Electrolyte and anode-electrolyte interphase in solid-state lithium metal polymer batteries: A perspective

Heng Zhang1 | Yuhui Chen2 | Chunmei Li3 | Michel Armand3

1 Key Laboratory of Material Chemistry for Energy Conversion and Storage (Ministry of Education), School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan, P. R. China
2 State Key Laboratory of Materials-Oriented Chemical Engineering, School of Energy, Nanjing Tech University, Nanjing, Jiangsu, P. R. China
3 Centre for Cooperative Research on Alternative Energies (CIC energiGUNE), Basque Research and Technology Alliance (BRTA), Gipuzkoa, Spain

Abstract
The interest for solid-state lithium metal (Li°) batteries (SSLMBs) has been growing exponentially in recent years in view of their higher energy density and eliminated safety concerns. Solid polymer electrolytes (SPEs) are soft ionic conductors which can be easily processed into thin films at industrial level; these unique features confer solid-state Li° polymer batteries (SSLMPBs, i.e., SSLMBs utilizing SPEs as electrolytes) distinct advantages compared to SSLMBs containing other electrolytes. In this article, we briefly review recent progresses and achievements in SSLMPBs including the improvement of ionic conductivity of SPEs and their interfacial stability with Li° anode. Moreover, we outline several advanced in-situ and ex-situ characterizing techniques which could assist in-depth understanding of the anode-electrolyte interphases in SSLMPBs. This article is hoped not only to update the state-of-the-art in the research on SSLMPBs but also to bring intriguing insights that could improve the fundamental properties (e.g., transport, dendrite formation, and growth, etc.) and electrochemical performance of SSLMPBs.

KEYWORDS
anode-electrolyte interphase, solid polymer electrolytes, solid-state batteries, solid-state lithium metal polymer batteries
1 | INTRODUCTION

Emanating from the “rocking-chair battery” concept, lithium-ion batteries (LIBs), comprising two intercalation electrodes with different redox potentials, have become the most prevalent battery technologies for electrochemical energy storage.1,2 The global market of LIBs has been steadily growing since their commercialization in 1990s, and is estimated to reach 1200 GWh in 2030, being six times higher than today’s size (ca. 200 GWh in 2020).3 This is mainly driven by a deeper penetration of LIBs in the application scenarios requiring large-format batteries (e.g., electric vehicles [EVs] and grid storage [GS]).3 Unfortunately, there has been an increasing number of fire incidents for EVs and GS caused by catastrophic thermal runaway of LIBs.4,5

Replacing organic carbonate-based liquid electrolytes, volatile and flammable solutions widely used in LIBs, with solid electrolytes (SEs) is believed to be an auspicious approach to overcome the aforementioned safety concerns at material level.5–8 Among all kinds of SEs, solid polymer electrolytes (SPEs) consisting of “soft” polymeric matrices and conducting salts are lighter (~1.3 g/cm³, close to those of liquid electrolytes), cheaper, and more processable.9–15 These merits have greatly incentivized the research and development of SPEs and their application as electrolytes for solid-state batteries—solid-state lithium metal (Li°) polymer batteries (SSLMPBs). Currently, SSLMPBs have been successfully utilized as power sources for EVs and GS by Bollore group (https://www.blue-solutions.com/en/), which strongly validates their technological suitability.

Due to lower ionic conductivities of SPEs (ca. 10⁻⁵ S/cm) compared to liquid electrolytes (ca. 10⁻² S/cm) at ambient temperatures, SSLMPBs have to be cycled at high temperatures (~80°C) with extra thermal controlling system, thus, reducing the practical energy density of SSLMPBs. For instance, for Li° | SPE | LiFePO₄ cells, only half of their theoretical values (~250 Wh/kg) could be accessible at pack levels (~120 Wh/kg) (https://www.blue-solutions.com/en/).9–14 Moreover, the growth of dendritic lithium, particularly at moderate to high currents (>0.5 C), severely limits the rate capability and long-term cycling stability of SSLMPBs.9–14

To improve the performances of SSLMPBs so as to contend with present LIBs in energy density and other critical metrics while keeping their inherent safety, considerable research activities have been devoted to search for highly Li-ion conductive SPEs and enhancing Li° anode/SPE stability. In this article, we overview recent progresses and achievements that have been made with respect to the improvement of ionic conductivity of SPEs and their interfacial stability with Li° anode. Moreover, we briefly present advanced in-situ and ex-situ techniques which could benefit the understanding of anode-electrolyte interphases in SSLMPBs.

