery (SSB) technology: the high cost and sustainability issues due to the use of highly reactive and expensive Li metal foil anodes.

In this work, surface modifications of the selected copper current collector (CC) have been performed by coating using composite layers, made of carbon and different metal nanoparticles. The impact of different coatings on the electrochemical performance of single layer solid-state anode free pouch cells (SS AFB, nominal capacity of ca. 30 mAh) based on a PEO electrolyte and $LiFePO_4$ cathode, has been systematically studied. With the best tested coating, composite layer containing Ag nanoparticles and carbon black in a 1:3 wt. ratio, the initial discharge capacity is doubled respect to bare CC, and the cells exhibit a coulombic efficiency above 99% after 50 cycles (**Fig. 1**).

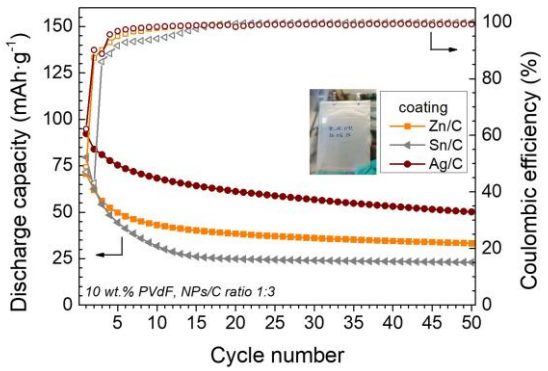

Figure 1. Discharge capacity and Coulombic efficiency of pouch-type SS AFB, using 15 µm coatings on anode CC, made with different metals nanoparticles and carbon black. LFP cathode with loading 0,6 mAh·cm^{-2}. Cycling conditions: 60°C, 1 N·m, DoD 100%, 2.5-3.8 V, 0.1C–0.1C.

Authors acknowledge to Basque Government under the ELKARTEK-CICe2021 KK 2021/00064 project for financial support.

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Designing cathode composite for oxide Li-metal battery

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Solid-state lithium metal battery has a huge potential to be a more energy-dense architecture, safety and fast charging capability relative to a current lithium-ion battery.

In particular, the cell interface made of oxide-based electrolyte and cathode is believed to withstand more tightly than any other ‘soft’ solid electrolytes (polymer, sulfide electrolytes) once optimized.

Sintering at high temperature is generally required to produce dense interfaces for oxide-based electrochemical devices; however, the poor chemical compatibility of the oxide electrolyte with common cathode active materials limits a wide range of material choice, processing and microstructure-performance relationship.

Here, potential processing strategies to fabricate oxide-based cathode composite are presented based on an infiltration of $LiCoO_2$ active material and $Li_7La_3Zr_2O_{12}$ catholyte through the porous scaffolds or a co-firing of both.

Discussion is aimed toward opportunities to meet important target parameters including low interfacial resistance, high-loading capability and specific capacity for high energy and power Li-metal battery.

Slurry-Cast Solid Electrolyte/Binder-Sheets as Separators in All-Solid-State Batteries – a Comparative Study

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In the present study, we report on the preparation of composite sheet-type separators for sulfidic all-solid-state batteries by a slurry-casted process, investigating three different sulfidic solid electrolyte systems (Li_6PS_5Cl, $Li_7P_3S_{11}$ and $Li_{10}SnP_2S_{12}$) in combination with different volume fractions of hydrogenated nitrile butadiene rubber (HNBR, φHNBR = 1.7 – 16.0 vol.-%) binder.[1-2] By means of the analysis of top-view and cross-sectional scanning electron microscopy (SEM) images of the prepared sheet-type separators, combined with energy dispersive X-ray spectroscopy (EDX), we characterize the influence of the slurry-coating process conditions as well as of the binder volume fraction on their morphology. Compaction of the obtained separator sheets is easily possible by uniaxial compression at room temperature, resulting in residual pore volume fractions of ≈ 3 – 12 %, depending on the respective solid electrolyte system. While increasing fabrication pressures lead to a reduction of void volume and an increasing contacting between the solid electrolyte particles, very high fabrication pressures (> 200 MPa) lead to a fusing of the SE particles and to nearly pore-free separator sheets. Apart from the micromorphology and porosity of the separator sheets, we investigate the dependence of HNBR binder content, processing as well as densification conditions on their ionic conductivity using potentiostatic electrochemical impedance spectroscopy (PEIS) measurements. As one would expect, the Li+-ion conductivity of the SE/HNBR separator sheets decreases with increasing binder volume fraction. Interestingly, however, the relationship between Li^+-ion conductivity and binder volume fraction (φ_{HNBR}) is essentially identical for the three different sulfidic electrolytes that are examined in our study.

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Investigations of negative electrode alternatives towards efficient anode-free solid-state batteries

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In recent times, anode-free batteries (AFB) have attracted increasing interest due to the elimination of a conventional negative electrode material from the cell, exploiting lithium inventory from a lithiated cathode. Such configuration implies a much simpler, cost-effective, and more sustainable approach, helping to overcome the main weak points of the solid state battery (SSB) technology: the high cost and sustainability issues due to the use of highly reactive and expensive Li metal foil anodes.

In this work, surface modifications of the selected copper current collector (CC) have been performed by coating using composite layers, made of carbon and different metal nanoparticles. The impact of different coatings on the electrochemical performance of single layer solid-state anode free pouch cells (SS AFB, nominal capacity of ca. 30 mAh) based on a PEO electrolyte and $LiFePO_4$ cathode, has been systematically studied. With the best tested coating, composite layer containing Ag nanoparticles and carbon black in a 1:3 wt. ratio, the initial discharge capacity is doubled respect to bare CC, and the cells exhibit a coulombic efficiency above 99% after 50 cycles (**Fig. 1**).

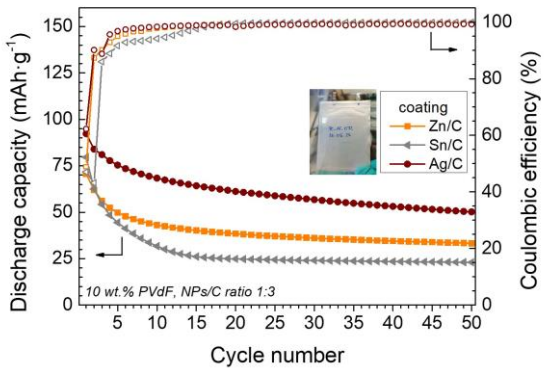

Figure 1. Discharge capacity and Coulombic efficiency of pouch-type SS AFB, using 15 µm coatings on anode CC, made with different metals nanoparticles and carbon black. LFP cathode with loading 0,6 mAh·cm^{-2}. Cycling conditions: 60°C, 1 N·m, DoD 100%, 2.5-3.8 V, 0.1C–0.1C.

Authors acknowledge to Basque Government under the ELKARTEK-CICe2021 KK 2021/00064 project for financial support.

Literature:

[1] O. García-Calvo et al. Frontiers in Chemistry, 2022, 10, 934365

Challenges in the Development of All-Solid-State 5 V Lithium Ion Batteries

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The development of all-solid-state high-voltage Li-ion batteries (> 4.8 V vs. Li/Li^+) is a challenge associated with a) the electrochemical stability window and Li^+ conductivity of solid electrolytes, b) the intrinsic stability of redox active cathodes at a high-operation voltage, c) the stability of the cathode-electrolyte interface upon operation of high-voltage batteries, d) Li^+ conductivity across the electrode/electrolyte interface, and e) the issues associated with the electrode/electrolyte contact.

Here, we present our novel results on functionality of all-solid-state thin-film batteries (ASSTFB) composed of $LiCoPO_4$ (LCP) cathode with olivine structure (redox potential ~4.8 V vs. Li/Li^+), metallic lithium as the anode. As solid electrolytes, the high-voltage ceramic $Li_{1.5}Ti_{1.5}Al_{0.5}(PO_4)_3$ (LATP) and amorphous lithium phosphorus oxynitride (LiPON) were used.

Chemical compatibility of the solid electrolytes with the LCP thin-film cathode, as well as their interfacial properties are *in-situ* studied by photoelectron spectroscopy. The redox peaks of the LCP cathode in all-solid-state battery are observed at 4.7 V and 4.9 V. Furthermore, electrochemical activity is compared to that of LCP battery with the hybrid electrolytes. The impact of coating as protection layer for the electrodes is studied. The impact of charging/discharging rate on the mechanical stability of the solid electrolyte is demonstrated. The possible degradation mechanisms occurring in the high-voltage all-solid-state batteries are presented.

The Role of Pressure and Temperature during Cell assembly on the Cell performance of sulfide based All-Solid-State-Batteries

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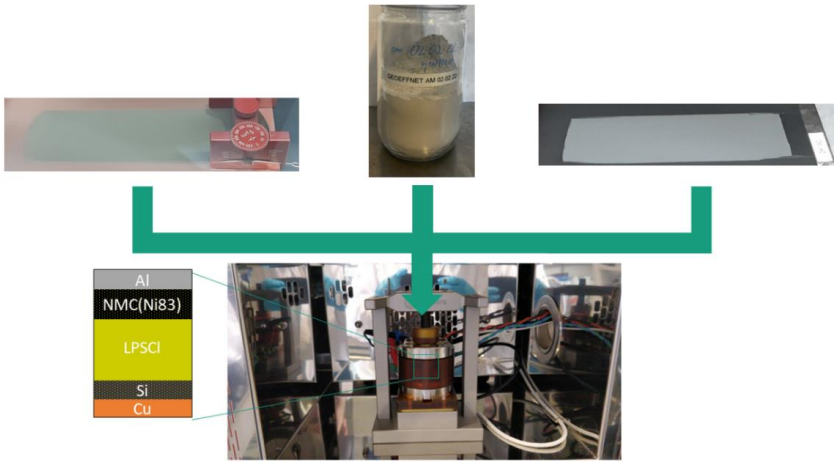
All-Solid-State-Batteries (ASSBs) are promised to be the successors of currently used lithium-ion-batteries. Still in development, different electrolytes are being studied as suitable candidates for the next-gen batteries. One class of them are sulfide based which demonstrate high ionic conductivity at room temperature as well as ductile behavior, allowing them to be compacted at low temperatures and pressures.
Substantial work has been done on the investigation of sulfide electrolytes themselves but fewer on the integration into ASSBs. Therefore, in this work we will demonstrate the cell assembly process of ASSBs with in-house developed electrode sheets for cathode (Ni-rich (Ni83) NMC) and anode (silicon), using an Argyrodite-type sulfide ion-conductor as electrolyte and separator (pellet-type). At that, we take a closer look on the parameters of applied pressure as well as temperature during the cell assembly. The effect will be analyzed using galvanostatic cycling methods as well as electrochemical impedance spectroscopy (EIS). Investigating these parameters will support optimizing industrial processes such as roll pressing and set up a thermal stability window for this cell chemistry.



Titanium sulfide-based ternary compounds as cathode active materials for SSB batteries

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Among the technologies currently under development for energy storage, solid-state batteries with sulfide cathodes offer a step increase in capacity and safety while employing sustainable and affordable materials. TiS_2 is one of the most promising materials to be used at the cathode of said batteries. [1]

Its ability to reversibly intercalate Li-ions at high capacity and its high conductivity put this material under the spotlight of battery research many decades ago already [1] although that place that was subsequently lost in favour of other newly developed intercalation compounds. However, the deeper understanding we now have of the functioning of batteries has caused a renewed interest in TiS_2 in the past years [2].

A possible development of this line of research could come from $TiX^z_yS_{2+(z/2)y}$ ternary compounds, where X is another transition metal (Fe, Mn, Zr,...) and z its oxidation state. Very few similar Ti-X-S ternary compounds have been investigated so far as electrodes [3]. With appropriate ratios and synthesis, the layered structure typical of TiS_2 is preserved in these compounds, which seems to indicate the new metal simply replaces some of the Ti in the structure. This approach seems to overcome some of the main shortcomings of TiS_2. In a few combinations we tested experimentally we could already notice a reduced capacity fading (through inhibition of the $Li + TiS_2 \rightarrow Ti + Li_2S$ conversion reaction) and increased air stability (through an increased voltage). Other beneficial effects (currently under investigations) are also not to be excluded, such as increased capacities (using electrochemically active metals), alternative reaction paths or improved conductivity.

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High-energy solid-state batteries by the use of nanostructured Si-C materials

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The high gravimetric and volumetric capacity of silicon makes it an attractive anode material for lithium-ion solid-state batteries (SSBs). [1,2] Herein, we present silicon carbon void structures (Si-C) as anode material for SSBs for the first time. The carbon matrix enables excellent cycling performance in solid-state cells with areal loadings as high as 7.4 mAh cm^{-2}. [3]

Si-C composite electrodes showed higher lithiation capacities, better rate stability and higher capacity retentions than pristine silicon nanoparticles (SiNPs), which rapidly degraded due to the immense mechanical stress upon charging and discharging. Hence, the volume changes of the SiNPs are well compensated by the carbon matrix, which also stabilizes the entire electrode. [3]

In full cells with nickel-rich NCM ($LiNi_{0.9}Co_{0.05}Mn_{0.05}O_2$, 210 mAh g^{-1}) as cathode, higher initial discharge capacities and coulombic efficiencies (72.7 % vs. 31.0 %) can be achieved compared to the liquid system. The solid electrolyte (Li_6PS_5Cl, 3 mS cm^{-1}) does not penetrate the whole carbon matrix of the Si-C particles resulting in less side reactions. Consequently, prelithiation of the Si-C anodes is not required in SSBs. By applying either a low (1.1) or rather high n/p ratio (2.0) capacity retentions of up to 87.7 % after 50 cycles could be reached. The herein presented Si-C composites, effectively compensating the volume changes of silicon, are a promising concept for stable, high-capacity SSB anodes. [3]

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Thin-film solid-state batteries: from efficient microbatteries to monolithically-stacked devices

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All-solid-state thin-film batteries (TFBs) combine several features of solid-state batteries, such as long lifetime, high charge/discharge rates, and safety, with the potential of large-scale manufacturing using physical vapor deposition (PVD) methods. The talk will review several recent highlights of new materials and interfacial phenomena investigated in the 2D thin-film geometry in our research group. These include Li-rich NMC811 cathodes that can be cycled for > 1000 cycles within a wide voltage range of 1.5…4.7 V [1], ultra-thin amorphous LLZO electrolytes to block lithium dendrites [2], and amorphous carbon interlayers at the Cu/LIiPON interface to facilitate homogeneous Li plating and stripping in an anode-free configuration [3]. At last, we will present an experimental proof-of-concept of monolithically stacked (so-called bipolar) TFBs entirely fabricated with PVD methods, which could resolve the principal handicap of the low specific and areal capacity in TFBs and enable a new type of high-power solid-state devices.

