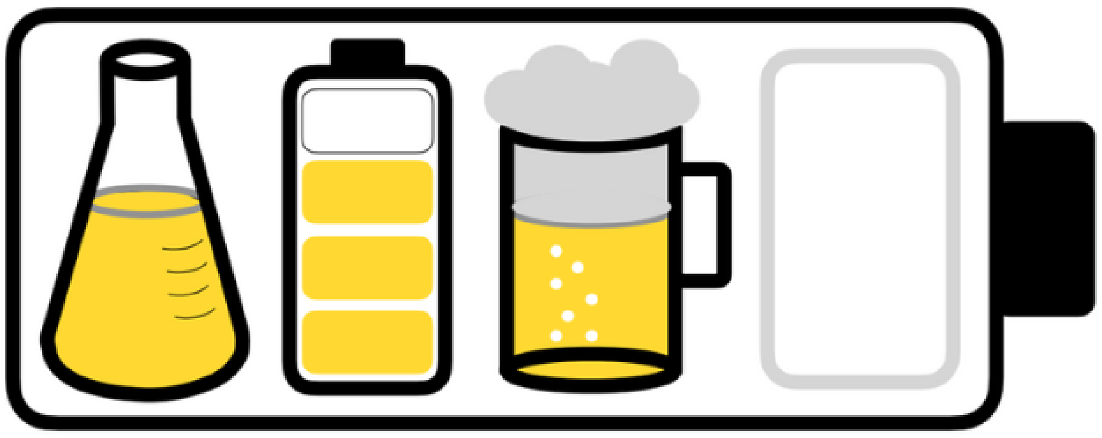
ESPE23

1st European Symposium on Polymer Electrolytes for Battery Applications

25 – 27 September 2023
Karlsruhe, Germany

Book of Abstracts

polymer,
batteries &
networking.



POLiS
Post Lithium Storage
Cluster of Excellence

Content

General Information

Polymer electrolytes have a long history in battery research and both material development and our fundamental understanding of ion transport mechanisms in polymers has evolved with it. Today, we are standing at the crossroads overseeing many possible winding paths down battery lane with a multitude of battery technologies to choose from. Diversification in many different cell chemistries opens new avenues to explore and encourages to revisit some concepts and findings of past days.

The pandemic has made it difficult for our community to meet and exchange, which has become clear during the International Symposium of Polymer Electrolytes (ISPE17) in Canada in October 2022. While we remain dedicated to other international communities, not least the ISPE, we, the Organizers, feel that a more limited meeting in terms of scope and geographical target group would be highly appreciated. It is our ambition to assemble primarily the European academic research community in this area, including a large number of PhD students, other newcomers, together with relevant researchers from industry, this year at the Karlsruhe Institute of Technology (KIT) in Germany for the first European Symposium on Polymer Electrolytes for Battery Applications (ESPE23) hosted from September 25th to 27th 2023.

We would like to give newcomers to the field the opportunity to meet leading experts, present their latest results, network and find new colleagues and friends to advance the development of polymer electrolytes together. Furthermore, we would like to encourage PhD students of our Center of Electrochemical Energy Storage (CELEST) as well as our research Cluster of Excellence for post-Li storage (POLiS) to join this meeting in the framework of a workshop module of the Graduate School of Electrochemical Energy Storage (GS-EES) to get in touch with the latest trends and advances in this exciting area.

Organizing Committee

Fabian Jeschull, Karlsruhe Institute of Technology
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Dominik Voll, Karlsruhe Institute of Technology

Institute for Chemical Technology and Polymer Chemistry (ITCP)

Christian Schmitt, Karlsruhe Institute of Technology

Soft Matter Synthesis Laboratory – Institute for Biological Interfaces III (IBG3)

Daniel Brandell, Uppsala University

Angström Advanced Battery Laboratory (AABC)

Program

Monday, 25th September 2023

Time (CEST)	Speaker	Title
12:45 pm	Opening ESPE23	
12:50 pm	**Stefano Passerini** HIU / Sapienza Università di Roma	Solvent-Free Ternary Polymer Electrolytes With High Ionic Conductivity For Sodium-Based Batteries Operating At Room Temperature
1:20 pm	**Felix Richter** Justus-Liebig-University Giessen	Considerations on Cell Types and the Roles of Polymers in Solid-State Batteries
1:40 pm	**Corsin Battaglia** EMPA	High-Voltage Lithium-Metal Batteries With Polymerized-Ionic-Liquid Based Polymer Electrolyte
2:10 pm	**Didier Devaux** Université Grenoble Alpes	Evolution of the Ionic Conductivity of Solid Polymer Electrolytes upon Elongation
2:30 pm	**Jonas Mindemark** Uppsala University	Polymer electrolytes beyond PEO, LiTFSI and LFP: A story of host materials, salts, additives and potentials
3:00 pm	Coffee Break	
3:30 pm	**Monika Schönhoff** Westfälische Wilhelms-Universität Münster	NMR transport measurements: Tracking ion migration in battery electrolytes
4:00 pm	**Anne Westphal** Fraunhofer Institute for Manufacturing Technology and Advanced Materials IFAM	Solvent Free and Catalyst Free Solid Polymer Electrolytes for Lithium-ion Batteries
4:20 pm	**Maria Martinez-Ibanez** CIC energieGUNE	Towards a rational design of lithium salts and polymer matrices for lithium metal solid-state batteries
4:50 pm	**Matteo Gandolfo** Politechnico Torino	Enhancing the safety of lithium metal batteries through the use of composite ionogels
5:10 pm	**Gabriele Lingua** POLYMAT	Polymer electrolytes based on protic poly(ionic liquid)s for lithium batteries
5:30 pm	**Daniel Brandell** Uppsala University	News from ISPE-18 in 2024
5:35 pm	Group Photo	
5:40 pm	Poster Session	
7:30 pm	End Day 1	

Tuesday, 26th September 2023

Time (CEST)	Speaker	Title
9:00 am	**Claudio Gerbaldi** Politechnico Torino	An Overview on Crosslinked Polymer-based Electrolytes with High Ionic Mobility for Safe Operation of Solid-State Batteries
09:30 am	**Jelena Popovic-Neuber** University of Stavanger	Ion Transport in Soft Matter Battery Electrolytes and Related Interphases
10:00 am	**Gunther Brunklaus** Forschungszentrum Jülich	Polymer Hybrid Concepts: Towards Higher Energy Densities with Oligomers and Grafted Ceramics
10:30 am	**Coffee Break**	
11:00 am	**Diddo Diddens** Forschungszentrum Jülich / Helmholtz Institute Münster	Improving the Ion Transport in Polymer Electrolytes by Modeling Insights
11:30 am	**Orpita Majumdar-Svensson** Uppsala University	Solvent Free and Catalyst Free Solid Polymer Electrolytes for Lithium-ion Batteries
11:50 am	**Federico Bella** Politechnico Torino	Exploring polymer electrolyte families for potassium batteries
12:20 pm	Lunch Break	

Program

1:40 pm	**Sabina Abbrent** Czech Academy of Science	The influence of ester versus ether crosslinkers on the physicochemical properties of electrolytes based on poly-2-oxazolines
2:10 pm	**Sergio Rodriguez Peña** CIC energieGUNE	Anion π–π Stacking for Improved Lithium Transport in Polymer Electrolytes
2:30 pm	**Vito di Noto** Università degli Studi di Padova	Polymer-based Electrolytes for Lithium Batteries and Beyond: New Materials and Conductivity Mechanisms
3:00 pm	Coffee Break	
3:30 pm	**Zora Chalkley** Helmholtz Centre Berlin	Probing interfaces in anode-free Li-ion batteries with polymer electrolyte by operando hard X-ray photoelectron spectroscopy
4:00 pm	**Simon Buyting** Westfälische Wilhelms-Universität Münster	Influence of Different Co-Solvents on Ion Transport in PEO and PCL polymer electrolytes
4:20 pm	**Laurent Rubatat** Université de Pau et des Pays de l'Adour	Block Copolymer Nanostructured Solid Polyelectrolytes From Equilibrium to Out of Equilibrium Strategies
4:50 pm	**Irune Villaluenga** POLYMAT	Confinement of Ionic Liquids into Copolymers for Flexible Solid-State Electrolytes for Li-metal Batteries
5:10 pm	**Patrick Théato** Karlsruhe Institute of Technology (KIT)	PEO based block copolymers as solid polymer electrolytes
6:00 pm	Symposium Dinner at Cantina Majolika	

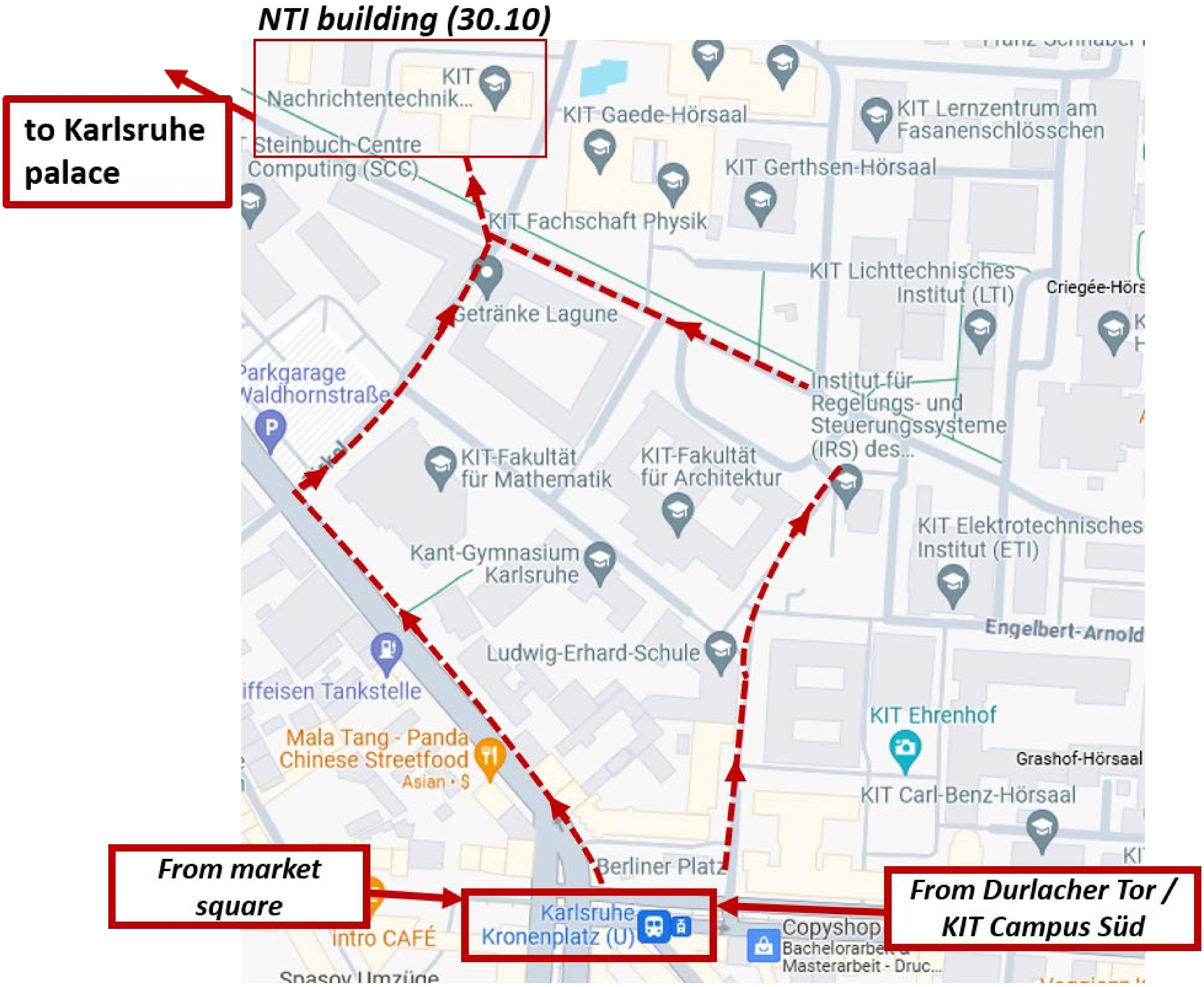
Wednesday, 27th September 2023

Time (CEST)	Speaker	Title
9:00 am	**Antonela Gallastegui** POLYMAT	Single-ion conducting Nanoparticles Electrolytes for Solid-State Lithium Batteries
09:30 am	**Władysław Wieczorek** Warsaw University of Technology	Development of Huckel type salts as components for polymeric electrolytes
10:00 am	**Guiomar Hernández** Uppsala University	Solubility and Stability Requirements for Solid Polymer Electrolytes
10:30 am	Coffee Break	
11:00 am	**Javier Carretero-González** Institute of Polymer Science and Technology – CSIC	Fluorine-Free K-Ion Polymer Electrolytes
11:30 am	**Maria Morant-Miñana** CIC energieGUNE	Electrochemical performance of dry- and wet- manufactured solid polymer electrolytes
11:50 am	**Dominic Bresser** Helmholtz Institute Ulm	Single-ion conducting polymer electrolytes – From an enhanced understanding towards their potential use in practical devices
12:20 pm	End of ESPE23	

How to get there

The campus south is located in the city center of Karlsruhe and can easily be reached by public transport. The closest stop is “Kronenplatz“.

From the event location at KIT Campus South it is a 15 minutes walk to the “Cantina Majolika” where the symposium dinner will take place on Tuesday evening.



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Partners

Center for Electrochemical Energy Storage | Ulm & Karlsruhe (CELEST)

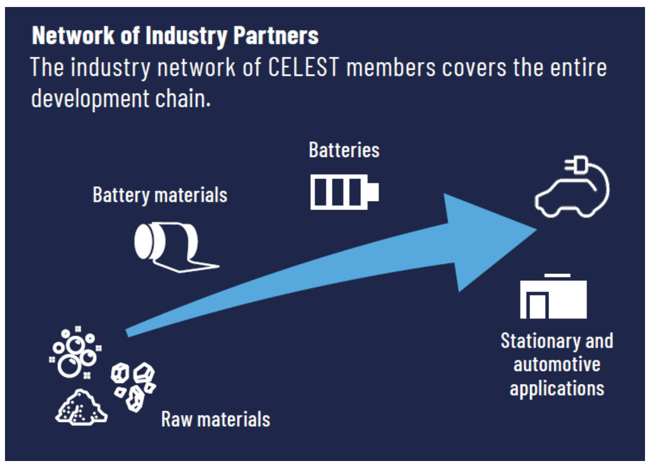
The Center for Electrochemical Energy Storage Ulm & Karlsruhe (CELEST) provides a broad platform for scientific collaboration and technology transfer in the field of electrochemical energy storage (EES) ranging from fundamental research to large-scale cell fabrication and testing.

Scientists in Ulm and Karlsruhe have complementary expertise extending from basic research on elementary processes at the atomic scale to multi-scale modeling of relevant processes over development of new storage materials and laboratory cells up to the largest pilot plant for battery cell manufacture in Europe at the ZSW. CELEST covers the research areas of “Lithium-ion technology,” “Energy storage beyond lithium,” and “Alternative technologies for electrochemical energy storage and conversion devices,” i.e. all highly relevant topics in the area of electrochemical energy storage.

Another focus lies on collaboration with industry partners for technology transfer, innovation, and commercialization of new technologies.

Within CELEST, our mission is:

- Working on the energy storage and conversion of the future
- Cooperating in interdisciplinary research and innovation in the field of EES ranging from basic research to technical applications
- Cooperating on students' qualification
- Planning, preparing, and organizing new joint endeavors in research, innovation, and technology transfer
- Acting as a platform to improve communication
- Coordinating and further developing joint activities with other universities and research institutions as well as the industry, at home and abroad



Network of Industry Partners

The industry network of CELEST members covers the entire development chain.

Abstracts Talks

- **Stefano Passerini, HIU | Sapienza Università di Roma**
  Solvent-Free Ternary Polymer Electrolytes With High Ionic Conductivity For Sodium-Based Batteries Operating At Room Temperature
- **Felix Richter, Justus-Liebig-University Giessen**
  Considerations on Cell Types and the Roles of Polymers in Solid-State Batteries
- **Corsin Battaglia, EMPA**
  High-Voltage Lithium-Metal Batteries With Polymerized-Ionic-Liquid Based Polymer Electrolyte
- **Didier Devaux, Université Grenoble Alpes**
  Evolution of the Ionic Conductivity of Solid Polymer Electrolytes upon Elongation
- **Jonas Mindemark, Uppsala University**
  Polymer electrolytes beyond PEO, LiTFSI and LFP: A story of host materials, salts, additives and potentials
- **Monika Schönhoff, Westfälische Wilhelms-Universität Münster**
  NMR transport measurements: Tracking ion migration in battery electrolytes
- **Anne Westphal, Fraunhofer Institute for Manufacturing Technology and Advanced Materials IFAM**
  PEGMEM as Reactive Polymer Electrolyte System for All-Solid-State Lithium Ion Batteries
- **Maria Martinez-Ibanez, CIC energieGUNE**
  Towards a rational design of lithium salts and polymer matrices for lithium metal solid-state batteries
- **Matteo Gandolfo, Politechnico Torino**
  Enhancing the safety of lithium metal batteries through the use of composite ionogels
- **Gabriele Lingua, POLYMAT**
  Polymer electrolytes based on protic poly(ionic liquid)s for lithium batteries
- **Claudio Gerbaldi, Politechnico Torino**
  An Overview on Crosslinked Polymer-based Electrolytes with High Ionic Mobility for Safe Operation of Solid-State Batteries
- **Jelena Popovic-Neuber, University of Stavanger**
  Ion Transport in Soft Matter Battery Electrolytes and Related Interphases
- **Gunther Brunklaus, Forschungszentrum Jülich**
  Polymer Hybrid Concepts: Towards Higher Energy Densities with Oligomers and Grafted Ceramics
- **Diddo Diddens, Forschungszentrum Jülich | Helmholtz Institute Münster**
  Improving the Ion Transport in Polymer Electrolytes by Modeling Insights
- **Orpita Majumdar-Svensson, Uppsala University**
  Solvent Free and Catalyst Free Solid Polymer Electrolytes for Lithium-ion Batteries
- **Federico Bella, Politechnico Torino**
  Exploring polymer electrolyte families for potassium batteries
- **Sabina Abbrent, Czech Academy of Science**
  The influence of ester versus ether crosslinkers on the physicochemical properties of electrolytes based on poly-2-oxazolines
- **Sergio Rodriguez Peña, CIC energieGUNE**
  Anion π–π Stacking for Improved Lithium Transport in Polymer Electrolytes
- **Vito di Noto, Università degli Studi di Padova**
  Polymer-based Electrolytes for Lithium Batteries and Beyond: New Materials and Conductivity Mechanisms
- **Zora Chalkley, Helmholtz Centre Berlin**
  Probing interfaces in anode-free Li-ion batteries with polymer electrolyte by operando hard X-ray photoelectron spectroscopy
- **Simon Buyting, Westfälische Wilhelms-Universität Münster**
  Influence of Different Co-Solvents on Ion Transport in PEO and PCL polymer electrolytes
- **Laurent Rubatat, Université de Pau et des Pays de l'Adour**
  Block Copolymer Nanostructured Solid Polyelectrolytes From Equilibrium to Out of Equilibrium Strategies
- **Irune Villaluenga, POLYMAT**
  Confinement of Ionic Liquids into Copolymers for Flexible Solid-State Electrolytes for Li-metal Batteries
- **Patrick Théato, Karlsruhe Institute of Technology**
  PEO based block copolymers as solid polymer electrolytes
- **Antonela Gallastegui, POLYMAT**
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  Development of Huckel type salts as components for polymeric electrolytes
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  Fluorine-Free K-Ion Polymer Electrolytes
- **Maria Morant-Miñana, CIC energieGUNE**
  Electrochemical performance of dry- and wet- manufactured solid polymer electrolytes
- **Dominic Bresser, Helmholtz Institute Ulm**
  Single-ion conducting polymer electrolytes – From an enhanced understanding towards their potential use in practical devices

Solvent-Free Ternary Polymer Electrolytes With High Ionic Conductivity For Sodium-Based Batteries Operating At Room Temperature

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Among the "beyond" lithium electrochemical storage systems, sodium-ion batteries (SIBs) are a promising technology, especially for large-scale stationary applications and light electromobility.[1] Transitioning to solid-state batteries using, e.g., polymer electrolytes, results in inherently safer devices and can facilitate the use of sodium metal anodes enabling higher energy densities. In this work, solvent-free ternary polymer electrolytes based on cross-linked polyethylene oxide (PEO), sodium bis(fluorosulfonyl) imide (NaFSI) or sodium bis(trifluoromethanesulfonyl) imide (NaTFSI) and N-butyl-N-methyl-pyrrolidinium-based ionic liquids (ILs, Pyr14FSI or Pyr14TFSI) are developed. Synthesized polymer membranes are thoroughly characterized, verifying their good thermal and electrochemical stability, as well as a low glass transition and crystallinity, thus high segmental mobility of the polymer matrix. The latter results in good ionic conductivities around 1·10-3 S cm-1 at 20 °C. The polymer electrolytes are successfully employed in (anode-less) sodium-metal battery (SMB) cells operating at room temperature (RT) in two rather different configurations, using either seawateror P2-Na2/3Ni1/3Mn2/3O2 layered oxide as the positive electrode.[2,3]

References:

[1] I. Hasa, S. Mariyappan, D. Saurel, P. Adelhelm, A. Y. Koposov, C. Masquelier, L. Croguennec, M. Casas-Cabanas, J. Power Sources 482 (2021), 228872.
[2] Y. Kim, M. Kuenzel, D. Steinle, X. Dong, G.-T. Kim, A. Varzi and Stefano Passerini, Energy Environ. Sci.15 (2022) 2610.
[3] D. Roscher, Y. Kim, D. Stepien, M. Zarrabeitia and Stefano Passerini, Batteries & Supercaps (2023)e202300092.

