

Moving Down Group 1: Analytical Challenges and Current Trends for Solid Polymer Electrolytes in Post-Li Battery Applications

Fabian Jeschull*^[a]

The solid polymer electrolyte (SPE) field has traditionally struggled with sufficiently high cation conduction at room temperature. The reason for this is that ion transport is usually coupled to polymer chain mobility and as such is strongly temperature dependent. The diversification of battery technologies from Li-ion into Na- and K-ion batteries has revived efforts in the 80s and 90s to develop a broad conceptual understanding and to find overarching trends of the ion transport properties of SPEs based on Group 1 elements, Li⁺, Na⁺, K⁺,

Rb⁺ and Cs⁺ (i.e. beyond Li). This development brings its own set of challenges, starting from additional constraints to measure heavier cations. With a clearer aim towards tangible battery applications, particularly electrochemical stability and interphase formation, and together with a rising sensibility of sustainability aspects, other parameters have gained more relevance and opened new vectors of research. The associated scientific challenges and recent developments of Group 1 based SPEs shall be reviewed.

Introduction

Battery technology development has strongly accelerated over the past decade in search of more sustainable, high-energy storage solutions that are free of critical raw materials, preferably without fluorine-containing compounds or other toxic, volatile chemicals. In particular, the raw material issue is a scientific challenge that post-lithium batteries could potentially solve and that has already led to commercial Na-ion batteries (NIBs) entering the market. Overall this can be viewed as a diversification into alternative cell chemistries and battery technologies.

At lower technology readiness levels (TRL), i.e. on laboratory scales, several other mono- and multivalent cell concepts have attracted strong interest from the battery community. For monovalent systems, these include K-ion batteries (KIBs)^[1] and even pioneering work on Rb-ion batteries.^[2] From a scientific point of view, comparisons between different cell chemistries, such as those currently being carried out within the alkali metal group, are extremely valuable because they reveal overarching trends and show the limits of what is scientifically feasible. One domain within battery research quite clearly illustrates the potential opportunities and major challenges of moving down the Group 1 elements is solid polymer electrolytes (SPEs). SPEs consist of a conductive salt and a polymer host matrix that

promotes ion transport in the solid state. These materials are used as flexible, ion-conducting thin-film separators in rechargeable batteries, enabling potentially safer (no volatile, liquid components) and denser cell configurations. However, ion transport is highly temperature dependent as it is coupled to the mobility of the polymer chains^[3] and therefore SPEs typically only reach sufficient ionic conductivity only at elevated temperatures. Nevertheless, SPE-based Li-ion batteries (LIBs) are the only commercialized solid-state LIB technology (Blue Solutions, Bolloré Group) and have been around for more than a decade.^[4]

Looking back at 50 years of SPE research, many previous experiments are revisited with current state-of-the-art polymers and electrolyte salts. Recent achievements include for example cycling of post-Li (NIB and KIB) SPE-based cells under near ambient conditions (~40–45 °C).^[5,6] Here, a comparative summary based on recent studies on the impact of different Group 1 cations on SPE properties will be outlined, with a strict focus on liquid-free systems (thus excluding gel polymer electrolytes). In addition, major challenges that have accompanied this field and that continue to pose problems are discussed, particularly in the context of characterizing SPE properties for post-Li systems. Equally important is an outlook on new research directions, especially in the light of increasing sustainability concerns.

Impact of Cation Size on Electrolyte Properties – a Case Study of PEO-based SPEs

Poly(ethylene oxide) is the unrivalled benchmark to assess the ion transport properties of polymer electrolytes for battery applications.

[a] Dr. F. Jeschull
Institute for Applied Materials – Energy Storage Systems (IAM-ESS)
Karlsruhe Institute of Technology (KIT)
Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen,
Germany
E-mail: fabian.jeschull@kit.edu

© 2024 The Authors. ChemElectroChem published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

Many overarching trends are thus studied in this reference system. While PEO:LiX (X=TFSI⁻, FSI⁻, ClO₄⁻, etc.) complexes have been studied extensively for more than 40 years,^[16] including pioneering work on a range of other mono- and multivalent cations,^[17–20] a steadily increasing number of studies is now appearing for PEO complexes from salts of heavier alkali metals, especially the triflimidates TFSI⁻ ((CF₃SO₂)₂N⁻) and FSI⁻ ((FSO₂)₂N⁻). The results from these studies deliver important puzzle pieces to understand in better detail polymer-cation interactions of Group 1 elements and their impact on ion transport.

Coordination and Salt Dissolution Properties. From early crystallographic works it is known that the coordination environment of the cation changes in dependence of charge and cation radius in crystalline PEO:A⁺ complexes (i.e. high electrolyte salt concentrations),^[21] ranging from 3 (Li), 4 (Na) to 5 (K, Rb), as well as two coordinating anions. For polyether chains to wrap around larger cations, changes in polymer conformation are necessary, which is then reflected in longer coordinate bonds. A comprehensive molecular dynamic study by Fortuin *et al.*^[14] recently supported these trends down the Group 1 elements (though the EO:A⁺ ratio of 20:1 was higher), i.e. with increasing cation size the coordinate bond distance and coordination number increase (in their study 6 (Li), 7 (Na) and 8 (K, Cs)). Interestingly, the study found weaker cation-anion interactions in PEO:ATFSI complexes of A=Na, K and Cs, suggesting (nearly) complete dissociation with an optimum for PEO:NaTFSI complexes. This appears to be in general agreement with decreasing ion pair dissociation energies of ATFSI salts with increasing cation size (from 591 kJ mol⁻¹ (Li) to 495 kJ mol⁻¹ (Na) and ~420 kJ mol⁻¹ (K)) on the basis of DFT calculations.^[7] Experimentally, Andersson *et al.*^[22] determined the Gibbs free energy of dissociation (ΔG^0) from ligand exchange experiments as a measure of the cation-PEO coordination strength. Due to a smaller entropic contribution, ΔG^0 at 25 °C is smaller for NaTFSI ($\Delta G^0 = -9.5$ kJ mol⁻¹) than for LiTFSI ($\Delta G^0 = -10.2$ kJ mol⁻¹). Overall, this should result in low ion pair formation, higher ion mobility, and improved ionic conductivities.

Ionic conductivities. Two recent studies^[7,13] concluded that the ionic conductivity of PEO:ATFSI complexes does not change significantly above the melting temperature of the SPE across the Group 1 elements Li, Na, K and Cs. A comparison over a



Fabian Jeschull is leading the 'Electrolytes and electrochemical Methods' group at the Institute for Applied Materials – Energy Storage Systems (IAM-ESS) at the Karlsruhe Institute of Technology (KIT). His research focuses on liquid and solid electrolytes for post-Li batteries with a focus on degradation processes that are studied by electrochemical and surface analytical techniques. Dr. Jeschull worked as a postdoc at the Paul Scherrer Institute (PSI), Switzerland in the Novák group and received his PhD in chemistry from Uppsala University, Sweden, under the supervision of Prof. Daniel Brandell.

small selection of recent studies in Figure 1A confirms this trend for PEO:ATFSI (20:1) complexes. Differences in ionic conductivity are more pronounced in samples of AFSI-based SPEs (Figure 1B). DC polarization measurements by Oteo *et al.*^[7] further suggest higher transference numbers of heavier cations (Table 1), which agrees well with the trends in ion coordination strength. However, using electrophoretic NMR (eNMR) instead, Mönich *et al.*^[23] obtained similar transference numbers for PEO:ATFSI complexes (A=Li, Na, K; M_n(PEO) = 4 kg mol⁻¹) in the range of 0.14–0.2 and contrarily concluded no substantial difference in cation-PEO interactions. In fact, accurate T₊ measurements are a major roadblock in post-Li systems, which will be further discussed below.