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Rapid Thermal Processing of Garnet-Based Composite Cathodes

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In the pursuit of safer batteries with a high energy density, the transition from liquid to solid electrolytes resulting in solid-state batteries (SSB) is probably one of the most promising directions in current battery research [1]. A promising Li-ion conducting oxide-ceramic is the garnet $Li_7La_3Zr_2O_{12}$ (LLZO). However, it needs to be densified in order to be used as separator or in composite cathodes of SSB, but suffer from lithium loss at elevated temperatures.

To address this issue, the sintering method “rapid thermal processing” (RTP) is used to fabricate ceramic composite cathodes of LLZO and $LiCoO_2$ (LCO), the cathode active material. Rapid thermal annealing techniques enable quick and non-contact processing of ceramic materials and are particularly promising for materials containing elements with high vapor pressure.

The cathodes were deposited on LLZO separators by screen-printing, a scalable industrial process for the fabrication of ceramic components. A detailed analysis by Raman spectroscopy and X-ray diffraction analysis confirms the successful mitigation of secondary phase formation between LCO and LLZO. The subsequent application of indium-metal anodes resulted in fully inorganic SSB that were electrochemically cycled.

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Implementation of a Li-Metal Reference Electrode in All-Solid-State Battery Pouch Cells for Half-Cell Potential Controlled Rate Tests

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The discharge rate capability is an important property of electrodes for all-solid-state batteries (ASSBs) and is often studied by a slow charge and a fast discharge rate. In order to guarantee that the end-of-discharge is truly defined by the cathode potential, either an anode that does not limit the rate or a cathode potential control via a reference electrode is required. However, the commonly used InLi alloy is known to have a limited delithiation capability at high current density.[1,2] Thus, when using InLi as counter electrode in discharge rate tests, the use of a reference electrode would be highly beneficial to ensure that the end-of-discharge is defined by the cathode potential. To date, however, the application of reference electrodes in ASSBs has only been performed in highly specialized setups,[1-3] as for a proper implementation various aspects have to be considered: first, the hardware for investigating ASSB components requires hermetic sealing and the capability to apply high pressures and, second, most ASSB cells are based on bulk-type electrodes, i.e., pressed powders. To overcome these issues and enable the use of reference electrodes in ASSB cells, we developed a straight-forward preparation method for a three-electrode setup. In our approach, sheet-type separators[4] and cathodes were used to assemble pouch cells with an InLi alloy anode. By extending the separator sheet beyond the electrodes, a piece of Li-metal could be attached, serving as a reference electrode with a stable potential. This setup is used to deconvolute the half-cell potentials during a rate test of a nickel-rich NCM composite cathode with sulfidic electrolyte (Li_6PS_5Cl) and an areal capacity of 3 mAh/cm^2. In discharge rate tests, current densities up to 3 C (9 mA/cm^2) are applied, where the InLi anode overpotentials are very large and thus lower the discharge capacity in cell-voltage-controlled rate tests. The latter will be compared with discharge rate tests where the lower cut-off potential is controlled by the cathode potential measured via the Li-reference electrode.

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Fabrication and Modification of Pouch-Type All-Solid-State Lithium Batteries

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High energy density for lithium-ion batteries (LIBs) has become critically important for the practical application of electric vehicles and energy storage systems. In terms of high energy density, Li metal batteries have been extensively studied. However, the intrinsic dendritic growth issues for Li metal anodes and the safety problems associated with flammable organic liquid electrolytes (LEs) have been major drawbacks. In this regard, all-solid-state batteries (ASSBs) using non-flammable solid electrolytes (SEs) have become promising alternatives for conventional LIBs. Especially, ASSBs using sulfide SEs are major candidates for practical applications owing to their high ionic conductivities and mechanical sinterability. Due to the high Young's modulus, it was believed that most SEs could prevent the dendritic growth of Li. However, it has been revealed that SEs cannot prevent it. Thus far, most studies on ASSBs have been reported using powder-based uniaxial-pressurized cells while pouch-type ASLBs cells using thin SE films are practically meaningful.

In this presentation, fabrication strategies for practical pouch-type ASLB cells employing thin sulfide SE films and corresponding electrochemical performances are presented.

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Towards Optimised Cell Design of Thin Film Silicon-Based Solid-State Batteries via Modelling and Experimental Characterisation

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Abstract

To realise high energy density solid-state batteries for use in wearable, portable electronic and Internet of Things devices, the use of an advanced negative electrode material such as Li or Si is required. However, these materials exhibit large volumetric expansions during cycling, causing significant mechanical stress and strains within the cell. The electrochemical and mechanical behaviour of these cells is poorly understood and insight into the electro-chemo-mechanical relationship is required to improve cell performance and durability.

Here I will present a 2D electro-chemo-mechanical model of a thin film SSB which is validated using experimental steady-state, transient and pulsed electrochemical methods.[1] The cell, consisting of an amorphous Si negative electrode, lithium phosphorus oxynitride (LiPON) solid electrolyte and lithium cobalt oxide positive electrode ($LiCoO_2$) is subjected to 1C cycling, high C-rate pulses, electrochemical impedance spectroscopy (EIS) and the galvanostatic intermittent titration technique (GITT) to extract key parameters for the model. A viscoplastic model is used to predict the strains and plastic deformation of Si due to (de)lithiation.

The validated model is used to explore the peak interfacial stress and strain which occur at the Li-Si alloy and LiPON boundary. The mechanical properties of the Li-Si alloy which forms during lithiation, is highly dependent on state of charge. Careful consideration of the Li-Si mechanical behaviour as a function of lithiation is modelled and the distinct electrochemical signature of the Li-Si alloy layer detected using distribution of relaxation times (DRT) analysis. The peak volumetric expansion increases from 69% to 104% during 1C cycling as a function of relative electrode thickness (up to a factor of 4). Future directions include using the model to vary the electrode thickness to understand its sensitivity on the stress-strain behaviour. This will help to further cell design and optimisation of solid-state battery technologies.

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The influence of molecular weight on the processing of PEO-based solid electrolytes with a slot die

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The constantly growing requirements on energy storage make an optimization regarding costs, safety, energy and power density inevitable. These optimizations can be achieved with all solid-state batteries (ASSB).

By replacing the liquid electrolyte with an ion-conducting solid, the major advantages such as an increase of safety, energy and power density can be reached. To fulfill these requirements, questions about production methods for homogeneous, thin solid-state electrolytes (SE) are becoming more important. The slot die process is already a prevalent coating process for the production of lithium battery electrodes. Therefore, the process offers a good basis for the realization for the production of SE by adapting this process. Further, the process is easy scalable which provides potential in terms of economic and upscaling by optimization of the process parameters. Additionally, limiting factors of the process are well known and applicable to non-Newtonian fluids, which makes the use of polymer based SE appropriate.

Poly(ethylene oxide) (PEO) based SE make a good model as PEO offers many advantages, such as its good availability on the global market, high solubility in solvents like methanol, cyclohexanone or acetonitrile and the capability to dissolve conductive salts like the alkali salt Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI).

In this work, the coating window is evaluated as a function of material properties, i.e. molecular weight of PEO and solution concentrations. For these solutions, material properties such as viscosity and surface tension are determined. Also design of experiment is used to investigate the influence of the process parameter on the layer quality. The layers are evaluated based on their thickness and ionic conductivity. Experimental results are compared to theoretical film break up models.

Computational Study of the Formation of Solid Electrolyte Interface from Polycaprolactone

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As for liquid electrolytes, studying the formation of the solid-electrolyte interface (SEI) and its implications is one of the most important topics in solid-state batteries. In this study, density functional theory (DFT) and ab-initio molecular dynamics (AIMD) calculations were performed to study the decompositions of polycaprolactone, one main constituent of the electrolytes, and its ending groups at the interface. Additionally, the computational lithium electrode (CLE) method [1] was applied to study the formation of the SEI under external voltage. The AIMD results suggest that the fragments are highly reactive on the Lithium slab where the fragmentation can be observed in less than 1 ps. The decomposition was triggered by the electrons transferred from the slab to the fragments. The electrochemical mechanism shows only slightly weaker energetics with respect to the non-electrochemical one, showing that pristine lithium readily reacts with the polymer. After the formation of passivation layers (Li_2O, LiF or Li_2CO_3) on top of the anode, the calculations show that only one monolayer protects the molecules from being decomposed at the interface at short interval of time, where the LiF layer seems to have the most robust protection as compared to the other layers. The electrochemical window and the decomposition of the polymer fragments in the presence of a Li cation, TFSI anion, or LiTFSI ion pair without explicit interface have also been also investigated. These cluster calculations show good accordance with results given by DFT and AIMD calculations at the interface.

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Scale-up of mechanochemical synthesis and demonstration of a continuous production process for sulfide-based solid electrolytes

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To establish solid-state batteries (SSB) as a technology for potentially safer and high-performing energy storage, there are still many challenges, such as upscaling the syntheses of solid electrolytes (SE) and production processes for electrodes [1-3]. Aiming at the availability of these highly demanded materials, the focus of this work was to evaluate scalable and continuous processing strategies to produce sulfide-based SE.

Sulfide-based SE have attracted broad interest because of their high Li^+ conductivity and compliant mechanical properties in SSB electrodes, but their syntheses are typically known as time consuming processes and mainly require toxic and inflammable solvents [1,4-6]. Within this work, the solvent-free mechanochemical synthesis of Li_3PS_4 and Li_6PS_5Cl was investigated and highly optimized in lab scale via high energy ball milling. A deeper understanding of process-structure-product-relations was gained by experiments and associated simulations of stressing conditions with the discrete-element-method (DEM). The coupling of the experimental and simulation results revealed a direct correlation between the existing stressing conditions for different parameter sets and the obtained product properties.

In a subsequent upscaling step the stressing conditions and suitable continuous processing strategies were investigated in scalable mill types. Based on the obtained insights, the solvent-free synthesis of sulfide-based solid electrolytes was successfully demonstrated in an upscaled mill type, which will thus facilitate the industrial production of SSB.

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Powder Aerosol Deposition, a Novel Way to Manufacture All-Solid-State Batteries

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Significant efforts have been made to develop ASSB by processing ceramic solid electrolyte powder into electrolyte films. Achieving electrolyte films with thicknesses below 20 µm is challenging and currently impedes the commercialization of ASSB.
Powder Aerosol Deposition (PAD) is a relatively new technology that can be applied for the production of ceramic films. The advantages of PAD are that very thin films can be easily manufactured and that the process itself requires relatively low temperatures. In PAD, deposition takes place at room temperature and in many cases high sintering temperatures, as required by conventional ceramic processing routes, are not necessary. [1] In first investigations, garnet-type electrolyte PAD films showed promising electrochemical properties [2,3].
Based on these results, we aim at showing that multilayer films can be produced by PAD and used in ASSB. Our films consist of a composite cathode layer (NMC/LLZO) as well as an electrolyte layer (LLZO). SEM images of the PAD multilayer show that a dense and nanocrystalline film structure is achieved. EDX data confirms that a composite cathode can be created by the simultaneous deposition of the electrolyte and the cathode material. The PAD films exhibit promising electrochemical performance against lithium metal anodes. In the next step we will introduce composition gradients into the cathode layer. It is expected that such gradients will help to improve the kinetics of ASSB and enable increased power and energy densities.

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Advanced co-sintering of a $LiNi_{0.5}Mn_{1.5}O_4$ and $Li_{0.33}La_{0.55}TiO_3$ composite cathode for all-solid-state Li batteries

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Oxide-ceramic electrolytes possess superior electrochemical properties for all solid-state Li batteries. A high temperature sintering step is required to obtain high-conductive grain boundaries. Unfortunately, the high temperature sintering can lead to the reaction of the oxide-ceramics with cathode active materials and the formation of low-conductive secondary interface layers.

Lower sintering temperatures are beneficial to maintain the pure electrolyte and cathode active material phases. However, lower sintering temperature prevent the dense sintering and the formation of high-conductive grain boundaries. Advanced sintering techniques are required to lower the sintering temperature while still achieving the good electrochemical properties. Such an advanced sintering technique is Field-Assisted Sintering Technology/Spark Plasma Sintering (FAST/SPS) which utilizes an applied mechanical pressure and electric currents to assist the sintering process. The advantage of FAST/SPS is furthermore the significantly reduced dwell times of hours to minutes.

Through the shorter dwell times and lower sintering temperatures, we were able to co-sinter $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) as the cathode material and $Li_{0.33}La_{0.55}TiO_3$ (LLTO) as the solid-state electrolyte material. The composite system was analysed in detail for its structure, phase, and electrochemical properties.

With this work we want to show an energy-efficient, fast, and simple co-sintering process for LNMO and LLTO and its potential to transfer our process to other material systems.

Enabling the Industrial Wet Coating Process for Sulfide-Based All-Solid-State Battery Components – An Experimental Study on Product-Process Correlations

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Abstract

Sulfide-based all-solid-state batteries are one of the most promising next generation energy storages. Especially the chlor-argyrodite material Li_6PS_5Cl and ceramic sulfide $Li_7P_3S_{11}$ are attractive solid electrolyte materials due to their high ionic conductivity. To date a lot of research in terms of material chemistry and cell design is presented in literature. From a production point of view, process parameter studies and process engineering are rarely addressed. To fabricate a thin-film sheet of the separator or composite cathode, conventional wet coating techniques from lithium-ion battery production can be applied. A process study showing interdependencies for the up-scaling of thin-film and large-scale sheets is omitted. Therefore, this paper reveals the correlation between product and process parameters for the design of an industrial wet coating process. Large-scale sheets of LPSCl and LPS separators with thicknesses down to 40 µm as well as composite cathodes on aluminum are coated and relevant parameters such as viscosities and coating velocities are varied to analyze correlations and pave the way for the industrial roll-to-roll coating process.

Scalable production of a polymer-based matrix-supported solid-electrolyte separator for use in all-solid-state-batteries

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All-solid-state batteries (ASSBs) are seen as a next-generation battery technology. Of the various ASSB variants, only polymer-based ASSBs have been successfully commercialized to date [1]. Currently, free-standing solid polymer electrolyte (SPE) membranes suffer from poor mechanical stability limiting processability and resistance against lithium-dendrites. Using a support-matrix enables the fabrication of thin but robust SPE separators [2], but literature focussing on scalable production is still scarce. Therefore, this work describes a scalable manufacturing method for ultrathin matrix-supported SPE separators for high-performance ASSBs.

The infiltration of commercially available conventional LIB separators was studied experimentally. Multiple process parameters such as the solvent content of the solid-electrolyte solution and the wet film thickness used for the infiltration of the support matrix were evaluated and their influence analysed. The production and characteristics of the matrix-supported membrane were studied with the use of scanning electron microscopy and electrochemical impedance spectroscopy.

The production of an ultrathin (< 8 µm) matrix-supported SPE separator using scalable processes was achieved in this work. A commercially available conventional LIB separator with a thickness of 7.4 µm was infiltrated with a PEO-based SPE using a doctor blade process. The resulting membrane measured less than 8 µm with a polymer cover layer of less than 1 µm. Using this ultrathin SPE separator symmetrical pouch cells with an area of 9 cm² were successfully cycled with a current density of 100 µA·cm². Electrochemical effects caused by the ultrathin separator and the used SPE were investigated and a possible explanation by the sand-equation [3] given.

