ABSTRACT: Lithium batteries with solid polymer electrolytes (SPEs) and mobile ions are prone to mass transport limitations, that is, concentration polarization, creating a concentration gradient with Li⁺-ion (and counter-anion) depletion toward the respective electrode, as can be electrochemically observed in, for example, symmetric Li//Li cells and confirmed by Sand and diffusion equations. The effect of immobile anions is systematically investigated in this work. Therefore, network-based SPEs are synthesized with either mobile (dual-ion conduction) or immobile anions (single-ion conduction) and proved via solvation tests and nuclear magnetic resonance spectroscopy. It is shown that the SPE with immobile anions does not suffer from concentration polarization, thus disagreeing with Sand and diffusion assumptions, consequently suggesting single-ion (Li⁺) transport via migration instead. Nevertheless, the practical relevance of single-ion conduction can be debated. Under practical conditions, that is, below the limiting current, the concentration polarization is generally not pronounced with DIC-based electrolytes, rendering the beneficial effect of SIC redundant and DIC a better choice due to better kinetical aspects under these conditions. Also, the observed dendritic Li in both electrolytes questions a relevant impact of mass transport on its formation, at least in SPEs.

KEYWORDS: solid polymer electrolyte, Li⁺ depletion and concentration polarization, immobilized anions, single-ion versus dual-ion conduction, Li⁺ diffusion versus Li⁺ migration, limiting current, Li dendrites

1. INTRODUCTION

Solid electrolytes are currently regarded as the most promising enabler of lithium metal batteries (LMBs), which, at least theoretically can offer enhanced specific energies and energy densities compared to state-of-the-art liquid electrolyte Li-ion batteries (LIBs). The poly(ethylene oxide)-based solid polymer electrolyte (PEO-based SPE) can be considered as the benchmark SPE system for LMBs, owing to, for example, high abundance, low cost, easy processing, established wettability, and good electrochemical compatibility with lithium metal. Moreover, contrary to many reports, the PEO-based SPE can be operated even in high voltage cells, for example, in a LiNi₀.₆Mn₀.₂Co₀.₂O₂ (NMC622)||Li cell, without the characteristic voltage noise failure, which is attributable to Li-metal dendrite formation and growth through the SPE. This can be practically realized either via using a spacer (= remaining distance) between the electrodes or via enhancing the mechanical robustness of the SPE, for example, by forming a polymer network. In all cases, the oxidation onset of PEO-based SPEs, indicated via a plateau, remains 4.6 V versus Li/Li⁺, as validated with practical composite electrodes.

The main challenge of SPEs remains their relatively poor ionic conductivity, which limits their application to lower current rates and/or higher temperatures. In addition, depending on their Li⁺ transport properties, SPEs reveal a characteristic limiting current density, which leads to a blocking-type overvoltage behavior represented by an almost vertical voltage profile (known as polarization) after a certain time (transition time). In this case, battery cells reach their pre-set cut-off condition defining the end of the charge (or discharge) process, which enormously diminishes the achievable specific capacity. In practice, this type of limitation can be attributed to ions, in particular, Li⁺ depletion at the SPE/electrode interface in the course of diminishing amount of transported Li⁺ toward the respective electrode within the SPE.
describing the onset of concentration polarization and the Li\(^+\) diffusion reach, respectively, the Li\(^+\) depletion depends on the SPE thickness, Li\(^+\) diffusion coefficient, Li salt concentration, and current density/rate.\(^{19,21,24-26}\) Finally, the transition time (= time until complete Li\(^+\) depletion) can be practically and mathematically confirmed and even predicted.\(^{21,24-26}\)

So far, the phenomenon of Li\(^+\) (and counter anion) depletion has been investigated in SPEs, where both the anions and cations are mobile (dual-ion conduction),\(^ {21,24}\) while the impact of immobile anions (single-ion conduction) on Li\(^+\) depletion is not fully clarified. In this work, this scenario is systematically investigated using a network PEO-based SPE, which allows an innovative simple and effective membrane preparation with mobile or immobile anions, respectively (Scheme 1). Fundamental differences between the two conduction types are discussed, and the observed beneficial effect of single-ion conduction, that is, the absence of concentration polarization, is finally evaluated according to its practical relevance.