Considerations on Cell Types and the Roles of Polymers in Solid-State Batteries

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Battey research is especially interdisciplinary, with a focus on bridging physics, chemistry and materials science. In addition, battery cells contain practically all types of materials: metals, carbon, oxides, polymers and liquids make up most cells. The key lies in finding the optimum composition and processing technology to combine the advantages of each material type as effectively as possible. Polymers, especially polymer electrolytes, contribute significantly to the functioning of batteries and their advantages and disadvantages are discussed considering the different roles they play in a cell, particularly in solid-state batteries.

Solid-state batteries are investigated for the promise of delivering more energy at a higher rate, thereby posing an appealing technology that may surpass the performance of present-day lithium-ion batteries. This is particularly true if a lithium metal anode can be implemented effectively and the stability in the composite cathode is improved by mitigating degradation processes and crack formation at the interfaces. What makes an electrochemical cell a solid state battery is not defined strictly, and the term is used liberally to be applied to next-generation battery technologies relying on a solidified electrolyte independent of its chemical composition. Therefore, basically all solids fall into this category, including polymers, oxides, thiophosphates and composite materials, even though they all have different properties and are processed differently. Here, a uniform typology of different cell types is proposed, which is based around the ion-conduction mechanism of the electrolyte with the aim to increase clarity of the scientific debate and expedite the exchange of results across all cell types.

References:

[1] I. Hasa, S. Mariyappan, D. Saurel, P. Adelhelm, A. Y. Koposov, C. Masquelier, L. Croguennec, M. Casas-Cabanas, J. Power Sources 482 (2021), 228872.
[2] Y. Kim, M. Kuenzel, D. Steinle, X. Dong, G.-T. Kim, A. Varzi and Stefano Passerini, Energy Environ. Sci.15 (2022) 2610.
[3] D. Roscher, Y. Kim, D. Stepien, M. Zarrabeitia and Stefano Passerini, Batteries & Supercaps (2023)e202300092.

High-Voltage Lithium-Metal Batteries With Polymerized-Ionic-Liquid-Based Polymer Electrolyte

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Integrating a lithium-metal anode and a high-voltage cathode into a solid-state battery remains a formidable challenge, especially when the battery is charged beyond 4 V. Most electrolytes genuinely do not possess such a wide electrochemical stability window, but have to rely on the formation of a passivating solid electrolyte interphase, require protective electrode coatings, or have to be combined with a secondary electrolyte to achieve stable dis-/charge cycling, adding complexity.

We recently employed a polymer electrolyte based on a polymerized ionic liquid to demonstrate a 4 V class solid-state battery with a lithium metal anode and a $LiNi_{0.8}Mn_{0.1}Co_{0.1}$ cathode operating at room temperature and delivering an initial capacity of 162 mAh/g and a capacity retention of 72% after 600 cycles to 4.4 V [1]. The polymer matrix consists of poly(diallyldimethylammonium) bis(fluorosulfonyl)imide (PDADMAFSI) and N-butyl-N-methylpyrrolidinium bis(trifluoromethylsulfonyl) imide ($PYR_{13}FSI$) is employed as plasticizer in combination with lithium bis(fluorosulfonyl)imide (LiFSI) as lithium salt. PDADMAFSI and $PYR_{13}FSI$ were selected because of their outstanding chemical stability and wide electrochemical stability window. Comparing to typical lithium-ion-coordinating polymer matrices, the positively charged $PDADMA^+$ chains reduce lithium-ion coordination with the polymer promoting high lithium-ion mobility. LiFSI also exhibits low binding energy between Li^+ and FSI^- and the ability to form stable interphases in contact with lithium metal. To confirm the high oxidative stability of this electrolyte, we also assembled a solid-state lithium-metal cell with a high-voltage spinel $LiMn_{1.5}Ni_{0.5}O_4$ cathode reaching an initial capacity of 132 mAh/g and a capacity retention of 76% after 300 cycles to an upper cut-off voltage of 5 V at room

References:

[1] C. Fu, G. Homann, R. Grissa, D. Rentsch, W. Zhao, T. Gouveia, A. Falgayrat, R. Lin, S. Fantini, C. Battaglia, Adv. Energy Materials 2022412 (2022)
[2] G. Homann, Q. Wang, A. Devincenti, P. Karanth, M. Weijers, F. Mulders, M. Piesins, T. Gouveia, A. Ladam, S. Fantini, C. Battaglia, submitted

Evolution of the Ionic Conductivity of Solid Polymer Electrolytes upon Elongation

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Trang Phan[2], Renaud Bouchet[a], Didier Devaux[a]

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Existing Li-ion battery technologies are limited for large scale application because of the presence of flammable liquid electrolytes (lithium salt in alkyl carbonate solvents). [1]Solid polymer electrolytes (SPEs) based on polyethylene oxide (PEO) directly address this issue but present a relatively low ionic conductivity (σ) at temperatures below the melting point (T_m) of about 55 °C with value typically lower than 10^{-5} S.cm^{-1}.

Strategies to increase the ionic conductivity of SPEs are typically based on the development of new polymer architectures, lithium salt natures, plasticizers, or additives. In addition, applying an external field such as magnetic, electric, pressure, or a mechanical deformation onto the SPEs can alter the resulting ionic transport properties.[2] For the later one, the main difficulty lies in obtaining the instantaneous evolution of the ionic conductivity coupled with the mechanical deformation and its geometrical change, especially when a striction domain appears.

Inspired by the pioneered work of Golodnisky and Peled [3, 4] to study SPE elongation under uniaxial stress, a dedicated sample environment was designed to perform tensile tests in an inert atmosphere on SPE membranes at given temperatures, typically below and above the PEO melting temperature. Moreover, a methodology to calculate the instantaneous in-plane ionic conductivity is proposed based on COMSOL simulations to back out the sample geometrical changes during elongation. A strong impact on the inplane ionic conductivity is observed when comparing PEO electrolyte architectures; from homopolymers to single-ion conducting block copolymer via binary conducting block copolymer electrolytes. Below the PEO melting temperature, a striction domain appears upon elongation whose conductivity is higher than the one of the bulk by a factor that depends on the SPE architecture.

References:

[1] F. Gebert, M. Longhini, F. Conti, A. J. Naylor, J. Power Sources 556 (2023) 232412
[2] M. J. Park, N. P. Balsara, Macromolecules 43 (2010) 292–298
[3] D. Golodnitsky, E. Peled, Electrochim. Acta 45 (2000) 1431–1436
[4] S. H. Chung, Y. Wang, S. .G Greenbaum, D. Golodnitsky, E. Peled, Electrochem. Solid-State Lett. 2 (1999) 553–555

Polymer electrolytes beyond PEO, LiTFSI and LFP: A story of host materials, salts, additives and potentials

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The most archetypical polymer-based solid-state battery undoubtedly consists of a PEO:LiTFSI electrolyte in a Li || LFP cell configuration. Despite the implementation of more high-voltage cathode materials such as LCO and NMC for commercial liquid-electrolyte cells, this has not been mirrored for solid polymer electrolytes. Instead, a shared feature of polymer electrolytes seems to be a tendency to experience difficulties when cycling vs. anything with a higher redox potential than LFP. Recent research has identified Li dendrite formation connected to insufficient mechanical stability of the electrolyte as the main factor [1–3], but electrochemical stability insufficiencies have also been identified [4], pointing to a tangled web of interconnecting factors that limit the use of higher-voltage cathodes together with polymer electrolytes.

But what if we lift our gaze away from the standard PEO:LiTFSI system; can changing the polymer electrolytes composition provide the sought-after stability required for utilizing cathode materials that are otherwise well-established in liquid-electrolyte cells but remain challenging for polymer systems? With a diverse set of established as well as more exotic host materials, and a range of different available salts, it is certainly possible to engineer electrolyte systems that differ considerably from PEO:LiTFSI. Of particular interest are host materials based on carbonyl coordination have a number of advantages over PEO in terms of ion transport properties, but it remains to see whether these advantages extend also to cell performance.

Or perhaps the solution is even simpler than mere electrolyte engineering…?

References:

[1] G. Homann, L. Stolz, K. Neuhaus, M. Winter, J. Kasnatscheew, Adv. Funct. Mater. 30 (2020) 1–8
[2] G. Homann, L. Stolz, J. Nair, I. C. Laskovic, M. Winter, J. Kasnatscheew, Sci. Rep. 10 (2020) 2–10
[3] L. Stolz, G. Homann, M. Winter, J. Kasnatscheew, Mater. Adv. 2 (2021) 3251–3256
[4] L. Seidl, R. Grissa, L. Zhang, S. Trabesinger, C. Battaglia, Adv. Mater. Interfaces. 2100704 (2021) 1–10

NMR transport measurements: Tracking ion migration in battery electrolytes

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Concentrated electrolytes play a major role in batteries, however, being rather complex liquids, an understanding of ion transport processes requires dedicated methods. Pulsed-Field-Gradient (PFG)-NMR is well suited for this purpose, as a detailed characterization of all constituent species is feasible by multinuclear (e.g. ^{1}H, ^{7}Li, ^{19}F) PFG-NMR. While diffusion coefficients of all species are easily accessible, they are often not sufficient to identify the conductivity contributions of specific ion species, since ion correlations complicate the transport behaviour. Electrophoretic NMR (eNMR), however, yields a direct measurement of ion drift velocities and thus electrophoretic mobilities and allows conclusions on distinct ion correlations [1,2].

This lecture first presents recent progress on ionic mobility measurements in liquid electrolytes, identifying the mechanisms governing transport, such as vehicular motion [2,3] or the role of ion-ion correlations [4]. In exemplary systems, even a quantification of Onsager coefficients is achieved, for example pointing out the role of ion-ion anticorrelations in solvate ionic liquids [5], and demonstrating superionic behaviour in salt-in-ionic liquid electrolytes with a coordinating cation [6].

In polymer electrolytes, eNMR serves as a suitable method to determine transference numbers, shedding light on current discrepancies in literature [7]. While the classical salt-in poly(ethylene oxide) system suffers from strong Li-chain coordination [7], higher transference numbers can be obtained with less coordinating chains such as poly(ε-caprolactone) or poly-(trimethylene carbonate), however, at the cost of a lower total conductivity. Interestingly, the partial lithium conductivity remains in a similar magnitude [8].

In all types of concentrated electrolytes care has to be taken as to interprete data in a suitable frame of reference. In contrast to momentum conservation being a general assumption in theoretical work, electrolytes in closed cells obey to the constraint of volume conservation under violation of momentum conservation, which requires a transformation of the frame of reference [9].

References:

[1] Gouverneur, M.; Kopp, J.; van Wüllen, L.; Schönhoff, M. Phys. Chem. Chem. Phys. 2015, 17, 30680-30686.
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PEGMEM as Reactive Polymer Electrolyte System for All-Solid-State Lithium Ion Batteries

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Reactive polymer electrolytes are a special class of polymer electrolytes that utilizes *in situ* polymerization of monomers on electrode surfaces. Monomers have a low viscosity enabling fast and easy mixing with conductive salts and a fully automated application on electrode surfaces where a good wetting for maximum interfacial contact is achieved.

Using *poly*-PEGMEM (PEGMEM: Poly(ethylene glycol) methyl ether methacrylate) , the balance between mechanical properties and ionic conductivity can be adjusted by the addition of cross-linkers. Pure PEGMEM10LiTFSI is viscous, electrochemically stable up to 5.2 V vs. Li/Li^{+} and has a Li+-conductivity of $8.7 \cdot 10^{-4}$ Scm^{-1} at 80 °C (Figure 1a). With the addition of di-, tri- or tetrafunctional acrylate-based cross-linkers the Young´s modulus increases (Figure 1b). The resulting electrolyte films are dimensionally stable, which also allows processing on a larger scale. The electrochemical and mechanical properties can be tailored by the structural nature and the amount of cross-linker. Thus, *poly*-PEGMEM represents a polymer with a high potential to be used as a solid electrolyte due to its high ionic conductivity. Featuring high mechanical properties and electrochemical stability at the same time makes it especially attractive as a protective layer for lithium metal anodes.

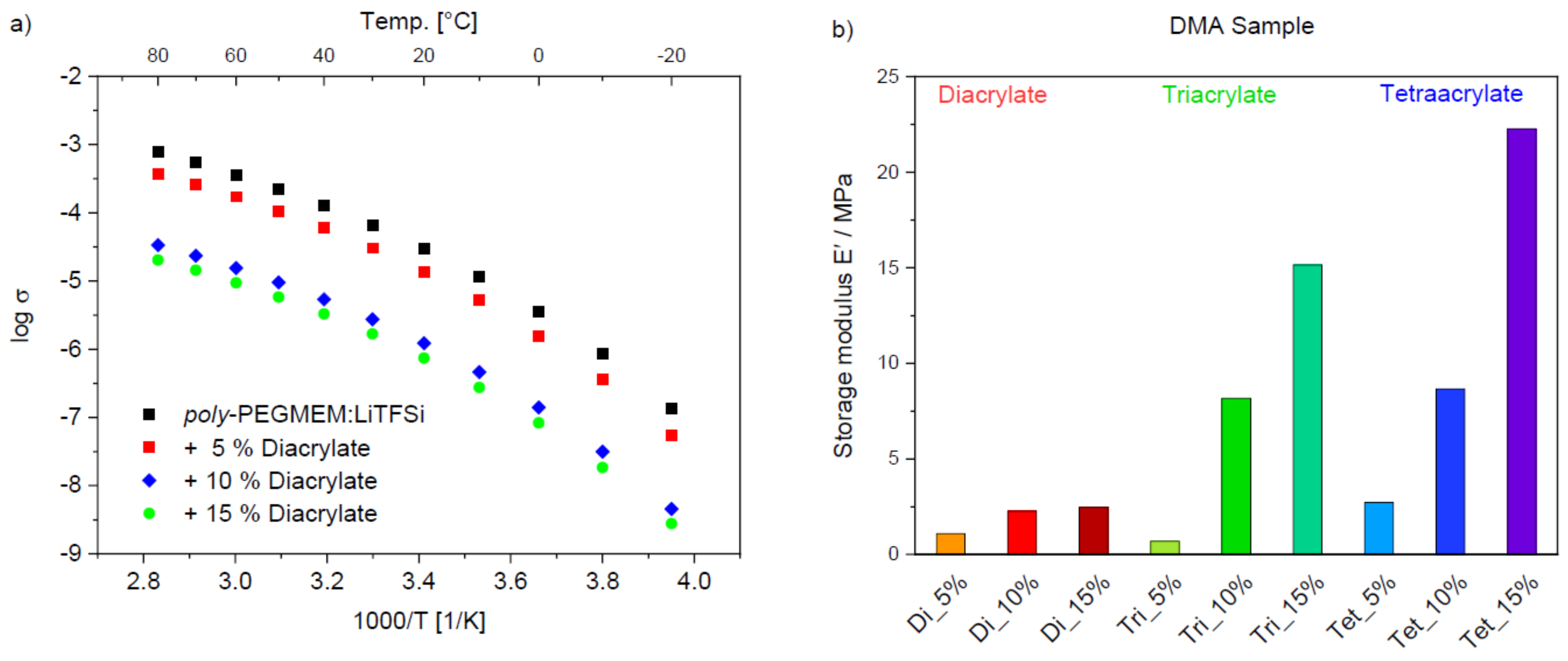

Figure 1. a) Ionic conductivities of *poly*-PEGMEM:LiTFSI with different percentages of diacrylatebased cross-linker and b) storage modulus E' in dependence of di, tri- und tetrafunctional acrylatebased cross-linkers and respective percentages by weight (5 %, 10 % and 15 %).

Towards a rational design of lithium salts and polymer matrices for lithium metal solid-state batteries

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The growing demand for finding new green energy sources to replace the excessively used fossil fuels has tipped the balance in favor of electrochemical energy storage. Among all the available electrochemical storage devices, lithium-ion batteries (LIBs) have been extensively investigated as the most suitable choice where a graphitized material as negative electrode, a lithium transition metal oxide as positive electrode, and a carbonate-based liquid solution as electrolyte are employed. However, the need of higher energy density batteries has attracted much interest in the use of materials with higher capacity [e.g., lithium metal, Li° (3860 mAh g^{-1}) vs. graphite (372 mAh g^{-1})]; and at the same time, avoid the use of flammable organic solvents due to their severe safety issues.[1]

In this regard, solid-state lithium metal polymer batteries (SSLMPBs) are believed to be the most promising technology to tackle all these concerns, being poly(ethylene oxide) (PEO) and $Li[(CF_3SO_2)2N]$ (LiTFSI), the preferred choice as polymer host and lithium salt, respectively. However, although LiTFSI/PEO is nowadays the most widely employed system, it still presents very low Li-ion conductivities (Li-ion transference number; T_{Li^+}, ca. 0.2), poor Li electrode compatibility and poor electrochemical stability against the Al current collector.[2]

Inspired by these challenges our work is devoted to the design and development of new polymer and lithium salt chemistries. Considering the lithium salt as a one of the key players on the overall electrolyte performance, several approaches have been undertaken to modify the anion chemistry towards the improvement of the Li-ion conductivity and overall cell performance: (1) additive-containing single Li-ion conductive (SLIC)-SPEs to balance T_{Li^+} while keeping an overall stable cycling performance, [3] and (2) novel Li-salt anions aiming to decrease the anion mobility and promote the Li-ion conductivity. [4] Additionally, the polymer matrix will dictate the battery operation temperature, for that reason deep research has been done towards the development of new matrices beyond PEO aiming to decrease the crystallinity and enhance the ionic conductivity at temperatures below 70 ºC. [5] In this presentation an extensive characterization is provided showing how a rational design of the lithium salts' anion structure or the polymer matrix, can substantially improve the SSLMPB performance.