The suitability of the matrix-supported solid electrolyte separator for its application in scalable ASSB production is discussed and further potential for research is shown.

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Modification of SE Films for Stable Li Metal Anode in All-Solid-State Lithium Batteries

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Abstract

Interests in lithium-ion batteries (LIBs) have been increasing with the development of next-generation energy storage. Opposed to conventional LIBs which face serious safety issues, all-solid-state batteries (ASSBs) have emerged as a promising alternative. Particularly, there has been outstanding development in sulfide solid electrolytes (SEs) as they have beneficial intrinsic properties of high ionic conductivities and mechanical ductility. In addition, ASSBs are advantageous to achieve high energy density with the employment of Li metal anode. However, there are many obstacles: e.g., poor reversibility, dendritic growth, and instability with SEs. Therefore, interface engineering to enable reversible dissolution/deposition of Li metal is imperative. While most studies on ASSBs have been conducted using pressurized pellet-type cells with thick SE layers (hundreds of micrometers), the employment of thin SE membranes (≤ 100 μm) is required for practical pouch-type ASSBs.

In this presentation, SE film modification strategies for pouch-type ASSBs employing Li metal anode is presented.

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Visualizing the structure evolution of CuS-based SSBs by 3D Tomography

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Solid state batteries (SSBs), especially those utilizing conversion-type active materials, are promising future energy storage systems.[1] However, the mechanical stability of SSBs upon electrochemical cycling are a great challenge. The periodic volume variation is known to deteriorate the physical contact between the active material and solid electrolyte (SE) particles which emphasizes the need for optimizing the mechanical properties.[2]

It has been shown, however, that with the right combination of materials even electrode reactions with large volume changes can be cycled in SSBs at room temperature. A peculiar example is CuS which shows an expansion of 75 % upon lithiation. This appears possible due to a favorable combination of several materials properties.[3] For example, CuS is an ionic (Cu^+) and electronic conductor and a soft material. Interestingly, lithiation of CuS leads to a phase separation including the formation of µm-sized Cu crystals. 3D tomography is an excellent tool for studying solid-state interfaces as it yields three-dimensional reconstructions of materials with spatial resolution.[4]

Herein, we study the reaction mechanism of CuS electrodes in Li-SSBs and the related crack formation by 3D tomography. Li is used as counter electrode and Li_3PS_4 as solid electrolyte. We find that the z-oriented expansion of the active material leads to cracks with preferred orientation perpendicular to the applied pressure. The crack formation is shown to be effectively mitigated by increasing the pressure. Preferred orientation is also found for the µm-sized copper crystals. We also find a z-oriented “back-and-forth” displacement of the CuS particles during cycling over several µm which is due to the plating/stripping of the Li counter electrode. Overall, CuS is found to be an ideal study case to follow chemical and structural changes during cycling of Li-SSBs

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Microscale-silicon anodes with high silicon content fabricated by water-based slurry processing for use in all-solid-state batteries

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In order to enable the market introduction of all-solid-state batteries, several anode concepts are under investigation to increase the energy density compared to graphite anodes, while maintaining longer stability and reducing the production costs. More and more interest is being directed towards materials that form lithium alloys, particularly silicon, which has a theoretical capacity of 3579 mAh/g.

In this work, anodes with 96w% silicon are prepared by coating water-based slurries which contain a microscale silicon as active material, the rest being made up of LiPAA as binder and C65 carbon as conductive additive, so that no solid electrolyte particles are present. [1] The combination of the water-based process and the microscale dimension of the silicon particles make this electrode concept easily scalable and cost-effective. To reach a competitive areal capacity in the range of 2-6 mAh/cm^2, with the full utilization of the silicon, only a thin layer is needed. In this case, the lithiation would start at the interface of the silicon particles with the LPSCl solid electrolyte separator, and the loss of lithium into the SEI should be minimized due to the limited silicon/SE contact area. During lithiation, the silicon-lithium alloy expands and fills all the pores present on the electrode. While, during the delithiation, it has been observed that the electrode assumes a columnar morphology that could guarantee the mechanical integrity of the electrode even upon extended cycling. [2] The thickness variation and the anode morphology is being investigated by examining cross-sectional SEM images at different states of charge. Cycling half-cells with InLi as counter and as reference electrode, the stability and the rate capability of the prepared silicon anodes will be compared when cycled at different cell compression pressures.

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Current-Dependent Lithium Metal Growth Modes in 'Anode-Free' Solid-State-Batteries at the Cu|LLZO-Interface

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Using lithium metal as anode material promises a drastic increase in energy and power density in solid-state batteries. However, handling and fabrication of cells employing lithium metal foils is very demanding due to strict atmospheric requirements to suppress surface passivation of lithium as well as ensuring safety due to its high reactivity.[1] A possible solution is the use of so-called "anode-free" or rather reservoir-free cells (RFCs). In these RFCs the lithium anode is deposited within the first charging step from lithium present in the cathode active material instead of mechanically applied during fabrication, which offers an elegant opportunity to circumvent the handling of pure lithium metal. This formation step, however, is difficult to control. Instead of a layered film growth of lithium, rather a heterogeneous combination of whiskers, dendrites and island growth is typically observed.[2]

Therefore, a powerful operando scanning electron microscopy technique was developed within this work, which allowed the observation of lithium nucleation and growth both from a top and cross-sectional perspective. Using this technique, the influence of applied current density and current collector thickness was investigated on the lithium plating at the Cu|$Li_{6.25}Al_{0.25}La_3Z_2O_{12}$ interface. A 6-fold increase in particle density and correlated decrease in average particle size was observed for increasing current densities. This may help with the growth of homogeneous films, especially if pressure is additionally applied during the experiment. Furthermore, it could be shown that a mechanically stable current collector needs to be employed, which suppresses the penetration of single lithium whiskers, as this would lead to inhomogeneous and irreversible lithium growth. In this case, a 10 µm thick copper foil is sufficiently resistant against whisker penetration.

Overall, this work not only presents an analysis of the growth of lithium at the electrolyte|metal interface, but also describes a technique for visualization of lithium growth in operando using electron microscopy. This technique can help to elucidate the influence of other parameters on lithium growth, such as applied stack pressure, crystal orientation and surface morphology, which guides the search for optimal deposition parameters in RFCs.

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Interface Engineering of Solid-state Batteries

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The solid-solid interfacial contact is a critical issue during the studies of solid-state batteries (SSBs), which greatly affects the electrochemical performance of SSBs, such as the coulombic efficiency, and cycle life. For flexible polymer/garnet electrolytes (PGEs), the interfacial issue mainly comes from the interactions between the inorganic fillers and the polymer matrix. The slow Li^+ transport through the polymer/garnet interface can lead to the low ionic conductivity of PGEs. While for garnet ceramic electrolytes (GCEs), the ceramic bulk with a relative density over 99% shows no obvious grain boundary, leading to the ionic conductivity over 10^{-3} S cm^{-1} at room temperature. Under this circumstance, the interfacial issue could be attributed to the poor interfacial contact between the GCEs and Li metal anodes. It can induce the large interfacial resistance as well as the lithium dendrite growth. In this presentation, I'll focus on the aforementioned interfacial issues, various targeted strategies will be introduced to construct the excellent interfacial structure, thus significantly improving the performance of SSBs [1-3].

Keywords: Garnet; Solid-state batteries; Interfacial engineering; Li dendrite suppression

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Halide-Sulfide Hybrid Catholytes for Ni-Rich Cathodes Designed by Digital-Twin for All-Solid-State Batteries

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Under the pressure of the European Emission Standards enacted by the European Union (EU), to decrease carbon emissions, demands for electric vehicles are largely increasing. However, conventional Li-ion batteries have intrinsic safety problems, owing to the use of flammable organic liquid electrolytes. Accordingly, all-solid-state lithium batteries (ASLBs) employing non-flammable inorganic solid electrolytes (SEs) are considered as promising next-generation batteries. Ni-rich layered oxides, $LiMO_2$ (M = Co, Ni, Mn, Al), and inorganic SEs are considered crucial components for high-performance ASLBs. Especially, sulfide SEs (e.g., $Li_{10}GeP_2S_{12}$, $Li_{5.5}PS_{4.5}Cl_{1.5}$) that exhibit a maximum Li^+ conductivity of $\approx 10^{-2}$ S cm^{-1} are expected to enable the commercialization of ASLBs. However, sulfide SEs suffer from serious interfacial degradation when combined with $LiMO_2$ cathodes, which originates from their low electrochemical oxidation stability (< 3 V *vs.* Li/Li^+) and chemical incompatibility. Despite the unsatisfactory ionic conductivity (max. 10^{-3}S cm^{-1}), halide SEs have been newly emerging due to their excellent electrochemical oxidation stability (> 4 V *vs.* Li/Li^+) with good compatibility with $LiMO_2$[1, 2].

In this presentation, a hybrid usage of sulfide and halide SEs to compromise their drawbacks for the application to $LiMO_2$ cathodes in ASLBs will be presented. A digital-twin 3D modeling will also be discussed.

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Studying lithium stripping and plating behavior of silver-carbon composite layer with solid polymer electrolyte

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Lithium metal as a promising anode candidate for solid state battery is widely studied for its ultra-high specific capacity (3862mAh/g). However, due to global inadequate lithium reserves, high manufacture cost as well as safety concerns on application of lithium metal, “anode free” concept with zero-excess lithium anode design gains its attention for further improved energy density and safety [1]. In 2020, the research team from Samsung proposed a solution with a silver-carbon composite layer to achieve the “Anode free” concept, the demonstrated ASSB shows long time cycling with coulombic efficiency over 99.8% over 1000 cycles [2].

In this poster, the lithium stripping and plating behavior of this silver-carbon composite layer was studied with the PEO-based solid polymer electrolyte in a pouch half cell format. The PEO-based solid polymer electrolyte was thermally polymerized with thermal initiator AIBN, which yielded the ionic conductivity of 0.376mS/cm^2 at 60 ℃. The reversible alloying and de-alloying of the silver nanoparticles with in-situ reduced lithium was observed with cyclic voltammetry, and this composite layer was further approved to regulate the lithium deposition over potential during the first discharging step (referring to half cell format), as well as enable reversible lithium stripping and plating over longer period of time.

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Anhydrous LiNbO3 Synthesis and Its Application for Surface Modification of Garnet Type Li-Ion Conductors

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In our work we demonstrate a facile, water-free synthesis of amorphous lithium niobate ($LiNbO_3$) layers. Our developed method also enables the coating of substrates in inert atmosphere with simple, industrial scalable methods. As verification, a 120 nm thin $LiNbO_3$ layer was deposited on the garnet type lithium ion conductor $Li_{6.45}Al_{0.05}La_3Zr_{1.6}Ta_{0.4}O_{12}$ (LLZTO) to improve its interface to lithium metal and reduce dendrite formation. The application of the thin film reduced the interface resistance between LLZTO and lithium metal to 1.02(13) $\Omega \cdot cm^2$ and increased the critical current density for dendrite formation to at least 0.5 mA cm^{-2}. The chemical stability of the $LiNbO_3$ thin film in contact with Li-metal was verified by SEM, XPS and ToF-SIMS.

Effect of Carbon Black on the Conductivity of a Li_6PS_5Cl-based Catholyte: A Percolation Study

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To achieve high energy densities with sufficient cycling performance in all-solid-state batteries, the fraction of active material has to be maximized while maintaining ionic and electronic conduction throughout the composite cathode [1]. In a previous study, C65 added to the composite-cathode showed the potential to enhance the capacity and rate capability [2]. In contrast, it is known that carbon additives can lead to faster decomposition of the cathode constituents in thiophosphate-based cells [3]. By determining the electronic percolation threshold of the conducting matrix, the C65 fraction shall be minimized. As a result, not only side reactions could be suppressed, but also it offers the possibility of increasing active material- or solid electrolyte (SE) content [4,5].

This study systematically investigated the microstructure and the conduction behavior of a catholyte containing the SE Li_6PS_5Cl and various fractions of C65. The SE was synthesized via the solid-state reaction. To prepare the catholyte, the as-synthesized SE powder was mixed with increasing fractions of C65. Those powder mixtures were sandwiched and densified in a symmetric cell setup between blocking electrodes and their temperature depended effective conductivity (σ_{eff}) was determined by electrochemical impedance spectroscopy (EIS) and evaluated as a function of the temperature and C65 content. The percolation threshold p_c is discovered to be about 4 wt.-% C65. It is suggested that below p_c the ionic contribution is dominant, which can be seen in temperature dependend σ_{eff} and blocked charge transfer. Above p_c, the impedance of the catholyte becomes frequency-independent, and the ohmic law applies.

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Impact of carbon additives' microstructure on sulfide solid electrolyte decomposition and its optimization for improved SSBs

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One of the main challenges that all-solid-state batteries (ASSB) have to overcome is achieving high specific capacity. For this, maximum utilization of the cathode active material (CAM) is mandatory. Carbon-based conductive additives are commonly used in composite cathodes due to their benefit on the initial capacity by improving the electronic conducting network. Nevertheless, their influence on several cell parameters, especially for different types of carbon additives, is not understood yet.

In this work, we analyze the impact of differently shaped and sized carbon additives on the overall cell performance and material composition in a cathode composite containing $Li(Ni_{0.6}Co_{0.2}Mn_{0.2})O_2$ as CAM and sulfide-based solid electrolytes (SE). In addition, a CAM-free model system was built to investigate the microstructure influence of the carbon additives on the SEs via cyclic voltammetry. To complete the study post mortem X-ray photoelectron spectroscopy was carried out on both cell systems.

For maximizing the use of the CAM in ASSB, a carbon additive with a fibrous shape and with the smallest possible electrochemical active surface area (EAS) is most suitable. With these properties, an interconnected network can be formed through the entire cathode composite causing the least amount of side reactions. The side reactions at the EAS are limited to the initial decomposition of the SE. Nevertheless, this leads to an increased loss of capacity during the ongoing cycles.

To prevent capacity fading, an insulating Al_2O_3 coating layer was applied on the additives by atomic layer deposition. With this approach, a reduction of the initial decomposition can be observed. Despite minor losses in utilization and a lower initial capacity, the improved cycle stability compensates this negative impact, resulting in an enhanced overall cell performance.