Thermal and Rheological Properties. For PEO:KTFSI blends melting temperatures as low as 37 °C (Table 1) were measured that lead to less marked decrease in ionic conductivity in the temperature region between 25–65 °C, which should have a positive impact on the polymer chain mobility and thus 'near ambient' cell cycling. However, the changes in the thermal behavior lead to marked differences in the rheological properties up to the point at which some compositions lose their mechanical integrity. In Figure 1C this behavior is exemplified for PEO:KTFSI composites, where a EO:K 12:1 formulation shows viscous-fluid properties (loss modulus, G'' > storage modulus, G') at low oscillation stress, rendering this composition unsuitable as separator. This motivated several revised material approaches, including PEO-based block copolymers,^[13,24] polymer blends^[25] or ceramic fillers^[5] to improve the mechanical properties. Especially, block copolymers with non-conductive segments imparting better mechanical properties have been widely explored for this purpose for Li-based SPEs.^[24,26] They also exhibit interesting anisotropic ionic conductivity behavior as a function of their microphase separated domains.^[27]

Furthermore, ion transport properties can significantly change when ether-oxygen groups are replaced by other coordinating groups, such as the carbonyl-units in polycarbonates,^[28,29] polyesters^[30] and their copolymers.^[31] These materials have had a considerable impact on the SPE field in the last decade and greatly contributed to a more diversified polymer portfolio.^[16] Electrophoretic NMR studies^[32] show that polymer-cation interactions carbonyl-coordinating groups are weaker. This leads to more ion pairing and lower degrees of dissociation, but on the other hand the dissociated cations exhibit higher mobilities. The focus on Li-SPEs is also here slowly shifting towards PEO alternatives for post-Li systems (e.g. ref^[33]), but does not come close to the number of studies on PEO-containing materials.

The Cell Challenge: Reproducibility, Comparability, Material Availability

It is a positive development that cell tests have become an integral part of SPE studies. Especially within the last decade the number of cell tests of SPE-based alkali-ion,^[6] alkali-metal (e.g. Li,^[29,34] Na,^[6,35] K^[9,13]) and anode-less^[36] battery configura-

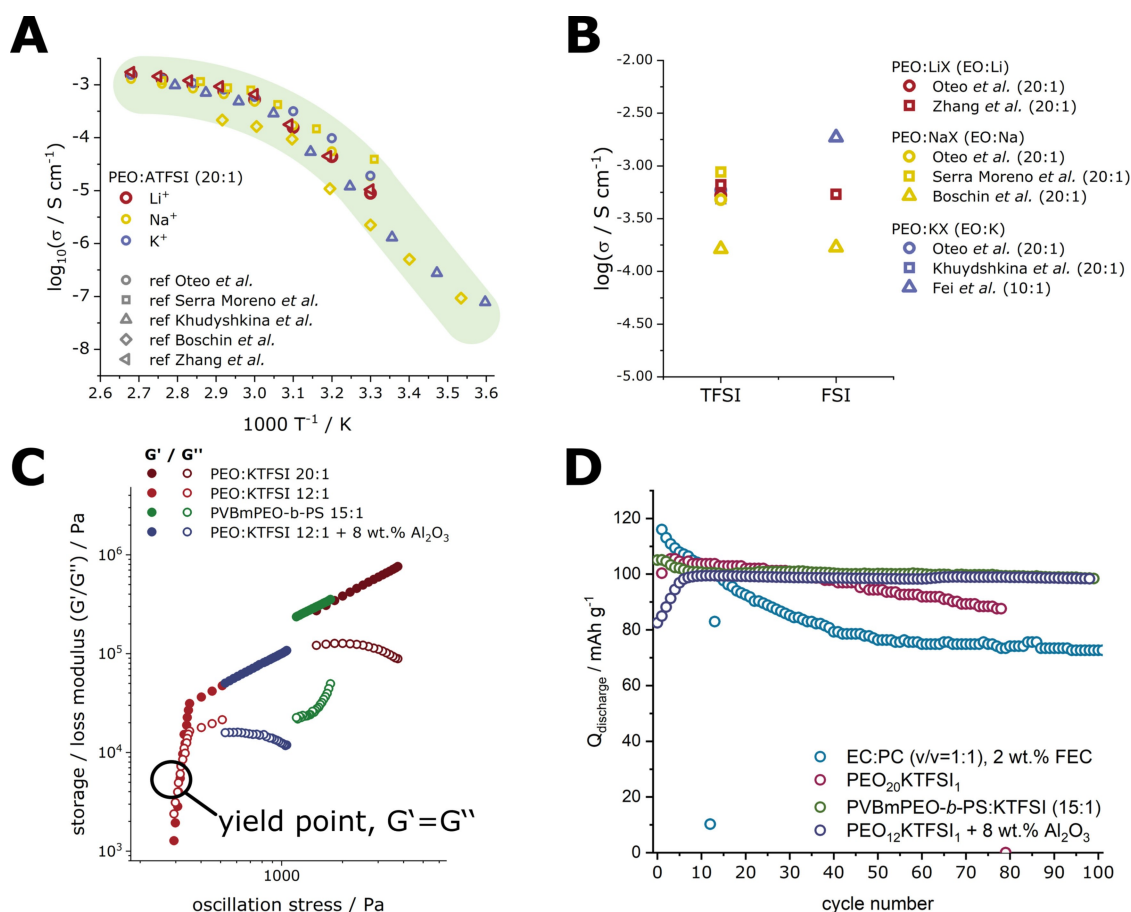


Figure 1. Results of a small meta study including references [7–11] on A) the ionic conductivities of PEO:ATFSI (EO:A = 20:1; A=Li, Na, K) electrolytes and B) the ionic conductivities of PEO:AX (EO:A = 20:1 or 10:1, A=Li, Na, K and X=TFSI or FSI) electrolytes for values reported in the temperature range from 55 to 60 °C. The data was extracted from the original publications using the WebPlotDigitizer online tool.^[12] The bottom row summarizes results from C) oscillatory rheology and D) cell testing in K|SPE|K₂Fe[Fe(CN)₆]₂ configurations at 55 °C against a corresponding liquid electrolyte system (750 mM KPF₆ in EC:PC, v/v = 1:1 + 2 wt.% FEC) from references^[5,9,13] for two different PEO:KTFSI compositions, a styrene-PEO based block copolymer and an PEO:KTFSI/Al₂O₃ composite.