2. **EXPERIMENTAL SECTION**

2.1. Materials. Poly(ethylene oxide) (PEO, MW: 100,000 Da), polyethylene glycol dimethacrylate (PEGDMA MW: 750 g mol\(^{-1}\)), 1-methyl-2-pyrrolidinone (NMP, anhydrous, 99.5%), and 2-hydroxy-2-
methylpropionophenone were purchased from Sigma-Aldrich, Germany. Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, 99.9%) and polyvinylidene difluoride (PVdF, Solef S130) were purchased from Solvay, France. Super C65 carbon black was received from Imerys, France. Lithium 3-(trifluoromethanesulfonyl)propyl methacrylate (LiMTFSI) was purchased from SynQuest Laboratories, USA. Mylar foil (100 μm thickness) was purchased from DuPont, USA. The active material LiNi0.6Mn0.2Co0.2O2 (NMC622) was purchased from Targray, Canada. Lithium metal (Albemarle) was used as the counter and reference electrodes. PEO was dried under vacuum (10⁻³ mbar) at 60 °C (24 h).

2.4. Solid-State NMR Spectroscopy. The solid-state ¹⁹F magic-angle spinning (MAS) nuclear magnetic resonance (NMR) experiments were performed on a Bruker XCP200 spectrometer operating at a magnetic field of 4.70 T, resulting in a Larmor frequency of 188.3 MHz. Samples were packed into ZrO₂ rotors (2.5 mm) and sealed with the Vespel drive and bottom caps. Experiments were performed using a Bruker 2.5 mm MAS triple resonance probe and a MAS frequency of 23.0 kHz. ¹⁹F chemical shifts and radio-frequency (rf) field strengths were calibrated using poly(tetrafluoroethylene) (PTFE) (−122 ppm) as a secondary standard. Calibration of the magic angle was performed using KBr. A π/2 pulse length of 3.0 μs was used for excitation, corresponding to a rf-field strength of 83.3 kHz.

2.5. Electrode Preparation and Cell Assembly. NMC622 electrodes consisting of 91 wt % NMC622, 4 wt % carbon black, and 5 wt % PVdF were prepared by dissolving PVdF in NMP, followed by the addition of carbon black and NMC622. The mixture was homogenized using a dissolver. The slurry was cast on aluminum foil using a doctor blade with a wet coating thickness of 30 μm. The electrode sheets were dried at 80 °C under vacuum for 3 h, punched into the circular electrode, and dried again at 120 °C overnight before use. The average active mass loading of NMC622 electrodes was ≈2 mg cm⁻².

The cells were prepared in a two-electrode setup (coin cell) using a NMC622-based positive electrode, the PEO-based SPE as the polymer membrane and lithium metal as the negative electrode. The cells were assembled using the polymer membranes (10 mm diameter) inside rings of (mylar foil) the spacer (outer diameter: 16 mm, inner diameter: 10 mm) sandwiched between lithium metal (overall 16 mm diameter, but active area is only 10 mm due to 10 mm SPE diameter) and NMC622 electrodes (10 mm diameter) and/or NMC622 electrodes (10 mm diameter) and/or...
between a further lithium metal in case of the symmetrical Li||Li cell configuration.

2.6. Electrochemical Measurements. All constant current (galvanostatic) and galvanodynamic experiments were conducted on an Arbin Instruments battery cell test system at 60°C in a climate chamber (Memmert). The used C-rates and corresponding specific currents or current densities are mentioned within the text and/or in the figure captions.

2.7. Ionic Conductivity Measurements. Electrochemical impedance spectroscopy (EIS) was conducted utilizing an Autolab PGSTAT302N with FRA32M high-frequency analyzer and MUX.SCNR16 16-fold multiplexer. The prepared SPE samples were sandwiched between stainless-steel (SS) blocking electrodes, and a PTFE spacer disc was used to keep the sample dimensions of 100 μm height and 10 mm diameter constant in the coin cell (CR2032) housing. The sample cells were preheated at 70°C for 2 h prior to the measurement to improve the surface wetting of the SS electrodes with the considered polymer samples. The EIS measurements were performed in the frequency range of 1 MHz to 1 Hz with an applied voltage amplitude of 10 mV in the temperature range of 0–70°C in 10°C steps. The temperature was controlled using a Binder MK53 climate chamber.

3. RESULTS AND DISCUSSION

Both SPE membranes were prepared according to Scheme 1, that is, with mobile or immobilized anions and were initially checked regarding their immobilization degree via the solubility test according to Scheme 2. As shown in Figure 1a, the SPE with mobile anions is expected to dissolve in the ACN solvent, except the insoluble PEO-based network, and theoretically yields an insoluble mass fraction of 28%. In the case of immobilized anions, the insoluble residue must additionally include the LiMTFSI salt and theoretically yields a mass fraction of 47%. Both mass fractions can be experimentally confirmed, as shown in Figure 1b, hinting to successful anion immobilization, that is, chemical attachment to the polymer network of the latter. The presence of anions, being the only fluorine-containing material within the membranes, is additionally validated and proven by means of 19F MAS NMR. As shown in Figure 1c, the 19F signal at ∼76 ppm is only notable for the SPE with immobilized anions, giving additional experimental evidence for the aimed difference in the prepared membranes.