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Enhancing the safety of lithium metal batteries through the use of composite ionogels

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Lithium-ion batteries (LIBs) represent the dominant technology in portable electronic devices, electric vehicles (EVs), and grid-scale energy storage systems due to their high energy density, long cycle life, and low self-discharge rate. However, LIBs are expected to reach their theoretical limits in the future in terms of gravimetric and volumetric energy density [1]. Lithium metal batteries (LMBs) are a promising candidate for battery next generation because of their high specific capacity (3860 mAh g^{-1}) and the lowest redox potential (-3.04 V *vs.* SHE) [2]. However, the practical application of LMBs has been hindered by the formation of lithium dendrites, which can cause short circuits, reduce battery lifespan, and create important safety concerns. Polymer electrolytes have attracted considerable attention as an alternative to liquid electrolytes in LMBs due to their ability to suppress dendrite growth and improve the stability against lithium metal anode. In this context, the combination of ionic liquids and polymer matrixes, creating ionogels (IGs), has shown increasing interest in the possibility to boost at the same time both the electrochemical performance and the safety of lithium metal batteries. Ionic liquids (ILs) have excellent thermal stability, low volatility and a wide electrochemical stability window compared to conventional organic electrolytes. At the same time, high Li^+ mobility and rate performance are still a challenge due to their high viscosities and transference number not comparable to conventional electrolytes [3].

In this framework, IGs are prepared via a one-pot preparation method mixing together butyl methacrylate (BMA) and poly(ethylene glycol) diacrylate (PEGDA) with PYR14TFSI. The polymer backbone is crosslinked through free-radical thermal polymerization with the incorporation of Al2O3 NPs as a passive filler. Even with the high content of IL in the formulation (80 wt.%), the produced IGs are self-standing with interesting ionic conductivity (10-4 - 10-3 S cm-1 at 20-60 °C). The addition of Al2O3 NPs increased the electrochemical stability window (5.1 V *vs.* Li^+/Li) and the lithium transference number (0.17). The improved Li+ transport kinetics in comparison with no filler electrolyte enhanced the performances in half-cell configuration with lithium metal anode and LFP cathode, reaching 125 mAh g^{-1} at room temperature with a good capacity retention after 500 cycles. The increased safety of the developed IGs was assessed through the flammability test showing better fire resistance behaviour compared to conventional carbonate electrolytes.

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Polymer electrolytes based on protic poly(ionic liquid)s for lithium batteries

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Ionic Liquid (ILs) are an interesting class of salt-like material having melting points lower than 100 °C, with major advantages over organic solvent electrolytes such as therma-stability or electrochemical stability window. [1] Nevertheless, a subset family of ILs, called protic ionic liquids (PILs), is receiving increasing attention in recent years because of the easily preparation by means of direct neutralization reactions of a Brønsted acid (proton donor) and a Brønsted base (proton acceptor), resulting in most cases in a nitrogen-containing organic cation singly or doubly protonated with corresponding counter anion. [2] The main advantage of PILs over Aprotic ones (AILs) comes from the presence of less shielded cations in the former ones, intrinsically responsible for the “cation competition effect”, which, in a mixture of PIL-Li salts, results in loosely coordinated Li^+ ions along with improved mobility. Furthermore, the elevate Li^+ ions mobility allows to achieve improved performance in term of specific capacity output especially at high C-rates (elevate current densities). [3]

Here we present the investigation on polymeric protic ionic liquids based on Diallylmethyl amine (DAMA). Specifically, through simple ion exchange procedure we obtained a new family of Protic Poly(Ionic Liquid)s with different counter anion ($PolyDAMAH^+$-X^-). [4] Then, polymer electrolytes were achieved by mixing the polymers with same counter anion salts in different molar ratios. Starting from the precursors, the different Protic Polymer electrolytes were fully characterized in terms of chemical-physical properties as well as electrochemical one. Finally, the most promising samples were selected for further analysis to evaluate the possible application as solid-state electrolytes in energy storage/conversion devices.

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An Overview on Crosslinked Polymer-based Electrolytes with High Ionic Mobility for Safe Operation of Solid-State Batteries

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Commercial secondary batteries use as ion transport media liquid electrolytes, which are based on toxic and volatile organic carbonate solvents, and their flammability raises safety concerns. The most striking solution at present is to switch on all solid-state designs exploiting polymer materials, films, ceramics, low-volatile, green additives, etc. The transformation from liquid-to solid-state architecture is expected to improve safety, fabrication, and temperature stability of energy storage devices, particularly if constraints of low ionic conductivity, low cation transport properties and stringent processing conditions are overcome [1]. Here, an overview is offered of the recent developments in our labs on innovative polymer-based electrolytes allowing high ionic mobility, particularly attractive for safe, high-performing, solid-state Li-metal batteries, and obtained by different techniques, including solvent-free UV-induced photopolymerization. Electrochemical performances in lab-scale devices can be readily improved using different kind of RTILs or other specific low-volatile additives. Cyclic voltammetry and galvanostatic charge/discharge cycling coupled with electrochemical impedance spectroscopy exploiting different electrode materials (e.g., LFP, Li-rich NMC, LNMO, Si/C) demonstrate specific capacities approaching theoretical values even at high C-rates and stable operation for hundreds of cycles at ambient temperature [2,3]. Direct polymerization procedures on top of the electrode films are also used to obtain an intimate electrode/electrolyte interface and full active material utilization in both half and full cell architectures. In addition, results of composite hybrid polymer electrolytes [4], as well as new single-ion conducting polymers [5] are shown, which are specifically developed to attain improved ion transport and high oxidation stability for safe operation with high voltage electrodes even at ambient conditions.

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Ion Transport in Soft Matter Battery Electrolytes and Related Interphases

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The development of next generation batteries depends heavily on the capability of electrolytes to quickly and selectively transport alkali and alkaline earth metal cations, and form stable electrochemical interfaces. In high energy density metal anode batteries, issues such as dendrite and continuous solid electrolyte interphase (SEI) growth can be addressed by suitable interfacial and electrolyte chemistry.[1]

In the first part of my talk, current understanding of ion transport mechanisms and related electrochemical measurement techniques (impedance spectroscopy, galvanostatic polarization) in soft matter battery electrolytes including liquids, polymers and hybrid (e.g. liquid/oxide and polymer/solid state electrolyte) materials will be discussed.[2-5] According to this discussion, I will give guidelines and examples of improvements of the relevant electrochemical properties including ionic conductivity and the cationic transference number.

In the second part of my talk, I will show recent findings related to the electrochemical and chemical growth and transport in SEIs on several alkali and alkaline earth metal anodes in contact with liquid and solid-state electrolytes.[6-13] The multitechnique approach involving the measurement of activation energy for ion transport showed that such SEIs are complex composite liquid/solid materials, with sometimes predominant ionic pathways in the liquid phase. The relevance of the native passive layer on alkali and alkaline earth metals, possibility of forming artificial SEIs (e.g. sulfides and Al_2O_3) and electrodeposition through porous SEI will be discussed. Finally, I will show a new modelling approach for treatment of impedance spectroscopy data of symmetric alkaline and alkaline earth metal cells.

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Polymer Hybrid Concepts: Towards Higher Energy Densities with Oligomers and Grafted Ceramics

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Current market demands for larger energy densities in battery applications necessitate polymer (hybrid) electrolytes that are compatible with Li metal anodes, mechanically robust and able to operate at lower temperatures.[1] Polymers are often 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-type electrolytes (Bolloré) require temperatures above 60°C, tailor-made polycaprolactones provide reasonable electrochemical performance already at 40°C. Also, PCL-based electrolytes are considered as biodegradable, affordable and are straightforward to produce.[2]

The importance of realistic benchmarks in energy density of polymer-based cells as well as key characteristics governing the cycling reversibility of cells are thoroughly discussed, evaluating projected energy densities of lab-scale and multi-layered pouch cells. Increased discharge capacities were realized with suitable hybrid materials and 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 11 mg/cm² and discharge capacities of >170 mAh/g at 0.1 C. Multi-layer pouch cells are projected to enable energy densities of up to 356 Wh L^{-1}, clearly superior to other reported polymer-based cell designs. In addition, grafted LATP particles enable superior miscibility of ceramics inside the polymer membrane, potentially stabilizing lithium metal anodes according to the Chazalviel model. A proof of concept was demonstrated in single-ion conducting polymer/oxide hybrid electrolytes utilizing a non-symmetrical membrane at 0.5 C.[3] Processing challenges of grafted LATP particles will be addressed and mitigation strategies for membrane mechanical stability presented.

The introduced hybrid cell concept based on oligomer infiltrated composite cathodes and grafted LATP particles is the key strategy to facilitate benefits of polymer-based solid-state batteries that can be achieved for a variety of polymer chemistries. Appropriate processing methods are essential for a timely transfer of solid-state electrolyte technology to industrial applications.

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Improving the Ion Transport in Polymer Electrolytes by Modeling Insights

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To overcome the current limitations of polymer electrolytes, the knowledge of the underlying ion transport mechanisms is vitally important. Complementary to experimental techniques, Molecular Dynamics (MD) simulations are a powerful tool to gain additional insights with atomic resolution. This presentation will give an overview how results from MD simulations can be harnessed to deliberately tune and enhance the lithium ion transport in polymer electrolytes experimentally. In particular, different strategies will be discussed:

The first part will demonstrate how archetypal polymer electrolytes based on poly(ethylene oxide) (PEO) can be improved by the addition of ionic liquids, which may either act as low-molecular weight plasticizers [1] or entirely liberate the lithium ions from the slow PEO chains, thereby acting as *ion shuttles* [2]. The findings from the MD simulations will be rationalized by an analytical ion transport model, by which the impact of different molecular processes on the lithium ion diffusion constant can be assessed quantitatively.

The second part of the talk will focus on the question how the lithium ion transport can be enhanced by modifying the polymer architecture, such as densely cross-linked polymer networks [3], salt-rich lamellar block-copolymer structures [4] or novel non-PEO polymer candidates [5]. In the context of the latter, an MD-based in silico screening approach, relying on a simple estimation of parameters relevant for ion transport, will additionally be illustrated.

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Solvent Free and Catalyst Free Solid Polymer Electrolytes for Lithium-ion Batteries

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In this work, we present the synthesis of poly(β-amino ester) based crosslinked Solid Polymer Electrolytes (SPEs) from off-stoichiometric acrylate-amine (1.3:1) formulations using one-step, catalyst and solvent free aza-Michael addition. This method is modular, generates zero side products and is environmentally friendly. The amines used in this study are ethanolamine (EA), propylamine (PA) and their mixtures along with 10 wt% of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) as the salt. The synthesized polymers yield free-standing and easy to handle electrolyte films. The resultant polymer chain can aid in the mobility of both the anion and the cation due to the presence of various functional groups in the structure (Figure 1). Films with and without LiTFSI were analysed using DSC, IR and impedance spectroscopy. The SPE employing just PA showed better ionic conductivity than the SPE using just EA. Surprisingly, the SPE with 90% PA and 10% EA displayed further enhancement in conductivity and was the best amongst all the analysed SPEs (Figure 2). The potential of materials that combine different functionalities is demonstrated by this deviation. We believe that the fine-tuning of the coordinating groups leads to improved ionic mobility and consequently improved ionic conductivity.

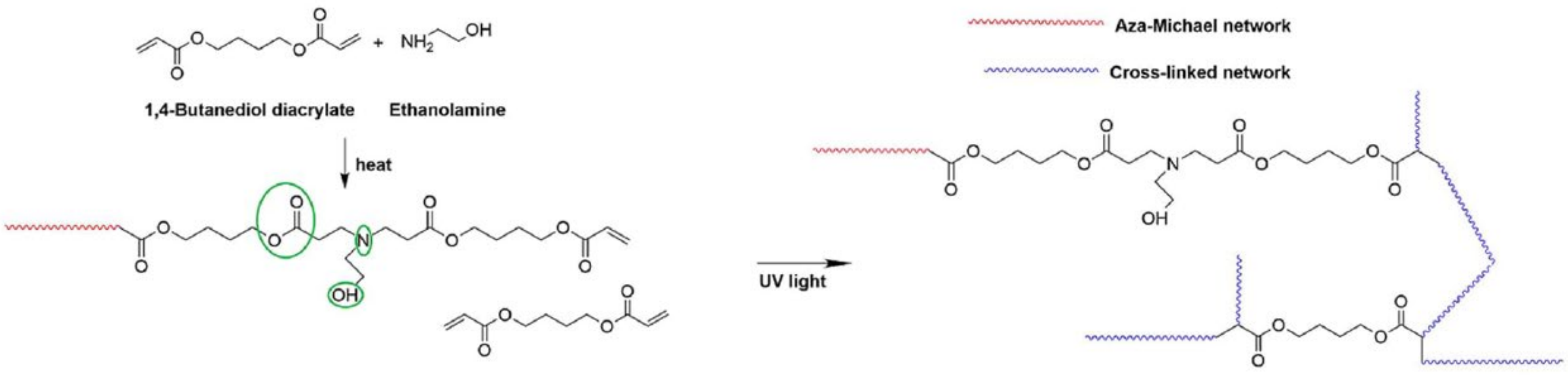

Figure 1: Example reaction scheme

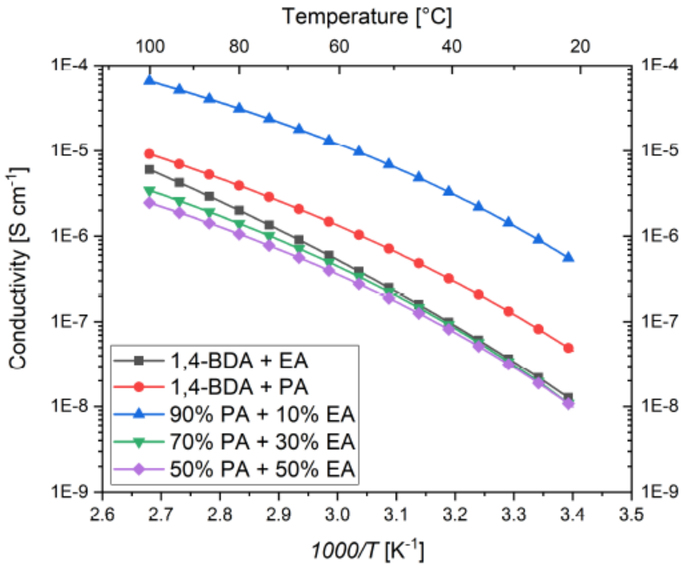

Figure 2: Impedance Spectroscopy Data

Exploring polymer electrolyte families for potassium batteries

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Rechargeable batteries are a key technology in the world rush toward the energy transition. Li-ion batteries (LIBs) have reached unprecedent targets of performance and safety, nevertheless it is not logical thinking that the LIB technology alone is able to provide for the whole world electrification, given lithium scarcity (0.0017 wt% in the Earth crust) and its uneven distribution.

In this scenario, it is not surprising the increasing attention coming from the research community on potassium-based batteries. Potassium is abundant on Earth (2.09 wt%), evenly distributed and characterized by a very low standard equilibrium potential (-2.93 V vs. SHE with respect to -3.09 V vs. SHE of Li^+/Li) and Lewis acidity (smaller solvated ions and thus faster conduction). Nonetheless, K-ion batteries have lower volumetric and gravimetric energy density with respect to LIBs, but this makes them perfectly suitable for stationary application. In light of this consideration, it is logical to already design potassium-batteries for large scale commercialization to be sustainable and low cost.

Herein, we present two polymer electrolyte systems for potassium batteries. The first is photocured gel polymer electrolyte obtained by the radical polymerization of acrylate and methacrylate monomers, which displayed a high ionic conductivity (17 mS cm^{-1}) and wide electrochemical stability window (up to 3.7 V *vs.* K^+/K) [1]. The thermal stability was suitable for potassium batteries and the glass transition temperature was low enough to ensure a good macromolecular mobility of the polymer chains. The electrolyte provided mechanical stability and was able to hinder the formation of potassium dendrites. All these features allowed the unprecedent achievement of 600 cycles with a capacity retention of 58%.

As a second case study, lignin-based gel polymer electrolytes are proposed [2]. Once these membranes were activated by soaking liquid electrolyte, the as obtained gel polymer electrolyte was fully characterized, showing suitable ionic conductivity exceeding 10^{-3} S cm^{-1}, excellent chemical compatibility and tremendous ability at suppressing the growth of metal dendrites. Its further implementation with molecular functionalities aiming at guaranteeing self-healing capacity is investigated and lab-scale cells cycling for more that 1000 cycles are demonstrated.

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The influence of ester versus ether crosslinkers on the physicochemical properties of electrolytes based on poly-2-oxazolines

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Current lithium-ion batteries (LIBs), commonly used in a wide range of electronic devices and electric vehicles, still face challenges related to safety and insufficient durability. Improving the electrolyte component of batteries is essential for the development of new LIBs that are durable, high-energy, and safe. The utilization of polymeric electrolytes, which also serve as separators, has emerged as a potential solution to the aforementioned issues in conventional LIBs. Gel polymer electrolytes (GPEs), composed of a polymer matrix plasticized with a solution containing lithium salt and/or additional low-molecular-weight compounds, are considered promising candidates for practical implementation in LIBs. They exhibit relatively high ionic conductivity, flexibility, and sufficient mechanical stability.

The present study focuses on the synthesis and characterization of novel GPEs based on copolymers of poly(2-Nonyl-2-Oxazoline-co-2-Dec-9'-enyl-2-Oxazoline). Cationic ring-opening polymerization (CROP) of the 2-Oxazolines with varying ratios of the comonomers was conducted, where the presence of double bonds in the dec-9'-enyl sidechains enables chemical cross-linking. Two different thiol-based crosslinkers containing ether and ester bonds respectively were used for the formation of crosslinked polymer networks that were swollen with 1M LiBOB solution of propylene carbonate. The samples were extensively studied in terms of ionic conductivity across a wide temperature range, as well as their thermal and mechanical stability. Ionic diffusion at different temperatures, Li-ion transference number, theoretical conductivity, and degree of salt dissociation for the different compositions were evaluated.