Cation	EO:A ratio	T _g (T _m)/°C	crystallinity ^{a)} / %	T ₊ ^{b)} (°C)	Ref
Li ⁺	20:1	−40 (57)	47	0.22 (70)	[7]
Na ⁺	20:1	−35.3 (61.4)	45.4	0.66 (70) ^[7]	[7,8]
				0.39 (75) ^[8]	
K ⁺	12:1	−34 (49.8/58.1)	1.5	–	[8]
	20:1	−48.1 (37/53)	34.7	0.32 (70) ^{c)}	[9,14]
	12:1	−47.7(39.5)	11.1	–	[9]

a) crystallinity was calculated based on the th. melting enthalpy of PEO. b) determined by the method reported by DC polarization.^[15] c) value determined by MD simulation, according to ref [14].

tions have increased sharply and has even moved beyond lab-scale testing.^[37] As with liquid electrolytes, the choice of cell setup and cell construction have profound effects on cell performance and lead to very different results even when the same material is being investigated.^[38,39] Moreover, pre-conditioning protocols have a significant impact on overpotentials and capacities in the first cycles,^[29] which is typically due to initial contact problems that disappear over time at elevated temperatures, as the polymer creeps into the remaining void

space of the composite electrode. Internal cell pressure, operating temperature, and rheological aspects thus affect the time required for establishing good contact significantly. Contrary to ceramic electrolytes, SPEs as soft materials show only little pressure dependence and can adapt more readily to morphological changes in electrode composites.

Alkali-Metal Batteries. As with most solid-state cell configurations, the use of a metallic electrode is considered advantageous from an energy density perspective. On a lab scale, this

typically means that cells are tested with a vast excess of charge carrier inventory at the negative electrode, particularly when the mass loading of the positive electrode is low. Therefore, irreversible losses can easily be masked, as they can be compensated over many cycles by the metallic electrode. In addition to a wide range of electrode mass loadings, different materials are used in the positive electrode. In LIBs these are mostly lithium iron phosphate (LFP) with a comparatively low redox potential (~ 3.5 V vs. Li^+/Li) and various layered oxides with potential cut-offs up to 4.3 V vs. Li^+/Li . As a result, the cell performance can turn out quite differently, depending on the anodic (oxidative) stability of the electrolyte under these conditions.^[40] In fact, the availability of commercial electrode materials for LIBs helps the reproducibility of research results over in-house synthesized materials. Unfortunately, electrode formulations can still vary widely, and although commercial electrode coatings are available, infiltration of such electrodes with a solid electrolyte is only a compromise, as the electrolyte phase is best mixed into the electrode slurry during preparation. In contrast, comparability across different cell chemistries is considerably more challenging to achieve, considering that the material availability and the material portfolio is greatly limited (NIBs) or not available at all (KIBs). In this case the only fallback option is to prepare electrode materials in-house, as is frequently done with Prussian blue analogues ($\text{A}_2\text{M}[\text{Fe}(\text{CN})_6]$, $\text{A}=\text{Na}, \text{K}$, $\text{M}=\text{transition metal}$, mostly Fe & Mn). For the limited material cases where the same active material class can be used for cell tests, differences in redox potentials and thus voltage windows can still cause different degrees of degradation. To avoid the use of the frequently cited standard hydrogen electrode (SHE) potentials, which refer to aqueous electrolytes, referencing against Li^+/Li is more practical in first approximation, using reported potential differences in non-aqueous electrolytes (e.g. $E(\text{Na}^+/\text{Na})=0.23$ V and $E(\text{K}^+/\text{K})=-0.09$ V vs. Li^+/Li ^[1]). The comparatively low average redox potentials of $\text{Na}_3\text{V}_2\text{PO}_4$ or $\text{Na}_2\text{Fe}[\text{Fe}(\text{CN})_6]$ (~ 3.4 V and ~ 3.2 V vs. Na^+/Na), are about 300 mV higher on a Li^+/Li scale (cut-off limits shift accordingly).

Anode-less or anode-free batteries are the logical outcome of alkali-metal batteries when aiming for high energy densities and taking into account the charge carrier excess of the metallic negative electrode. During the charge process alkali metal is deposited onto the current collector foil. This process is associated with several issues regarding the deposition process. Because there is no excess alkali metal inventory, the Coulombic efficiency needs to be exceptionally high from the start to maintain high capacity retention. Uniform and reversible deposition strongly depends on the substrate and the reactivity between freshly plated alkali metal and electrolyte components^[41] (see also below). Incidentally, the commonly used Cu current collector at the negative electrode performs poorly, at least for Li-deposition, compared to 'lithiophilic' materials such as Zn, Ag or Au.^[36]

The Transference Number Challenge: Expanding the Toolbox

The most fundamental parameters for evaluating the characteristics of an SPE are its transport properties, defined by the A^+ transport number, t_{A^+} , and its transference number T_{A^+} . The transport number, t_{A^+} , describes the charge fraction of a unit Coulomb that is transferred across the electrode interface by a single non-blocked ionic species (cations in batteries). As SPEs are not dilute systems (< 0.01 M), ion pairing to form solvent-separated contact ion pairs (SSIPs and CIPs), and charged clusters in (super-)concentrated environments is common.^[42] In this case a variety of non-blocked ionic species, which include the migration of triplets or ion clusters, contribute to the ion transport, as illustrated in Figure 2A. Most techniques cannot distinguish between these different species. The sum of their individual contributions is expressed in the transference number, T_{A^+} .^[42] It is a measure of the maximum load (current) that an electrolyte can support.^[42] Under these non-ideal conditions, transport and transference number are not the same. In practice, however, the assumptions of an ideal electrolyte are prevalent and the theoretical basis for prominent experimental approaches.^[43] Electrochemically transference numbers are determined by a DC polarization technique introduced by Bruce and Vincent^[15] in symmetric cells with metallic electrodes (to exclude influences from electrode tortuosity). Although the presence of interphases is accounted for and appears to hold reasonably well for Li-systems, the deviations and issues with the technique become critical in more reactive systems of Na- and K-symmetric cells, where surface layer resistances are significantly larger. Moreover, the cell impedance changes strongly under applied current (Figure 2B). This makes an accurate determination of the required parameter set from electrochemical impedance spectroscopy (EIS) more challenging.^[13,23,44]

An alternative approach are solid-state NMR (ssNMR) techniques, e.g. pulse-field gradient NMR (PFG-NMR) to measure (self-)diffusion coefficients and electrophoretic NMR (eNMR) to measure cation migration in an electric field. Both techniques encounter challenges when moving from the NMR-active ^7Li nucleus to the heavier Group 1 elements ^{23}Na and ^{39}K , as the nuclei exhibit too short relaxation times.^[8,13,23] In such cases, it mostly the ^{19}F signals of fluorine-containing anions that provide meaningful information. Diffusion coefficients for Na- and K-ions could be obtained indirectly if the total ionic conductivity (e.g. from EIS) and the anion partial conductivity are known.^[13,23] Another approach are moving-boundary-type experiments, like the radiotracer method or *operando* Raman microspectroscopy as introduced by Fawdon *et al.*,^[45] that track time-dependent concentration gradients of cation, anion or both to derive the transport and thermodynamic electrolyte properties (Figure 2C).

