

Comprehension-driven design of advanced multi-block single-ion conducting polymer electrolytes for high-performance lithium-metal batteries

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The continuously growing importance of batteries for powering (hybrid) electric vehicles and storing renewable energy has prompted a renewed focus on lithium-metal batteries (LMBs) in recent years, as its high theoretical specific capacity of about 3860 mA h g⁻¹ and very low redox potential (−3.04 V vs. the standard hydrogen electrode) promise substantially higher energy densities compared to current lithium-ion batteries (LIBs) [1]. However, lithium metal electrodes face severe challenges associated with the risk of dendritic lithium deposition and the high reactivity with traditional organic liquid electrolytes, resulting in a continuous loss of electrochemically active lithium and a relatively low Coulombic efficiency [2]. To address these challenges, solid inorganic and polymer electrolytes have emerged as a potentially safer alternative.

Among the most investigated solid electrolyte systems are those comprising polyethylene oxide (PEO) and a lithium salt [3–5]. PEO is a cost-efficient, widely available polymer that allows for dissolving substantial amounts of the lithium salt owing to its high dielectric constant ($\epsilon = 5$) and a facile processing at the industrial level [6]. The Li⁺ conduction occurs through the segmental motion of the Li⁺ coordinating polymer chains and Li⁺ hopping from one coordination site to another according to the “free volume” model, thus, offering suitable ionic conductivity values at temperatures approaching (or beyond) the melting point of the PEO/Li salt composite [7]. As this means, however, that the battery needs to be heated to about 60 °C and higher during charge and discharge, not least as the operation at lower temperatures favors the formation of a detrimental concentration gradient of the lithium cation and the (more mobile) anion in the electrolyte [8], the use of PEO-based LMBs has been limited so far to car sharing programs and buses [9]. An additional challenge for PEO-based electrolyte systems is their limitation to “low-voltage” cathode materials such as LiFePO₄, as the ether group tends to get oxidized at potentials beyond 4 V vs. Li⁺/Li [10,11]. While the latter challenge remained essentially unsolved so far for polymer-based elec-

trolyte systems, several strategies have been proposed to address the first two challenges, i.e., the limited ionic conductivity and the formation of detrimental concentration gradients, including (i) decoupling the charge transport and the segmental dynamics of the polymer and (ii) the covalent tethering of the anionic function to the polymer backbone, yielding a Li⁺ transference number of unity, i.e., single-ion conductivity, which theoretically promises a dendrite-free lithium deposition owing to the essentially infinite Sand’s time [8,12].

In our work on single-ion conducting block copolymer electrolytes (SIPEs), we achieved a (partial) decoupling of the charge transport and the segmental dynamics of the polymer by introducing small molecules with a high dielectric constant such as ethylene carbonate (EC) or propylene carbonate (PC) [13,14]. These small molecules preferably coordinate the ionophilic block of the nanostructured SIPE and, hence, effectively coordinate the Li⁺ cations, thus, facilitating the Li⁺ hopping from one highly dissociative, bis(trifluoromethanesulfonyl)imide (TFSI) type anionic coordination site to another via a vehicle-type mechanism, hence, addressing the prevalent issue of insufficient ionic conductivity in SIPEs. In other words, the charge transport is decoupled (to a great extent) from the polymer dynamics and, instead, coupled to the high mobility of these small molecules. For this reason, we termed them “molecular transporters”. The chemical structure of the SIPE backbone is based on poly(arylene ether sulfone), as depicted in Fig. 1, owing to its self-extinguishing properties and by this enhancing the safety of the electrolyte system [13,15]. The ether unit in the polymer backbone, which is important for the flexibility of the polymer chains [16], but prone to oxidation beyond 4 V vs. Li⁺/Li [10], is stabilized by the electron-withdrawing effect of the fluorinated arylene moiety next to it. This has been confirmed by a combined theoretical and experimental investigation of the corresponding model compounds, which also revealed that the presence of fluorine in the backbone simultaneously enables the formation of a stabilized, LiF-rich interphase at the interface with lithium metal [17]. In sum, each functional group and moiety in these multi-block SIPEs plays an important role for the performance:

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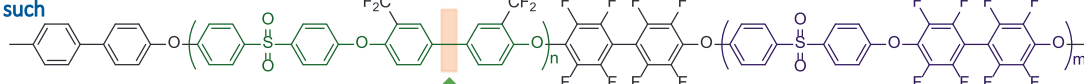
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1. Introduction of the “molecular transporters”

Facilitated ion dissociation and hopping from one anionic site to another, i.e., reduced activation energy

Enhanced mobility of the anionic side chains, further facilitating the hopping from one anionic site to another

Increase in segmental dynamics of the ionomer as such

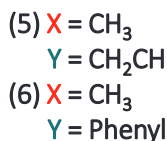
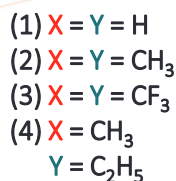


2. Modification of the ionophilic block

Single-ion conductivity

Facilitated charge transport

Enhanced electrochemical stability towards oxidation and formation of a stable interphase with lithium



3. Introduction of an ionophobic block

- Self-extinguishing properties

- High mechanical stability

- High electrochemical stability towards oxidation

- Formation of a stable interphase with lithium

Fig. 1. Illustration of the general design and the herein discussed modification of poly(arylene ether sulfone)-based SIPEs.