The temperature-dependent conductivity values are depicted in Figure 2a. The SPE with immobilized anions has a notably lower ionic conductivity compared to the SPE with mobile anions and reveals measurable values only above 50°C, showing that a major fraction of the overall ion transport in the dual-ion conducting electrolyte is due to the anion movement, as known in the literature. The initial charge profile of both SPEs in LiNi0.6Mn0.2Co0.2O2 (NMC622)||Li cells at 60°C is depicted in Figure 2b. Given the enhanced overvoltage, the anion-immobilized SPE reaches a significantly lower specific charge capacity than the SPE with mobile anions.

![Figure 2](https://example.com/figure2.png)

**Figure 2.** (a) Conductivity as a function of temperature for both SPEs, that is, with mobile or immobilized anions. (b) Voltage profiles of the initial charge of NMC622||Li cells with both SPEs at 60°C at a specific current of 15 mA g⁻¹.

![Figure 3](https://example.com/figure3.png)

**Figure 3.** Galvanostatic charge of Li||Li cells with varied current densities at 60°C with an SPE using (a) mobile and (b) immobile anions. The SPE with immobile anions does not suffer from concentration polarization contrary to the SPE with mobile anions, which is seen by the almost vertical increase in overvoltage (polarization) for a current density of 700 μA cm⁻² in (a).
Hence, the immobilization of anions in the SPE can be regarded as practically disadvantageous; however, a systematic comparison of both SPE systems allows valuable insights into the behavior/mechanism of Li+ transport.

Under limiting conditions (e.g., at high current density, large SPE thicknesses, and/or low diffusion coefficients), Li+ ions (and the anions) deplete toward the electrode within conventional SPEs where anions and cations are mobile,\textsuperscript{23,24,26} as indicated by a blocking-type polarization behavior as exemplarily shown in Figure 3a for 700 μA cm\(^{-2}\). At current densities below the cell characteristic threshold, no concentration polarization appears due to sufficient Li+ mass transport toward the electrode, as, for example, seen for 400 and 200 μA cm\(^{-2}\).

The onset of complete Li+ depletion above the threshold, expressed by the transition time (τ), obeys the Sand and diffusion equations, as discussed in our previous studies.\textsuperscript{23,24,26} Mechanistically, Li+ depletion can only occur as long as the anion can simultaneously leave the Li+ depleted region to obtain electroneutrality. In the case of single-ion conduction, Li+ cannot deplete in the first place as the anions are immobile, which consequently continuously forces Li+ to migrate in order to retain electroneutrality. In fact, though higher Ohmic resistance, the SPE with immobile anions does not suffer from concentration polarization, as shown in Figure 3b for similar current densities and operates without reaching the cut-off conditions (even at 700 μA cm\(^{-2}\)).

We would like to emphasize that this study does not regard any difference in the Li electrode/electrolyte interface behavior or in the solid electrolyte interphase formation,\textsuperscript{27,38} composition, electrochemical behavior, and the resulting cell behavior, which are due to the presence or absence of anions at these interfaces and will be part of continuous work. The cell voltage of 10 V suggests the anode and cathode potential of 5 and −5 V versus Li/Li\(^+\), respectively, and such anodic stability is indeed possible for PEO-based SPEs on planar surfaces.\textsuperscript{11} Moreover, the oxidation process and mechanism during limiting conditions need to be mechanistically unraveled, which is part of future work.

A more expedient and effective way to force and observe concentration polarization is the galvanodynamic method, as shown in Figure 4a, where the current density is progressively increased with a scan rate of 1 μA cm\(^{-2}\) s\(^{-1}\). The SPE with mobile anions is again limited by concentration polarization at a current density of ≈700 μA cm\(^{-2}\), while the SPE with immobile anions only suffers from Ohmic overvoltage without any hints for concentration polarization, that is, for depleting ions (Figure 4b), consequently pointing to an obvious theoretical benefit of single-ion conduction.

Nevertheless, a practical benefit of single-ion conduction can be reasonably debated. It is worth to note that the apparent disadvantage, that is, concentration polarization in dual-ion conducting SPEs is only notable at current densities above the threshold.\textsuperscript{11,23,24,26} In other words, under convenient conditions, that is, below the threshold currents, the dual-ion conducting SPE does not suffer from such transport limitations, and the concentration polarization practically does not occur.

In this context, a speculated further disadvantage of mobile anions, that is, the possibility of electric field-driven anion transport (and intertwined retardation of Li+ transport) in electrolytes toward the positive electrode needs to be debated as well because the electric field drops off within the Helmholtz double layers (nanometer range) at the electrode/electrolyte interfaces, rendering the bulk anion movement in the membranes (micrometer range) less relevant, as well.\textsuperscript{39,40}

Overall, the notably lower Ohmic polarization of dual-ion conducting SPEs (Figures 3 and 4) under convenient conditions reasonably suggests even better interfaces and overall kinetic aspects, finally a better choice from the practical point of view.