Anion π−π Stacking for Improved Lithium Transport in Polymer Electrolytes

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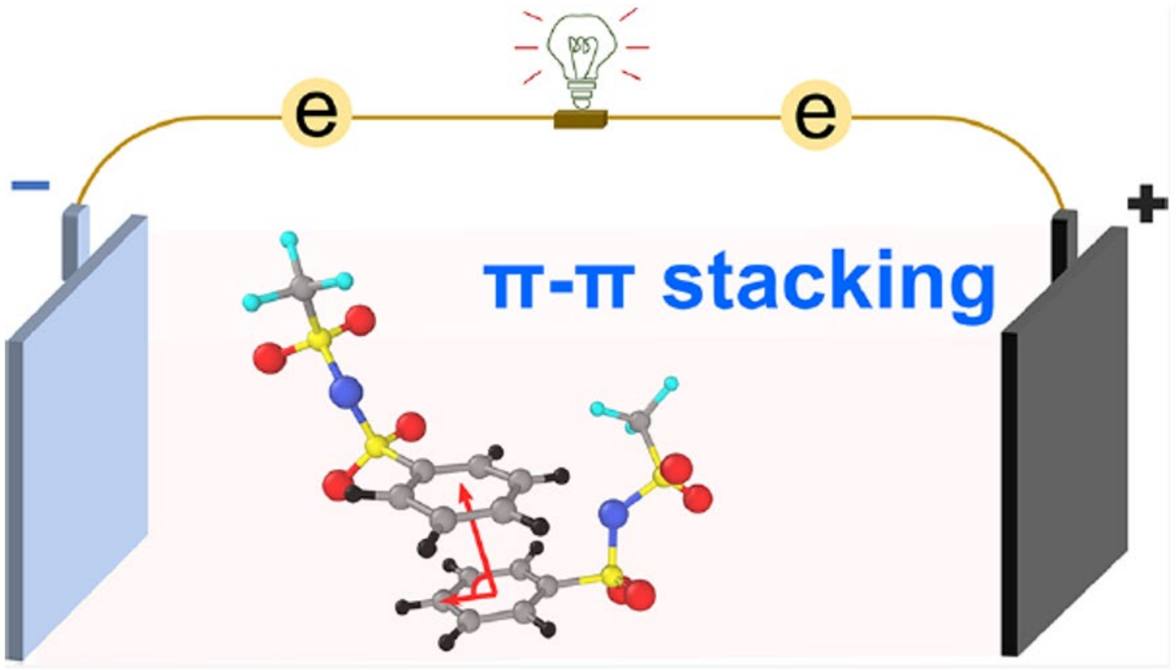
The increment demand for energy storage coming from the necessary development of the electric vehicles and the continuously growing market of portable devices have overcome the actual technology of lithium-ion batteries (LIBs)[1]. The substitution of the common graphite anode used in most LIBs for lithium metal (Li^0) can multiply by ten the theoretical capacity (3860 mAh g^{-1} of Li° vs 372 mAh g^{-1} of graphite)[2]. But these lithium metal batteries (LMBs) suffer from many problems when used with liquid electrolytes (LEs)[3].

Polymer electrolytes (PEs) with excellent flexibility, processability, and good contact with Li° anodes have attracted substantial attention in both academic and industrial settings. However, conventional poly(ethylene oxide) (PEO)-based PEs suffer from a low lithium-ion transference number (T_{Li^+}), leading to a notorious concentration gradient and internal cell polarization[4].

Here, we report two kinds of highly lithium-ion conductive and solvent-free PEs using the benzene-based lithium salts, lithium (benzenesulfonyl)-(trifluoromethanesulfonyl)imide (LiBTFSI) and lithium (2,4,6-triisopropylbenzenesulfonyl)(trifluoromethanesulfonyl)imide (LiTPBTFSI), which show significantly improved TLi+ and selective lithium-ion conductivity. Using molecular dynamics simulations, we pinpoint the strong π−π stacking interaction between pairs of benzene-based anions as the cause of this improvement. In addition, we show that Li°‖Li° and Li°‖LiFePO4 cells with the LiBTFSI/PEO electrolytes present enhanced cycling performance[5]. By considering π−π stacking interactions as a new molecular-level design route of salts for electrolyte, this work provides an efficient and facile novel strategy for attaining highly selective lithium-ion conductive PEs.



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Polymer-based Electrolytes for Lithium Batteries and Beyond: New Materials and Conductivity Mechanisms

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Electrochemical energy storage systems have attracted significant attention due to their potential to play a crucial role in global efforts to decarbonize the mobility and energy sectors. Of particular interest are secondary batteries utilizing alkaline and alkaline-earth anodes, known for their high specific energy and power, as well as extensive cyclability [1]. However, the widespread adoption of this technology is hindered by the need for suitable ion-conducting materials (ICMs) that can offer sufficient ion conductivity, appropriate chemical and electrochemical stability, and excellent compatibility with other functional materials used in the device assembly [1].

The ion conductivity mechanism in ICMs takes place through a series of different possible processes, with the most dominant ones being: i) the migration of ions between coordination sites in the host materials, and ii) the increase in conductivity due to relaxation phenomena involving the dynamics of the host materials [2-4]. The efficient motion of ions to new coordination sites relies on the concurrent relaxation of their occupying domains through reorganizational processes, which are generally coupled with relaxation events related to the host matrix dynamics. These phenomena are effectively and accurately identified and described using the broadband electrical spectroscopy (BES) technique [5].

This lecture presents an overview of the outcomes obtained from applying BES to investigate the charge transfer mechanisms in different types of ICMs. These include: (i) classical polymer electrolytes based on alkaline and alkaline-earth ions [2,6]; (ii) highly structured 3D Hybrid Inorganic-Organic Networks as Polymer Electrolytes [7]; (iii) Single-Ion Nano-Composite Polymer Electrolytes [8]; and (iv) “hybrid gel” polymer electrolytes for Li^+ ion conduction [4].

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Probing interfaces in anode-free Li-ion batteries with polymer electrolyte by operando hard X-ray photoelectron spectroscopy

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Anode-free solid-state lithium metal batteries with composite polymer electrolyte (CPE) are promising replacements for current lithium Li-ion batteries due to higher energy densities and mitigation of safety issues. In the anode-free design Li metal (Li^0) is deposited (plated) from the cathode on the anode current collector (CC). Plating of Li results in degradation of the CPE and formation of a solid electrolyte interphase (SEI). A common CPE is lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in a polyethylene oxide (PEO) matrix that has limited electrochemical stability and ionic conductivity. Developing a new sample environment for the HIKE endstation located at the KMC-1 beamline of BESSY II, enabled us to directly probe the Li/CPE interface and monitor the SEI formation by synchtron-based hard X-ray photoelectron spectroscopy (HAXPES, Figure 1a) under operating conditions. In our study we particularly focussed on the impact of the addition of lithium bisterephthalate (LiDTP), acting as an anion immobilizer improving ionic conductivity of the CPE, on the chemical structure of the Li/CPE interface and the formed SEI. For the operando HAXPES study, a 5 nm Cu CC was deposited by electron beam on the CPE surface (Figures 1 b,c). Cycles of Li plating/stripping were performed in a stepwise “titration” procedure at potentials of -0.1 V and 0.1 V vs Li/Li^+, respectively. HAXPES spectra were recorded while the cell was set to open circuit voltage (OCV); selected Li 1s spectra confirming successful cell cycling are shown on Figure 1 d. In this presentation, it will be discussed what information about SEI composition and thickness can be extracted by *operando* HAXPES, revealing insights into the underlying mechanism of LiDTP addition induced SEI stabilization.

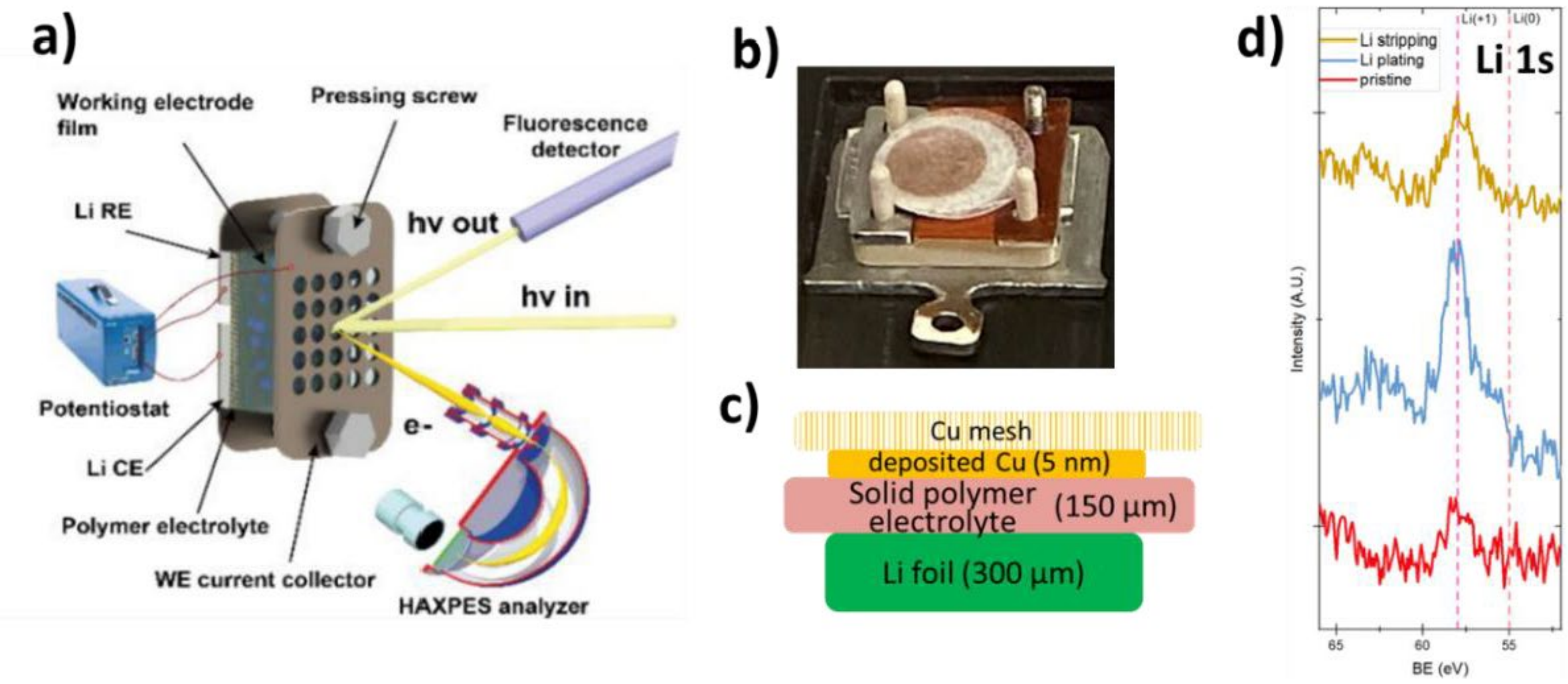

Figure 1 a) *Operando* sample environment developed for HIKE. b) Photograph of the cell with 5 nm of Cu deposited as current collector. c) Schematics of the cell for the proof-of-concept experiment. d) Li 1s spectra acquired at hv=2100 keV of a pristine sample and after Li plating followed by stripping.

Influence of Different Co-Solvents on Ion Transport in PEO and PCL polymer electrolytes

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The widespread commercial application of solid polymer electrolytes is currently largely impeded by their low conductivities and lithium ion transference as well as contact losses to the electrodes. For that reason, low molecular weight co-solvents are researched to be incorporated, forming gel polymer electrolytes. But facing the vast range of different polymers and polymer architectures studied, much less attention is drawn to the co-solvents itself.

Herein, we compare multiple diverse co-solvents, ranging from carbonates, sulfoxides and ethers to protic co-solvents, regarding their effects on ion transport in concentrated polymer electrolytes. To shine a light on the influence of the polymer's coordination strength, a comparison of electrolytes comprised of poly(ethylene glycol) (PEG) and poly(ε-caprolactone) (PCL) with incorporated lithium bis(trifluoromethane-sulfonylimide) (LiTFSI) is drawn. Results gained by nuclear magnetic resonance (NMR) diffusion measurements as well as Raman spectroscopy reveal a beneficial behavior of the co-solvents 15-crown-5 (15C5), tetraethylene glycol dimethyl ether (G4), N,N-dimethyl formamide (DMF), dimethyl sulfoxide (DMSO) and sulfolane. The results are supplemented by the co-solvents' binding constants determined by NMR titration.

An even deeper understanding of the ongoing transport processes in the polymer electrolytes is gained by application of electrophoretic NMR, yielding distinct electrophoretic mobilities of each molecular species. For the co-solvents in PEG, high lithium ion transference numbers and effective charges are obtained for some co-solvents and indicate advantages of smaller, less coordinating co-solvents. This observation holds true for PCL as well and especially sulfolane turns out to be extraordinarily well performing.

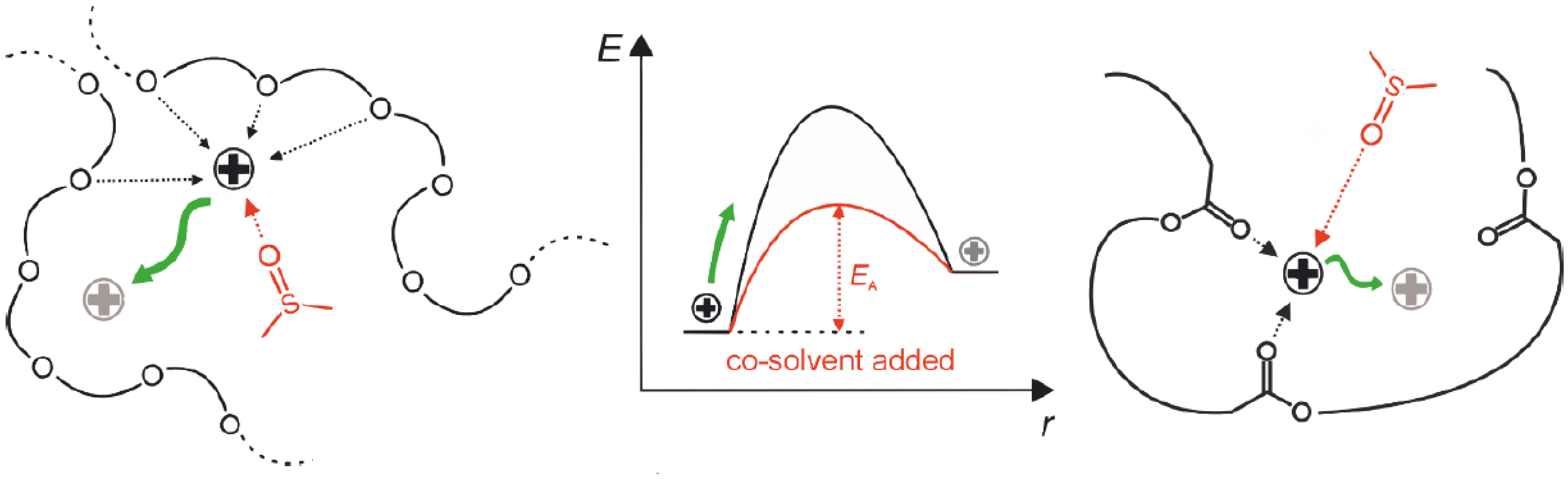

Figure: Mechanism of facilitation of Li+ ion hopping with the aid of a weakly coordinating co-solvent.

Block Copolymer Nanostructured Solid Polyelectrolytes From Equilibrium to Out of Equilibrium Strategies

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In the context of a significant growth of the battery market, solid polyelectrolytes (SPE) are foreseen to replace the flammable liquid electrolytes. There are two main advantages for all solid-state batteries: bring a higher safety level (no solvent, prevent dentrites growth, etc.) and increase energy density (lithium metal battery). That will ultimately bring improved security and autonomy to battery for end-users. The challenge is then to associate SPE mechanical strength with sufficient ionic conductivity to maintain the performances. Unfortunately, in most cases improving one leads to the degradation of the other. Among polymers, block copolymers (BCP) can be an alternative to decouple those antagonist properties.[1] Indeed, in BCP, functional blocks are associated along the polymer chains that self-assembled into nano-domains exhibiting each of them specific properties. Most often BCPs are considered at thermodynamical equilibrium since it gives stable and well-defined morphologies. More recently, out of equilibrium strategies were reported, such as Polymerization Induced Microphase Separation (PIMS).[2,3] This solvent free process based on liquid formulations (macro-initiator or pre-synthesized block copolymers and lithium salt solubilized in monomer), leads after polymerization to kinetically arrested morphologies. In the presentation we will go through examples of equilibrium and out of equilibrium SPEs based on star-like polymer architectures compared with linear analogues.[4] Additionally, the advantages and limitations of the PIMS strategy will be discussed.

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Confinement of Ionic Liquids into Copolymers for Flexible Solid-State Electrolytes for Li-metal Batteries

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Crude oil and petroleum products have the highest share of energy consumption in the EU. The transport sector accounts for about three-quarters of the EU's final consumption of petroleum products. Increased electrification in the transport sector will thus play a massive role in reducing the imports of energy from foreign sources, while simultaneously decreasing greenhouse gas emissions and improving local air quality. The need for safer, lower cost, higher energy density batteries to power such electrified vehicles is widely recognized. Lithium-ion batteries (LIBs) have been used in an increasingly diverse array of products, including automotive applications and represents the current state of the art. However, this architecture is reaching its limit, and a new cell architecture that replaces conventional intercalation negative electrodes in lithium-ion batteries with lithium metal is one of the most promising strategies to achieve specific energies above 300 Wh/kg.

Organic liquid electrolytes used in current LIBs have been extensively studied for the past four decades. However, they are not stable versus lithium metal electrode and generally, the lithium growth is heterogeneous that results in catastrophic battery failure. The solid-state electrolytes based on polymers with ionic liquids has emerged as a promising alternative to the current liquid electrolytes for lithium-metal batteries.[1] Intense efforts have been made to combine the ionic liquids and polymers in order to achieve both high mechanical properties and high electrochemical performance for practical applications. The combination of phosphonium-based ionic liquids with poly(ionic liquid)s exhibits very interesting properties due to their electrochemical stability with lithium-metal anodes.[2] However, the phosphonium-based ionic liquids present low compatibility with uncharged (non-ionic) polymers (such as PEO, etc). The ionic liquid easily exudes from the PEO polymer network, and it cannot maintain the properties of the material for long, which is quite unfavorable from the viewpoint of application. In this study, we propose a flexible solid-state electrolyte composed by a copolymer of isobutylene and maleic anhydride (ISOBAM) and trimethyl(isobutyl)phosphonium bis(fluorosulfonyl)imide (P_{111i4} FSI) as ionic liquid with LIFSI as salt. Solid-state electrolytes with different amounts of ionic liquid were prepared. The mechanical properties and transport properties of the optimal composition (20wt% of ISOBAM and 80wt% of (P111i4 FSI)/LiFSI) were studied. Finally, the optimized solid-state electrolyte was tested in lithium symmetric cells and a full cell based on lithium iron phosphate (LFP) and lithium-metal.

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PEO based block copolymers as solid polymer electrolytes

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Poly(ethylene oxide) PEO is a readily investigated polymer in numerous applications. One of them being its utilization as an electrolyte for solid-state batteries. However, not much is known on structural variants of PEO in regard to the utilization as polymer electrolytes. Herein, we present the synthesis of some novel PEO-based polymer architectures and their utilization as polymer electrolytes.

Single-ion conducting Nanoparticles Electrolytes for Solid-State Lithium Batteries

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Achieving solid-state lithium batteries with higher energy density and improved safety compared to conventional liquid lithium ion batteries is one of the primary research and development targets set for next-generation batteries in this decade. In this sense, polymeric electrolytes have been extensively investigated as solid electrolytes due to their excellent processability, flexibility and low weight. With high cation transfer numbers, single-ion conductive polymer electrolytes (SICPE) have enormous advantages compared to polymer electrolyte systems due to its potential to reduce the buildup of ion concentration gradients and suppress growth lithium dendrites.

Sulfonylimide based monomers, over carbonates or sulfonates mainly, dominate the recently developed field because their expanded conjugated structure can delocalize the negative charge in a relatively efficient manner and hence decrease the binding energy with Li-ions. In this work we present the synthesis of polymeric nanoparticles (NPs) of very small size functionalized in different quatities with lithium sulfonamide groups in order to prepare two systems that may compete nowadays with the state of the art of single-ion systems: we synthesized nanocompositės with the NPs and PEO and also printable single-ion conducting gel polymer electrolyte employing NPs and different organic solvents.

First, polymer nanocomposites based on the mixture of NPs and PEO were investigated as polymer electrolytes without the addition of extra salt to the system. The distribution of the NPs within the PEO matrix was first investigated. Then, a deep understanding on how the NPs affected the crystallization of PEO was carry out. The ionic conductivity of the nanocomposite polymer electrolyte was evaluated as a function of its composition, as well as the lithium-ion transference number for the electrolyte evaluated in a lithium battery. The nanocomposite all-polymer electrolyte with the best ratio between ionic conductivity and mechanical properties was finally evaluated in a lithium-metal battery as a salt-free solid electrolyte using a LFP as cathode material.