Polymer interlayer design to stabilize reactive interfaces between carbon additive and inorganic solid electrolyte

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Large-scale industrialization of solid-state batteries requires reducing degradation at the interfaces between inorganic solid electrolytes and anode/cathode materials, and components within cathode composites. In parallel, maintaining a percolative conductive network inside cathode composites, homogeneous ion flux across the solid-solid battery interfaces and a decrease in the dendritic growth of metals are pertinent challenges. [1]

One approach to stabilizing reactive interfaces is to apply a conformal coating between cathode composite components (cathode active material, carbon additives, and inorganic solid electrolytes) to decrease capacity loss. A newly developed polymer interlayer is introduced for carbon additives as a chemically stable coating for nonreactive interfaces between carbon additive and solid electrolyte interfaces. [2]

The microscopic structure of polymer-coated additives, the stability of polymers in the context of performance evaluation in solid state battery are investigated by employing SEM, battery cycling and ex-situ XPS. The broad impact of such a newly developed coating strategy is important for future-generation hybrid-type solid-state batteries, employing a combination of polymer interlayers and inorganic materials.[3]

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Polymer Coating of NCM to Improve the Cycling Stability in Solid-State Batteries

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Solid-state batteries (SSBs) with NCM-type high-nickel ternary cathode material represent a promising next-generation energy storage technology due to their expected high energy density and improved safety. However, a significant problem that needs to be overcome on the way to large-scale application is the rapid capacity fading. In this work, a polymer coating on NCM has been prepared to stabilize the interface between NCM and the solid electrolyte. The polymer coating achieves a significant improvement in long-term cycling performance and active mass utilization compared to uncoated NCM. Thereby, the coating can effectively suppress cell degradation, as shown by time-of-flight secondary ion mass spectrometry (ToF-SIMS). Furthermore, the galvanostatic intermittent titration technique (GITT) and focused ion beam scanning electron microscopy (FIB-SEM) indicate the reasons for the improved performance. Overall, such a polymer coating on NCMs is demonstrated as a scalable process for high-performance and stable SSBs.

Evaluation method of effective surface area for solid state battery cathode layer

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All-solid-state battery (ASSB) technologies are for future EV application, because of their safety and high energy/power density. Most importantly, high-rate performance is greatly desired, because quick chargeability is one of the most important requirements for EV application. Thus, it is necessary to understand the overpotential of ASSBs in order to improving the high-rate performance, since there is a disparity between the expectation and the present status. The effective reaction surface area of the cathode active material is one of the key parameters to understanding the cause of the overpotential. FIB-SEM and X-ray tomography have been utilized to analyse the microstructure of composite electrodes to clarify the effective reaction surface area. [1-2] However, such visualization methods have some limitations from a quantitative point of view, since they are destructive analysis techniques and only partial structural information is obtained resulting in rack of representativeness.

We have herein tried to construct an electrochemical measurement method which enables us to evaluate the effective surface area in the cathode layer quantitatively. In this study, double layer capacitance in the cathode composite electrode was focused on as an indicator of effective reaction surface area, and the applicability of the double layer capacitance evaluation method using the electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) was verified with various cathode compositions.

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Investigations of Li-ion migration in the novel electrolyte of GCD-PCL in Bulk and at Interfaces using Molecular Dynamics

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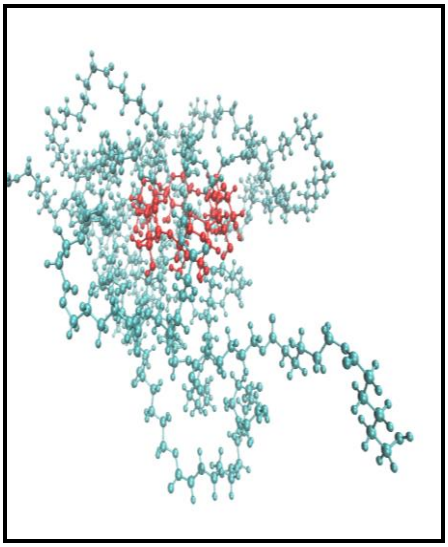
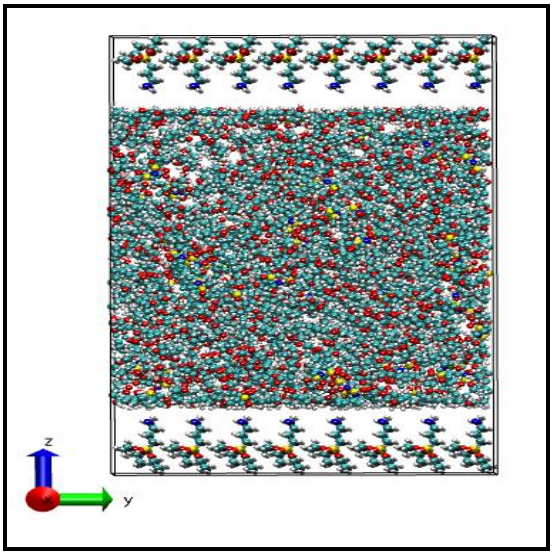
Several studies have been performed to obtain novel materials that can lead to the higher performance of the solid-state batteries in terms of ionic conductivity. Cyclodextrins grafted with polycaprolactone polymer chains are one among such materials which shows a promising increase in performance as compared with Polyethylene Oxide (PEO) experimentally. We have investigated the properties such as diffusivity and ionic conductivity of this novel material using molecular dynamics simulation for an All-Atom Model and Coarse-Grained model at different temperature ranges.

We employed the time-temperature superposition principle to determine the ionic conductivity at lower temperatures that matches well with the experimental findings. Furthermore, we have also investigated the impact of coating surfaces on the ion transport in the presence of other solid electrolytes like LLZO. This work provides insights into the Li-ion transport in the vicinity of internal interfaces in hybrid electrolytes.



All-Atom Model for GCD-PCL



Electrolyte with APTES Interface

Ionically Conducting Inorganic Binders (ICIB) for Solid-State Batteries

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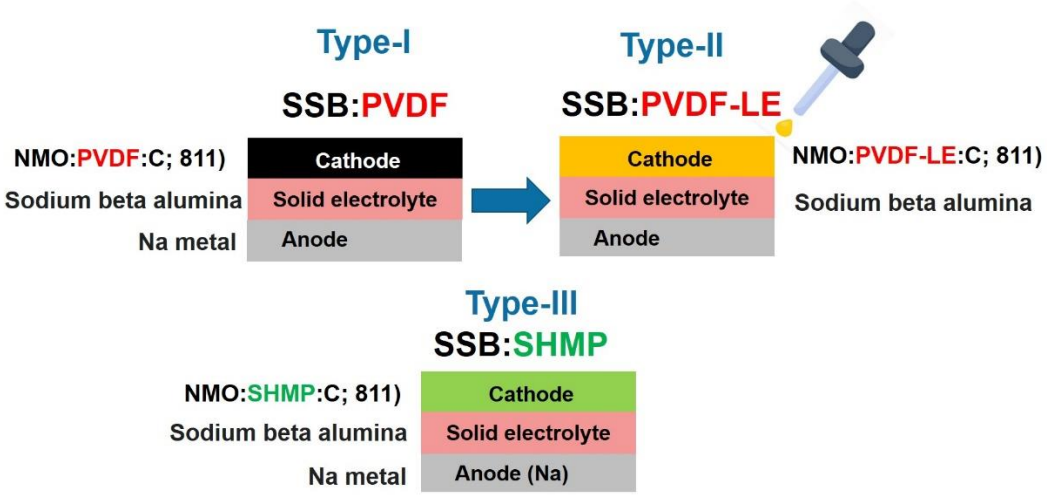
Abstract: Solid-state batteries (SSB) offer high energy density and in general considered safe as compared to conventional non-aqueous batteries. Most of the SSB use organic binders like PVDF which are ionically insulating in nature. To fabricate SSB, cathode layer (e.g., $NaMnO_2$:C: PVDF) is coated on one side of the solid electrolyte (SE) pellet and anode (e.g., Na metal) is pressed on the other side of it. This type of SSB (type-I) does not work because there is no ionic conductivity in the cathode layer. In general, two strategies are adopted in the literature to induce ionic conductivity. The first approach is mixing and sintering solid electrolyte (30-40%) in the cathode layer to induce sufficient ionic wiring in the cathode[1]. This battery functions well but the added SE would remain electrochemically inactive and only lead to mechanical rigidity and volume changes. In second and most common approach (type-II), a small drop of liquid electrolyte is added on the cathode side to induce ionic conductivity in the cathode layer[2]. This is however not fundamentally different than non-aqueous batteries and poses safety issue as reported recently[3]. Therefore, we fabricated SSB using a new class of aqueous binder, ICIB which has high thermal stability (>1000°C) and intrinsic ionic conductivity[4]. This is classified as type-III SSB and does not need addition of liquid electrolyte or SE to the cathode layer. In this type, we coated a cathode layer of $Na_{0.7}Mn_{0.9}Mg_{0.1}O_2$ (NMO): SHMP:C on one side of SBA (sodium beta alumina) pellet and Na metal on the other side of it. The cell worked well due to intrinsic ionic conductivity of SHMP (sodium hexa meta phosphate) binder. SSB of type-III are relatively safe due to high thermal stability of the binder used.



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Insight into the Li-LiPON-interface at molecular level: interfacial decomposition and reconfiguration

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All-solid-state batteries (ASSBs) have the potential to provide many advantages over the currently used liquid Li-ion battery technology, including faster charging, higher energy density, increased cycle life, reduced battery costs, and greater flexibility. [1] An important task in the development of ASSBs is to improve the interfaces between the Li-metal anode and/or solid-state electrolytes (SSE). These interfaces can determine the cell properties of ASSBs, but are not well understood. Lithium phosphorus oxynitride (LiPON) represents an interesting SSE for ASSBs and has also proven useful as a passivation layer for Li metal anodes. [2]-[3] Experimental efforts at the Li-LiPON interface revealed the decomposition products Li_2O, Li_3N, Li_3P, and Li_3PO_4. [4] However, there is still a lack of deep theoretical understanding on the Li-LiPON interface, especially on the interfacial decomposition and reconfiguration.

To take a step toward understanding ASSBs interfaces, we aim to gain a deep insight into the interfacial stability of the Li-LiPON interface by exploring in detail the role of different interfacial compositions and morphology caused by decomposition reactions. For this purpose, we investigate and characterize all possible occurring Li-LiPON interfaces (including Li-Li_2O, Li-Li_3N, Li-Li_3P and Li-Li_3PO_4) and LiPON-LiPON interfaces (including Li_2O-Li_3N, Li_2O-Li_3P, Li_2O-Li_3PO_4, Li_3N-Li_3P, Li_3N-$LiPO_4$ and Li_3P-$LiPO_4$) using density functional theory (DFT) calculations. We believe that our study could provide a fundamental understanding to guide the future design of solid electrolytes and interfaces in ASSBs.

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A hybrid LLZO-LSPS-based solid-state battery

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The combination of more than one type of solid electrolyte to form a hybrid solid electrolyte-based cell concepts are a very promising approach to realize high performance batteries. The oxidic garnet $Li_7La_3Zr_2O_{12}$ (LLZO), for example, has a high electrochemical stability, most outstanding in contact with a metallic lithium anode, making it the perfect choice as thin separator on the lithium-anode side. For the cathode side, which is typically thicker than the separator, solid electrolytes like $Li_{10}SnP_2S_{12}$ (LSPS) have clear advantages due to their higher ionic conductivity compared to LLZO. Furthermore, LSPS can be processed at room temperature, but is instable upon contact with elemental lithium. Therefore, both electrolyte types can complement each other in a hybrid battery cell. In a previous work we studied the interface between LLZO and LSPS and could show that very low interfacial resistances can be achieved [1]. Here, we show how a full cell, including a lithium anode, LLZO separator, and an LSPS-based cathode with NCM811 ($Ni_{0.8}Co_{0.1}Mn_{0.1}O_2$) as active material, can be achieved and that such a cell can be charged and discharged for more than 20 times. The cycling behavior was studied with different applied pressures, and 12-25 MPa was identified as an optimal range. We furthermore will discuss the implications of pressure on this hybrid batter concept which must be carefully selected. For example, LSPS requires sufficient pressure for proper contact between particles and to the active material, whereas too high pressures result in short circuiting of the cell, probably due to lithium dendrite formation during lithium plating.

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Improving Li-ion interfacial transport in hybrid solid electrolytes online abstract

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The development of commercial solid-state batteries has to date been hindered by the individual limitations of inorganic and organic solid electrolytes, motivating hybrid concepts. However, the room-temperature conductivity of hybrid solid electrolytes is still insufficient to support the required battery performance. A key challenge is to assess the Li-ion transport over the inorganic and organic interfaces and relate this to surface chemistry. Here we study the interphase structure and the Li-ion transport across the interface of hybrid solid electrolytes using solid-state nuclear magnetic resonance (ssNMR) spectroscopy. In a hybrid solid polyethylene oxide polymer–inorganic electrolyte, we introduce two representative types of ionic liquid that have different miscibilities with the polymer. The poorly miscible ionic liquid wets the polymer–inorganic interface and increases the local polarizability. This lowers the diffusional barrier, resulting in an overall room-temperature conductivity of 2.47×10^{-4} S cm^{-1}. A critical current density of 0.25 mA cm^{-2} versus a Li-metal anode shows improved stability, allowing cycling of a $LiFePO_4$-Li metal solid-state cell at room temperature with a Coulombic efficiency of 99.9%. Tailoring the local interface environment between the inorganic and organic solid electrolyte components in hybrid solid electrolytes seems to be a viable route towards designing highly conducting hybrid solid electrolytes.

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Impacts of cell physical parameters on the cycling performance of thin metallic lithium in sulfide-based all-solid-state batteries

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For all-solid-state batteries, the use of thin metallic lithium as anode holds the promise to enable high energy density (> 500 Wh Kg^{-1}). In order to achieve stable cycling performance and long lifetime at high current density (> 3 mA cm^{-2}), the rapid failure of the cell caused by the dendritic Li formation needs to be better addressed. [1,2] In this work, the impacts of cell physical parameters on the short circuit are concluded. Systematic investigation is carried out by varying (i) the protection of the edge, (ii) the solid electrolyte thickness and densification, (iii) the applied pressure during cycling, and (iv) the current density and area capacity. The electrochemical measurements are performed on symmetric cells using Li_6PS_5Cl and 50 µm metallic lithium coated on Cu.

The insulating polymer placed around the metallic lithium prevents the preferential dendritic Li on edge. For the fabrication pressure of the solid electrolyte pellet, a compromise between the thickness and porosity needs to be considered because of their opposite effect. With low stack pressure from 10 MPa to 20 MPa, the symmetric cells using 350 µm thick Li_6PS_5Cl and a disk protective edge of HDPE exhibit reliable plating and stripping behaviour at 0.1 mA cm^{-2} and 0.1 mAh cm^{-2} over 500 cycles. At increased current density (0.5 mA cm^{-2}) and area capacity (0.4 mAh cm^{-2}), the cells short earlier. Formation cycles at low current density helps to improve subsequent cycling at high current density (1 mA cm^{-2}). These results serve as baseline to form a guideline toward cell configuration, assembly process and cycling conditions. Finally, our study will contribute to improve the cycling reproducibility and provide guidance to further improve the cycling performance of metallic lithium in all-solid-state batteries.