2 | IMPROVEMENT OF LI-ION CONDUCTIVITY

Generally, ionic conductivities are determined by the concentration of mobile ions and their mobility under electric field. However, this principle could not be straightforwardly translated into SPEs. Unlike crystalline and glassy SEs, ionic conduction in SPEs mainly takes place in amorphous phases via dynamic percolation model and, therefore, crystallinity of SPEs turns to be a decisive factor.80 To improve the concentration of mobile ions, lithium salts with low dissociation energy is a prerequisite, in addition to other requirements such as good chemical stability, anodic and cathodic stability, and so on. In this regards, the weakly coordinating anion, bis(trifluoromethanesulfonyl)imide {[N(SO₂CF₃)₂]⁻, TFSI⁻}, has been proved to be the optimal choice and has been widely used as conducting salt for SPEs.16 However, the perfluorinated TFSI⁻ anion does not interact with polymer matrices and, thus, is highly mobile, the contribution of cationic conductivity normally is lower than 20%—low Li-ion transference numbers (T_Li⁺) of ca. 0.2 for TFSI-based SPEs.17 To improve the mobility of ions, polymers with low-glass transitions are of great interest because of their high segmental mobility (i.e., ease in conformational changes being required for transporting ions). Poly(ethylene oxide) (PEO) with a low T_g of ~60°C has been the benchmark polymer throughout the past 40 years’ research of SPEs.5,31 Unfortunately, PEO-based SPEs possesses low degree of amorphicity due to the semicrystalline nature of the neat PEO matrix (e.g., ~60% crystallinity at room temperature17). Below, we present several interesting alternatives to LiTFSI and PEO, which have been recently described in literature with promising performances in SSLMPBs.

2.1 | Alternatives to LiTFSI

Attempts on improving the T_Li⁺ of TFSI-based SPEs were made by increasing the chain length of perfluoroalkyl group, that is, replacing –CF₃ with –C₂F₅, –C₄F₉. Gorecki et al.18 synthesized a series of lithium salts with sulfonimide anions, [N(SO₂CₙF₂m+1)(SO₂CₙF₂m+1)]⁻ (n, m = 1, 2, 3, and 4), and observed that the corresponding SPEs obtained by blending these salts with PEO were characterized with very comparable T_Li⁺ values, for example, T_Li⁺ = 0.25 for the largest anion [N(SO₂C₄F₉)₂]⁻ (ca. 250 Å³)18 and TFSI⁻ (ca. 147 Å³)19 at a salt content
of EO/Li = 8. This clearly indicates the “slippery” feature of perfluorinated sulfonimide anions, as schematically shown in Figure 1A.

By adding Lewis acidic anion traps, Figure 1B, the migration of anionic species could be reduced but at a high cost of total ionic conductivity ($\sigma_{\text{total}}$), therefore, causing low Li-ion conductivities ($\sigma_{\text{Li}^+} = \sigma_{\text{total}} \times T_{\text{Li}^+}$) of $<10^{-5}$ S/cm at 70°C. For example, Blażejczyk et al. reported that the addition of calixarene-type supramolecular compounds as anion traps could greatly suppress the mobility of $\Gamma^-$ ions in LiI/PEO but with a low $\sigma_{\text{Li}^+}$ close to $10^{-5}$ S/cm at 95°C. By chemically tethering anions to polymer backbones, Figure 1C, for example, grafting a TFSI-like (i.e., CF$_3$SO$_2$N$^{(-)}$SO$_2$) moiety to polystyrene, polyacrylates, could sufficiently immobilize negative charges and approach $T_{\text{Li}^+}$ close to unity. The polymer core could be also replaced by inorganic nanoparticles, that is, nanoalumina, nanosilica, etc., Figure 1D, high $T_{\text{Li}^+}$ values are also reported. Both approaches, however, lead to a dramatic decrease in $\sigma_{\text{total}}$, notwithstanding arduous synthetic processes required to access these polysalts.

Recently, we introduced several new types of sulfonimide anions functionalized with specific groups for forming secondary bonds (e.g., hydrogen bond, van der Waals interactions, etc.) between salt anions and polymer backbones, thereby slowing the motion of anionic species. The ether-functionalized anion, with a frog-like shape, was found to be self-agglomerated or entangled with PEO via dipole–dipole interactions (Figure 1E). In addition to markedly reduced anionic conductivities, the $\sigma_{\text{Li}^+}$ remained as high as $10^{-4}$ S/cm at 70°C. In another work, one –CF$_3$ group of TFSI$^-$ was replaced with –CF$_2$H group, giving the (difluoromethanesulfonyl)trifluoromethanesulfonyl)imide anion ([$N(\text{SO}_2\text{CF}_2\text{H})\text{(SO}_2\text{CF}_3)$]$^-$, DFTFSI$^-$). The strong electron-withdrawing ability of F atoms and SO$_2$ group imparts the hydrogen atom in –CF$_2$H group good H-donicity, thus, enabling the formation of hydrogen bond between DFTFSI$^-$ and PEO. The $\sigma_{\text{Li}^+}$ of LiDFTFSI/PEO was found to be higher than that of conventional LiTFSI/PEO (Figure 1F), due to the enhanced $T_{\text{Li}^+}$ (0.35 at 70°C) with nearly negligible compromise of $\sigma_{\text{total}}$. These inspiring results suggest that connecting the structural design of new anions to the nature of the selected polymer matrices would be of prime importance for attaining highly cation conductive SPEs.
2.2 Alternatives to PEO