Later, single-ion conducting gel polymer electrolytes were evaluated by mixing lithium sulfonamide nanoparticles with carbonates and sulfolane. All the systems were studied regarding their mechanical, thermal stability and conductivity properties, among others. A special attention was paid under the successful development of printable systems on top of cathode materials like LFP and NMC, and their evaluation on lithium methal batteries.

Development of Huckel type salts as components for polymeric electrolytes

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Lithium salts are essential components of all electrolytes used in lithium-ion batteries. In our group in co-operation with CIC (Michel Armand) and Chalmers University (Patrik Johansson) various salts based on heterocyclic compounds with five-membered rings, such as 4, 5-dicyanoimidazole or 4, 5-dicyanotriazoles derivatives were obtained and investigated. The novel, promising concept of the application of new anions is based on the application of so called "Hückel anions" [1].

Our idea was to design structure that would not have disadvantages of big bulky anions causing high viscosity when dissolved in organic solvents, therefore a decrease in conductivity. Also, ions of new salts should not form agglomerates after dissolution, due to ion pairs' and triplet's which negatively affect ionic conductivity of an electrolyte, and high transference number of a lithium cation.

Electrochemical properties of the systems doped with 4, 5-dicyano-2-trifluoromethyl imidazole lithium salt (LITDI) were most intensively studied both in liquid and polymeric electrolytes. Crystallographic studies allowed for a better understanding of electrochemical properties of TDI salts. Despite of these studies more detailed examination of the interactions between [Li(glyme)]+ complex cations and weakly Lewis basic anions are still necessary to gain further insight into the ion coordination structure and transport mechanism in liquid and polymeric electrolytes containing LITDI as a dopant.

As a further extension of the previously mentioned studies we have introduced a new family of fluorine-free solid polymer electrolytes for use in sodium battery application 2. Systems are based on three novel sodium salts: sodium pentacyanopropenide (NaPCPI), sodium 2,3,4,5-tetracyanopirolate (NaTCP) and sodium 2,4,5-tricyano-1,3-imidazolate (NaTIM) which were dissolved in poly (ethylene oxide) to simulate viable solid-polymer electrolytes for sodium-ion batteries. Salts were selected with respect to their fluorine-free composition and diffuse negative charges and in consequence offered special „tailored" structure leading to better performance in electrolyte sytems. Due to this "liquid-like" high conductivities (> 1 mS cm-1) were obtained above 70 ˚C for solid-polymer electrolytes.

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Solubility and Stability Requirements for Solid Polymer Electrolytes

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A solid polymer electrolyte (SPE) consists of a salt dissolved in a polymer matrix and its purpose is to transport ions between the two electrodes during battery operation. For this to happen, the salt should be soluble in the polymer, that is, the polymer should have functional groups able to coordinate to the cation and break the ion–ion interaction. The most typical example where this occurs is polyethylene oxide (PEO). But with the aim to find alternative hosts with improved properties, new materials have been proposed although they lack the coordinating ability to lithium ions. This presentation will cover the case of poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP) to answer the question if non-coordinating polymers function as host materials for SPEs [1].

In addition, the SPE should be electrochemically stable under the battery operating conditions. The most common technique to investigate this is linear sweep voltammetry. However, in this technique the potential is ramped linearly versus time – not representing the real operating voltage profile of the battery and without the active material as working electrode – not representing the real environment. To circumvent these limitations, this presentation will focus on alternative more realistic methods that were used to investigate the electrochemical stability of LiTFSI-based PEO and poly(trimethylene carbonate) (PTMC) [2].

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Fluorine-Free K-Ion Polymer Electrolytes

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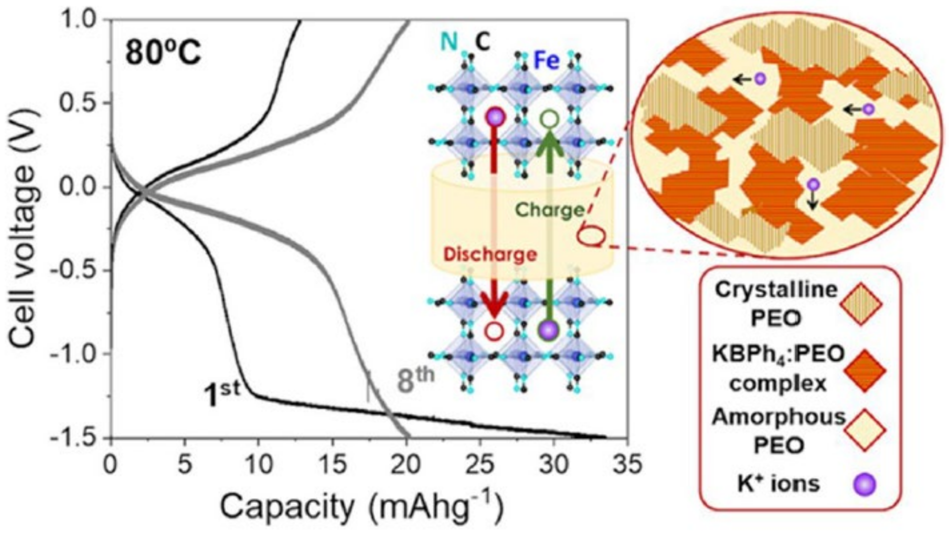
Solid polymer electrolytes (SPEs) could play a major role in the transition to safer and highenergy-density potassium-based batteries [1]. However, most polymeric K-ion electrolytes are based on fluorine-containing anions and flammable organic solvents, whose safety is nowadays in question. In this talk, we report a facile solvent-free synthesis of a series of several poly(ethylene oxide) (PEO)-based SPE solid solutions with KBPh4 salt as potassiumion source, including the formation of two crystalline (PEO)n/KBPh4 complexes [2]. The ionic conductivity of these novel K-ion SPEs above and below the melting point of PEO is rationalized in light of their glass-transition temperature and chemical composition. We highlight that below the melting point of PEO, the crystalline complexes may not be intrinsically ionically conducting, but they act as ion sinks preventing the polymer crosslinking and the formation of contact ion pairs and lower the glass-transition temperature leading to a conductivity of 1.1×10^{-4} S cm^{-1} at 55 °C. A high ionic conductivity of 1.8×10^{-3} S cm^{-1} is achieved at 80 °C for the optimum (PEO)30/KBPh$_4$ composition (3.2 mol % KBPh$_4$). Besides, the SPE compositions were found to be stable up to 4 V vs K0 metal electrode at 60 °C. The (PEO)30/KBPh4 composite electrolyte employed in an all-solid-state symmetric cell with Prussian Blue electrodes showed reversible K$^+$-ion (de)intercalation, where a reversible capacity of 20 mAh g^{-1} and low voltage hysteresis were achieved for 20 cycles. Considering the material availability, ease of synthesis, and promising electrochemical properties, this work may encourage future research on fluorine-free polymer electrolytes for K-ion batteries.



Charge-discharge curves of a symmetric cell where the composition (PEO)30/KBPh$_4$
is used as electrolyte and the electrode is Prussian Blue.

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Electrochemical performance of dry- and wet- manufactured solid polymer electrolytes

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Solid-state batteries (SSBs) are expected to be the next-generation systems in the fast-growing battery market.[1] To reach these expectations, solid polymer electrolytes (SPEs) which combine high ionic conductivity, good mechanical properties, and good interfacial behavior with lithium metal electrodes must be developed by the scientific community.[2] Traditionally, high molecular weight polyethylene oxide (PEO) is employed for the preparation of SPEs by solution casting. This procedure requires the use of solvents that should be evaporated and recycled. Therefore, greener methods such as extrusion are desired to scale-up the fabrication of the SPE without using volatile solvents obtained from fossil sources. Extrusion occurs with the reagents in the melt state, resulting in large differences in temperature, residence times and applied shear rates compared with the ones applied by solvent casting. As a result, despite employing the same reagents, the properties of the obtained SPEs are different and strongly dependent on the way in which the SPEs are prepared.

We will report the preparation and characterization of PEO-LiTFSI-based SPE by extrusion, and the comparison of their properties with the ones obtained by solvent casting (Figure 1). The morphology, crystallization behavior, rheological and thermal properties of the extruded and cast SPEs will be evaluated for SPEs consisting of a mixture of two different Mw (4,000 kg mol^{-1} and 300 kg mol^{-1}), with and without ceramic fillers. Finally, several SPE formulations will be assembled in pouch cell, proving how the manufacturing method affects the degradation mechanism and the essential role of the SPE mechanical properties to extend the cell cyclability.

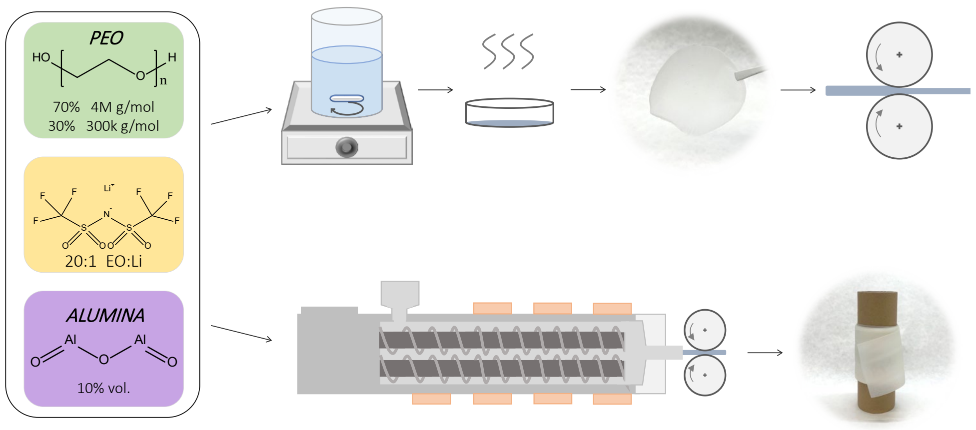

Figure 1. Processing methods employed for the manufacturing of the SPEs: solvent casting (up) and extrusion (down).

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Single-ion conducting polymer electrolytes – From an enhanced understanding towards their potential use in practical devices

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Single-ion conducting polymer electrolytes (SIPEs) are among the most promising candidates for high-energy lithium-metal batteries. Nevertheless, their commonly limited ionic conductivity and electrochemical stability hamper their practical application [1,2]. Recently, we have reported a nanostructured block copolymer electrolyte that shows an ionic conductivity of about 10^{-3} S cm^{-1} at 30 °C when introducing highly mobile small molecules with a high dielectric constant such as ethylene carbonate or propylene carbonate, excellent electrochemical stability towards Ni-rich high-energy cathodes like $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ (NMC811), and self-extinguishing properties, thus, enabling the realization of Li|SIPE|NMC_{811} cells that provide stable performance for hundreds of cycles even at 0 °C or when elevating the anodic cut-off to 4.5 V [3,4]. Herein, the step-by-step investigation of the impact of the different functional groups and the chemical nature of the block copolymer as such is presented, including inter alia the chemical nature of the ionic block, the number of ionic side chains attached to this block, and the fluorination of the polymer backbone. Eventually, the first results towards practically meaningful Li|SIPE|NMC_{811} cells with reasonable cathode active material mass loadings of >10 mg cm^{-2} will be presented, underlining the great promise of such electrolyte systems for next-generation lithium batteries.

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Abstracts Poster

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ESPE#P01	**Liping Wang | Zhirong Zhao-Karger**	Designing Gel Polymer Electrolyte with Synergetic Properties for Rechargeable Magnesium Batteries
ESPE#P02	**Harish Gudla**	Understanding the mechanical properties of polymer electrolytes from atomistic simulations
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ESPE#P17	**Hanyu Huo**	Interface Design Enabling Stable Polymer/Thiophosphate Electrolyte Separators for Dendrite-Free Lithium Metal Batteries
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ESPE#P20	**Simone Peters**	Cross-linking studies of a polymer electrolyte: influence on electrochemical properties
ESPE#P21	**Jinju Chen**	High Ionic Conductivity Quasi-solid Ternary Polymer Electrolytes for Potassium-based Batteries
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ESPE#P23	**Andreas Thum**	Molecular Dynamics Simulations of Polymer Electrolytes Close to Electrodes: Impact of Electrode Charge and Chain Length
ESPE#P24	**Elmar Kataev**	Probing interfaces formed in anode-free Li-ion batteries with polymer electrolyte by operando Hard X-ray Photoelectron Spectroscopy
ESPE#P25	**Ping Feng**	Di-Lithium Terephthalate (DTP)-based Solid Polymer Electrolyte for All Solid-State Li Metal Ba
ESPE#P26	**Daniel Döpping**	Solvent-free composite polymer electrolyte membrane preparation
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ESPE#P31	**Ujjawal Sigar**	Study of the interface between inorganic and polymer solid electrolytes for enhanced ion transport
ESPE#P32	**Benjamin Heyne**	Polymer Ceramic Electrolytes and Electrodes for Medium Temperature Sodium-Batteries
ESPE#P33	**Sylvio Indris**	From lithium to potassium: Comparison of cations in PEO-based block copolymer electrolytes

Designing Gel Polymer Electrolyte with Synergetic Properties for Rechargeable Magnesium Batteries

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Rechargeable magnesium batteries (RMBs) have emerged as attractive candidates among post-lithium batteries because of the particular features of metallic magnesium (Mg) as a metal anode. However, the realization of practical Mg batteries remains challenging and exploration of suitable electrolyte is imperatively necessary.

Recently developed non-corrosive magnesium tetrakis (hexafluoroisopropyloxy) borate $Mg[B(hfip)_4]_2$ (hfip = $OC(H)(CF_3)_2$) electrolyte exhibits outstanding electrochemical performance and good chemical compatibility in Mg-based systems.[1] The discharge/charge chemistry with this electrolyte has been demonstrated with the sulfur (S) cathode, which is considered as one of the most promising cathode materials, due to its high theoretical capacity (1675 mA h g^{-1}), low toxicity and high abundance. Nevertheless, Mg−S batteries with a liquid electrolyte are still facing critical issues correlated with the dissolution of the sulfur species during the discharging/charging process, so-called polysulfide shuttle effect, which leads to self-discharge and capacity fading.

The development of gel polymer electrolytes (GPEs) may provide a promising solution to alleviate the above issues. A GPE designed by trapping solvent molecules in a polymerized gel network may limit the dissolution and diffusion of soluble electrode materials. For Mg−S batteries, the utility of GPE could be an efficient approach to inhibit the diffusion of the polysulfide. Moreover, GPEs have some additional advantages, including improved safety (less internal short-circuit and less electrolyte leakage) and mechanical durability for electrochemical devices.

Herein, a novel magnesium tetrakis(hexafluoroisopropyloxy)borate ($Mg[B(hfip)_4]_2$)-based non-corrosive gel polymer electrolyte has been developed by an in situ polymerization method.[2] Polytetrahydrofuran (PTHF) is chosen as backbone to build the GPE, denoted as $Mg[B(hfip)_4]_2$-PTHF-GPE. This gel polymer electrolyte exhibits unprecedented 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. Moreover, the gel polymer electrolyte shows good compatibility with sulfur cathode. The stable open circuit potential of the Mg−S cells using $Mg[B(hfip)_4]_2$-PTHF-GPE demonstrates that the GPE can largely suppress the self-discharge of the cell. Furthermore, this GPE can be simply prepared from a liquid electrolyte and easily integrated into devices, which opens a new avenue for the development of magnesium batteries.

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Understanding the mechanical properties of polymer electrolytes from atomistic simulations

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Self-healing polymers have caught much attention for potential applications in electrochemical energy storage systems because of their superior mechanical properties. However, unlike ion transport properties where much has been understood recently with the aid of atomistic simulations [1-3], the understanding of mechanical properties of polymer electrolytes at the atomistic level remains elusive. In this ongoing work, a model polymer electrolyte system, i.e., poly(ethylene oxide)-LiTFSI, was considered for a systematic study of the impact of molecular weight, temperature, and salt concentrations on mechanical properties, such as Young's modulus, storage, and loss modulus with both non-equilibrium and equilibrium molecular dynamics simulations. This work will provide a benchmark for computing the mechanical properties of polymer electrolyte systems and shed light on the molecular mechanism of self-healing polymers.

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Clarifying the Beneficial Effect of Fillers Inside Polymer Electrolyte by the Use of Neutron Scattering and Synchrotron Tomography Experiments

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State-of-the-art Li-ion battery is showing limitations regarding application as energy storage devices for electric mobility.1 Overcoming these limitations could be possible by using metallic Lithium as the negative electrode. A strategy that possibly meet prerequisites for such anode would be the use of a solid electrolyte. They could prevent dendrite growth thanks to their solid state and have higher safety by avoiding flammable solvents. In this context, polymer electrolytes are appealing solid-state materials but they still lack sufficient Li ion conductivity. Blending poly(ethylene oxide) (PEO) with alumina fillers has shown enhanced conductivities, an effect attributed to beneficial interactions between the filler surface and the polymer/Li-salt system. It was suggested that acidic groups on the filler surface increase the amount of free Li ions2, but also that particles create faster conduction pathways surrounding them by changing the PEO structure and segmental mobility. 3 However, to optimize the design of composite polymer electrolyte toward higher conductivities, there is still a need for detailed understanding of the relative effect of filler surface interactions and changes in the polymer mobility.

This study aims at clarifying the effects of filler surface interactions and changes in dynamics at the molecular-scale level on the ionic conductivity by means of combined lab-scale and large-scale facility experiments on a model composite electrolyte. Our system is composed of poly(trimethylene carbonate) (PTMC) as the polymer matrix, and several types of alumina nanoparticles as the filler. Compared to the typical PEO-based electrolyte, the role of the filler might differ, because of the fully amorphous state of PTMC electrolytes and the weaker coordination strength between carbonate units and Li+.4 As in PEO systems, we observed enhanced ionic conductivities with alumina added inside the PTMC-based electrolyte. The degree of improvement depends on the alumina type, its concentration, as well as on the preparation method. We investigated some physico-chemical properties of the PTMC-alumina composites (IR, DSC, SEM), and probed their microstructure by synchrotron nano-holotomography at the ESRF (ID16a). Segmentation of the tomograms gives us access to the state of dispersion of the particles in the polymer matrix from which we computed quantitative parameters. We found that the ionic conductivities of the electrolyte correlate to the total surface developed by the filler, thus indicating the importance of the surface interactions. Further understanding at the molecular-level was acquired using quasi-elastic neutron scattering, a technique suited to probe dynamics in polymers.5 The experiments were performed at the ILL (IN5 and IN16b) on a series of composites along with reference samples of pure PTMC and electrolyte without fillers. We found that the Li salt hinders the intrinsic motion of PTMC, while composite samples containing alumina recover a molecular-scale dynamic. This process probably contributes to facilitate a more efficient ion transport within the composite.

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Synthesis and characterization of gel polymer electrolytes based on crosslinked poly(2-Nonyl-2-Oxazoline-co-2-Dec-9'-enyl-2-Oxazoline)

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Today's lithium-ion batteries (LIBs), found in a large variety of electronic devices and electric vehicles, still suffer from safety and insufficient durability issues [1]. An electrolyte is a key component of batteries and its further improvement is crucial for the development of new durable, high-energetic and safe LIBs. Usage of polymeric electrolytes which also act as separators is considered to be capable of solving the above-mentioned issues of conventional LIBs [2]. Gel polymer electrolytes (GPEs) comprising a polymer matrix plasticized with a solution containing Li salt and/or additional low-molecular-weight compounds are deemed good candidates for potential practical use in LIBs because of their relatively high ionic conductivity and flexibility combined with sufficient mechanical stability [3].