Radiotracer experiments or Hittorf-type methods usually require sectioning of the electrolyte to determine concentration changes. The former was used for example by Bastek *et al.* to determine the Rb^+ diffusion in $\text{PEO}_{30}\text{RbI}$ electrolytes.^[46]

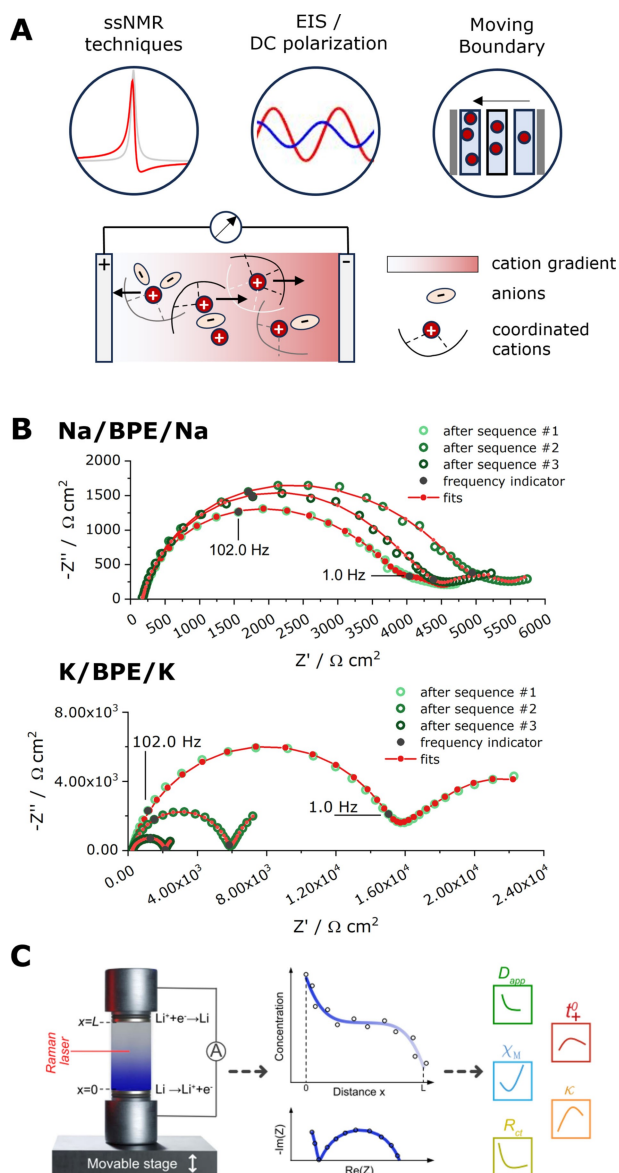


Figure 2. A) Illustration of different cationic species formed in a SPE and a selection of commonly used analytical techniques to measure transference numbers. B) EIS spectra of Na/Na and K/K symmetric cells with a PEO-based block copolymer solid electrolyte (BPE) recorded at 55 °C after three consecutive cycling sequences comprising of 10 cycles at 10, 20 and 50 $\mu\text{A cm}^{-2}$, respectively (Reprinted with permission.^[44] Copyright 2024, Xing *et al.*). C) Operando Raman microspectroscopy setup to determine transport and thermodynamic electrolyte properties (Adapted with permission.^[45] Copyright 2021, Fawdon *et al.*).

A Stability Challenge for Polymer Hosts and Salts

The formation of passivating electrode surface layers, namely the solid electrolyte interphase (SEI) on negative electrodes and the cathode electrolyte interphase (CEI) on positive electrodes, is arguably the most challenging part of achieving batteries with long cycle life and high capacity retention, regardless of the type of electrolyte employed. This challenge is twofold, as both the electrolyte medium and electrolyte salt either need

broad electrochemical stability windows or need to form protective interphase layers to prevent recurrent degradation processes. The reactivity of alkali metals generally increases down the Group 1 elements, as demonstrated by the observation of parasitic heat flow in symmetric cells by isothermal calorimetry.^[44] Polyethers typically display high cathodic stability towards alkali metals,^[47] contrary to polycarbonates (e.g. PEC and PPC) which have been reported to depolymerize.^[48] A major driver for this process might not be the alkali metal itself, but the fact that surface groups, like oxides and hydroxides,^[49] initiate the degradation. The role of the electrolyte salt should not be underestimated with respect of the formation of protective surface layers, which becomes most apparent in multivalent systems:

Anions prone to reductive degradation, such as FSI^- , are increasingly used to improve the reversibility of metallic electrodes.^[47] Their stability can be tuned as a function of salt concentration and choice of solvent that affect the degree of ion pairing. Compared to the cathodic electrolyte stability, the anodic stability at potentials above 4 V vs. Li^+/Li , is widely recognized as a considerable roadblock, as the number of polymers (or salts) that show sufficient inertness with increasing upper voltage cut-off limits (up to 4.3–5.0 V vs. Li^+/Li) becomes small. Unfortunately, the onset of electrolyte degradation is difficult to pinpoint, as it is poorly defined, highly dependent on the electrochemical technique used, and influenced by settings (e.g. scan or current density) and the positive electrode material itself.^[52] Qiu *et al.*^[53] therefore proposed surface coatings on layered oxides as a means of suppressing surface-mediated polymer degradation. Their findings indicated that polyanionic compounds are more benign in this regard. Instead of searching for a universal material to cover the entire electrochemical window, Arrese-Igor *et al.*^[54,55] introduced double-layer polymer electrolytes with a polyether layer on the negative electrode side and a polycarbonate-based electrolyte as catholyte, which greatly improved the capacity retention of Li-NMC622 configurations. To navigate the vast chemical space of potentially stable monomers and polymer architectures, the SPE field appears to lack clear design principles from methodically classifying degradation of polymer building blocks beyond electrochemical testing. Furthermore, stability tests are performed with a wide range of different electrolyte compositions, which is reasonable given that each polymer-salt combination has different physicochemical properties. However, this further dilutes the chances of finding overarching trends, either across systems with different cationic species or across polymeric materials.

The Interphase Challenge: Electrolyte Degradation At Buried Interfaces

The study of interfacial properties is particularly challenging when the surface region is difficult to access, as it is hard to separate the electrolyte from the electrode after cycling without damaging the interphase layer. The pool of available techniques

is comparatively limited. Although various electrochemical techniques can correlate the onset of degradation with potential (voltametric techniques^[40,56]) and parasitic currents, heat flow (microcalorimetry^[44]), gas evolution (online electrochemical mass spectrometry, OEMS^[56]) or resistance changes (e.g. electrochemical impedance spectroscopy, EIS^[44]). Zaghib and coworkers took a more visual approach, using *in-situ* scanning electron microscopy (SEM) experiments to investigate the surface layer evolution, dendrite growth and associated changes in electrolyte and electrode layer thickness.^[4,57] Complementary microscopy and chemical analysis, e.g. ion milling or sputtering coupled with X-ray photoelectron spectroscopy (XPS) or time-of-flight secondary ion mass spectrometry (ToF-SIMS),^[58,59] may introduce artefacts from surface roughening due to different sputter rates of organic and inorganic compounds, sputter-induced degradation of SEI components,^[60] and specifically in SPEs there is a risk of degradation due to local heat generation. Eliminating sample preparation bias is thus a considerable challenge and a setback for established techniques like XPS, where the high surface sensitivity (< 10 nm for in-house spectrometers) becomes a problem, as the region of interest is buried underneath a solid electrolyte layer. Recent studies have therefore aimed to move beyond post-mortem XPS experiments^[31,61] and bypass sample preparation issues by studying interfaces formed after deposition of Li metal onto polymer electrolyte films (Figure 3A),^[41,62] as previously demonstrated in the ceramic electrolyte field.^[51]