The ethylene oxide (EO) repeating unit has a moderate donor number (i.e., a thermodynamic measure of Lewis basicity) of ca. 22 and strong complexing ability by chelating alkali metal cations and forming favorable configurations in terms of entropy, which endow PEO with outstanding solvating power toward various kinds of alkali metal salts, including lithium halides except lithium fluoride, sodium bromide, potassium iodide, lithium thiocyanate (LiSCN), etc. The main drawback of PEO is the presence of crystalline phase which largely hinders the ion transport of PEO-based SPEs. Either blending PEO with a second polymer or copolymerizing EO-containing monomers with foreign monomers could effectively decrease the crystallinities and improve ionic conductivity of the corresponding SPEs. This has been well scrutinized in other review articles and book chapters.

However, reaching an ionic conductivity of $>10^{-4}$ S/cm at ambient temperatures (%40°C) tends to be a ceiling for PEO-based SPEs.

Recently, we developed a new family of comb-like polymer matrices comprising commercial polyetheramines (Jeffamine®) as side moiety and poly(ethylene-alt-maleimide) as backbone Figure 2A. These Jeffamine-based polymers were found to be nearly totally amorphous with a second polymer or copolymerizing EO-containing monomers with foreign monomers could effectively decrease the crystallinities and improve ionic conductivity of the corresponding SPEs. This has been well scrutinized in other review articles and book chapters.

![Chemical structure of Jeffamine-based polymer](image)

![Ionic conductivities of Jeffamine- and PEO-based SPEs](image)

![Cycling performance of the Li⁺ || LiFePO₄ cells using LiFSI/Jeffamine and LiFSI/PEO at various temperatures](image)

![Chemical structure of the Jeffamine-based block polymers](image)

![Nanofiber reinforced polymer electrolyte (NRPE)](image)
with low-glass transitions (ca. \(-55°C\)), owing to the presence of flexible but highly disordered poly(propylene oxide) (PPO) unit which could remarkably prevent the packing of PEO lamellae.\(^{30}\) At room temperature, the Jeffamine-based SPEs utilizing discrete salts, like LiTFSI or lithium bis(fluorosulfonylimide) [Li[N(SO\(_2\)F\(_2\)]\(_2\), LiFSI], exhibited more than one order of magnitude higher ionic conductivities than the respective PEO-based SPEs (Figure 2B). Together with superior SEI layer formed in the LiFSI/Jeffamine electrolyte, the assembled Li\(^+\) || LiFePO\(_4\) cells were successfully cycled down from 70°C to ambient temperature (Figure 2C).\(^{31}\) To improve the mechanical strength of Jeffamine-based SPEs, we introduced polystyrene block into Jeffamine-based SPEs (Figure 2D) and observed only a slight decrease in ionic conductivity but a great enhancement in mechanical stability, obtaining self-standing membranes.\(^{32}\) Alternatively, with poly(vinylidene fluoride) (PVDF) nanofibers, we could also obtain highly conductive, self-supporting membranes containing Jeffamine-based polymers (Figure 2E).\(^{33}\) These nanofibers reinforced Jeffamine-based SPEs allowed the cycling of the Li\(^+\) || LiFePO\(_4\) cells with decent areal capacity at low C-rates (\(-0.8\) mAh/cm\(^2\) at C/20) at 30°C.

Apart from polyether-type polymers, polycarbonates and polyesters have emerged as interesting candidates for building robust SPEs with high ionic conductivities at ambient temperatures.\(^{34}\) For example, Mindemark et al.\(^{37,38}\) developed a type of polyester-based copolymers consisting of \(\varepsilon\)-caprolactone (CL) and trimethylene carbonate (TMC) units, poly(CL-co-TMC). The SPEs of LiTFSI/poly(CL-co-TMC) showed a low \(T_g\) (around \(-40°C\), Figure 3A) and decent ionic conductivities (e.g., \(4 \times 10^{-5}\) S/cm at 25°C) and high \(T_{Li^+}\) (ca. 0.6 at 40°C). The Li\(^+\) || LiFePO\(_4\) cells using LiTFSI/poly(CL-co-TMC) (80 mol% CL unit) delivered good specific capacity at lower C-rates (C/50, C/20), Figure 3B.\(^{37}\) It is noticeable that a highly salt-concentrated SPE containing LiFSI and poly(ethylene carbonate) (PEC) was reported to be highly conductive at room temperature, reaching a high ionic conductivity of \(10^{-4}\) S/cm at 25°C, enabling the cycling of SSLMPBs at room temperature.\(^{39,40}\) Yet, Zaghib et al.\(^{41}\) proved that PEC and its analogue poly(propylene carbonate) (PPC) readily undergo depolymerization in the presence of lithium salt, trace amounts of water, and heat, giving low-molecular-weight monomer, ethylene carbonate (EC) and propylene carbonate (PC), respectively, as shown in Figure 3B, which significantly increased the ionic conductivity of PEC-based SPEs particularly, in the salt-rich region. Along with this critical report, Cui and coworkers.\(^{42}\) also showed that, in contact with Li\(^+\) anode, PPC degraded to short-chain oligomers or even PC monomer via either chemical or electrochemical pathways (Figure 3C). These results imply that more critical evaluations on the physicochemical and electrochemical properties of polycarbonate-based SPEs are of utter importance for identifying their practical suitability for SSLMPBs.