Current work covers the synthesis and characterization of new GPEs based on poly(2-Nonyl-2-Oxazoline-co-2-Dec-9'-enyl-2-Oxazoline) copolymers. A series of samples were synthesized by cationic ring-opening polymerization (CROP) of the respective 2-Oxazolines with different ratios of the comonomers. The presence of double bonds in the dec-9'-enyl sidechains allows further chemical crosslinking with thiol-based crosslinkers. Therefore, the samples were crosslinked using thiol-ene click reaction [4] and two types of crosslinkers and further swollen in 1M solution of LiTFSI salt. The samples were investigated in terms of ionic conductivity in a wide temperature range, and thermal and mechanical stability. In addition, pulse-field gradient (PFG) NMR spectroscopy was used for probing the ion diffusion at various temperatures as well as for evaluation of Li-ions transference number, theoretical conductivity and degree of salt dissociation. Finally, lithium striping-plating experiments were performed to evaluate the compatibility of the chosen GPEs with the Li electrode in terms of the functioning of the symmetric Li/GPE/Li test cell. In these experiments, the influence of the nature of lithium salt on the stability of solid electrolyte interphase (SEI) was also investigated by preparation and further testing of the GPEs containing LiBOB salt. The comparison of electrochemical properties of GPEs containing fluorinated LiTFSI and non-fluorinated LiBOB salts has been done. Promising samples possessing relatively high conductivity (~10^{-4} S/cm at 25 ^{o}C) and good stability were obtained within this research.

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Carbonate swollen Lithiated Nafion Electrolyte for Lithium-Sulfur Batteries

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The formation of polysulfide intermediates during operation of lithium-sulfur battery is prevented by confining sulfur into ultramicroporous (UMP) carbon.[1] By size restriction physical entrance of typically used electrolyte solvents is hindered.[2] That minimizes direct contact of sulfuric species with electrolyte solvent to the entrance of pores.

Due to the reduced sulfur-solvent contact, carbonate solvents can be used with such sulfur cathodes. Electrophilic carbonates are harmless and non-toxic compared to typical ether electrolyte solvents. But they react irreversibly with nucleophilic polysulfides (PS) of lower order to form thioethers (cyclic carbonates) or sulfonium (linear carbonates).[3] Their use in conventional sulfur cathodes is therefore not possible. Gas-infiltrated micro/ultramicoporous carbon sulfur composite cathodes show excellent cyclability and stability of capacitance.[4] The use of carbonate solvent further creates an advantageous protective layer on the pore opening, preventing solvent penetration at the limit of pore size <0.7nm (UMP) / >0.7nm (supermicropores). However, active material is also irreversibly lost, which is not available as an electron carrier and limits the specific capacity of the sulfur cathode.

Single lithium-ion conducting solid polymer electrolytes (SLIC-SPEs) based on lithiated Nafion membrane have been investigated, utilizing the chemical and thermal stability of this kind of ionomers. A mixture of ethylene carbonate (EC) and propylene carbonate (PC) was tested as membrane swelling solvent and was beneficial compared to glycol ether or linear carbonates in terms of high ion mobility while avoiding phase separation issues and undesired leaching. The combination of Li-Nafion_EC:PC membrane with sulfur-infiltrated ultramicroporous carbon composite cathodes facilitating a quasi-solid-state lithium-sulfur full cell. Comprising carbonate compatibility and high active material utilization due to reduced amount of solvent in the cell and spatial concentration in the membrane and its interfaces.

Electrochemical performance of the full cell was investigated elaborately and compared with a reference system using conventional liquid EC:PC electrolyte. While rapid capacity fading can be observed for the liquid electrolyte cell, an enduring high capacity is found in the lithiated Nafion system. For better understanding of these effects, cycling analysis was accompanied by implementing impedance spectroscopy upon galvanostatic cycling. The electrochemical characterization indicates the formation of a stable film and high degree of reversibility during cycling of the lithiated-Nafion cell whereas an increased film resistance due to sulfur cross over and electrolyte decomposition was observed within the liquid electrolyte system.

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Correlation between the cation transference number and the ion coordination strength for post lithium electrolytes

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To satisfy the increasing demands of lithium ion batteries (LIBs) and meet the rising cost and scaling requirements, on top of the lithium abundancy concern, the exploration of the so-called “beyond Li-ion” area has emerged. Although LIBs will not be replaced, they will most certainly be accompanied by other alkali/alkaline metal technologies in combination with solid-state batteries, including solid polymer electrolytes (SPE) to complement current liquid-based LIBs. Interesting alkali and alkaline metal ions to accompany Li^+ on the market are Na^+, K^+ and $Mg2^+$, which are all on different stages in the development process and all face different types of challenges. To make it more challenging, these cation technologies can be implemented along with SPEs, where the ionic conductivity already is limited compared to liquid-based LIBs.[1]

Considering the ionic conductivity, it is predominantly the partial cationic conductivity that is of importance, since it is the cation that is electrochemically active and generating electrical current in a battery. The partial cationic conductivity can be accessed by determining the cationic transference number (T_+) in the SPE, which describes the net charge carried by the cation species. There are several ways to obtain the T_+, and whereas all in practice should reveal the same T_+ for identical systems, the reality disagrees due to theoretical assumptions and errors in the methods.[2-3]

Among the methods to determine the T_+, the electrochemical methods are most practically approachable and are (therefore) most widely used for Li-systems. However, when employed for above mentioned “beyond Li-ion” systems, reactivity and/or passivation issues limits the utilization of these methods and therefore new methods are required.[4-5]

In this study, a combination of NMR spectroscopy, that independently have been used for Li-systems, and electrochemical impedance are utilized to determine the T_+ for Na_+, K_+ and $Mg2_+$. Moreover, it is investigated if the same correlation observed between the ion coordination strength and the T+ for Li+ is maintained for these cations, where strong coordination strength entails low T+ and vice versa.[6]

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Ionic Transport in Solid Polymer Electrolytes filled with Li Polysulfides

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Lithium sulfur (Li-S) batteries, make use of the readily available, non-toxic, high-capacity sulfur positive electrode and Li metal negative electrode to theoretically deliver energy densities (2500 Wh/kg) ten times higher than what the current Li-ion battery can deliver. However, this promising technology faces tremendous challenges mostly due to the intermediate reaction products, lithium polysulfides (Li_2S_x, $2 \leq x \leq 8$), originating from the positive electrode that dissolve and migrate through the electrolyte up to the negative electrode in a process referred to as "redox shuttle effect". At the negative electrode, these Li2Sx react with the Li metal to form an insulating layer impairing the electrochemically active surface area and increase the internal resistance of the cell. This leads to a strong decay of the Coulombic efficiency and capacity. The "Li_2S_x shuttle" can be mitigated using functionalized solid polymer electrolyte (SPE) by capitalizing on the mechanical properties of triblock copolymer polystyrene-poly(ethylene oxide)-polystyrene (PS-PEOPS) as well as other functionalities arising from single-ion conducting SPE such as PSTFSI-PEO-PSTFSI where the anion of the Li salt is directly grafted onto the PS units [1]. As the Li_2S_x are ionic in nature and their "shuttling" behaviour is dependent on the nature of the electrolyte, it is thus of high interest to investigate the interactions between the Li_2S_x and these SPEs starting by their ionic transport properties.

In this work, the ionic transport properties of lithium polysulfides within several SPE hosts (PEO, PS-PEO-PS, PSTFSI-PEO-PSTFSI) have been characterized by differential scanning calorimetry to have access to thermodynamical properties such as glass transition and melting temperature which are correlated to the three main transport properties: *i)* ionic conductivity, *ii)* transference number [3], and *iii)* ambipolar diffusion coefficient [4]. The goal of this study is to gain insight into the ionic transport that takes place in Li-S batteries in an effort to mimic the battery failure mechanism [2]. In addition, Small Angle X-ray Scattering (SAXS) characterization of SPE/Li_2S_x mixtures have been carried out to investigate the effect of the Li2Sx on the mesostructure of the SPEs.

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The effect of molecular weight on ion transport in polycarbonates compared to polyethers

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Polymer electrolytes are among the most interesting alternatives to realizing solid-state batteries due to their low cost, high processability and low density. Despite this, it remains challenging to design polymer electrolytes that fulfill a sufficient ionic conductivity at ambient temperature. Therefore, a better understanding of the ion transport in different polymers is needed. The ion transport in most polymers is governed by the segmental motion of the polymer chain, but also the coordinating interactions between the salt and the polymer.[1]

Poly(ethylene oxide) (PEO) is the most explored polymer host due to its excellent ability to solvate Li^+, reasonable ionic conductivity, and rather good compatibility with Lithium metal. However, it suffers from a low transference number (T_+) and crystallization below 60 °C. Alternative polymer hosts, such as polyesters and polycarbonates have shown to exhibit significantly higher T_+. In particular, polycarbonates (e.g. PTMC) can exhibit T_+ as high as 0.8. A key reason to the differences in T_+ between PTMC and PEO is the weaker interaction between the cation and carbonyl group. However, the total ionic conductivity of salt doped PTMC is low, due to the higher chain rigidity. [1]

Although the differences between PEO and PTMC are rather established on the polymeric level, the effect of molecular weight (M_n) and end group has been less explored. [2, 3] In a study by Devaux et. al., the transition from low M_n glymes to PEO was explored. [4] The study showed that a transition in ionic conductivity, viscosity and T_+ all occurred up to a critical Mn. The change in T_+ was correlated to the transition from vehicular transport at low M_n to coupled ion transport at higher M_n. In this study, we explore this transition for a strongly (PEO) and weakly (PTMC) Li coordinating material. The changes in ionic conductivity, viscosity and T_+ are mapped out together with the coordination strength of the two hosts. The effect of the polymer host on the transition as a function of M_n is thereby evaluated. In addition, the effect of the end groups at different M_n is explored for both PEO and PTMC.

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Synchrotron PES measurements of SPEs: in-situ deposition and practical considerations

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A hindrance to the implementation of solid polymer electrolyte (SPE)-based lithium batteries is the performance of the electrolyte decomposition layer that forms at their lithium metal anodes. This decomposition layer and the process of its formation has a large impact on the long-term stability of the cell, and while a growing collection of studies exist (*e.g.* [1-3]) there is still lots to be done in order to understand this interface. In this work the application of in-situ lithium deposition photoelectron spectroscopy (PES) in order to investigate of the anode|electrolyte interface is discussed.

The first part of this work discusses the results from a study[5] in which three different SPEs, PEO:LiTFSI, PCL:LiTFSI, and PTMC:LiTFSI, were investigated using the in situ deposition PES method. The results found that while the PTMC:LiTFSI displays the most decomposition, its decomposition layer is more stable over time, indicating that a SPE prone to decomposition can still be beneficial for cell performance.

In the second part of this work, three different SPEs, PEO:LiBF4, PEO:LiBOB, and PEO:LiDFOB were investigated using the in situ deposition PES method. The analysis was aided by the results from a newly developed ab initio molecular dynamics (AIMD) protocol and later also connected to cycling performance. PEO:LiDFOB decomposed the least at the interface while displaying the highest coulombic efficiency out of the three SPEs. Together with the first study this indicates that the amount of electrolyte decomposition is secondary to the stability of the decomposition layer itself.

The third part of this work is concerned with practical considerations of these measurements and of synchrotron measurements of the anode|electrolyte interface of SPEs in general. Beam damage effects in materials which are not considered radiation sensitive when exposed to soft x-rays is are presented.

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Polymerized Ionic Liquids as Solid Electrolyte Membranes in Lithium-Ion Batteries

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Ionic liquids (ILs) feature many advantages over conventional liquid electrolyte systems but also exhibit several drawbacks, like high toxicity and environmental persistence in case of leakage. By polymerization of monomeric ionic liquids (mIL), the ionic liquids are fixed within a covalent network of polymerized ionic liquids (PIL). Our ambition is to develop PIL based solid electrolyte membranes as a replacement for conventional separator-electrolyte systems. PILs preserve important material benefits of the ionic liquids, like high electrochemical stability, high thermal stability and tunability while also featuring safety benefits like non-flammability and leakproofness. While PILs feature many advantages over conventional electrolyte systems, low ionic conductivity values of these materials are still challenging. In order to improve the ionic conductivity, a general understanding of structure-property-relationships of PILs is essential. Therefore, we investigated eight polymerizable ionic liquids featuring either a polymerizable acrylate or methacrylate group and varying alkyl chain lengths at the quaternary ammonium function.

We found that the ionic conductivity values of the monomeric ionic liquids decrease with increasing chain length. After UV-induced bulk-polymerization, there is a clear tendency of the opposite behaviour. The ionic conductivity values were measured at temperatures between 20 °C and 60 °C and are in the order of 10^{-5} mS cm^{-1} at 25 °C and 10^{-3} mS cm^{-1} at 60 °C. For future application of the membranes in Li-ion batteries, the addition of a conducting salt to the PIL matrix is indispensable. Therefore, we evaluated the influence of varying LiTFSI concentrations on the ionic conductivity values of the membranes. Our studies reveal that there is a strong influence of the amount of additional conducting salt on the ionic conductivity, but the conductivity value also depends strongly on the structure of the applied mIL. DSC analysis indicated that the glass transition point is shifted to lower temperatures with increasing amounts of conducting salt in the PIL matrix.

Development of fluorinated polyetherimides: Synthesis, characterization and electrochemical properties

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Polymer electrolytes (PE) consisting of lithium salt dissolved in polymer matrix are widely recognized as attractive electrolyte materials for the next generation of solid-state energy storage devices. PE offer several advantages, including flexibility, enhanced safety, ease of membrane formation, and excellent electrochemical stability. Over the past 50 years, poly(ethylene oxide) (PEO) has emerged as a favourable choice for PE application due to low glass transition temperature, chain flexibility, remarkable electrochemical stability against lithium metal, and great solubility for conductive lithium salts. Aromatic polyetherimides (PEI) are well-known high-performance polymers widely used in areas such as membrane separation, adhesive, electrical insulation, gas transport, oil storage and composite matrices, due to their excellent thermal and chemical resistance in combination with good mechanical properties Therefore, in this work we aimed to synthesise PEI-PEO copolymer to increase mechanical properties and stability of PE.

To introduce PEO chain into copolymer Jeffamine ED-2003 was utilised with average molecular weight of 1900 g/mol. For PEI block, 4,4'-(Hexafluoroisopropylidene) diphthalic anhydride and 4,4'-(Hexafluoroisopropylidene)bis[(4-aminophenoxy)benzene] were used due to presence of flexible ether linkage and bulky fluorinated substituent in their chemical structure. The general synthetic route shown at Figure 1. By variation of monomers concentrations, copolymers with different molar ratios of PEI/PEO block were prepared. Scheme of synthesis shown in Figure 1 (where x = 0.05; 0.15; 0.3).

The structures of copolymers were confirmed via 1H NMR and FT-IR spectroscopy. By tweaking the PEO content, the glass transition temperature can be adjusted in the range from 24 to 195 °C. Our results show that the thus prepared polymers are able to dissolve high amounts of Li-salts (up to 70%wt) to form “polymer in salt compositions” with intriguing electrochemical properties such as a wide electrochemical stability window for high volt application.

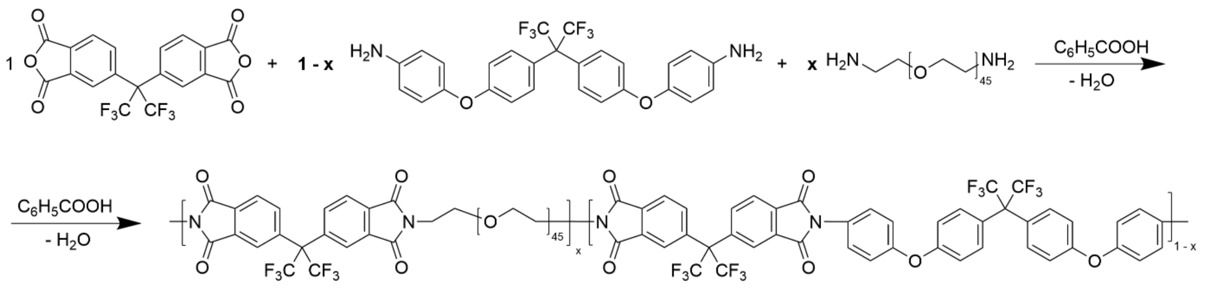

Figure 1. General synthesis route of polymers (simplified structure of Jeffamine ED-2003).

Understanding carbonate degradation: Using PES, computations and cell cycling to explore the degradation of different polycarbonate electrolytes in anodeless cells

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Degradation of the electrolyte is a major challenge in any lithium-based battery. Generally, the electrolyte is only kinetically stable and its continuous degradation is prevented by a solid electrolyte interface (SEI). Thus, the formation of a stable SEI is of high importance in any lithium battery. This issue is exacerbated in anodeless systems as there is no excess lithium available to repeatedly reform the SEI and any side reactions directly lead to a loss of capacity.

In recent years there started to be more and more research exploring polycarbonates as solid polymer electrolytes (SPE) to be used in combination metallic lithium as an anode.[1] As SPEs generally allow the utilization of metallic lithium as an anode and to forego using separators, there are clear incentives in regards to energy density as well as cost savings.[2] When comparing different options for SPEs, polycarbonates compare quite competitively: They offer quite good conductivity and a high cationic transference number due to a relatively low coordination strength of the carbonyl oxygen with lithium cations.[3]

Then, the question arises which is the optimal spacing of the carbonate groups along the polymer chains to minimize unnecessary degradation in an anodeless battery? Should they be separated by two methylene groups, three or even four? The respective polycarbonates (poly ethylene carbonate (PEC), poly trimethylene carbonate (PTMC) and poly tetramethylene carbonate (PTeMC)) have been synthesized and analyzed using several methods: photo electron spectroscopy (PES), computations (ab initio molecular dynamics (AIMD)) and cell cycling.

Using lithium deposition in combination with a synchrotron light source allows for the analysis of the SEI formed at the contact area between the polycarbonate and metallic lithium that would be formed in a battery cell during cycling. Due to the thin layer of lithium deposited it is also possible to track the stability of the formed SEI over time. Here, it can be observed that hydrocarbons form at the contact area between lithium and the polymer, but that the surface of the polymers return to their original states over time. The AIMD simulations can calculate the molecular breakdown products in a system containing polycarbonates, a lithium salt and metallic lithium, giving more detailed insight in how the respective carbonates break down and over what time frame. Here it is notable that PEC forms ethylene as a breakdown product which the other two polymers don't and that PTeMC keeps reacting with the lithium over a longer period of time. Lastly, cell cycling experiments relate the data obtained from the methods above to real systems, using cells consisting of each polycarbonate and cycling them in an anodeless setup with LFP cathodes. These findings can give insight in the importance of functional group spacing in SPEs as well as the feasibility of polycarbonates as candidates for their use as SPEs in anodeless batteries.

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Investigation of poly(acrylonitrile-co-butadiene) rubbers as polymer matrix for solid Mg-electrolytes

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Solid-state polymer electrolytes have received significant interest for application in next-generation energy storage devices due to their enhanced safety and compatibility. In this study, we investigate the feasibility of utilizing poly(acrylonitrile-co-butadiene) (NBR) rubbers as a host matrix for solid Mg-polymer electrolytes. Our investigation primarily focuses on the mechanical and electrochemical characteristics of NBR polymers with varying concentrations of Mg salts, coupled with an examination of the alterations in behavior subsequent to the modification of NBR through thiol-ene reaction.