Through the possibility of varying the excitation energy at synchrotron facilities, surface layer compositions can be investigated at different probing depths. For building chemically stable polymers, this technique has its merits in identifying monomer units that exhibit high stability or decompose in 'benign' degradation products. In the SPE field this work was so far limited to processes at the Li/SPE interface. Future activities are thus likely to expand to the positive electrode and into other battery chemistries. The recent progress further motivates the next leap forward: *operando* XPS experiments on the basis of current collector and metallic surface deposits at the negative electrode (Figure 3B)^[50] and also in composite electrodes at the positive electrode^[63] have been introduced in the ceramic electrolyte community.

The Sustainability Challenge: Fluorine-Free, Energy-Efficient, Abundant and Recyclable

To develop better materials for tomorrow, their development today has to follow increasingly stringent sustainability criteria to enable resource-efficient and environmentally friendly material platforms. In battery research this issue is often associated with critical raw materials for cathode active materials, including cobalt or nickel, and energy-intensive synthesis processes, especially process heat or purification and handling of production waste. However, what is sometimes neglected in the case of supposedly 'green' materials based on of more abundant and sustainable raw material platforms is the

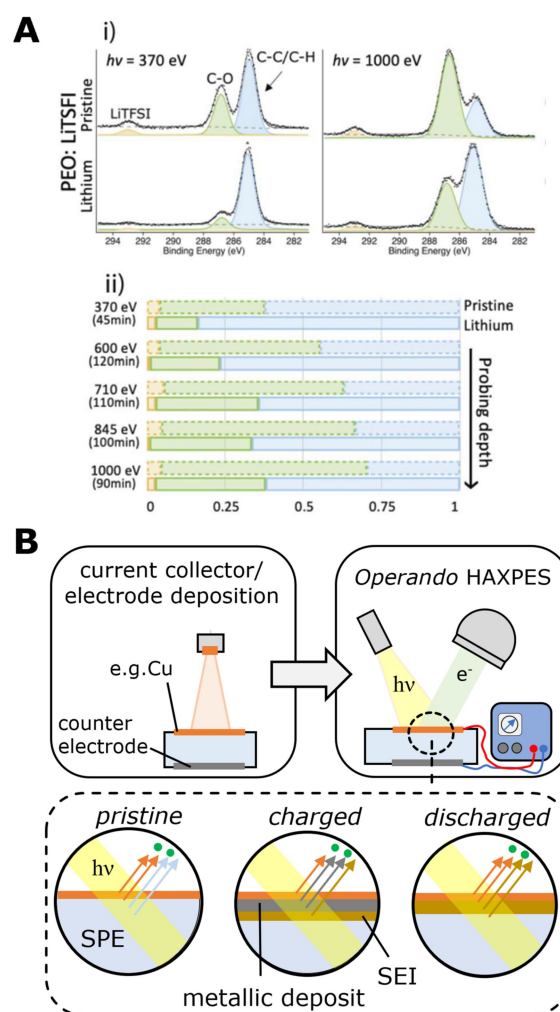


Figure 3. A) Chemical degradation of PEO:LiTFSI SPE in contact with deposited layers of lithium studied by photoelectron spectroscopy at two different photon energies before and after the deposition (i). (ii) illustrated compositional changes in the surface layer as a function of probing depth. Adapted with permission from ref.^[41] Copyright 2021, Andersson *et al.* B) Schematic of in-situ/operando experiments reproduced and edited from ref. [50,51].

fact that their environmental impact may still be worse than the materials they intended to replace if this is at the cost of compromises in capacity or average potential.^[64] In this case, larger amounts of active materials and other electrode components are needed, more energy is required during production and more waste is generated to produce 1 kWh of battery.^[65] Ironically, moving to less critical materials may render recycling activities less attractive, both economically and environmentally, in terms of the cost of beneficiation of battery materials, and may become critical for materials such as LiFePO₄ (LFP)^[66] or Prussian blue analogues (e.g. A₂Fe[Fe(CN)₆], A=Na, K). Consequently, it is misguided to assess post-Li battery technologies solely on the basis of the materials they avoid, as the overall environmental impact along the battery value chain is much more complex.

The challenges for electrolyte components are equally big:

- fluorine-containing electrolyte salts or monomer segments ought to be replaced,
- synthesis procedures based on 'green' material platforms under the use of non-hazardous solvents and energy-efficient conditions,
- recycling procedures for solid-state batteries, particularly SPE-based, is still in its infancy

Per- or polyfluoroalkyl substances (PFAS – the 'forever' chemicals) are anthropogenic compounds that are particularly persistent bioaccumulation and have a high ecotoxicological potential. Fluorinated compounds are ubiquitous in batteries, as binders (e.g. poly(vinylidene difluoride), PVDF), electrolyte salts (e.g. LiTFSI),^[67] electrolyte additives or solvents (e.g. fluoroethylene carbonate, FEC)^[68] and as undefined organic fluorinated degradation products and inorganic fluorides in the SEI layer.^[69,70] This is a double-edged sword, considering that in copolymers fluorinated groups or blocks have been shown to improve electrochemical stability and electrode interfaces.^[71,72] Although, perfluorinated polymers display comparatively low toxicity levels, their synthesis involves more potent fluorinated compounds.^[73,74] In recycling processes there is a risk of fluorinated compounds entering the waste stream and accumulation in nature.^[75] In this context, the synthesis of PEO and many polycarbonates from ethylene oxide as a platform chemical of the petrochemical industry also needs to be critically reviewed.^[76]

The fluorinated FSI- and TFSI-anions dominate the SPE-field for their non-coordinating and plasticizing nature, thus promoting improved ion transport. Alternative fluorine-free salts have been considered and are likely to play a more prominent role in the future, including percyano-anions (e.g. 2,4,5-tricyanoimidazole, TIM or 2,3,4,5-tetracyanopirrolate, TCP^[77,78]) and various bis(chelate)borates including the well-known bis(oxalate)borate, BOB,^[79] or tetraphenylborates (BPh₄⁻).^[80] Many of these salts have already found their way into post-Li applications, such as NaTIM^[78] or KBPh₄,^[80] which is an important step towards fluorine-free cell concepts.