In complement, alternative polymers, such as polyetheramines and polyesters, own advantages in terms of enhancing ionic conductivities at room temperature as compared to PEO due to their amorphous nature. The higher transference numbers of polycarbonate-based SPEs would be linked to the inherent chemistry of carbonate group—lower solvating ability toward lithium salts resulting in strong ion aggregates which could improve the transport of cationic species.\(^{43}\) Besides, there have been extensive research efforts dedicated to new polymer hosts, such as polymerized ionic liquids (PILs), with/without plastic crystals. These interesting topics have been covered in recent excellent review articles\(^{44-47}\) and therefore are not discussed in this article.

## 3 | ENHANCEMENT OF THE STABILITY OF SPE VERSUS LI ANODE

Besides the ionic conductivity, the stability of SPE versus Li\(^+\) anode is another important requirement when developing a new SPE. An enhanced stability between the two means a desired reduction of SPE components happens on Li\(^+\) anode that leads to a robust SE interphase (SEI) layer, which acts as a protection layer on Li\(^+\) electrode to enable a longer cycle life in SSLMPBs. The key criteria for such layer are: (1) electron insulating and Li-ion conducting; (2) compact, mechanically stable, and homogeneously deposited; (3) form a chemically stable and inert film. This protection layer could be formed in situ via the decomposition of electrolyte components (e.g., salts and additives), or ex situ via an artificial SEI fabricated on Li\(^+\) anode. Different approaches and recent progress are discussed in the following sections.

### 3.1 | Novel salts

By tuning the chemical structures of salt anions, one could change the SEI components as well as the reduction potential of the salt, hence, the choice of the salt is very crucial for a robust SEI formation in SSLMPBs. Besides the benchmark LiTFSI, its derivative lithium (difluoromethanesulfonyl) (trifluoromethanesulfonyl)imide [Li[N(SO\(_2\)CF\(_3\)]\(2\), hereafter LiDFTFSI] has been mentioned in the Section 2.1, was tested in Li-S batteries by our group.\(^{21,48,81}\) LiDFTFSI has to be considered as LiTFSI, in which the fluorine atoms in one –CF\(_3\) group is replaced by a hydrogen atom. The Li\(^+\) deposition morphology in LiDFTFSI/PEO is more compact and homogenous...
FIGURE 3 Properties of some representative polycarbonate- and polyester-based SPEs. (A) Ionic conductivities of LiTFSI/poly(CL-co-TMC) at 25°C. (B) Charge/discharge capacities and Coulombic efficiencies for the Li$^+$ | LiTFSI/poly(CL-co-TMC) (80 mol% CL) | LiFePO$_4$ cell cycled at various C-rates at room temperature. (C) Possible depolymerization reactions of polycarbonates (R = H for PEC, R = CH$_3$ for PPC) in the presence of salt and heat, as suggested by Zaghib et al.$^{41}$ (D) Possible chemical and electrochemical degradation pathway of PPC-based SPEs, as suggested by Cui et al.$^{42}$ Figure 3A and B is reproduced from Ref.$^{[37]}$ with permission. Copyright 2015, Elsevier. Figure 3C is reproduced from Ref.$^{[41]}$ with permission. Copyright 2019, Elsevier. Figure 3D is reproduced from Ref.$^{[42]}$ with permission. Copyright 2018, Elsevier
compared to the one with LiTFSI salt. The SEI layer is composed with not only mechanically stable LiF, but also ionically conductive LiH (Figure 4A), which facilitates an enhanced Li⁺ electrode/SPE interfacial stability, leading to a Li stripping and plating for 600 h at 70°C with a low overpotential, less than 40 mV at 0.2 mAh/cm².⁸¹ Other two types of LiTFSI-derivative salts, LiFSI and lithium (fluorosulfonyl)(trifluoromethanesulfonyl)imide [Li[N(SO₂F)(SO₂CF₃)]], LiFTFSI,⁴⁹⁻⁵¹ even if they are not “novel,” their integration into SPEs are recently developed. LiFSI has been proved to be a good candidate to result in a firm LiF-rich SEI formation on Li⁺ anode in PEO-based SPE at 70°C by its relatively easier cleavage of S–F bond compared to C–F bond in LiTFSI.¹⁷,⁴⁹,⁵⁰ Although LiF is essential for a firm and stable SEI layer, its low ionic conductivity of approximately 10⁻⁴ S/cm could lead to a high resistance of SEI, hence, large overpotentials of the full cell. The chemical structure of LiFTFSI combines the characters of both LiTFSI (i.e., CF₃SO₂ moiety) and LiFSI (i.e., FSO₂ moiety), as a consequence, the Li⁺ anode/SPE interfacial properties are also sitting in-between the ones in LiTFSI/PEO and LiFSI/PEO cells with an optimum amount of LiF formed, meaning balanced the mechanical stability and interfacial resistance.⁵¹ Moreover, Zhou et al.⁵² studied lithium (trifluoromethanesulfonyl)(n-nonfluorobutanesulfonyl) imide [Li[(CF₃)SO₂(n-C₄F₉SO₂)N], LiTNFSI] in LiFSI/POE electrolyte which also showed a stable Li⁺ electrode/SPE interface at 60°C at 0.4 mAh/cm². The Li stripping and plating test lasted for 400 h (100 cycles) at an overpotential lower than 70 mV.