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HfO_2 Nanoparticle Coating for Stabilizing Layered Ni-Rich Oxide Cathodes in Solid-State Batteries

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Improving the interfacial stability between cathode active material (CAM) and solid electrolyte (SE) is required for developing high-performance thiophosphate-based solid-state batteries. Here we report on the preparation of characterization of a protective coating (made from preformed HfO_2 nanoparticles) on a Ni-rich CAM, $LiNi_{0.85}Co_{0.1}Mn_{0.05}O_2$ (NCM85), which is capable of preventing detrimental side reactions from occurring during battery operation. The surface-modified NCM85 shows superior performance in terms of reversibility, capacity, longevity, and rate capability over its uncoated counterpart in bulk-type SSB cells with argyrodite Li_6PS_5Cl as SE. The effectiveness of the nanoparticle coating in mitigating electro-chemo-mechanical degradation was investigated using a suite of characterization techniques. In addition, wet processing of the coated NCM85 is demonstrated for slurry-cast SSB cathodes.

Origin and growth of lithium dendrites at grain boundaries in garnet solid electrolytes

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All-solid-state batteries with lithium metal as anode material are attracting more and more attention because of their potentially higher energy, power density and safety. Among all-solid-state batteries, solid electrolytes play the most important role. Garnet-type solid electrolytes based on $Li_7La_3Zr_2O_{12}$ are widely regarded as one of the most promising solid electrolyte class due to its relatively high lithium ion conductivity, wide voltage stability window and chemical compatibility with lithium metal. However, lithium dendrites penetrate into garnet-type solid electrolyte during battery operation, especially along grain boundaries, which is still not understood [1].

Mechanical and electrical conduction properties of grain boundaries in garnet-type solid electrolyte are assigned to be the reason for lithium dendrites formation. However, theoretical simulations and traditional electrochemical characterizations are contradictory on grain boundaries electrical conduction [2-3].

We used operando scanning force microscopy (SFM) techniques to clarify the role of the conduction properties for lithium dendrite formation and growth. SFM features a high spatial resolution allowing to compare properties of grains and grain boundaries. We found

(i) that grain boundaries and grains have similar lithium ionic conduction property.

(ii) an electrical potential drop at grain boundaries close to the counter lithium electrode. We attribute this potential drop to a stronger electron capture ability of grain boundaries.

(iii) preferential metal lithium expulsion growth at grain boundaries under electron beam irradiation because of different grain boundaries electron conduction properties.

Based on these novel experimental findings, we provide a model, which explains why grain boundaries are “hot spots” for lithium dendrite formation [4].

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Investigation of the Exchange Current Densities in Bulk-Type All-Solid-State Batteries

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Bulk-type all-solid-state Li batteries (ASSBs) are currently of great interest due to the improved battery safety compared to conventional lithium-ion batteries containing liquid electrolytes. [1] Furthermore ASSBs can potentially achieve higher energy densities than state-of-the-art lithium-ion batteries. [1,2] The performance of ASSBs depends critically on the contacts between cathode active material (CAM) particles and solid electrolyte (SE) particles inside the composite cathodes. The Li^+ exchange current density at the CAM | SE interfaces is determined by these contacts. Nonetheless experimental studies on Li^+ exchange current densities are almost non-existent for ASSBs, which is most likely due to the poor understanding of the impedance spectra of such batteries.

In order to obtain more information on exchange current densities, a comparative case study was carried out using different cathode active materials (CAM), namely single crystalline $LiCoO_2$ particles and single crystalline $LiNi_{0.83}Mn_{0.06}Co_{0.11}O_2$, an In-Li alloy as anode, and a sulphide-based solid electrolyte. The determination of the cathode exchange current density is based on: (i) Impedance measurements on In−Li | SE | In−Li symmetric cells in order to determine the anode impedance together with the anode | separator interfacial impedance; (ii) Variation of the composite cathode thickness in order to differentiate between the ion transport resistance and the charge transfer resistance of the composite cathodes; (iii) Impedance simulations based on the transmission-line model [3-5]. We show that under the application of stack pressures in the range of 400 MPa, the Li^+ exchange current densities can compete with or even exceed those obtained for CAM | liquid electrolyte interfaces.

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Thermal, mechanical, and dielectric properties of PVDF-LiTFSI-based solid polymer electrolyte membranes for lithium ion batteries

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Abstract. With the significant demand for high-capacity lithium-ion batteries (LIBs) and the integration of LIBs in essential everyday use, there is also a growing obligation to improve the other aspects of performance and safety standards within pre-existing LIBs. The electrolyte component in LIBs is a critical variable that acts as a medium for the movement of ions across the battery and is a facilitating location for reactions and side reactions such as the formation of the solid-electrolyte interface (SEI) amongst many other functions [1,2]. Sufficient evidence and documentation suggest there have been successes for well-established liquid electrolytes in revealing optimal performances within LIBs. However, the solvent composition of liquid electrolytes gives way to questionable drawbacks. As such would be the combustible and toxic properties of organic solvents consequently leading to fires, explosions, and electrolyte leakage whilst aqueous solvents tend to decompose at high working voltages thereby restricting the energy density of the battery As an alternative to liquid electrolytes, solid polymer electrolytes (SPEs) are effective at assisting the transfer of ions and functioning as a separator in lithium-ion batteries (LIBs) with the added safety. SPE membranes, derived from a mixture of polyvinylidene fluoride (PVDF) with poly(vinylpyrrolidone) (PVP) or poly(4-vinylpyridine) (P4VP), were prepared to examine their efficacy after the addition of a Li salt, namely lithium bis(trifluoromethanesulfonyl)imide (LiTFSI). Characterization results obtained from Fourier-transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD) studies revealed transformations to an amorphous structure induced by the addition of LiTFSI. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out to determine the performance of the SPE membranes, which showed enhanced heat resistance and inhibition of PVDF endotherms with higher levels of LiTFSI added. In terms of mechanical property, higher LiTFSI quantity was found to be unfavorable due to the reduced tensile strength. Moreover, the addition of LiTFSI was shown to boost dielectric and conductive properties within a wide working voltage range of 0.5-3.64 V vs. Li^+/Li. The effects of incorporating metal oxides (Al_2O_3, SiO_2, ZrO_2) as additives in SPE membranes were also investigated.
Keywords. Solid Polymer Electrolytes; PVDF blends; LiTFSI salt; thermal stability; dielectrics; electrochemical stability.

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Thermal transport in solid state battery materials: A case study of Na_3PS_4

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The transport of charged particles (electrons and ions) through a material results in the generation of heat due to the various microscopic interactions broadly categorized as resistance. Known as Joule heating, the rate at which electrical energy is converted to thermal energy is proportional to both current and voltage, meaning that “high-rate” and “high-voltage” batteries will inherently generate more heat. Additionally, this thermal energy generated inside the battery will tend to accumulate over time if the rate of heat removal is slower than the rate of production. The intrinsic ability of battery materials to dissipate heat depends on the magnitude of their effective thermal conductivity, where higher thermal conductivity is desirable for faster heat removal. Altogether, the thermal management of a battery is necessary to control the operational temperature, suppress degradation and prevent battery failure.

While thermal management is actively considered in conventional Li ion batteries, it is rarely discussed in solid state batteries, in part due to the limited knowledge of the thermal transport properties of its components. In this work, the thermal conductivities of Na_3PS_4, representing a model system for moisture sensitive solid electrolytes, have been determined experimentally as a function of sample porosity. Overall, thermal conductivities comparable to liquid electrolytes can be found, showing that heat generation at the electrochemical interfaces in solid state batteries can be expected. The presented experimental procedures can be easily extended to other material systems, e.g., the Li argyrodites, using common techniques of thermal conductivity analysis.

In addition to the case study of Na_3PS_4, a general perspective about thermal management in solid state batteries is given in this work.

Solid electrolyte based on 2-adamantanone for all-solid-state lithium-ion 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.

Within the recent past, several material classes, such as oxide ceramics, sulfides and polymers, have attracted a lot of attention with prominent representative materials in each class being investigated intensively, with each material having certain advantages and disadvantages.

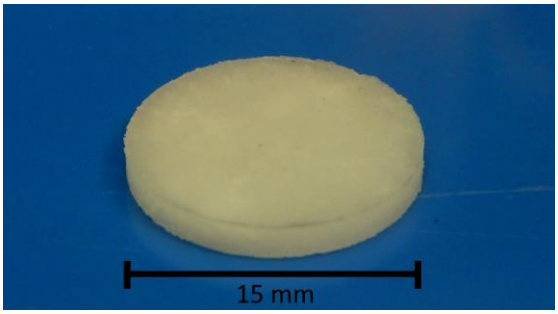

Fig. 1 Photograph of a pressed pellet containing 2-adamantanone and LiTFSI

Besides the established material classes, plastic crystals, organic compounds of low molecular weight, have recently garnered attention. Similar to polymer-based electrolytes, they work as a suitable matrix material to dissolve Lithium salts and achieve high ionic conductivity. Furthermore, their organic nature and facile processing opportunities make them a cost efficient option for solid-state electrolytes.

Within this contribution, a new plastic crystal, 2-adamantanone, is introduced as basis for a solid electrolyte. Its large temperature window from −95 °C to +255 °C for its plastic (conductive) state and the high dipole moment of 3.4 D make it a promising material for battery application. [1]

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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 and Dick and Overhauser's shell model was used to account for ionic polarization. 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 all 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 concentrations of antisite defects in the Li_xOBr_y set are lower than expected, based on the Li_xOCl_y series findings for counterpart structures. Molecular dynamics simulations are currently ongoing to assess ion transport in these materials.

Literature:

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Garnet Li7La3Zr2O12 based electrolytes for all-solid-state lithium-ion batteries

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The rapid development of electronic devices and electric transportation increases the demand for safe and high energy density rechargeable batteries. All solid-state batteries comprising of solid-state electrolytes, such as ceramic electrolytes and polymer electrolytes, can meet these requirements. The electrochemical stability of solid-state electrolytes enables the use of lithium-metal anodes and high voltage cathodes to increase the energy density in lithium-based batteries.
Garnet Li7La3Zr2O12 (LLZO) ceramic electrolyte constitutes one of the most promising solid-state electrolytes for all-solid-state batteries. This is due to its good ionic conductivity, convenient stability against lithium metal anodes, and a wide electrochemical window of operation [1]. However, the use of LLZO ceramic electrolytes in all-solid-state batteries remains a challenge. This is because the hard, brittle and rigid nature of LLZO results in high interfacial resistance and poor physical contact with both electrodes. To address these challenges, polyester and polycarbonate-based polymers are incorporated in the garnet Al-doped LLZO ceramic electrolyte with the ambition of leveraging on the advantages of these polymers to fabricate a ceramic-polymer composite electrolyte with improved performance [2,3]. Additionally, the problematic lithium carbonate formation on the LLZO surfaces when exposed to moist air hinders the full development of the LLZO electrolyte. The effect of the modification of the LLZO surface with conductive species to improve the interfacial properties of the electrode-electrolyte and ceramic-polymer interfaces is also investigated.

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Pressure induced strain engineering of ion transport in Li^+ argyrodites

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The understanding and development of Li^+ solid ionic conductors are important for solid-state batteries[1]. In the search for novel solid electrolytes for solid-state batteries, lithium argyrodite ionic conductors have been in recent focus owing to their high ionic conductivities and processability[2]. Although atomic site disorder has been systematically studied in these materials[3], the influence of internal strain resulting from microstructural defects such as dislocations has not. Characterizing the effects of internal strain on ion transport is particularly important given the prevalent use of high energy ball milling in the synthesis and processing of solid-state electrolytes for solid state batteries[4], [5]. In this work, we systematically study the effects of internal strain on the bulk ionic transport of the Li_6PS_5Br argyrodite. We are able to reproducibly induce internal strain by applying uniaxial pressures of 250 – 1500 MPa. Quantification of the bulk internal strain occurs in parallel with a local structural analysis by pair distribution function analysis. The changing ionic conductivity of the different materials is assessed by electrochemical impedance spectroscopy and the lithium-ion mobility is probed by NMR spectroscopy. Together, these results show that the high lithium-ion mobility in Li_6PS_5Br is quantifiably affected by external pressure that results in straining of the material. Not only does this work show that strain engineering may be a new methodology for tuning ion conductors without changing the composition of the material itself, it also shows that the external pressures during solid state battery formation may affect the solid electrolyte permanently.

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plastic-crystalline electrolytes for batteries

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Ion-conduction in the solid-state, in so-called solid-electrolyte materials has been under intense (re)investigation in the past decade, motivated by potential applications in batteries and other electrochemical devices. One emerging theme of research lately consists in the attempts to establish a link between the lattice dynamics (i.e. phonons, incl. anharmonicity) and the atomistic processes of ion transport [1]. Particularly, many solid electrolytes under study can be considered molecular-ionic crystals of the mobile cations (Li^+, Na^+) and polyanions (e.g. PS_4^{3-}). In this context, the role of rotational vibrations of the polyanion on the cation long-range conduction are being studied [2].

In certain cases, said molecular crystals can undergo first-order transitions to mesophasic polymorphs called “plastic crystals”, with structure, dynamics and properties in between those of classical solids and classical liquids. One such example is γ-Na_3PS_4, stable at ~500<T<750 °C at ambient pressure [3,4]. The local structure of plastic crystals is liquid-like with anions and cations exhibiting incoherent, diffusive dynamics: translational for the cations and rotational for the polyanions. Consequently, such plastic-crystalline polymorphs typically exhibit large ionic conductivity/diffusivity, making them appealing as electrolytes for electrochemical applications.

This work aims to better understand the factors that lead to the existence/stabilization of plastic polymorphs with the main goals of 1) understanding the interplay between anion-cation dynamics, 2) discovering new plastic-crystalline electrolyte materials and 3) rationally depressing the plastic-transition temperature for these systems.

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Effects of the Processing Route on the Structure and Dynamics of $Na_3Zr_2Si_2PO_{12}$

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Sodium-ion batteries (SIBs) are an emerging post-lithium technology considered ecologically and economically favorable with respect to raw material abundance and cost [1]. Conventional cell configurations use flammable liquid electrolytes and are susceptible to a high degree of dendrite formation against sodium metal [2].Chemically stable solid electrolytes (SE) with a high ionic conductivity are promising for enhancing the safety and operating lifespan of SIBs. $Na_3Zr_2Si_2PO_{12}$ is a promising SE with a scatter of reported conductivities obtained via different processing conditions [3].

Herein, the effect of three processing routes on the structure and conductivity of $Na_3Zr_2Si_2PO_{12}$, $Na_{3.4}Zr_2Si_{2.4}P_{0.6}O_{12}$, and a range of doped (Mg, Mo, and F) compositions was investigated by employing X-ray Diffraction (XRD), ^{23}Na Nuclear Magnetic Resonance (NMR) relaxometry and Electrochemical Impedance Spectroscopy (EIS).