Recycling is key to keeping critical raw materials from active materials and electrolytes in the loop of a battery economy, especially when their mining, extraction and purification is energy intensive.^[81] In SPE-based cells the polymer itself is of relatively low value compared to electrolyte salt and active materials and the polymer matrix can be difficult to separate. For example, high-molecular PEO, although biodegradable, only dissolves slowly in solvents like acetonitrile. In contrast, ceramic solids can be dissolved or leached, allowing to redirect solid and liquid fraction in further mechanical, hydrometallurgical or direct recycling steps.^[82,83] The difficulties in dealing with the polymer matrix may be one reason why there are no prominent examples of recycled SPE-based cells yet. Even in recycling processes of liquid-electrolyte-based cells the recovery rates of liquid components can be low^[82] or, the organic materials are incinerated in pyrometallurgical recycling processes.^[84] On the other hand, chemical upcycling of plastic waste is also a route to more sustainable polymers for SPE applications, as Saito *et al.*^[85] recently demonstrated on a depolymerization strategy

of a bisphenol A-polycarbonate thermoplast to first produce poly(trimethylene carbonate) and then corresponding SPEs.

Summary and Outlook

With the increasing interest in post-Li battery systems, the largely Li-dominated SPE field is also shifting towards other monovalent (and multivalent) cation conductors. New information on the underlying transport processes can be gained by examining the overarching trends of Group 1 cations in SPEs by looking back at more than 40 years of research and by creating new perspective by leveraging methodological advances. Questions about cation transport, ion pairing, and transport numbers still remain unsatisfactorily answered in post-Li systems, where such studies face additional experimental challenges. However, at a practical level, the integration of SPEs into post-Li batteries operating at near ambient temperature has already been demonstrated and appears more probable than in corresponding Li systems. As a result, a number of scientific questions related to the (electro)chemical stability at the buried electrode-SPE interfaces have become more relevant in recent years. A deeper understanding of the degradation pathways of different monomer types could provide valuable insights into future polymer design strategies, which control material properties beyond ion transport and will increasingly need to incorporate sustainability considerations as well. A discussion on this aspect would certainly warrant a separate review. Furthermore, experimental work could greatly benefit from more theoretical work addressing ion transport in post-Li SPE systems, especially for polymer systems other than PEO. For instance, further development of SPE-based cells on the device level would greatly benefit from a deeper understanding of ion transport in particle-polymer matrices (e.g. with respect to tortuosity factors).

Acknowledgements

I would like to express my gratitude to my wonderful team members, the postdocs, PhD and undergraduate students of the 'Electrolytes and Electrochemical Methods' group at IAM-ESS, for their contributions and hard work over the past 5 years. Furthermore, I'd like to extend my gratitude to my collaborators at KIT, Prof. Patrick Théato, Dr. Dominik Voll, and at Uppsala University, Prof. Daniel Brandell, Dr. Guiomar Hernández and Dr. Jonas Mindemark. This work contributes to the research performed within the Post Lithium Storage Cluster of Excellence (POLiS), funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) under Germany's Excellence Strategy – EXC 2154 – Project number 390874152 and DFG grant #448719339, as well as to the research performed at the Center for Electrochemical Energy Storage Ulm-Karlsruhe (CEL-EST). Open Access funding enabled and organized by Projekt DEAL.

Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

Keywords: solid polymer electrolyte (SPE) · post-Li batteries · solid-state batteries (SSB) · ion transport · electrochemical stability