Solid polymer electrolytes were prepared by solvent casting method. The resulting films were analyzed by electrical impedance spectroscopy (EIS) to characterized their conductivity behavior at different temperatures with different salt concentrations. Fourier transformed infrared spectroscopy (FT-IR) measurements of the electrolytes were conducted to investigate the Mg-salt dissociation and differential scanning calorimetry (DSC) measurements were used to analyze changes in the thermal properties. Furthermore, thiol-ene reactions were used to modify the polymer with ethanethiol. The resulting polymers were used to prepare new polymer electrolyte membranes, of which the change in ionic conductivity was studied.

Our findings shed light on the potential of NBR rubbers as host matrices for solid Mg-polymer electrolytes. The systematic investigation of the electrochemical behavior of these electrolytes offers insights into the design and optimization of solid Mg-polymer electrolytes for advanced energy storage applications.

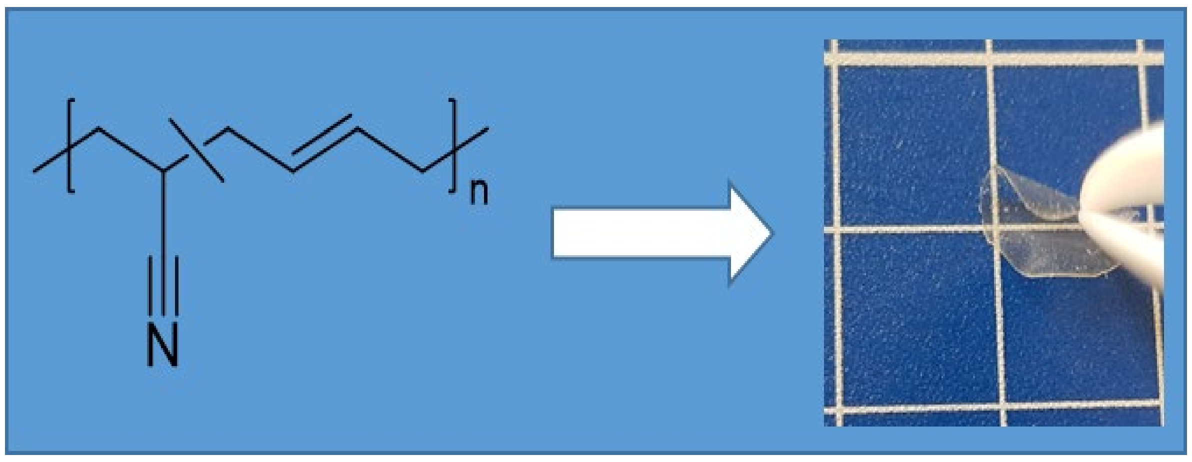

Figure 1: Schematic representation of NBR film forming properties.

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Interface Design Enabling Stable Polymer/Thiophosphate Electrolyte Separators for Dendrite-Free Lithium Metal Batteries

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Organic/inorganic interfaces greatly affect Li+ transport in composite solid electrolytes (SEs), while SE/electrode interfacial stability in general plays a critical role in the cycling performance of solid-state batteries (SSBs). However, incomplete understanding of interfacial (in)stability hinders the practical application of composite SEs in SSBs. Herein, interfaces based on polymer/thiophosphate composite SEs are designed to facilitate dendrite-free lithium metal batteries. Chemical degradation between Li6PS5Cl (LPSCl) and poly(ethylene glycol) (PEG) is revealed. The high nucleophilicity of PEG changes the electronic state and structural bonding of the PS43− tetrahedra, thus triggering a series of side reactions. Polyethylene glycol dimethyl ether (PEGDME) with a substituted terminal group not only stabilizes the PEGDME/LPSCl interface but also extends the electrochemical window of the composite SE. Moreover, a LiF-rich protection layer formed in situ by the introduction of mixed lithium bis(trifluoromethanesulfonyl)imide/lithium bis(fluorosulfonyl)imide (LiTFSI/LiFSI) salts can effectively prevent side reactions at the Li/SE interface and suppress lithium dendrite growth. The stable interfaces in the PEGDME/LPSCl composite SE enable homogeneous lithium plating/stripping for both lithium symmetric cells and Li/$LiNi_{0.85}Co_{0.1}Mn_{0.05}O_2$ cells. The results provide insights into the chemical stability of polymer/sulfide composites and demonstrate an interface design to achieve dendrite-free lithium metal batteries.

Prospective Life Cycle Assessment of Magnesium Batteries using Gel Polymer Electrolytes

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Concerns regarding global environmental problems like climate change drives the energy and mobility transitions with the goal to decrease the use of fossil fuels in the future. Batteries are considered as key technology for the energy and mobility transition. Over the last three decades, lithium-ion batteries (LIBs) with different chemistries are being used for many different applications such as portable consumer electronics, stationary storage systems and within the mobility sector. In recent years there has been increased interest in post lithium batteries due to the major drawbacks related to environmental (including resource availability), social, and safety aspects of conventional lithium-based batteries.

Emerging solid state batteries (SSBs) with different solid electrolytes are seen as potential option to overcome some of the sustainability related limitations. The magnesium–sulfur (MgS) SSB emerges as one of the alternatives, with much lower safety concerns in comparison to LIBs with fluid electrolyte. Information about the potential environmental impacts of these emerging batteries is rarely available in the literature, especially for batteries with a gel polymer electrolyte.

In our study we apply the prospective life cycle assessment (LCA) methodology to analyze potential environmental impacts in an early development stage. We investigate different environmental impact indicators and cumulative energy demand. The functional unit is Wh of the storage capacity of a lab scale MgS battery for the different scenarios. The battery is modelled based on an existing prototype MgS pouch cell (baseline scenario) and is optimized hypothetically in elements such as share of the electrolyte, casing and separator exploring future improvement potentials according to the current state of mass production of lithium-ion batteries (LIB). From the LCA results global warming potential (GWP) impacts for the baseline scenarios are 13.35 kg of CO_2 eq./Wh of energy storage while for the different optimized scenarios GWP varies from 0.2-1.1 kg of CO_2 eq./Wh of energy storage. It turns out, that as expected the initial (non-optimized) prototype cell cannot compete with current LIB in terms of energy density or environmental performance, mainly due to the high share of non-active components, decreasing its technical performance substantially. But, if the assumed optimization of the MgS cell composition would be achieved for the considered scenarios, MgS could be competitive to existing LIBs. The discussion of the results will also include further environmental impact categories, to provide a broader picture of the comparison. Overall, MgS study with gel polymer electrolytes provides useful insights to technology developers from environmental perspective in an early stage of technology development.

Center for Electrochemical Energy Storage | Ulm & Karlsruhe (CELEST) – A unique Research and Innovation Platform for the Energy Storage of the Future

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Electrochemical Energy Storage (EES) is a key technology of the 21st century. In 2018, the Center for Electrochemical Energy Storage | Ulm & Karlsruhe (CELEST), one of the most ambitious research platforms in this area worldwide, has started operation. It is the joint research and innovation platform in the field of EES of the three partners Karlsruhe Institute of Technology (KIT), Ulm University and Center for Solar Energy and Hydrogen Research Baden-Württemberg (ZSW). CELEST provides a broad space for scientific collaboration, education and training, technology transfer and science communication in the field of EES from basic research to application as well as sustainability issues. The more than 60 CELEST members come from over 30 institutes of the participating three partner institutions at the Ulm and Karlsruhe sites. One strength of CELEST is the complementary expertise that our members bring to the table. In addition to research activities in the fields of lithium and post-lithium batteries, CELEST members are also active in hydrogen research, because the EES landscape of the future will consist of a portfolio of storage concepts.

Within CELEST, the GS-EES – Graduate School for Electrochemical Energy Storage supports doctoral researchers doing their PhD in the field of electrochemical energy storage at one of the partner institutions. The GS-EES offers excellent graduation conditions including support of a three-month research stay abroad, an annual Summer School, workshops on scientific or method-related topics and on professional skills as well as an interdisciplinary block course. More details about the CELEST activity fields can be found on our homepage [1].

In this work, the CELEST activity fields are presented in an overview and coherent manner.

References:

[1] https://www.celest.de/en/

Cross-linking studies of a polymer electrolyte: influence on electrochemical properties

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State-of-the-art lithium-ion batteries are considered promising energy storage systems for managing the energy transition, both in the transport sector and for storing energy for renewable energy. Compared to conventional lithium-ion batteries, solid-state batteries are seen as the next generation of battery technology with the promise of high energy density and improved safety. To achieve these goals, high-capacity negative electrodes, e.g., silicon or lithium, need to be combined with high capacity and high voltage positive electrodes, e.g., Ni-rich NMC. This combination of active materials provides a number of significant challenges for the solid-state electrolyte. If silicon is used as the anode active material, significant volume changes during lithiation/delithiation occur. These volume changes lead to a variety of problems including irreversible loss of lithium and eventual disintegration of the electrodes, resulting in capacity fade. Therefore, the electrolyte must be sufficiently elastic to buffer these changes.

Polymer electrolytes offer higher thermal stability and more safety compared to standard liquid electrolytes. Compared to ceramic solid electrolytes, which usually have high ionic conductivity and mechanical strength, polymer electrolytes offer higher flexibility, which is important for maintaining contact between the electrolyte and the electrodes to ensure long cell life.

The approach in the ASTRABAT project is based on inorganic-organic hybrid polymers. This class of polymers is an ion-conducting material consisting of inorganic and organic nanodomains formed by a sol-gel reaction of functionalised alkoxysilanes. The majority of the silane side chains consist of polyethylene oxide (PEO) chains that promote ionic conductivity in the polymer electrolyte, while a smaller portion of the silanes are functionalised with terminal organic groups to provide additional cross-linking of the prepolymer after the siloxane backbone has been established. The solid electrolyte is prepared by mixing the polymer precursor with a suitable lithium salt and a small amount of ionic liquid and cross-linking via the polymerisable moieties (e.g. epoxide group). The resulting structure consists of cross-linked oligosiloxane networks with attached polyether chains. The high degree of mixing between inorganic and organic domains prevents reorganization of the polyether domains (which leads to crystallization) and results in a very flexible polymer electrolyte.

Here we present deeper insights into the mechanistic pathways of the cross-linking process of the polymer material along with the impact on the electrochemical properties of the final polymer electrolyte.

High Ionic Conductivity Quasi-solid Ternary Polymer Electrolytes for Potassium-based Batteries

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As society develops, more attention is paid to developing, storing, and using clean and sustainable energy sources. In recent decades, batteries have been the emerging devices expected to lead the energy storage era [1]. Potassium-ion batteries (PIBs) have attracted great attention in the past few years [2] due to the fact that potassium is more abundant and widely distributed on Earth crust than lithium, and K/K+ has a lower reduction potential (−2.93 V vs. SHE) than sodium. This suggests that PIBs can be an alternative to lithium- and sodium-ion batteries for high operating voltage applications [2,3].

Solid/quasi-solid electrolytes offer several advantages over non-aqueous electrolytes, including better safety, thermal stability, and strong impact resistance. They also prevent the dissolution of organic/inorganic species into electrolyte, which might enhance battery cycling stability [4]. Among them, PEO-based solid/quasi-solid polymer electrolytes (SPEs) are gaining attention for their ability to combine the benefits of liquid and inorganic solid electrolytes [5], such as high solubility and ability to complex with various salts at high concentrations, along with its good processability and mechanical properties. The main disadvantage of SPEs is the poor ionic conductivity (10^{-5}-10^{-7} S cm^{-1}) at room temperature [4,5].

This work focuses on developing quasi-solid ternary polymer electrolytes consisting of PEO, potassium salt, and ionic liquid, with the aim of achieving high ionic conductivity at room temperature. The developed quasi-solid ternary polymer electrolytes were physicochemically and electrochemically characterized, showing ionic conductivities of around 6.21 x 10^{-4} S cm^{-1} at 20°C. In addition, the quasi-solid ternary polymer electrolytes were tested in a potassium-metal cell using a Prussian White cathode at room temperature as a proof of concept.

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Nanocomposite Solid Polymer Electrolytes with Polymer Blend (PVDF-HFP/Pluronic) as Matrix and GO as Nanofiller: Preparation, Structural Characterization, and Lithium-Ion Conductivity Analysis

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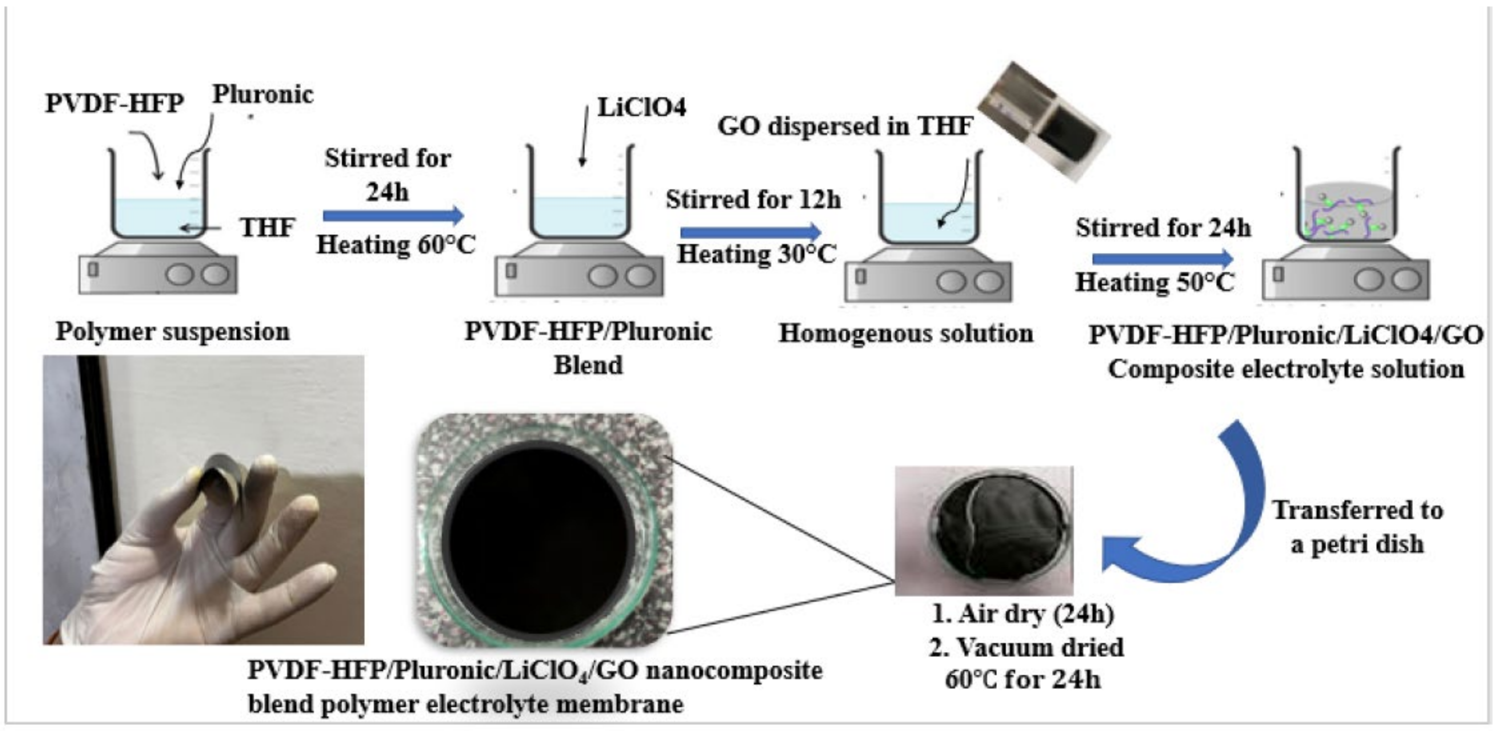
Nanocomposite solid polymer electrolytes (NSPEs) with PVDF-HFP/Pluronic as blend polymer matrix, graphene oxide (GO) as nanofiller, and LiClO$_4$ are reported. FTIR spectroscopy reveals the crystal phase transformation of PVDF-HFP from nonpolar a phase to electroactive g phase upon salt addition that suggests the ion-dipole interaction between the salt and the matrix. Further, Pluronic not only hinders the PVDF crystallization that increases the amorphous character of the matrix but also interacts with the salt and hence assists in salt dissociation in the blend matrix. The dc conductivity of PVDF-HFP/Pluronic/LiClO$_4$ blend SPE improves with increasing the Pluronic content reaching 0.73 μScm^{-1} at room temperature with 60 wt.% Pluronic. The dispersion of GO in the same blend SPE leads to a significant jump in room temperature ion conductivity (~ 1.2 μScm^{-1}) with 0.4% GO. Temperature dependent ion conductivity of the NSPEs reveals an Arrhenius type thermally activated process. The dc polarization data indicates that the conductivity is predominantly due to ions. Impedance plots exhibit a distorted semicircle at higher frequency and a tilted spike at lower frequency. The spike is an indication of ion diffusion and electrode polarization effect. Further, GO also has enhanced the mechanical properties of the fabricated NSPEs. Thus, the fabricated polymer membranes provide a good compromise between mechanical strength and ionic conductivity due to incorporation of GO and main polymer matrix of PVDF-HFP.



Scheme 1: Schematic presentation of the various steps involved in the fabrication of PVDF-HFP/Pluronic/LiClO4/GO nanocomposite polymer electrolyte films by solution casting technique.

Molecular Dynamics Simulations of Polymer Electrolytes Close to Electrodes: Impact of Electrode Charge and Chain Length

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Polymer electrolytes are intensely investigated as (quasi-)solid electrolytes in lithium-ion and post-lithium-ion batteries. However, little is known about the structural and dynamical properties of polymer electrolytes in the vicinity of electrode surfaces. Here, we study poly(ethylene oxide) (PEO) with lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) confined between two oppositely charged graphite-like electrodes using atomistic molecular dynamics simulations [1]. To answer the question how polymer electrolytes behave differently near electrode surfaces than low-molecular-weight liquid electrolytes, we vary the chain length of PEO from two to 128 ether oxygens per chain. At chain lengths of six to eight and around 60 ether oxygens per chain qualitative changes in the behaviour of many properties are observed. Thereby, structural properties show generally a weaker chain-length dependence than dynamic properties. For instance, all investigated electrolytes exhibit a similar component-specific layer structure near the electrode surfaces. This layer structure goes along with the emergence of free energy barriers which reduce the lithium-ion dynamics. Dynamic properties like layer residence times show a strong chain-length dependence but usually plateau at long chain lengths.

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Probing interfaces formed in anode-free Li-ion batteries with polymer electrolyte by operando Hard X-ray Photoelectron Spectroscopy

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Solid-state lithium-ion batteries with polymer composite electrolytes (PCE) hold great promise as safe, stable, and high-energy density storage systems to power the future society. However, their development still faces challenges that require an in-depth understanding of the underlying electrochemical reactions. Here we combine hard X-ray photoelectron spectroscopy (HAXPES) with hard X-ray absorption spectroscopy (hXAS) to provide insights into the reaction mechanism of MnS2 in novel PCEs consisting of a polyethylene oxide matrix (PEO), a lithium diterephthalate (LIDTP) anion immobilizer, and a lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) salt.

Di-Lithium Terephthalate (DTP)-based Solid Polymer Electrolyte for All-Solid-State Li Metal Batteries

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Despite the widespread use of commercial liquid electrolytes in lithium-ion batteries (LIBs), there is a growing demand for the next generation of batteries with exceptional features such as lightweight design, high energy density, wide working potential range, rapid charging capability, enhanced safety, and environmental friendliness.[1, 2] One promising solution in response to these demands is the development of all-solid-state lithium batteries (ASSLBs), known for their potential to provide reliable electrochemical performance and enhanced safety.[3, 4] Among the various solid electrolyte options, polyethylene oxide-based solid polymer electrolyte (PEO-SPE) has gained significant attention in the battery market due to its excellent properties.[5]

Herein, a di-lithium terephthalate (DTP) filler was introduced into the conventional PEO-SPE. The resulting SPE, referred to as DTP-SPE, is a self-supporting membrane with a thickness of ~90 µm (Figure a). It is believed that the DTP filler weakens the interaction between the "active" Li^+ cations and PEO through Coulombic interactions, leading to an improved ionic conductivity in DTP-SPE (3.27×10^{-4} S cm^{-1} at 60°C) compared to pure PEO/LiTFSI (referred to as Ref-SPE, 9.9×10^{-5} S cm^{-1} at 60°C), as shown in Figure b.