Different processing conditions for the parent $Na_3Zr_2Si_2PO_{12}$ result in variations in the conductivity over an order of magnitude, whereas the highest ionic conductivity of 3.5 mS/cm was observed in the Mg-doped composition $Na_{3.6}Zr_{1.8}Mg_{0.2}Si_{2.2}P_{0.8}O_{12}$. ^{23}Na NMR relaxometry probes the hopping rate of the sodium ions from one interstitial site to another and reveals several temperature-dependent Na^+ hopping processes. These insights allow us to correlate the structure and dynamics of the systems and are therefore valuable in developing strategies for optimizing the conductivity and improving the next generation of solid electrolytes.

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Solution-Processed Non-Crystalline Thin Film Solid Electrolytes for Li and Na Metal Batteries

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Advanced batteries containing lithium and sodium metal anodes (LMA and NMA) are needed to enable the clean economy and meet ambitious climate targets. Currently, both LMA and NMA batteries are limited by dendrite propagation due to the non-uniform plating and stripping of Li and Na, which is detrimental to cell performance. The non-crystalline solid electrolyte (SE), lithium phosphorus oxynitride (LiPON) has demonstrated stable Li plating/stripping at appreciable rates, aiding in the inhibition of dendrite propagation. However, LiPON is typically produced via expensive and low throughput vacuum deposition methods, limiting its wide application and study.

Here, we report a study on non-crystalline thin films with the compositions, Li-Al-P-O (LAPO) and Na-Al-P-O (NAPO), which are synthesised via spin coating from aqueous solutions and subsequent annealing in air. Homogenous, dense, flat layers can be synthesised with sub-micron thickness at temperatures as low as 230 ℃ (LAPO) and 300 ℃ (NAPO). We have demonstrated a relatively high room temperature ionic conductivity (σ_{ion}) (>10^{-7} S cm^{-1}) for LAPO, with a 3-fold reduction for NAPO (~10^{-10} S cm^{-1}). We will discuss the various approaches used to optimise the σ_{ion} of LAPO, including compositional engineering, and controlled thermal processing conditions. Utilising EIS and in-situ XPS with Li deposition we report that in contact with Li metal, LAPO is found to form a stable, but high impedance passivation layer comprised of Al metal, Li-P and Li-O species. Our findings relating to LAPO should be of value when engineering non-crystalline SEs for Li-metal batteries with high energy and power densities. Whilst the current findings relating to NAPO are promising, future work improving the σ_{ion}, as well as investigating the stability with Na, will provide valuable information regarding the use of NAPO in Na-metal batteries.

Highly Conducting Argyrodite Based Composite Membranes with Excellent Mechanical and Electrochemical Behaviour

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Abstract:

Due to the current trend in the energy transition from the fossil fuel-based system to the renewable resources as well as the increased energy demand, there is an increasing interest in developing all-solid-state lithium batteries (ASSLB). They not only can exceed the energy density of conventional LIBs with liquid electrolyte, they are also much safer due to the use of a solid electrolyte (SE).[1] However, there are three main problems: (1) the inevitable parasitic reactions at the interface between the SE and the electrode material, (2) the electrochemical stability of the electrolyte and (3) dendrite growth. A promising solution is the use of polymer-based hybrid solid electrolyte that can provide sufficient mechanical stability and inhibit the dendrite growth.[3,4] In this study, a new scalable fabrication route for flexible thiophosphate-polymer separator membranes is demonstrated. By infiltrating different commercially available porous polymer membranes with highly conductive $Li_{5.5}PS_{4.5}Cl_{1.5}$ (~10mS/cm)[2], an ionic conductivity of 1mS/cm is realized. The different 3D structures of the polymers can have an influence on the infiltration process and thus on the electrochemical properties of the membrane. Nevertheless, we have been able to perform a homogeneous infiltration with subsequent cold pressing and produce flexible thiophosphate-polymer hybrid separators with promising electrochemical behaviour for ASSBs.

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Cycling demonstration of Sequential Deposition Synthesis-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.

Defect chemistry and disorder in Li_3AlP_2 Solid electrolytes

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The material development of solid electrolytes is a critical challenge for advanced batteries, as it could enable a Li metal anode as well as improved safety. However, stringent requirements such as high ionic conductivity, stability against Li metal and ability to inhibit Li dendrite growth hinder commercialization [1]. Sulfides, oxides and phosphides are popular solid electrolyte candidates which are widely studied.

Phosphides are selected in this study because of its numerous desirable features, such as easy processing, elemental abundance as well as formation of a Li_3P interlayer phase when reacted with Li metal [2]. As we show, these materials are also amenable to mechanochemical processing, allowing metastable phases to be accessed. However, their defect chemistry is poorly understood as is how to engineer these materials as solid electrolytes.

In this work, we study the crystallinity and defect chemistry of Li_3AlP_2, which had previously been reported as an ionic insulator [3], through mechanochemical synthesis and post-annealing as well as theoretical calculations. The ionic conductivity and electronic conductivity are measured for a range of Li stoichiometries with various degrees of crystallinity. We show that crystalline Li_3AlP_2 forms above 500℃, and although it can be engineered to have measurable ionic conductivity (~10^{-8}S/cm), two orders of magnitude higher ionic conductivity can be achieved in the disordered phase, formed via mechanochemical synthesis without post annealing. These results should motivate the study of other ion conductors whose crystalline phases have poor ionic conductivity and expand our library of solid electrolytes.

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Development of Recycling Strategies for All-solid-state Li-ion Batteries with Oxide- and Halide based solid electrolyte

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All-solid-state lithium-ion batteries (ASSLIBs) with solid electrolytes (SEs) are promising candidates for high density applications e.g. electric vehicles, along with their higher safety compared to organic liquid electrolytes [1]. Different types of SE chemistries have been of interest for their potential application within ASSLIBs i.e. sulfides, oxides, halides, etc. Despite several advantages, an important aspect currently neglected by the scientific community is the use of several critical elements (i.e. lithium, rare earth elements, cobalt, …) within such ASSLIBs, which are necessary to the development and industrial scale application of such batteries. Hence, it is important to address the issue of recycling and thus the sustainability of these valuable materials [2]. In this contribution, different recycling strategies have been developed with respect to two promising SEs, $Li_{3x}La_{2/3-x}TiO_3$ (LLTO) and Li_3InCl_6. Here, $Li_4Ti_5O_{12}$ (LTO) and $LiFePO_4$ (LFP) were used as the anode and cathode material, respectively. For the LLTO containing system, a hydrometallurgy-based approach using H_2SO_4 was found to be suitable for the recovery of all the cell components. In comparison, a direct recycling approach based on solution separation using H_2O for halide-based Li_3InCl_6 was developed, that allowed the separation of the electrolyte from the active electrode materials. Additionally, different electrode materials i.e. LTO, LFP, LCO and NMC were combined with Li_3InCl_6 to confirm the compatibility of the process. The recovered materials were characterized for their phase purity via X-ray diffraction along with their electrochemical properties via electrochemical impedance spectroscopy. The process developed here has a potential for large scale application.

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Hybrid Solid Electrolytes for Room-Temperature Application

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Polymer electrolytes (PEs) belong to the most promising Li-ion conductors, and are cheap, flexible, and have better physical interfacial contact with electrodes compared to ceramic-based electrolytes. However, these PEs, in particular polyethylene oxide (PEO)-LiTFSI electrolytes show a high crystallinity, restricting the segmental motion of ether groups and thus resulting in a poor ionic conductivity at ambient temperature. One solution is the incorporation of ceramic filler particles into the polymer matrix to hinder crystallization of the polymer.

Herein, a novel hybrid electrolyte based on a cross-linked copolymer (pentaerythritol tetraacrylate (PETEA) + tri(ethylene glycol) divinyl ether (TEG)), polymer-grafted oxide filler particles (functionalized $Li_7La_3Zr_2O_{12}$ (F-LLZO)), and Li conducting salt is introduced. The electrolyte shows ionic conductivity of 1.1 × 10^{-3} S cm^{-1} at 20 °C, which is 100 times higher than that of a PEO-LiTFSI electrolyte. The ionic conductivities of polymer-based electrolytes and the developed hybrid electrolyte were compared (Fig. 1). The electrochemical properties of the developed cross-linked polymer-based electrolytes as alternative to PEO-based electrolytes will be presented with their potential application in Li-S batteries.

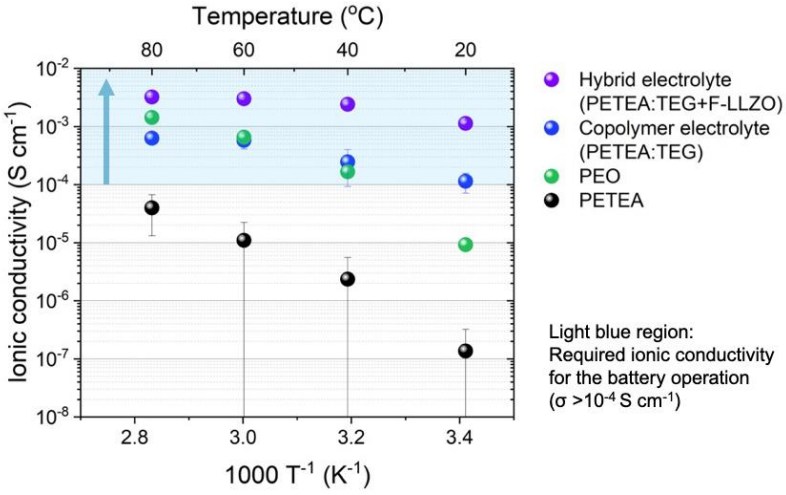

Fig. 1. Ionic conductivity of polymer-based electrolytes at different temperatures

Novel electrospun PAN/PEO-based solid polymer electrolytes for Lithium-ion application

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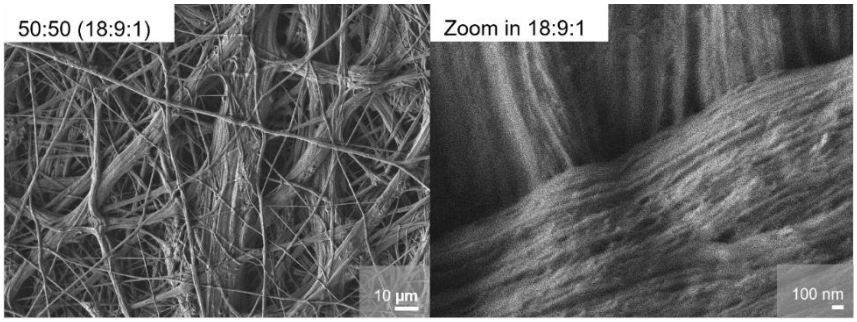
The world is currently facing the challenges of the energy transition, which came faster than expected. With the political limitation of fossil energy sources, the importance of energy storage increases dramatically. The effective and safe storage of electrical energy from green sources would create a real alternative to fossil fuels, and accessibility in a larger scale can be achieved. Researching effective energy solutions is the way out of the dependence on fossil fuels, building the basis of a future with the same life standards that society is used to. The state of the art battery is the lithium ion battery, which possess safety concerns regarding toxic decomposition products that can be produced from the reactivity of the anode against the electrolyte. Another risk of lithium batteries is their flammability, which leads to a catastrophic failure and poses health risks. To minimize those problems, all-solid-state batteries are being intensely researched. In these systems, the liquids are substituted by solid alternatives, such as solid polymer electrolytes. In this project, solid electrolytes based on PAN were synthesized using electrospinning with the goal of a solid electrolyte with high conductivity and high thermal and mechanical stability.



Systems with different PAN to PEO ratios were investigated in this work. A change in the conduction mechanism was found for samples with a ratio of 50:50 wt % PEO:PAN. The products were characterized by X-ray diffraction and their conductivity was determined by impedance spectroscopy. Furthermore, the activation energies for the conduction processes in these materials were determined using the Arrhenius equation. The fibers were analyzed using SEM. Increasing the PAN amount from 30 wt % to 50 wt % showed a great impact in mechanical stability and conductivity of the electrolyte. A conductivity of 10^{-2} S/cm at 55 °C was reached. The membranes showed a dense fiber structure with an elastic character.

Influence of the sintering procedure on the solid electrolyte's microstructure and its grain and bulk resistance

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Solid state batteries lithium-ion batteries (SLIBs) are envisaged as next-generation to current liquid electrolyte based batteries due to their supposed enhanced safety. The search for solid electrolyte materials is a very active research topic due to several reasons. Firstly, the material needs to have appropriate lithium-ion conduction while having good chemical/ electrochemical stability. Secondly, the material should have decent mechanical properties, so it would be possible to sinter it under reasonable conditions. [1]

In order to chemically tailor improved materials for SLIB electrolytes, it is important to be able to separate and quantify the different contributions of the solid electrolyte's overall lithium-ion conductivity. Consequently, the first aim of this study is to separate grain and bulk ionic contributions of different popular sulphide-based electrolyte materials (Li_3PS_4, Li_6PS_5Cl, $Li_{10}GeP_2S_{12}$, $Li_7P_3S_{11}$) using electrochemical impedance spectroscopy (EIS), and subsequent analysis via the distribution of relaxation times (DRT).

Secondly, it is important to analyse the sintering procedure for different electrolyte materials as the voids resulting from improper sintering lead to lower the ionic conductivity or even lead to crack formation during electrochemical cycling. In this work the electrolyte's sintering procedure's influence both on the ionic conductivity and the microstructure was studied using EIS coupled with DRT and scanning electron microscopy.

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A polymer electrolyte based on a new dinitrile poly(ethylene glycol) plasticizer for solid-state batteries

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The flammable and volatile nature of liquid electrolytes based on non-aqueous organic solvents is a major drawback in lithium-ion batteries, which causes a safety deficiency, degradation processes, and dendrite growth. As an alternative, polymer electrolytes exhibit advantages in terms of safety, density, flexibility, and lithium dendrite suppression [1]. Poly(ethylene oxide) (PEO)-based solid polymer electrolytes belong to the most popular electrolytes, but their fundamental ionic conductivities are too low for practical battery applications.

The amorphous state of a PEO-based matrix was enhanced by the addition of a novel plasticizer in order to increase ionic mobility and electrochemical performance. The synthesized plasticizer 4,7,10,13-tetraoxahexadecane-1,16-dinitrile (bCN-PEG4) and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) were incorporated into an acrylate-based polymer matrix. The quasi-solid polymer electrolyte (QSPE) was prepared by UV-induced copolymerization and exhibited a highly uniform morphology, high thermal (> 200 °C) and electrochemical stability (> 5 V vs. Li/Li^+), the ionic conductivity of 1.3 x 10^{-3} S cm^{-1} at 80 °C and a low glass transition temperature (– 55.7 °C). Overall, the QSPE meets the requirements for an application in solid-state lithium-ion batteries and shows the capability of the plasticizer bCN-PEG4 to enhance important properties of PEO-based electrolytes.