- [1] S. Komaba, T. Hasegawa, M. Dahbi, K. Kubota, *Electrochem. Commun.* **2015**, *60*, 172–175.
- [2] D. Igarashi, R. Tataru, R. Fujimoto, T. Hosaka, S. Komaba, *Chem. Sci.* **2023**, *14*, 11056–11066.
- [3] Z. Song, F. Chen, M. Martinez-Ibañez, W. Feng, M. Forsyth, Z. Zhou, M. Armand, H. Zhang, *Nat. Commun.* **2023**, *14*, 4884.
- [4] P. Hovington, M. Lagace, A. Guerfi, P. Bouchard, A. Mauger, C. M. Julien, M. Armand, K. Zaghib, *Nano Lett.* **2015**, *15*, 2671–2678.
- [5] A. D. Khudyskhina, U.-C. Rauska, A. J. Butzelaar, M. Hoffmann, M. Wilhelm, P. Theato, F. Jeschull, *Batteries & Supercaps* **2024**, *7*, DOI 10.1002/batt.202300404.
- [6] C. Sångeland, R. Younesi, J. Mindemark, D. Brandell, *Energy Storage Mater.* **2019**, *19*, 31–38.
- [7] U. Oteo, M. Martinez-Ibañez, I. Aldalur, E. Sanchez-Diez, J. Carrasco, M. Armand, H. Zhang, *ChemElectroChem* **2019**, *6*, 1019–1022.
- [8] J. Serra Moreno, M. Armand, M. B. Berman, S. G. Greenbaum, B. Scrosati, S. Panero, *J. Power Sources* **2014**, *248*, 695–702.
- [9] A. D. Khudyskhina, P. A. Morozova, A. J. Butzelaar, M. Hoffmann, M. Wilhelm, P. Theato, S. S. Fedotov, F. Jeschull, *ACS Appl. Polym. Mater.* **2022**, *4*, 2734–2746.
- [10] A. Boschini, P. Johansson, *Electrochim. Acta* **2015**, *175*, 124–133.
- [11] H. Zhang, C. Liu, L. Zheng, F. Xu, W. Feng, H. Li, X. Huang, M. Armand, J. Nie, Z. Zhou, *Electrochim. Acta* **2014**, *133*, 529–538.
- [12] A. Rohatgi, n.d.
- [13] A. D. Khudyskhina, A. J. Butzelaar, Y. Guo, M. Hoffmann, T. Bergfeldt, M. Schaller, S. Indris, M. Wilhelm, P. Théato, F. Jeschull, *Electrochim. Acta* **2023**, *454*, 142421.
- [14] B. A. Fortuin, J. Otegi, J. M. López del Amo, S. R. Peña, L. Meabe, H. Manzano, M. Martínez-Ibañez, J. Carrasco, *Phys. Chem. Chem. Phys.* **2023**, *25*, 25038–25054.
- [15] J. Evans, C. A. Vincent, P. G. Bruce, *Polymer* **1987**, *28*, 2324–2328.
- [16] J. Mindemark, M. J. Lacey, T. Bowden, D. Brandell, *Prog. Polym. Sci.* **2018**, *81*, 114–143.
- [17] F. M. Gray, *Polymer Electrolytes*, Royal Society Of Chemistry, United Kingdom, **1997**.
- [18] F. Jeschull, C. Hub, T. I. Kolesnikov, D. Sundermann, G. Hernández, D. Voll, J. Mindemark, P. Théato, *Adv. Energy Mater.* **2023**, *2302745*, 1–17.
- [19] N. S. Schausser, R. Seshadri, R. A. Segalman, *Mol. Syst. Des. Eng.* **2019**, *4*, 263–279.
- [20] B. Park, J. L. Schaefer, *J. Electrochem. Soc.* **2020**, *167*, 070545.
- [21] J. B. Thomson, P. Lightfoot, P. G. Bruce, *Solid State Ionics* **1996**, *85*, 203–208.
- [22] R. Andersson, G. Hernández, J. Mindemark, *Phys. Chem. Chem. Phys.* **2022**, *24*, 16343–16352.
- [23] C. Mönich, R. Andersson, G. Hernández, J. Mindemark, M. Schönhoff, *JACS* **2024**, DOI 10.1021/jacs.3c12272.
- [24] A. J. Butzelaar, P. Röring, T. P. Mach, M. Hoffmann, F. Jeschull, M. Wilhelm, M. Winter, G. Bruncklaus, P. Théato, *ACS Appl. Mater. Interfaces* **2021**, *13*, 39257–39270.
- [25] H. Fei, Y. Liu, Y. An, X. Xu, G. Zeng, Y. Tian, L. Ci, B. Xi, S. Xiong, J. Feng, *J. Power Sources* **2018**, *399*, 294–298.
- [26] M. Singh, O. Odusanya, G. M. Wilmes, H. B. Eitouni, E. D. Gomez, A. J. Patel, V. L. Chen, M. J. Park, P. Fragouli, H. Iatrou, N. Hadjichristidis, D. Cookson, N. P. Balsara, *Macromolecules* **2007**, *40*, 4578–4585.
- [27] R. Jeanne-brou, J. Deseure, T. N. T. Phan, R. Bouchet, D. Devaux, *Electrochim. Acta* **2022**, *434*, 141268.
- [28] Y. Tominaga, K. Yamazaki, *Chem. Commun.* **2014**, *50*, 4448–4450.
- [29] B. Sun, J. Mindemark, K. Edström, D. Brandell, *Solid State Ionics* **2013**, 2–6.
- [30] A. Bergfelt, M. J. Lacey, J. Hedman, C. Sångeland, D. Brandell, T. Bowden, *RSC Adv.* **2018**, *8*, 16716–16725.
- [31] I. L. Johansson, C. Sångeland, T. Uemiya, F. Iwasaki, M. Yoshizawa-Fujita, D. Brandell, J. Mindemark, *ACS Appl. Energy Mater.* **2022**, *5*, 10002–10012.
- [32] M. P. Rosenwinkel, R. Andersson, J. Mindemark, M. Schönhoff, *J. Phys. Chem. C* **2020**, *124*, 23588–23596.
- [33] C. Sångeland, R. Mogensen, D. Brandell, J. Mindemark, *ACS Appl. Polym. Mater.* **2019**, *1*, 825–832.
- [34] K. Kimura, M. Yajima, Y. Tominaga, *Electrochem. Commun.* **2016**, *66*, 46–48.
- [35] R. Tataru, H. Suzuki, M. Hamada, K. Kubota, S. Kumakura, S. Komaba, *J. Phys. Chem. C* **2022**, *126*, 20226–20234.
- [36] L. Bertoli, S. Bloch, E. Andersson, L. Magagnin, D. Brandell, J. Mindemark, *Electrochim. Acta* **2023**, *464*, 142874.
- [37] M. C. Morant-Miñana, G. Liendo, M. Cabello, A. Quintela, J. Blanco, S. Martín-Fuentes, M. Armand, L. Otaegui, A. Villaverde, *Energy Technol.* **2021**, *9*, 1–8.
- [38] A. Smith, P. Stübke, L. Leuthner, A. Hofmann, F. Jeschull, L. Mereacre, *Batteries & Supercaps* **2023**, *6*, DOI 10.1002/batt.202300080.
- [39] T. Marks, S. Trussler, A. J. Smith, D. Xiong, J. R. Dahn, *J. Electrochem. Soc.* **2011**, *158*, A51.
- [40] G. Hernández, I. L. Johansson, A. Mathew, C. Sångeland, D. Brandell, J. Mindemark, *J. Electrochem. Soc.* **2021**, *168*, 100523.
- [41] E. K. W. Andersson, C. Sångeland, E. Berggren, F. O. L. Johansson, D. Kühn, A. Lindblad, J. Mindemark, M. Hahlin, *J. Mater. Chem. A* **2021**, *9*, 22462–22471.
- [42] K. Xu, *Commun. Mater.* **2022**, *3*, 1–7.
- [43] M. D. Galluzzo, J. A. Maslyn, D. B. Shah, N. P. Balsara, *J. Chem. Phys.* **2019**, *151*, DOI 10.1063/1.5109684.
- [44] S. Xing, A. Khudyskhina, U. Rauska, A. J. Butzelaar, D. Voll, P. Theato, J. Tübke, F. Jeschull, *J. Electrochem. Soc.* **2024**, *171*, 040516.
- [45] J. Fawdon, J. Ihli, F. La Mantia, M. Pasta, *Nat. Commun.* **2021**, *12*, 1–9.
- [46] J. Bastek, N. A. Stolwijk, T. K. J. Köster, L. van Wüllen, *Electrochim. Acta* **2010**, *55*, 1289–1297.
- [47] S. Ko, T. Obukata, T. Shimada, N. Takenaka, M. Nakayama, A. Yamada, Y. Yamada, *Nat. Energy* **2022**, *7*, 1217–1224.
- [48] B. Commarieu, A. Paoletta, S. Collin-Martin, C. Gagnon, A. Vijn, A. Guerfi, K. Zaghib, *J. Power Sources* **2019**, *436*, 226852.
- [49] J. Popovic, *J. Electrochem. Soc.* **2022**, *169*, 030510.
- [50] K. N. Wood, K. X. Steirer, S. E. Hafner, C. Ban, S. Santhanagopalan, S. H. Lee, G. Teeter, *Nat. Commun.* **2018**, *9*, 1–10.
- [51] S. Wenzel, T. Leichtweiss, D. Krüger, J. Sann, J. Janek, *Solid State Ionics* **2015**, *278*, 98–105.
- [52] G. Hernández, I. L. Johansson, A. Mathew, C. Sångeland, D. Brandell, J. Mindemark, *J. Electrochem. Soc.* **2021**, *168*, 100523.
- [53] J. Qiu, X. Liu, R. Chen, Q. Li, Y. Wang, P. Chen, L. Gan, S. Lee, D. Nordlund, Y. Liu, X. Yu, X. Bai, H. Li, L. Chen, *Adv. Funct. Mater.* **2020**, *1909392*, 1–8, DOI 10.1002/adfm.201909392.
- [54] M. Arrese-Igor, M. Martínez-Ibañez, J. M. López del Amo, E. Sanchez-Diez, D. Shanmukaraj, E. Dumont, M. Armand, F. Aguesse, P. López-Aranguren, *Energy Storage Mater.* **2022**, *45*, 578–585.
- [55] M. Arrese-Igor, M. Martínez-Ibañez, E. Pavlenko, M. Forsyth, H. Zhu, M. Armand, F. Aguesse, P. López-Aranguren, *ACS Energy Lett.* **2022**, *7*, 1473–1480.
- [56] L. Seidl, R. Grissa, L. Zhang, S. Trabesinger, C. Battaglia, *Adv. Mater. Interfaces* **2022**, *9*, 2100704.
- [57] S. Kaboli, H. Demers, A. Paoletta, A. Darwiche, M. Dontigny, D. Cle, A. Guer, M. L. Trudeau, J. B. Goodenough, K. Zaghib, *Nano Lett.* **2020**, *20*, 1607–1613.
- [58] S. K. Otto, Y. Moryson, T. Krauskopf, K. Peppler, J. Sann, J. Janek, A. Henss, *Chem. Mater.* **2021**, *33*, 859–867.
- [59] D. Schäfer, K. Hankins, M. Allion, U. Krewer, F. Karcher, L. Derr, R. Schuster, J. Maibach, S. Mück, D. Kramer, R. Mönig, F. Jeschull, S. Daboss, T. Philipp, G. Neusser, J. Romer, K. Palanisamy, C. Kranz, F. Buchner, R. J. Behm, A. Ahmadian, C. Kübel, I. Mohammad, A. Samoson, R. Witter, B. Smarsly, M. Rohnke, *Adv. Energy Mater.* **2024**, *2302830*, DOI 10.1002/aenm.202302830.
- [60] K. Edström, M. Herstedt, D. P. Abraham, *J. Power Sources* **2006**, *153*, 380–384.
- [61] B. Sun, C. Xu, J. Mindemark, T. Gustafsson, K. Edström, D. Brandell, *J. Mater. Chem. A* **2015**, *3*, 13994–14000.