The anticipated benefit of suppressing Li dendrites by circumventing mass transport limitations \textit{via}, for example, single-ion conduction should be treated with caution, as well. As known from the literature, Li+ depletion during concentration polarization is supposed to facilitate high-surface area lithium (HSAL), for example, dendrite and formation growth.\textsuperscript{51} In this regard, it is believed that immobilization of anions may suppress Li dendrite formation \textit{via} suppression of Li+ depletion. However, it should be generally noted that severe formation of HSAL including Li dendrites also takes place below any threshold current, that is, \textit{via} other mechanisms than that being induced by concentration polarization, as for example known from liquid electrolytes.\textsuperscript{12,13,32−35} However, even at mass-transport-limiting
conditions (during concentration polarization, as seen in Figures 3 and 4), no indications for noisy-like over-limiting currents (attributable to Li dendrite formation at least in liquid electrolytes)\(^{41,47}\) can be detected.

On the other hand, even for the case when concentration polarization is circumvented via, for example, immobile anions, still the resulting cells do undergo a short circuit, as shown in Figure 5a. These time-delayed arbitrary voltage noises and voltage decays toward 0 V can be attributed to Li dendrite-induced short circuits, as schematically illustrated in Figure 5b and thoroughly discussed in previous studies.\(^{11,16−18,48}\) The immobilization of anions may have a theoretical/potential benefit in terms of reducing/avoiding concentration polarization but is obviously not the sole solution to suppress Li dendrites. More likely, factors influencing the homogeneity of Li plating, either via SEI or electrolyte,\(^{17,49,50}\) can be more relevant and should be considered and investigated in future studies for solid electrolytes.

4. CONCLUSIONS

In this work, the impact of anion immobilization on concentration polarization/Li\(^+\) depletion is systematically investigated by means of electrochemical polarization experiments. For this purpose, network-based SPEs were synthesized and prepared with mobile and immobile anions, respectively. The anion detachment/attachment within the SPE resulting in mobile/immobile anions was proven via solvation tests and NMR.

As expected, the SPE with mobile anions showing dual-ion conduction suffers from concentration polarization, visible through a blocking-type polarization during galvanostatic and galvanodynamic operation in Li\textsubscript{L1}Li cells. This process comes with Li\(^+\) depletion toward the electrodeelectrolyte interface and obeys the Sand diffusion equations. In contrast, concentration polarization does not appear in the single-ion conducting SPE with immobile anions, which implies the absence of Li\(^+\) depletion and concentration polarization. For this type of SPE, the Sand diffusion coherences are invalid, and Li\(^+\) transport proceeds via migration instead.

From a practical point of view, it needs to be noted that the apparent benefit of the single-ion conducting SPE only emerges at impractically high currents, that is, above the threshold, where concentration polarization only occurs. In other words, under practical conditions (below the threshold), the concentration polarization in dual-ion conducting SPE with mobile anions is not pronounced. As schematically illustrated and summarized in Scheme 3, the lower Ohmic resistance and overall better kinetics under practically convenient conditions, that is, before the onset of concentration polarization, render dual-ion conducting SPE even a better choice. Moreover, Li dendrite formation induced by mass transport limitations is not relevantly pronounced in SPEs, instead other forms of HSAL are present for both types of SPEs, being both prone to short circuits, that is, independent of the conduction mechanism.

\[\text{Li}^{+} + \text{electrode} \rightarrow \text{electrolyte} + \text{Li}\]

\[\text{Anode} \rightarrow \text{Migration} \rightarrow \text{Cathode}\]

**Figure 5.** (a) Galvanostatic charge of Li\textsubscript{L1}Li cells with varied current densities at 60 °C using an SPE with mobile and immobile anions. (b) Short circuits can be attributed to Li dendrite penetrations through the SPE. The assumed suppression of Li dendrite formation and growth when using immobile anions can be debated for the shown case of a single-ion conducting SPE.

**Scheme 3.** Overview of the SPEs with Mobile and Immobile Anions, That is, Dual-Ion and Single-Ion Conduction in Li\textsubscript{L1} Li Symmetric Cells, Where One Li Electrode Serves as the Anode and the Other as the Cathode, Respectively\(^{**}\)

**The single-ion conducting SPE can in fact prevent Li\(^+\) depletion, that is, concentration polarization. Nevertheless, under conditions before the onset of the concentration polarization, the dual-ion conducting SPE reveals overall better kinetic aspects, rendering it more beneficial for the cell performance from a practical point of view.**
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