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Understanding densification of oxide and phosphate-based solid electrolytes under low-temperature

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Solid-state lithium batteries are becoming a mature technology with potential use in stationary and electromobility applications thanks to the advances on new highly-conducting solid electrolytes. Oxide and phosphates have appealing properties as solid electrolytes, exhibiting high Li ion conductivity, wide electrochemical stability and compatibility with Li metal anode. For practical application in a solid-state device, these materials need to be densified under high temperatures above 1000ºC. Such requirement hampers their processing into composite cathodes with active materials usually having a narrower thermal stability, thus being a bottleneck for the upscaling of the technology.
In this work we will discuss our recent findings regarding oxide and phosphate-based ion-conductors, including the recent synthesis and characterization of a new form of crystalline LiPON [1]. Besides, we will focus on the impact that the processing of garnet-type electrolytes under temperatures below 500 ºC has on the ionic conductivity, taking a close look to the grain growth and boundary interconnection as main responsible for the ionic conductivity.

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Local structure and transport of record-holding Na^+ ion conductor $Na_{2.9}Sb_{0.9}W_{0.1}S_4$

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$Na_{2.9}Sb_{0.9}W_{0.1}S_4$ is up to date the best conducting sodium solid electrolyte with a conductivity of 41 mS/cm at room temperature. [1] But the underlying factors for the remarkably high conductivity are still not completely understood. While pristine Na_3SbS_4 crystallizes in a tetragonal structure, the substituted $Na_{2.9}Sb_{0.9}W_{0.1}S_4$ seems to exhibit a cubic structure based on its X-ray diffractogram. By allowing 3D diffusion pathways, the cubic structure was assumed to be one driving forces for the conductivity enhancement in $Na_{2.9}Sb_{0.9}W_{0.1}S_4$. [2]

Here, we show by performing pair distribution function (PDF) analysis that the near-range order of $Na_{2.9}Sb_{0.9}W_{0.1}S_4$ remains tetragonal despite the change in the Bragg diffraction pattern. The introduction of vacancies and W-Sb site disorder disturbs the tetragonal motif leading to a cubic average structure, a similar effect as previously observed for ball-milled Na_3PS_4. [3]

While showing no differences in the local structure, quasi-elastic neutron scattering (QENS) and nuclear magnetic resonance (NMR) measurements revealed drastically improved diffusivity and decreased activation energies for $Na_{2.9}Sb_{0.9}W_{0.1}S_4$. These results underline that aliovalent substitution does not only increase the concentration of charge carriers but also affects the ionic diffusion.

This work emphasizes how important the investigation of local structure and transport is for assessing structure-transport relationships in order to improve current solid electrolytes.

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A short annealing step leads to a strong Li^+ conductivity enhancement in the amorphous system 0.33 LiI + 0.67 Li_3PS_4

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Compared to conventional lithium-ion batteries containing liquid electrolytes, all-solid-state batteries (ASSBs) exhibit potentially a higher safety and a higher energy density. The research in this field was boosted by the discovery of sulfide-based crystalline solid electrolytes with ionic conductivity in the range of 10-25 mS/cm [1,2] However, in the case of crystalline solid electrolytes, much effort has to be put in finding optimized annealing protocols at elevated temperatures in order to reduce grain boundary resistances. Amorphous solid electrolytes, like Li_2S-P_2S_5-based glasses, which can be easily synthesized, e.g. by mechanical milling [3], do not exhibit grain boundary resistances, but the bulk ionic conductivity is often lower than for the crystalline counterparts. The addition of LiI increases the ionic conductivity [4] and lowers the interfacial resistances in contact to metallic lithium.[4,5]

In this work, we show that the ionic conductivity of solid electrolytes in the system 0.33 LiI + 0.67 Li_3PS_4 can be increased by a factor of about 7 by means of a short annealing step, while the sample is still mostly amorphous. The combination of electrochemical impedance spectroscopy, powder X-ray diffractometry, ^{7}Li NMR spectroscopy and positron annihilation lifetime spectroscopy shows that the increase of the conductivity is caused by an annealing-induced formation of monovacancies in the bulk amorphous phase.[6] Our results show that amorphous electrolytes in the system 0.33 LiI + 0.67 Li_3PS_4 are promising materials for ASSB applications.

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Fast ion conduction in metal hydride/metal oxide nanocomposites: Interplay between hydride and oxide properties

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Solid-state electrolytes are crucial for next generation batteries. Their compatibility with Li metal and sulfur cathode make them suitable for high-capacity batteries such as Li-S batteries. Also, they could potentially lead to safer batteries by eliminating the use of flammable organic solvents in current electrolytes, and minimizing/elimination dendrites. Complex hydrides such as $LiBH_4$, $NaBH_4$, and $LiCB_{11}H_{12}$, have recently gained attention as solid-state electrolytes due to their attractive ionic conductivity and good interface properties arising from their softness. However, increasing their often poor room temperature ionic conductivity, is pivotal to application, hence the focus of several research groups.

In this contribution, I will show that the room temperature ionic conductivity of complex metal hydrides can be increased to several orders of magnitude via nanocomposites formation with metal oxides [1-2]. Interestingly, the nanocomposite electrolytes show better performance in all-solid-state Li batteries than the pure compounds[1, 3]. Using selected examples and a variety of characterization techniques, I will discuss how the ion conductivity enhancement is related to structural/polymorphic phase stabilization, or interface reaction leading to high defect concentration and/or formation of tertiary phase(s) at the hydride/oxide interface [3-5]. Finally, I will show that the effects are a complex interplay between the properties of the metal hydride and the oxide.

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Controlling densification of Li-garnet electrolyte thin-film for all-solid-state batteries

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Assembling the electrode and electrolyte films with desired structure and phase is essential to design a thin-film based all-solid-state Li-ion battery (SSB) for high power and energy densities, and good cycle stability. Solid electrolyte film has to be thin and highly ionic conductive in order to enhance the Li ion transport properties across the electrolyte, and a dense and defect free structure is required to suppress the internal Li dendrite formation. Among the solid electrolytes, ceramic Li-garnet is a promising candidate for SSB due to its high Li-ion conductivity and structural and electrochemical stability in a wide range of temperature and working voltage. One way to achieve a cubic phase of Li-garnet thin-film with ~10^3 S/cm of Li-ion conductivity is introducing multilayer of Li_3N as Li reservoirs into a Li-garnet film through pulsed laser deposition (PLD) technique. However, this approach leaves a nanoporous structure inside the film formed by decomposing of Li_3N layers during a post annealing process. Although closed pores formed in the Li-garnet film have not affected its Li ionic conductivity significantly, it could give other potential issues such as providing sites for Li dendrite growth. Here, we developed a new thin-film fabrication technique to control the porosity of the Li-garnet film while keeping the desired cubic phase with high Li ionic conductivity. We investigated how this new ceramic processing approach affects the atomic structural properties and the correlation with its Li ion transport kinetics. This gives a new perspective on developing advanced Li-ion solid-state electrolyte thin-film, which can contribute to designing safer and longer cycle life of SSB architecture allowing more room for cathode volumes.

Effects of Mechanical Reinforcement utilizing Polymer Blends, Inorganic Fillers, and Block Copolymerization in Bottlebrush Polymer Electrolytes

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All-solid-state lithium-metal batteries (ASSLMB) are of high research interest in the field of electrochemical energy storage, due to improved safety aspects and increased energy density. In this regard, polyether-based solid polymer electrolytes are often used because of their low glass transition temperature as well as high solubility and capability of dissociating of lithium salts. However, at high molecular weights, poly(ethylene oxide) (PEO) shows a high degree of crystallinity which limits the application to temperatures above its melting point of around 65 °C. [1] Contrarily, low molecular weight poly(ethylene glycol) (PEG) exhibits improved low temperature applicability at the expense of reduced mechanical strength.

Bottlebrush polymers enable high molecular weight polymers with reduced crystallinity, yet the mechanical stability of such bottlebrush polymers is insufficient. Therefore, we compared three different strategies to improve the mechanical properties of bottlebrush polymers. [2,3] Firstly, the bottlebrush homopolymer (poly(Nb)$_{40}$-*graft*-PEGME) was blended with polynorbornene (poly(Nb)$_{90}$), secondly TiO_2 nanoparticles were added as fillers, and thirdly a block copolymer was prepared to yield poly(Nb)$_{40}$-*graft*-PEGME-*block*-(Nb)$_{68}$. The incorporation of reinforcing constituents resulted in increased storage and loss moduli, with a maximum increase by two orders of magnitude for the bottlebrush block copolymer. Both the bottlebrush homopolymer and the reinforced electrolyte systems showed similar specific capacities in all solid state lithium metal battery cycling experiments, indicating that battery performance is not compromised by fillers or by the block copolymerization strategy.

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Oligoethylene oxide functionalized vinylphosphonic esters as solid polymer electrolytes with adjustable flexibility

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Solid-state polymer electrolytes show great potential for next-generation high-energy rechargeable lithium batteries due to the advantages of high safety, good mechanical flexibility, and easy film-formation ability. Among all the polymers, polyethylene oxide (PEO) is demonstrated to be a feasible polymer host, based on its high dielectric constant and strong lithium salt dissolving ability. However, the practical application of PEO in all-solid-state lithium batteries is limited mainly by its low ionic conductivity at room temperature, resulting from its semi-crystalline character. In this study, we synthesized a solid polymer electrolyte based on a vinylphosphonate backbone functionalized with oligoethylene oxide side chains. Hereby, the side chains are responsible for the ionic conductivity, while the phosphonate polymer backbone contributes to high chain flexibility, electrochemical stability and flame retardancy, therefore increasing the safety aspect. The resulting polymers are characterized *via* differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and size-exclusion chromatography (SEC). Consequently, polymer films are prepared by solution-casting with $LiBF_4$, $LiClO_4$, LiOTf and LiTFSI. The resulting polymer films are analyzed by electrochemical impedance spectroscopy (EIS). The polymers are thermally stable up to 260 °C and exhibit a low glass transition temperature (T_g) of –67 °C while no melting temperature (T_m) is observed, therefore lacking any crystalline domains. With the precisely adjustable catalytic polymerization the synthesized polymers can be optimized in their mechanical and electrochemical properties by introducing various side chains at the phosphonate unit without affecting the polymerization procedure. The completely amorphous character of the free-standing polymer films is one major advantage over pure poly(ethylene oxide) (PEO) as the ion conduction occurs in the amorphous regions of a polyelectrolyte. In addition, the low T_g indicates high chain flexibility, resulting in high ionic conductivity already at room temperature.

Systematic investigation of sensitivity of sulfide-based solid electrolytes for lithium-ion batteries towards humidity

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All-solid-state lithium-ion batteries (ASSLIBs) attract huge interest of researchers and battery manufacturers since they are the most promising candidates for future safe energy storage devices with high energy density for electric transport [1]. However, an important obstacle for wide commercialization of sulphide-based solid electrolytes (SSEs) for LIBs is their extremely high reactivity with traces of humidity leading to toxic H_2S evolution. Therefore, a deep understanding of reactivity of SSEs with water is a key factor to optimise intrinsic characteristics of SSEs as well as a production process of ASSLIBs ensuring its safety and reliability. Very limited amount of literature data is available on the topic [2, 3].

In this work, reactions between SSEs and water were investigated with high precision using a home-made test assembly. Commercially available SSEs, such as Li_3PS_4, $Li_7P_3S_{11}$, $Li_{10}GeP_2S_{12}$, Li_6PS_5Cl and Li_6PS_5Br were investigated at different scales (from few milligrams to 1g). The developed test assembly is based on gas flow-through cell for the analysis of SSE powders and pellets and continuous H_2S measurements thanks to ultra-sensitive laser detection equipment. Specific attention was paid to reproducibility of the results. The levels of humidity were chosen to mimic a dry room atmosphere. A strong relationship was found between the composition of SSEs, their surface area and reactivity towards humidity. Passivation phenomena were observed in some cases upon exposure to H_2O. Additional advanced characterisation methods helped to understand the differences in reactivity of SSEs with water.

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Single-step ball milling synthesis of highly Li^+ conductive $Li_{5.3}PS_{4.3}Cl_{1.7}$ glass ceramic electrolyte

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All-Solid-State-Batteries (ASSB) are promising candidates for the next generation of batteries due to the favourable properties of solid electrolytes (SE) regarding safety concerns and due to the potential usage of a Li metal anode. Nevertheless, several challenges remain, like maximizing the ionic conductivity while simplifying the synthesis route to make it applicable at industry scales. [1] Argyrodite-type SEs Li_6PS_5X (X = Cl, Br, I) are of great interest, since fast ion transport (10^{-3} – 10^{-2} mS·cm^{-1}) together with good mechanical properties can be achieved from inexpensive educts. The conductivity may be further enhanced by cation doping or by preparing halide-rich $Li_{6-x}PS_{5-x}X_{1+x}$ (> 10^{-2} mS·cm^{-1}) SEs. However, it is important to note that these high conductivity values are only achieved by multi-step syntheses and by solid electrolyte pellet annealing prior to measurements, which impedes industrial application. [1-3]

In this work, we present a simple synthesis of glass-ceramic (GC) $Li_{5.3}PS_{4.3}Cl_{1.7}$ ($LPSCl_{1.7}$) via mechanochemical ball milling. Impedance measurements of a cold-pressed SE pellet yield a Li^+ conductivity of 4.4 mS·cm^{-1} at room temperature, hence it is a promising contestant for the application in ASSB alongside with GC-$Li_{5.3}PS_{4.3}ClBr_{0.7}$ (previous work). [4] We also show results for the pressure-dependent conductivity of cold-pressed $LPSCl_{1.7}$ between two In/Li electrodes. The usage of $LPSCl_{1.7}$ leads to an ASSB cathode impedance of 10 Ω·cm^2 and a stable discharge capacity of 180 mAh·g^{-1} at a rate of 0.1C.

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XRD-CT Investigation of LPSCl degradation occurring during cycling

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Sulphur based solid electrolytes (SE) are a promising candidate for realising solid state battery systems as they exhibit both reasonable ionic conductivity[1] and ease of processability. These solid electrolytes are unfortunately not fully stable upon cycling, due to their narrow electrochemical stability, causing electrochemical degradation during cycling which reduces their long-term electrochemical performance. Despite current investigation, the link between structural and morphological changes and electrochemical performance is yet poorly understood especially during lithiation and delithiation[2].

X-ray diffraction computed tomography (XRD-CT) carried out at ID15a at the European Synchrotron Radiation Facility allows distribution of specific chemical species within a material to be resolved spatially. The focus of this work, in which ex-situ half cells of L_6PS_5Cl have been examined using XRD-CT after 50 charge-discharge cycles against lithium-indium, in both reduction and oxidation and compared to a pristine sample, is to observe the localisation of chemical changes as a function of the depth of the reaction in the cells and gain insight into how they affect the morphology.