Since LiF is a sword with two sides, stability of novel F-free salts in SPE is also investigated in SSLMPBs seeking for alternative anion reduction products which could facilitate a superior SEI film.³³,⁵⁶,⁵⁷ Lithium tricyanomethanide [LiC(CN)₃], LiTMC] has a fairly stable structure of a triple C≡N group; however, it can be reduced by Li⁺ electrode in PEO-based SPE at 70°C forming a C = N network and Li₃N-rich SEI layer. Due to the high Li⁺ ionic conductivity of Li₃N, Li stripping and plating of such cell has an extremely low overpotential of 10 mV at 0.2 mAh/cm² at 70°C (Figure 4B).⁵³ It is worth mentioning that conjugated C = N network can be electronically conductive at some extent leading to continuous decompositions of the salt.⁵⁰ Another interesting study is to combine LiTFSI and lithium bis(oxalate)borate (LiBOB) in presence of glutaronitrile (GN), and poly(ethylene glycol)diacylate (PEGDA) as prepolymer host.²⁹ A free-standing SPE was obtained through a crosslinking reaction. Li⁺ electrode/SPE interface was probed at 30°C by stripping and plating test, which lasted for more than 1300 h at 0.075 mAh/cm², thanks to a thin layer of deposited lithium and better dendrite mitigation.

Other salts, such as lithium 2-trifluoromethyl-4,5-dicyanoimidazolate (LiTDI), have been studied in SPEs, but with a main focus on their physicochemical properties and effects on ionic conductivities.¹⁶,⁵⁸,⁵⁹ It would be a great interest to further explore their contributions on the stability toward Li⁺ anode in SSLMPBs.

3.2 Electrolyte additives

Using additives in the electrolyte to stabilize anode is a well-known and common approach in liquid LIBs.⁶⁰,⁶¹ However, it is much less in SSLMPBs. Ceramic fillers (<10 wt.% of total composite SPE), such as Al₂O₃, SiO₂, and LLZO, etc., can be considered as one type of additives in SPE, numerous literatures have reported their significant effects on suppressing Li dendrite growth.⁵²,⁶³ Since the exact reason behind such effect is not clearly proven, one of the most reasonable models is that the various types of ceramic additives simply act as a physical barrier for Li dendrite to grow.⁶⁴,⁶⁵ Moreover, most studied fillers are in the nanosize range, hence, their high surface area could effectively trap water and impurities from the SPE, which is another important reason for the onset of Li⁺ dendrite growth.⁵²

Comparing to the number of works on ceramic additives, the studies of lithium salt additives in SPE are much less. In 2017, we investigated the impact of adding 2 wt.% of lithium azide (LiN₃) as additive in PEO-based SPE, and found that Li₃N-rich highly conducting SEI was formed leading to a low overpotential of 10 mV at 0.2 mAh/cm² at 70°C in Li⁺ symmetric cell (Figure 4C).⁵⁴ Recently, lithium trifluoro(perfluoro-tert-butyloxyl) borate (Li[(CF₃)₂COBF₃], LiTFPFB) has been employed as 5 wt.% additive in LiTFSI/PEO SPE. The Li⁺ symmetric cell with such SPE showed stable cycles for 600 h at charge of 0.25 mAh/cm² per cycle at 60°C, in which the SEI formation involves decomposition of both –CF₃ and –BF₃ groups (Figure 5B).⁵⁵