In the coin cell tests, NCM811/Li half-cell assembled with DTP-SPE achieved an impressive initial specific discharge capacity of ~180 mAh g^{-1} at a current rate of 200 mA g^{-1} (60°C). In contrast, the specific discharge capacity of Ref-SPE was only ~150 mAh g^{-1} and was maintained for 10 cycles (Figure c). This work highlights the potential of the DTP-based electrolyte membrane for further development in ASSLBs applications.

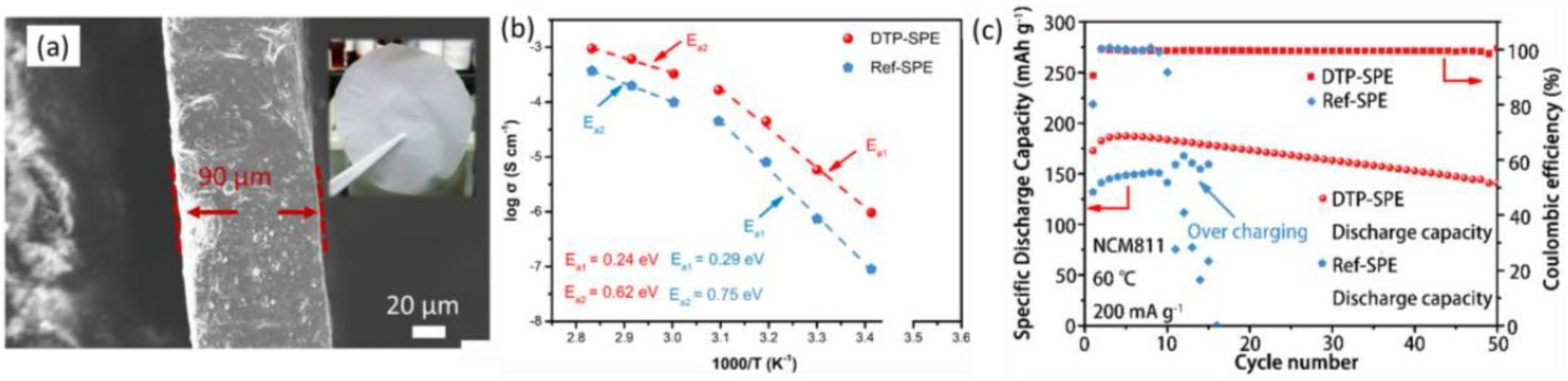

Figure (a) SEM image and digital image of the DTP-SPE. (b) Arrhenius plots of DTP-SPE and Ref-SPE at different temperatures. (c) Cycling performance of NCM811 cathode in half-cells using DTP-SPE or Ref-SPE at a current density of 200 mA g^{-1}.

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Solvent-free composite polymer electrolyte membrane preparation

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Composite polymer electrolyte membranes (CPE) play a pivotal role in energy storage and conversion devices, such as fuel cells and batteries. However, traditional methods of preparing CPEs often involve the use of volatile organic solvents, which pose environmental and safety concerns. Further, solvent-free methods are preferable for industrial up-scaling due to the increased safety and production speed.1

Herein, we propose a method that involves silane functionalized polymers to incorporate oxide nanoparticles into a polymer matrix of poly(ethylene oxide) (PEO), poly(caprolactone) (PCL), and poly(tetrahydrofuran) (PTHF), aiming to enhance ion conductivity and mechanical properties. The nanoparticles are uniformly dispersed within the polymer matrix through a facile mixing process, ensuring homogeneity and optimal ionic transport pathways. The ratio of nanoparticles and polymers can be chosen freely and various active and inactive oxide nanoparticles (e.g., LLZTO, SiO_2, M_oO_3) can be used. The absence of solvents in this process eliminates the need for solvent evaporation steps, simplifying and accelerating the membrane fabrication process and reducing its environmental impact. Conductivity measurements show that the solvent-free composite polymer electrolyte membranes exhibit competitive ion conductivity compared to conventionally prepared membranes.

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

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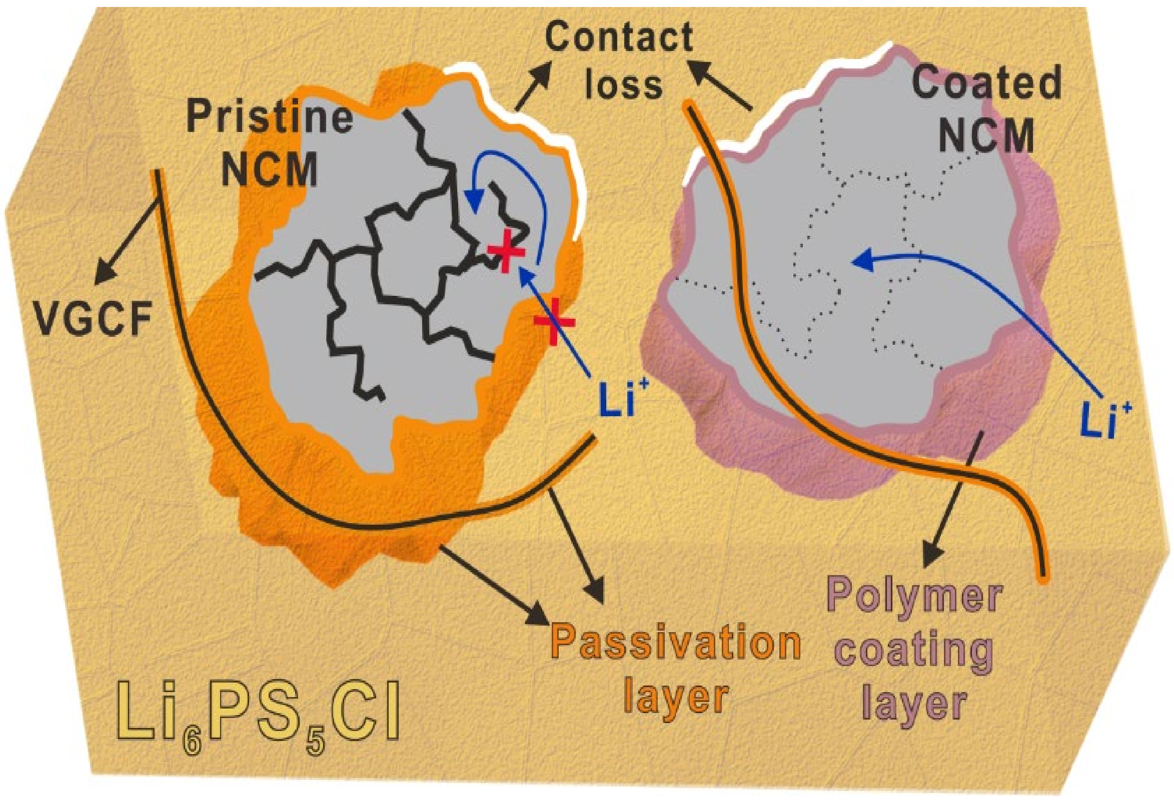
Thiophosphate-based solid-state batteries (SSBs) with high-nickel ternary cathode materials $LiNi_{1-x-y}Co_xMn_yO_2$ (NCMs) represent a promising next-generation energy storage technology due to their expected high specific discharge capacity and improved safety. However, rapid capacity fading caused by contact loss through interphase and crack formation during cell cycling is a significant problem hindering stable SSB cycling and high-energy-density applications.

During cell cycling, the passivation layer at the interface of NCM and Li6PS5Cl and cracking within the NCM particles inhibit the lithium transport into the NCM particles, increasing the lithium diffusion pathway length. The passivation layer also causes contact loss, giving rise to active mass loss during cycling. In this work, a uniform coating of poly((4-vinyl benzyl)trimethylammonium bis(trifluoromethanesulfonylimide)) (PVBTA-TFSI) on NCM is obtained via a spray-drying process. This exceptionally thin cationic polymer coating of only 2 nm to 4 nm thickness on NCM helps stabilize the interface between NCM and the Li_6PS_5Cl solid electrolyte (SE). Electrochemical tests confirm a significant improvement in long-term cycling performance and active mass utilization compared to uncoated NCM. In addition, the polymer coating effectively suppresses the degradation of the NCM/SE interface, particularly the formation of oxygenated species, and reduces the extent of particle cracking. Overall, these results highlight a new approach to mitigate SSB degradation using a thin cationic polymer coating on NCM for SSBs.



Molecular Dynamics Study of Lithium Ion Transport in Concentrated Block–Copolymer Electrolytes

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Insights into the ion transport in block–copolymer electrolytes with lamellar microstructure and high salt loadings will be presented on this poster contribution. Amorphous poly(ethylene oxide) (PEO) is often used as solvent in conventional solid polymer electrolytes (SPEs). PEO shows favorable interactions with lithium salts commonly used in electrolytes and allows ion transport between chains as well. Many other polymers have been investigated to improve conductivity and safety of the electrolyte. Generally, operational safety of the battery is improved when using rigid polymers. These polymer types can suppress dendrite growth and provide mechanical stability. Unfortunately, the rigidity directly impedes the ion mobility due to decreased segmental dynamics. Block copolymers provide the ability to tune the mechanical and ion–transport properties of the blocks independent from each other. We report results about the ion transport in block–copolymer electrolytes with lamellar microstructure which experimentally have displayed very high conductivities. In those observations the ionically conducting PEO domain consists of short PEO chains that can accommodate high salt concentrations. Upon addition of large amounts of salt, a salt–rich layer forms within the lamella. From the preparation of the lamellae there remains non–volatile Tetrahydrofuran (THF) too [1,2]. We employ Molecular Dynamics (MD) simulations to understand the ion transport mechanism and compare our findings to earlier MD simulations of classical PEObased SPEs [3-5]. The role of the remaining THF and the unique properties of salt–rich lamellar structures are presented.

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Investigation of Ion Transport Properties of Li-ion in Hybrid Electrolyte Interfaces using Molecular Dynamics Simulation

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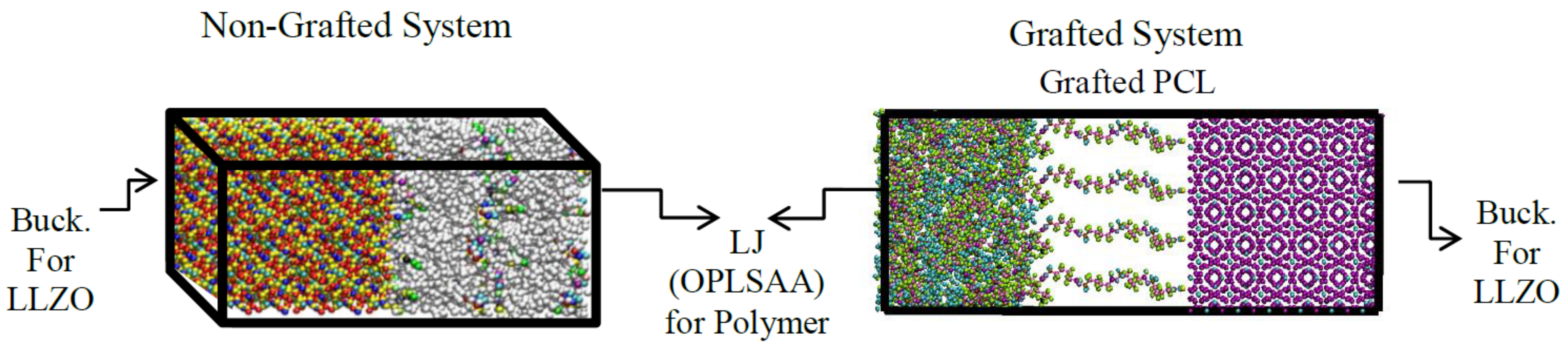
Several studies have been conducted to develop novel materials for use as electrolytes, aiming to enhance the performance of batteries in terms of ionic conductivity. Although polymers play a predominant role in electrolytes, the superior mechanical stability of solid electrolytes has spurred the development of hybrid electrolytes that combine the best attributes of both phases. In our work, we are investigating the interface between a Li salt containing polycaprolactone polymer and LLZO ($Li7La3Zr2O12$) solid electrolyte, using molecular dynamics simulations. Experiments have shown that polycaprolactone (PCL) exhibits better conductivity when grafted onto solid electrolytes in hybrid systems, compared to non grafted systems. We employed different Buckingham potential sets for LLZO and standard OPLS AA parameters for the polymers to examine the interfaces in these hybrid systems. Furthermore, we varied the number of grafted polymer chains on the solid surface to compare the behavior of grafted and non grafted interfaces. These simulations were carried out using the LAMMPS simulation software. Different force field sets for the solid electrolytes have shown considerable impact on Li ion migration both at the interface and within the solid phase at a consistent temperature. This is mainly attributed to the presence of different predominant phases, such as tetragonal or cubic, within the solid electrolyte.

Hybrid System with LLZO and

Polycaprolactones (PCL) with LITFSI salt



In-situ and Operando Analysis of the Potassium-Polymer Electrolyte Interface

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Potassium-ion batteries (KIBs) are considered a promising post-lithium battery technology. It has a list of advantages; one of them being its high abundance leading to potentially lower material costs. Moreover, it can work at high operating voltages [1]. Modern liquid-organic battery electrolytes suffer from recurrent irreversible electrolyte degradation reactions at the solid electrolyte interfaces (SEIs), causing significant interface resistances, dendrite growth, and fast electrolyte consumption, culminating in a rapid capacity fade [2]. However, it was found for post-Li battery technologies (e.g. Na- or K-ion batteries) that the protection by the SEI layer is insufficient leading to notably shorter battery life. In this respect, solid polymer electrolytes (SPE) offer significantly improved (electro)chemical stability [3]. The stability of functional polymer materials at the highly reactive potassium metal interface is not fully understood and challenging to study by conventional means [4-6]. The degree of irreversible reactions is highly relevant, especially in so-called anode-free setups because of the limited potassium supply. Although post-mortem photoelectron spectroscopy (PES) is often used to study the degradation of liquid electrolytes and subsequent SEI formation, the high adhesion between the PEO-based SPE and the metallic interface prevents easy access to the interface required for this surface-sensitive technique. Therefore, to access the interface region and to evaluate electrolyte stability at the electrode-SPE interface a novel approach is examined herein: thin layers of Ni are deposited onto a SPE to serve as permeable current collector for photoelectrons generated at the electrode-electrolyte interface, leveraging the higher probing depths of hard X-ray PES (HAXPES) at the KMC-1 beamline at BESSY II. This anode-free KIB configuration allows both in-situ or operando PES studies to observe the growth of metallic potassium at the interface under high vacuum conditions and at elevated temperatures. This technique has the potential to classify polymer building blocks according to their (electro)chemical stability to mitigate high irreversible losses in next-generation SPEs by tailored design. In this contribution, we demonstrate the feasibility of in-situ/operando experiments on anode-free polymer-based solid-state KIBs by investigating the potassium plating at the negative electrode and the electrode-electrolyte interface evolution.

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Study of the interface between inorganic and polymer solid electrolytes for enhanced ion transport

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In recent times, solid-state batteries (SSBs) have become popular among the battery community. Unlike lithium-ion batteries (LIBs), they have a high energy density and are less flammable. The idea behind SSBs is to replace the liquid electrolyte with a solid electrolyte. Inorganic solid electrolytes (SE) and polymer electrolytes (PE) are the two established categories of SE. SEs have high ionic conductivity but are brittle. On the other hand PEs have low ionic conductivity but possess softness and flexibility, which adds up to a benefit for easy fabrication. Therefore, combinations of SE and PE, so-called hybrid electrolytes (HEs) may have the advantages of both categories.

The performance of HEs is limited by the interfacial resistance between PE and SE. The PE/SE interface is not yet extensively studied in the literature so far. In this study, we investigate the PE/SE interface utilizing surface-sensitive techniques, including time-of-flight secondary ion mass spectrometry (Tof-SIMS) and four-electrode electrochemical measurements, such as electrochemical impedance spectroscopy (EIS). This comprehensive exploration of the electrochemical and chemical properties of the interface/interphase allows for enhanced optimization of ionic conduction in HEs. To study this, NASICON-type LAGP pellets are synthesized, PEO-LiTFSI polymer films are prepared using a solvent-free method, and cells are assembled with lithium metal electrodes. The PE/SE interface is studied using EIS. The equivalent circuit model is used to understand different contributions in the EIS spectrum. Arrhenius measurements are performed to analyze the dependency of the PE/SE interface resistance on temperature. Additionally, Tof-SIMS depth profiles of PE and SE after disassembling of the cells revealed the chemical composition of the interphase formed between both materials.

Polymer Ceramic Electrolytes and Electrodes for Medium Temperature Sodium-Batteries

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The development of rechargeable high-performance batteries is one of the major challenges of the present time. In contrast to the state-of-the-art Li-ion based battery systems, sodium-ion batteries have lower manufacturing costs, a higher safety, and require less or no critical resources. However, the typically used liquid organic electrolyte pose a serious safety risk due to the high chemical reactivity of the metallic sodium-anode. Side reactions can cause dendrite growth, which can lead to short circuits and ultimately to a fire. All-solid-state sodium-ion batteries (ASIB, Figure 1) provide a solution by integrating polymer- or/ and inorganic solid electrolytes (SE).

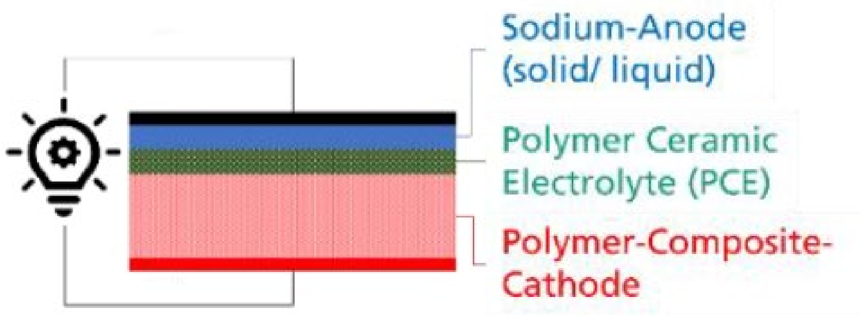

Figure 1: Scheme of an all-solid-state sodium-ion battery

These are not flammable, and the energy density of sodium batteries can be improved significantly. When inorganic SEs are integrated into a polymer electrolyte, their positive properties of strength and high conductivity are combined with high flexibility. [1,2] Publications on the use of inorganic oxide particles, for example NASICON (Na Super Ionic Conductor) based structures or Na-ß-aluminate, as ionic conductors in PCEs for ASIB are rare and need a better understanding. [3,4] The high conductivity (~4x10-4 S/cm at 60 °C) of PCE with Na-ß-aluminate systems displays the high potential for use in ASIB. In this study, Na-ß-aluminate electrolytes are dispersed into a solvent-free UV cross-linkable PEO matrix including a dissolved sodium salt to achieve the high conductivity, which will be presented in detail. The next key challenge in this effort will be integrating the PCE with cathode to form the composites. As a result, selecting an appropriate cathode that exhibits stable redox behavior over a wide temperature range and electrochemical stability in the polymer matrix is very critical for achieving high safety, high specific capacity, and long cycling life. [5] For this purpose we have chosen Na3V2(PO4)3 (NVP) with a NASICON structure as a potential suitable candidate for ASIB and the initial findings will be described in detail.

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