- [62] E. E. Ushakova, A. Frolov, A. A. Reveguk, D. Y. Usachov, D. M. Itkis, L. V. Yashina, *Appl. Surf. Sci.* **2022**, *589*, 153014.
- [63] X. Wu, C. Villeveille, P. Novák, M. El Kazzi, *Phys. Chem. Chem. Phys.* **2018**, *20*, 11123–11129.
- [64] J. F. Peters, M. Baumann, J. R. Binder, M. Weil, *Sustain. Energy Fuels* **2021**, *5*, 6414–6429.
- [65] C. Vaalma, D. Buchholz, M. Weil, S. Passerini, *Nat. Rev. Mater.* **2018**, *3*, 18013.
- [66] M. Mohr, J. F. Peters, M. Baumann, M. Weil, *J. Ind. Ecol.* **2020**, *24*, 1310–1322.
- [67] U. Oteo, M. Martínez-Ibañez, I. Aldalur, E. Sanchez-Diez, J. Carrasco, M. Armand, H. Zhang, *ChemElectroChem* **2019**, *6*, 1019–1022.
- [68] L. Gehrlein, C. Njel, F. Jeschull, J. Maibach, *ACS Appl. Energ. Mater.* **2022**, *5*, 10710–10720.
- [69] Y. Surace, D. Leanza, M. Miolo, Ł. Kondracki, C. A. F. Vaz, M. El Kazzi, P. Novák, S. Trabesinger, *Energy Storage Mater.* **2022**, *44*, 156–167.
- [70] F. Lindgren, C. Xu, J. Maibach, A. M. Andersson, M. Marcinek, L. Niedzicki, T. Gustafsson, F. Björefors, K. Edström, *J. Power Sources* **2016**, *301*, 105–112.
- [71] A. Mayer, H. D. Nguyen, A. Mariani, T. Diemant, S. Lyonard, C. Iojoiu, S. Passerini, D. Bresser, *ACS Macro Lett.* **2022**, *11*, 982–990.
- [72] X. Dong, Z. Chen, X. Gao, A. Mayer, H. P. Liang, S. Passerini, D. Bresser, *J. Energy Chem.* **2023**, *80*, 174–181.
- [73] Alex Tullo, *C&EN Glob. Enterp.* **2023**, *101*, 20–22.
- [74] X. Song, R. Vestergren, Y. Shi, J. Huang, Y. Cai, *Environ. Sci. Technol.* **2018**, *52*, 9694–9703.
- [75] A. Rensmo, E. K. Savvidou, I. T. Cousins, X. Hu, S. Schellenberger, J. P. Benskin, *Environ. Sci. Process. Impacts* **2023**, *25*, 1015–1030.
- [76] W. H. Faveere, S. Van Praet, B. Vermeeren, K. N. R. Dumoleijn, K. Moonen, E. Taarning, B. F. Sels, *Angew. Chem. Int. Ed.* **2021**, *60*, 12204–12223.
- [77] M. Armand, P. Johansson, M. Bukowska, P. Szczeciński, L. Niedzicki, M. Marcinek, M. Dranka, J. Zachara, G. Żukowska, M. Marczewski, G. Schmidt, W. Wieczorek, *J. Electrochem. Soc.* **2020**, *167*, 070562.
- [78] A. Bitner-Michalska, G. M. Nolis, G. Żukowska, A. Zalewska, M. Poterała, T. Trzeciak, M. Dranka, M. Kalita, P. Jankowski, L. Niedzicki, J. Zachara, M. Marcinek, W. Wieczorek, *Sci. Rep.* **2017**, *7*, 40036.
- [79] X. L. Wu, S. Xin, H. H. Seo, J. Kim, Y. G. Guo, J. S. Lee, *Solid State Ionics* **2011**, *186*, 1–6.
- [80] M. Elmanzalawy, E. Sanchez-Ahijón, O. Kisacik, J. Carretero-González, E. Castillo-Martínez, *ACS Appl. Energ. Mater.* **2022**, *5*, 9009–9019.
- [81] D. Larcher, J.-M. Tarascon, *Nat. Chem.* **2014**, *7*, 19–29.
- [82] D. H. S. Tan, P. Xu, H. Yang, M. cheol Kim, H. Nguyen, E. A. Wu, J. M. Doux, A. Banerjee, Y. S. Meng, Z. Chen, *MRS Energy Sustainability* **2020**, *7*, 1–10.
- [83] A. I. Waidha, A. Salihovic, M. Jacob, V. Vanita, B. Aktekin, K. Brix, K. Wissel, R. Kautenburger, J. Janek, W. Ensinger, O. Clemens, *ChemSusChem* **2023**, *16*, 1–13.
- [84] T. Georgi-Maschler, B. Friedrich, R. Weyhe, H. Heegn, M. Rutz, *J. Power Sources* **2012**, *207*, 173–182.
- [85] K. Saito, C. Jehanno, L. Meabe, J. L. Olmedo-Martínez, D. Mecerreyes, K. Fukushima, H. Sardon, *J. Mater. Chem. A* **2020**, *8*, 13921–13926.

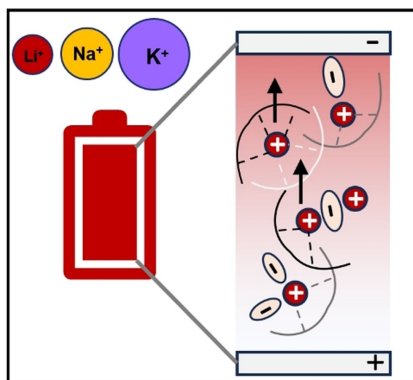
Manuscript received: March 21, 2024

Revised manuscript received: April 23, 2024

Version of record online: ■ ■ ■ ■

CONCEPT

Group 1 Cations Inside: Physical and electrochemical properties of solid polymer electrolytes (SPEs) change with the size of the cation. On the rocky road towards polymer-based solid-state batteries, the transition from Li to post-Li battery technologies, presents itself as an opportunity to study the ion transport properties and changes in electrochemical stability methodically and as a means to expand our analytical toolbox.



Dr. F. Jeschull*

1 – 10

Moving Down Group 1: Analytical Challenges and Current Trends for Solid Polymer Electrolytes in Post-Li Battery Applications