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On the role of binder in all-solid state battery using sulphide based electrolytes

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Nowadays, Li-ion batteries have started reaching their limitation in term of safety and electrochemical performance requesting the development of novel electrochemical energy system. To ensure a transition to safer and more energetic electrochemical system, solid state batteries using solid electrolyte have been declared as the most suitable solution. In theory the cell should be safer due to the replacement of the flammable liquid electrolyte into a solid state one and the employment of Li metal at the negative electrode, since no dendrites should be generated in the solid-state batteries[1]. Unfortunately, the transition to liquid based electrolyte to solid state electrolyte is causing several issues, among them, a chemical instability as the electrochemical stability windows of sulphide electrolyte is very narrow[2] and a mechanical instability caused by the "solid" aspect of the cell. Indeed, making a solid electrolyte implies the sintering of the electrolyte avoiding voids that could generate later on fracture once lithiation/delithiation occurs due to the stress propagation. In this work, we propose to use a binder to improve the ductility of the sulphide electrolyte (Li_6PS_5Cl). Through this poster, we will be showing the impact of the polymer on the physico-chemical characteristics of the LPSCl solid electrolyte, among them, the ionic conductivity, the 3D morphology, the grains boundaries investigation and the electrochemical stability windows.

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Designing Gel Polymer Electrolyte with Synergetic Properties for Rechargeable Magnesium Batteries

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The rapid market expansion for consumer electronics and electric vehicles urges the development of electrochemical energy storage devices with high energy density, low cost and safety. In this regard, the development of multivalent−ion batteries is one feasible solution for such goals, and among them magnesium (Mg) battery is one of the most promising candidates. However, the realization of practical Mg batteries remains challenging and advanced material design strategies are imperatively necessary. One of the main issues with liquid electrolyte in Mg battery is the dissolution and diffusion of active materials, for example, the so-called polysulfide shuttle effect in Mg−S batteries.

The development of gel polymer electrolytes (GPEs) may provide a promising solution to circumvent the above issues. With an in-situ polymerization, a novel magnesium tetrakis(hexafluoroisopropyloxy)borate ($Mg[B(hfip)_4]_2$)-based non-corrosive gel polymer electrolyte has been developed as a kind of Cl-free gel polymer electrolyte.[1] This gel polymer electrolyte exhibits unprecedented electrolytic properties in terms of high ionic conductivity (10^{-3} S cm^{-1}), reversible Mg plating/stripping capability (Coulombic efficiency ~99%, 1000 cycles) and low electrochemical overpotential. Simultaneously, the polymeric matrix can prevent dissolution and diffusion of soluble electrode materials. Moreover, it can be extended to other polymer backbones and incorporated with other cathodes for improving battery performance.

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Synthesis-dependent polymorphism of the sodium ionic conductor Na_2ZrCl_6

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Na-conducting rare-earth-containing halides have stimulated growing interest and the mechanochemical synthesis (e.g. ball milling) method has been widely employed to prepare these sodium halide solid electrolytes recently. The subsequent heating step can effectively tune the structure and transport property of the ball-milled material. Here, we synthesized a series of Na_2ZrCl_6 with ball milling and subsequent annealing at different temperatures. The structural evolution of Na_2ZrCl_6 was investigated using X-ray diffraction and Rietveld refinement. Na_2ZrCl_6 crystallizes in an unusual monoclinic structure ($P2_1/n$ space group) at a specific annealing temperature (400 °C) while it forms a trigonal structure ($P\bar{3}m1$ space group) adopting other annealing temperatures. The monoclinic Na_2ZrCl_6 exhibits a higher conductivity and lower activation energy compared to its trigonal isomer because of the Na^+ carrier density difference. Moreover, the trigonal Na_2ZrCl_6 crystals annealed at different temperatures show various ionic conductivities, which can be expected that the size effect is at play.

Identifying limiting factors on the cell performance of all-solid-state batteries by microstructural resolved simulations

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All-solid-state batteries (ASSBs) are predicted to play an important role in future battery applications, because they potentially provide high energy densities and an enhanced safety in operation. The ceramic electrolyte LLZO is a promising choice for the solid electrolyte (SE), as it is stable against Li-metal and shows a high ionic conductivity which is essential for a high cell performance. However, experimental results still show low capacities for garnet-based ASSBs at room temperature and a severe capacity fade after the cycling of the cells [1,2].

In this contribution we explore the reasons for the observed limitations and show possible optimization strategies by continuum modelling and simulations. First, we perform microstructural-resolved simulations on a set of virtual composite cathodes to identify the limitations of the underlying microstructure. In doing so we want to provide advantageous target values for the cell production regarding active material content, sinter density and particle sizes. Furthermore, we focus on the role of secondary phases in the composite cathode that can form as a result of degradation phenomena at the interface between the SE and cathode active material (CAM). By extending our simulation environment with an interface model, we show that a resistive layer at the interface SE/CAM resulting from secondary phase formation is a plausible explanation for the low measured capacities at room temperature. An increase in layer thickness when cycling the cell due to electrochemical degradation is a possible mechanism for the observed capacity fade.

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3D Impedance Modelling of Solid-State Battery Components

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Impedance spectroscopy is particularly suitable to systematically investigate solid-state battery components. Individual impedance contributions of phases and interfaces can be separated from each other if they differ in their frequency-dependent behavior. Therefore, it is the method of choice to investigate the charge transport in solid electrolytes and more complex solid-state systems like composite separators, composite cathodes, composite anodes or even full cells.[1] Quantitative results are regularly obtained by fitting the experimental impedance spectrum using simple mostly 1D equivalent circuits models which do not consider the 3D microstructure of the system.

Therefore, we developed a 3D electric network model in order to investigate the impact of the microstructure on the impedance response of the system considered.[2] We present an overview of case studies to highlight the significant impact of current constriction effects on the interface behavior of lithium metal anodes.[3-5] Moreover, we provide an outlook on possible applications of the developed network model with respect to solid-state battery research.

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Phase Evolution and Thermodynamics of Al-doped cubic LLZO studied by High-Temperature X-ray Diffraction

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Synthesis of phase pure $Li_7La_3Zr_2O_{12}$ (LLZO) is challenging due to easy formation of secondary phases, such as the pyrochlore $La_2Zr_2O_7$. While much work on LLZO has been done to understand the electrochemical performance of LLZO, the thermodynamics of the synthesis and formation of LLZO is poorly understood.

Here we report a high-temperature X-ray diffraction (HTXRD) study on 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. The resulting powders 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 1000 °C. Upon heating the pyrochlore phase gradually transforms to cubic LLZO. We performed two analyses of the sample with 10 % excess Li by HTXRD, with normal and thinner deposition thickness. In the thinner sample, cubic LLZO appears at a lower temperature. The pyrochlore phase does not fully disappear but instead reappears and crystallizes at the highest temperatures investigated, indicating extensive Li loss from the thinner sample. These observations suggest that atmospheric exposure and the 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:

$$6.25\ Li_2CO_3 + 0.25\ Al_2O_3 + 2\ La_2Zr_2O_7 + La_2O_2CO_3 \rightarrow$$
$$2\ Li_{6.25-x}Al_{0.25}La_3Zr_2O_{12-0.5x} + 7.25\ CO_2(g) + x\ Li_2O(g).$$

The enthalpy, entropy and Gibbs energy of the reaction were calculated from literature data and DFT calculations and agree with the experimental observations. Finally, we discuss the impact of the highly disordered Li sublattice for the entropy of cubic LLZO.

Investigating diffusion pathways, mechanochemical milling and the electrochemical stability window for the $Li_5NCl_2/Li_9N_2Cl_3$ solid electrolyte[1]

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Solid electrolytes which are thermodynamically stable against lithium metal may be key to stabilizing lithium-metal/solid-electrolyte interfaces which is crucial for realizing all-solid-state batteries with competitive energy densities. An extensive body of research has been dedicated to "halide" solid electrolytes in the past 4 years. But no recent report of lithium nitride-halides exists despite their thermodynamic stability against lithium metal. We thus decided to revisit a lithium nitride phase (cubic Li_5NCl_2) that had in previous investigations shown the highest ionic conductivity. [2]

We synthesized Li_5NCl_2 and initial electrochemical impedance spectra confirmed the ionic RT conductivity ($1x10^{-6}$ S cm^{-1}) and activation energy (0.47 eV) that were previously reported. [2] Interestingly, ^{7}Li NMR line narrowing measurements (Figure 1b) suggest a much lower activation energy (0.21 eV) and higher RT conductivity ($1x10^{-3}$ S cm^{-1}). To resolve this discrepancy, we turned to ab-initio molecular dynamics simulations and found a broad manifold of different jump events in Li_5NCl_2. The N/Cl disorder in Li_5NCl_2 means that the N/Cl composition of tetrahedra around the Li sites varies and the migration energies for different jumps span a wide range from 0.2 to 0.5 eV (Figure 1c). We concluded that fast Li diffusion between sites connected by low-E_a jumps (captured by NMR) is present in Li_5NCl_2 but percolation is limited by high-E_a jumps resulting in the low observable 3D macroscopic conductivity (captured by EIS).

We investigated the effect of mechanochemical milling on Li_5NCl_2 and that a milling step after ampoule synthesis as well as a "direct" mechanochemical synthesis (without any annealing step) improve the ionic conductivity by a factor of 10. We also investigated the anodic limit of Li_5NCl_2 combining calculations and experiments and based on our findings reflect on the applicability of Li_5NCl_2 in solid state batteries.

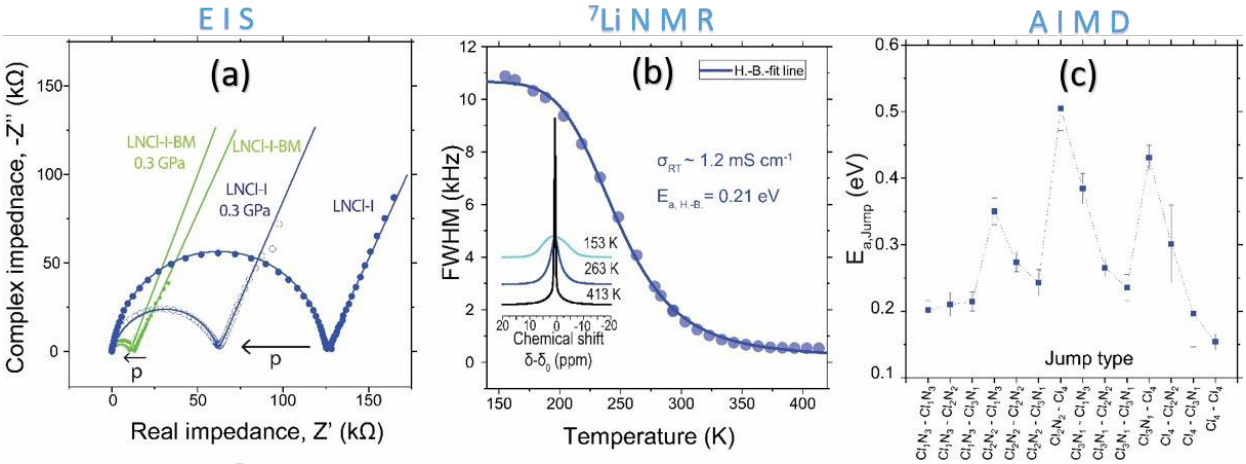

Figure 1. (a) EIS , (b) ^{7}Li NMR and (c) the migration energies for the different jumps in Li_5NCl_2 from AIMD.

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Evaluating Charge Transport and Microstructure of Composite Cathodes for Solid State Batteries

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As an energy storage device with high energy and power density, ASSBs (all-solid-state batteries) have recently received increased attention. Sufficient and short ionic and electronic transport pathways in composite cathode for ASSBs are essential for the active material utilization and (dis-)charging kinetics respectively, because cathode active material particles that are either electronically or ionically isolated cannot contribute to the charging or discharging process. Because ASSB cathodes rely solely on solid-to-solid contacts, achieving percolation is more difficult, than by infiltration of porous electrodes with a liquid electrolyte. Additionally, residual porosity that blocks charge transport of ions and electrons has to be minimized. Thus, optimizing cathode microstructures becomes increasingly important for the improvement of all-solid-state batteries.

In this study, we investigated both ionic and electronic percolation in composite cathodes made of an intercalation type active material and a thiophosphate based solid electrolyte . Different cathode microstructures were created by varying the particle size distribution of the solid electrolyte. Partial conductivities were then used to evaluate the effectivity of the electronic and ionic conduction pathways.

To quantify the respective partial conductivities, we used electronically as well as ionically blocking electrodes with which to carry out electrochemical impedance spectroscopy measurements. From the obtained partial conductivities, we calculated tortuosity factors and correlated them to cell performance with complementary cycling data of all-solid-state batteries in order to determine charge transport bottlenecks. By FIB-SEM tomography of a composite cathode we could generate a detailed 3D reconstruction of the cathode microstructure and found the particle size of the solid electrolyte to influence the charge transport and electrochemical performance of these cathodes.

Investigating safety of solid state batteries via 3D modeling

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The current energy transition trend towards renewable but intermittent energy resources requires advanced battery technologies to store energy electrochemically. On the other hand, the rapid increase in the application and production rate of Electric Vehicles (EVs) further increases the need for safe and reliable battery technologies. Lithium-ion batteries (LIBs) having high specific capacity constitute 95-99% of batteries used for transportation purposes [1]. However, the organic liquid electrolyte used in LIBs raises serious safety concerns such as fire and explosion occurrence in case of malfunction or damage. Solid state batteries (SSBs) using inorganic solid electrolytes are considered to be safer than conventional LIBs, although their thermal behaviors related to electrical, thermal, and mechanical abuse cases are still under debate. In this contribution, several abused scenarios related to safety aspects (pinhole formation and overheating) in a pouch SSB cell will be presented via a 3D modelling approach. In specific, key quantities such as electric potential, current density, and temperature profiles are analyzed and benchmarked with a normal case. The modeling results provide some insights for better designing SSB cells in the first step and will need to be validated using experimental data in the future. The presented 3D modeling methodology can be expanded to further cell chemistries, geometries, and abuse scenarios.

Literature:

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Sulfide-based All-Solid-State Battery Pouch Cell Production – An Environmental Assessment

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All-Solid-State batteries (ASSB) are a promising technology for reaching targets for capacity, fast-charging capability and safety of batteries. However, methods for a holistic evaluation of potential production routes and their transferability to industrial scale are still subjects to research. The investigation of different production concepts mainly focuses on the processing based on sulfide, oxide, polymer and hybrid-based solid electrolytes. The sulfide-based process chain is promising based on the high ionic conductivity and processing properties of the electrolyte for a scalable production [1, 2]. However, the release of H_2S during production makes this route challenging, so safety parameters for sulfidic solid electrolytes are also being investigated.

The focus of this work is to assess the environmental impacts and identify key hotspots of a potential sulfide-based production route for ASSB pouch cells. Therefore, a cradle-to-gate Life Cycle Assessment has been conducted. Expert opinions on the processes, laboratory-scale energy measurements, as well as background data from the ecoinvent database have been incorporated into the python-based modeling using Brightway2. The results show that especially the electricity demand and the consumption of argon represent a high environmental impact. The high argon demand is driven by the use of an inert environment required in the processing of the highly reactive sulfides and metallic lithium. Hence, optimizations in terms of energy and process efficiency are among the main challenges. Based on this, recommendations are developed by considering potential micro environments and scale effects to pave the way for high-energy and sustainable battery production.

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