- The self-extinguishing properties of the poly(arylene ether sulfone) backbone ensure a superior safety.
- The introduction of an ionophobic block with a very high glass transition temperature of more than 200 °C provides high mechanical stability, thus, enabling the realization of self-standing membranes.
- The TFSI-type anionic group facilitates the ion dissociation.
- The introduction of the “molecular transporters” further supports the charge transport by decoupling it from the segmental dynamics of the polymer and coupling it to the high mobility of these small molecules.
- The selective coordination of these “molecular transporters” in the ionophilic domains further supports their beneficial impact on the charge transport, while at the same time preserving the high mechanical stability of the eventual electrolyte membranes.
- The fluorination of the arylene groups neighboring the ether-type bonds leads to a high electrochemical stability towards oxidation well beyond 4 V, while simultaneously enabling the formation of a stable interphase with lithium metal.

As a result of this smart design, self-standing, mechanically solid SIPE membranes have been obtained that provide ionic conductivities of about $10^{-3} \text{ S cm}^{-1}$ at 30 °C (depending on the kind of molecular transporter and its content) and stable cycling of $\text{Li}||\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ (NCM₁₁₁), $\text{Li}||\text{Li}[\text{Ni}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}]\text{O}_2$ (NCM₆₂₂) and $\text{Li}||\text{Li}[\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}]\text{O}_2$ (NCM₈₁₁) cells for hundreds of cycles [13,14,18] – even at elevated current densities, anodic cut-offs of up to 4.5 V, and at temperatures as low as 0 °C [14,18].

Motivated by this outstanding performance, we aimed for an in-depth understanding of the role of each functional group, moiety, and electrolyte component to further improve the performance, facilitate the large-scale fabrication and processing, and generally deepen our understanding of polymer electrolytes beyond PEO. To start with, we kept the chemical nature of the ionic side chain

constant for the sake of comparability and focused on the modification of the chemical design of the ionophilic block by varying the number of ionic side chains and introducing a (fluorinated) propyl group in-between the ionic side chain bearing phenyl rings, which can be achieved by using different precursors for the synthesis of the ionophilic block, e.g., providing only one or two reaction sites for the initial bromination, before subsequently attaching the ionic side chain via an Ullmann coupling reaction [19]. The results showed that the presence of two ionic side chains in close vicinity rather than only one per repeating unit is beneficial for the charge transport in terms of ionic conductivity and limiting current density, presumably due to the intrinsically shorter hopping distance for the cations and the favorable statistics to have two anionic sites in sufficiently close proximity. Moreover, the results confirmed the importance of fluorine in the backbone for the electrochemical stability towards oxidation when employing Ni-rich NCM cathodes and in contact with lithium metal as a result of the formation of fluorine-stabilized interphases. Interestingly, a similar effect on the stability of the lithium|SIPE interface was observed when introducing even bulkier alkyl-type groups such as $-C_2H_5$, $-CH_2CH(CH_3)_2$, or $-C_6H_5$ (i.e., bisphenol B, DMB or AP) [20], which might be beneficial for forming a more electronically insulating, i.e., passivating interphase. These bulkier substituents enabled the stable cycling of symmetric $\text{Li}||\text{Li}$ cells for up to 1000 h with an essentially constant overpotential; though at the expense of electrochemical stability towards oxidation, which has been attributed to the greater thermodynamic stability of the resulting decomposition products [20]. Using the fluorinated propyl group at this stage, providing a good compromise between very small substituents (yielding a higher ionic conductivity and higher electrochemical stability towards oxidation) and large substituents (yielding a better interfacial stability with lithium metal) [20], symmetric $\text{Li}||\text{Li}$ cells showed stable stripping and plating for more than 1600 h and NCM₈₁₁ electrodes containing the SIPE with an active material

mass loading as high as 10.6 mg cm^{-2} – to the best of our knowledge the highest reported mass loading so far – could be cycled for 100 cycles with a capacity retention of more than 86% and an average Coulombic efficiency of 99.8% [21].

This is certainly just an intermediate step towards a potential commercialization of such SIPEs, since commercial electrodes contain more than double of this mass loading and as commercial battery cells should provide stable cycling for several hundred or better several thousand cycles. Moreover, the introduction of innovative molecular transporters or flame-retardant additives might further enhance the safety of such systems and yield further stabilized interfaces and interphases, while the fluorine content in the SIPE should be reduced as much as possible with regard to cost, ease of synthesis and sustainability. However, this will be particularly challenging for the ionic side chains – comparable to the search for non-fluorinated lithium salts for liquid electrolyte systems. Alternatively, the development of efficient recycling or reuse strategies might be a suitable approach to address these issues.

In sum, the results highlight the critical importance of a thoughtful chemical design of SIPEs, including the number of ionic side chains and the chemical nature of both the ionophilic and the ionophobic block to balance ionic conductivity, limiting current density, electrochemical stability, and the availability of decomposition products that stabilize the interphase (and, hence, the interface) with the two electrodes, especially the lithium-metal electrode. Apparently, even minor changes have a substantial impact on the electrochemical properties and the interfacial stability. In return, this also highlights the great potential to further optimize these SIPEs (and polymer electrolytes in general) by tailoring the chemical composition and, thus, achieve all the key performance indicators that may enable their commercial use in next-generation LMBs. With regard to a further improvement of the electrochemical stability, for instance, a comprehensive screening via theoretical calculations might provide a very suitable and efficient strategy to further optimize these SIPEs, as our results have shown a very good agreement with the experimentally obtained data and trends. To further enhance the ionic conductivity and charge transport, while ideally reducing the amount of molecular transporters, an increase of the charge carrier concentration and/or an optimization of the hopping distance might be a promising approach. In any case, such further improvement and the realization of commercially relevant electrodes and cells as well as the scale-up of the synthesis in a cost-efficient fashion will require concerted efforts from scientists and engineers with highly complementary skills and expertise – just like for any, eventually commercially successful technology.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The authors would like to acknowledge financial support from the Federal Ministry of Education and Research (BMBF) within the FestBatt project (03XP0175B) and the FB2-Poly project (03XP0429B), as well as the Helmholtz Association.

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