3.3 Other novel SPEs

Due to the stable structure of PEO and good mechanical properties, it is the most used polymer matrix in SSLMPBs. Therefore, the novel salts and additives are commonly studied based on PEO system. However, PEO is not the only solution, there are SPEs based on other alternatives that could also stabilize Li⁺ anode and provide promising performance in SSLMPBs. For example, the Jeffamine-based polymers mentioned in Section 2.2 could also be used as coating layer for improving the physical contact between Li anode and SPE, and thereby
FIGURE 4 Strategies for improving the stability of SPE versus Li\(^+\) anode. (A) Comparison between LiDFTFSI- and LiTFSI-based SPEs in Li-S batteries. Reproduced from Ref.\textsuperscript{[81]} with permission. Copyright 2019, Cell Press. (B) The SEI on Li\(^+\) anode formed in LiTCM-based SPE. Reproduced from Ref.\textsuperscript{[53]} with permission. Copyright 2019, Wiley-VCH. (C) LiN\(_3\), as electrolyte additive for PEO-based SPEs in Li-S batteries. Reproduced from Ref.\textsuperscript{[54]} with permission. Copyright 2017, Wiley-VCH. (D) LiTFPFB-added SPEs for protecting Li\(^+\) anode. Reproduced from Ref.\textsuperscript{[55]} with permission. Copyright 2019, Wiley-VCH. (E) Jeffamine-based polymer as coating layer for SSLMPBs. Reproduced from Ref.\textsuperscript{[33]} with permission. Copyright 2019, Elsevier
extending the cyclability of SSLMPBs (Figure 4E). A novel membrane has been fabricated by employing cellulose acetate membranes as the backbone and polymer-in-salt polysiloxane copolymers as the ionic conductive materials. The obtained SPE not only has the high ionic conductivity at room temperature \((7.8 \times 10^{-4} \text{ S/cm})\), but also ensures an improved \(\text{Li}^+\) anode/SPE interfacial properties. The Li stripping and plating test lasted for more than 300 h at current density of 0.5 mA/cm\(^2\). Furthermore, the Li-S batteries containing such SPE, delivered a good CE and 500 mAh/g at the end of 80 cycles.

4 CHARACTERIZING TECHNIQUES FOR UNDERSTANDING ANODE-ELECTROLYTE INTERPHASE

Recently, numerous methods have been developed to investigate the anode-electrode interphase and tremendous progress has been made in understanding the underpinned science at the interface. However, most studies focused on the interface using liquid electrolyte rather than the solid-state electrolyte, particularly polymer-based electrolyte. Some characterization techniques are not applicable to the polymer-based electrolytes due to their different physical properties from liquid electrolytes such as slow mass transport, high viscosity, low ionic conductivity, etc. For example, in-situ scanning probe microscope (SPM), including atomic force microscope (AFM) and scanning tunneling microscope (STM), are powerful tools to study the reactions at the surface with an atomic scale resolution and can identify the formation of \(\text{Li}^+\) dendrites in the liquid electrolytes. The high viscosity of polymer electrolytes, however, makes it difficult for the SPM probe to approach the surface of Li and move along the interface. So far, only a couple of techniques have been successfully applied in the in-situ or in-operando studies of the interface between \(\text{Li}^+\) anode and polymer electrolyte, which will be discussed in the context below.
In-situ SEM is the most common and helpful technique that directly monitors the morphology change and dendrite formation in the study of polymer electrolytes. By replacing the typical liquid electrolytes with polymer electrolytes and constructing a solid-state cell, the risk of leaking of liquid electrolyte under vacuum can be avoided. Because of the limited ionic conductivity of polymer electrolytes, the cathode and anode have to be close to each other and, thus, the in-situ cell is based on the sandwich structure that have the polymer electrolyte placed between two electrodes. The cross-sectional profiles of the sandwich cell were recorded during discharging and charging.

Zaghib and coworkers have done substantial work in this field. They studied the discharging and charging process of cells with Li anode, PEO-based polymer electrolyte, and various cathode like NMC, LiFePO₄, LiV₃O₈ (LVP) (Figure 5A), etc. The formation and evolution of the SEI and dendrites have been clearly demonstrated. In the case of using NMC cathode, SPE based on LiTFSI/PEO keeps decomposing from the contact location between the NMC and polymer, releasing gaseous fragments of by-products (Figure 5B). The thickness of the polymer electrolyte increases on charge and decreases on discharge but not linearly with the depth of discharging and charging. Because of the decomposition of polymer electrolyte made of LiTFSI/PEO, the thickness steadily decreases during the life span. The similar decomposition was not observed in the cells using LFP and LVP cathodes.

In-situ SEM could visualize the growth of dendrite directly, providing us a visual image of the formation and evolution of dendrites under the influence of various factors such as current density, stack pressure, and temperature. The sample surface, however, will be easily charged under the electron beam without gold sputtering owing to the limited electronic conductivity of polymer electrolyte, and thus, researchers are struggling to study the SEI layer and interface directly on the basis of low-resolution SEM images. Alternatively, in situ SEM can be strengthened by combining with focused ion beam (FIB) technique to observe the dendrites closely. Zaghib and co-workers observed a new active Li edge on the grain boundary based on the morphological change on the polymer electrolyte and they claimed that the Li⁺ dendrite pierced the polymer, melted, and then reduced the polymer (Figure 5C). Balsara and coworkers found the formation of globular Li structures above the faceted impurity particles at the interface during Li plating and striping by combining SEM and FIB.

X-ray tomography

SEM only exhibits the side view of the interface, which does not represent the entire interface. More importantly, it is only able to identify the pattern that forms at the edge of cell without FIB. To overcome this problem, X-ray tomography was applied to obtain the transmission images of the Li⁺ anode/electrolyte interface. By using the hard X-ray, the sample was sliced and the cross-sectional images of each slices were obtained to reconstruct the 3-D tomography of the electrode-polymer electrolyte interface with a high spatial resolution of up to 1 μm. Balsara and coworkers, for the first time, successfully identified the subsurface structures that hide underneath the dendrites of Li⁺ anode, which is impossible for merely using in-situ SEM. During cycling, the Li⁺ dendrites appeared at the sites where the subsurface structures were and they grew underneath the surface at the beginning. At this stage, the dendrites were invisible at the surface. Later, the dendrites grew rapidly during cycling and penetrated the separator eventually. This work changes our understanding of the dendrite growth, which is doomed to take place at the certain localization of the Li⁺ anode. The authors hypothesized that the impurities, such as Li₃N in metallic Li⁺ anode, are the source of substructure and Li⁺ dendrite.

In-situ Raman spectra provide sufficient chemical information and identify the reaction intermediates and products in reactions. Studies of in-situ Raman on the Li-polymer interface are scarce, and possible barriers are the weak signal and difficulties of waiving the background and noise from the side view of cells. Besides that, Raman can quantify the concentrations of Li and anions by their peak intensities to produce the corresponding mapping. Cheng et al. applied stimulated Raman to visualize the distribution of Li⁺ at the interface during Li plating (Figure 6). The stimulated Raman combines the high sensitivity of ions, high spatial resolution of 0.5 μm, and a fast imaging speed, which is an excellent method to track the real-time change of Li⁺ concentration near the electrode surface. By manipulating the focal plane, the 3-D model of Li⁺ dispersion was reconstructed and visualized. Cheng et al. identified a transitional stage between the no depletion of Li⁺ and the depletion of Li⁺ in the conventional model. During this stage, Li⁺ was partially depleted at some parts of Li⁺ surface, exhibiting a spatial heterogeneity of Li⁺, which encouraged the uneven Li⁺ growth following a positive feedback mechanism. This process is self-accelerated until Li⁺ is fully depleted and dendrites grow.
4.4 Challenges for in-situ analysis

In-situ analysis is crucial to investigate battery reactions; however, it is difficult to obtain the top-view profiles of the entire Li surface as the process occurs in a cell using liquid electrolytes owing to the restriction of the in-situ cells with polymer electrolytes using sandwich structure. The signals, that is, electron beam, laser, emitted electrons by X-ray, gas evolution, etc., are likely to be blocked by the electrode at both sides of the polymer electrolyte, either by a piece of Li or a composite cathode. Therefore, mostly studies are based on the side view of the cells as in the case of in-situ SEM, bringing in edge effects. For SEM, researchers are only able to watch the exposed side of cells and they cannot obtain the overview of the whole interface. Even if FIB is applied, only a couple of sites of interest can be studied and it is a destructive technique. In-situ TEM has been extensively applied to the study on the solid-state battery and Li\(^{\circ}\) dendrite.\(^{30,73}\) Although some polymers, such as PEO, might decompose under the electron beam, the cryo-TEM is a good option. Synchrotron X-ray imaging allows researchers to watch the side face of cells in a transmission mode yet it still gives a 2-D images of Li\(^{\circ}\)-dendrite formation and evolution. X-ray tomography allows researcher to reconstruct a 3-D model of the Li\(^{\circ}\) surface with admirable spatial resolution and, thus, have a more comprehensive visualization of the details in dendrite growth. However, these in-situ techniques only provide information on morphology, which is helpful to visualize the dendrite growth, but it is not enough to figure out the unpinning reasons for dendrite evolution due to the lack of chemical information. While in situ Raman is a good complement to identify chemical composition, at least two challenges remain: one is the low sensitivity of Raman without enhancement; the other is that the interface is very thin in the side view of a sandwich cell, which is smaller than the typical laser spot size of Raman (ca. 1 \(\mu m\)), hindering the use of in-situ Raman spectra. There are a few methods to improve the sensitivity of Raman signal such as enhancement by special surface nanostructures, AFM tips, etc. Nevertheless, the physical properties of the polymer electrolyte indeed introduce technical challenges to obtain the enhanced Raman spectra.

As a technique for bulk materials, plain Li nuclear magnetic resonance (NMR) provides quantitative results of dendrite formation, yet NMR itself does not provide spatial information.\(^{74,75}\) Magnetic resonance imaging (MRI) can provide both quantitative and spatial information. Jerschow, Grey, and coworkers have put in evidence the microstructure of Li\(^{\circ}\) anode in the cell with a liquid electrolyte using \(^{7}\)Li MRI, but it delivers an unsatisfactory resolution of 60 \(\times\) 376 \(\mu m\) in the x and y directions.\(^{76}\) Recently, Jerschow and coworkers studied the SEI growing process and exchange of Li ion between Li\(^{\circ}\) anode and LP-30 electrolyte (i.e., 1.0 M LiPF\(_6\)-ethylen carbonate [EC]/ethyl methyl carbonate [EMC] (30/70, v/v)) using in-situ \(^{7}\)Li/\(^{6}\)Li NMR.\(^{77}\) Little work about in-situ NMR/MRI in polymer electrolyte has been demonstrated so far. In case using \(^{6}\)Li, neutron beam-based techniques can be used.\(^{75,78}\) Neutron beam has a strong penetration capability and reacts with \(^{6}\)Li to release \(\alpha\) particles and \(^{3}\)H particles. It is suitable for the depth profile characterization in LIBs. It exhibited a high resolution of 72 nm in a cell with metal oxide cathode and liquid electrolyte although it is only in one dimension.\(^{78}\)

The ex-situ techniques for the polymer electrolyte are almost same as those for the cell using liquid electrolyte. The characterizations of bulk materials, such as X-ray diffraction (XRD), NMR, are not affected in the polymer-based electrolyte, whereas the surface analysis, such as X-ray photoelectron spectroscopy (XPS), Raman, have to deal with the barriers of removing the residue polymer electrolyte stuck tightly to the Li\(^{\circ}\) surface and obtaining a clean surface of Li\(^{\circ}\) anode. Although the sticky SPEs can be removed by using some volatile solvents, like acetonitrile, dimethoxyethane, tetrahydrofuran, dimethyl...
carbonate, these solvents change the chemical composition of SEI and even might react with Li\(^{\circ}\) anode, introducing some new side reactions. Therefore, characterizations of Li\(^{\circ}\) anode, the SPE-based cell without damaging the SEI layer are still challenging and require more efforts.

5 | CONCLUDING REMARKS AND OUTLOOK

SSLMPBs with good scalability at battery pack level have been intensively studied over the past 40 years, and the main progress and advances with respect to the electrolyte and anode-electrolyte interphase have been briefly discussed in this article. Despite the achievements mentioned in above sections, further actions in the following aspects would be of benefit for enhancing the performance of SSLMPBs.

1. Rather than simply searching for highly conductive SPEs, attention needs to be paid to the selectivity of Li-ion transport. A high \(T_{Li^+}\) favors low-polarization cycling of SSLMPBs with possibly dendrite-free Li\(^{\circ}\) deposition and dissolution processes. In this regard, the design of novel anions with low anionic mobility would be of importance.

2. Combination of various electrolyte salts and additives may result in synergistic effects in stabilizing Li\(^{\circ}\) anode interphase; hence, selectively formulating SPE with dual salts or dual additives is believed to be an elegant approach to largely improve the cyclability of SSLMPBs. Nonetheless, profound understanding on the nature of SEI layer formed in SSLMPBs and correlations between structure-property relations would be required for a more efficient design of SPEs.

3. The highly reactive nature of Li\(^{\circ}\) anode could be partially alleviated by utilizing SPEs due to slow reaction kinetics, while comparative studies on anode-electrolyte interphase between SPEs and the corresponding liquid analogues are seldom performed; this however could be intriguing to shed more light on the properties of SEI layer.

4. Advanced characterization techniques being developed for batteries using liquid electrolytes would sometimes encounter certain difficulties when directly applied for SSLMPBs. However, NMR/MRI techniques could certainly provide insights in anode-electrolyte interphase properties in SSLMPBs. More importantly, due to the unique properties of SPE, it is worth exploring some in-situ techniques for interface studies, which is not applicable in cells with liquid electrolytes but practical for SSLMPB. SPEs are compatible with high vacuum, which is not the case of liquids.

We anticipate that with continuous effort paid to aforementioned aspects, the performance metrics of SSLMPBs could be remarkably enhanced and thereby meet the requirements, particularly eliminating safety threats and enhancing energy density, imposed by emerging applications such as EVs.

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ORCID

Heng Zhang @ https://orcid.org/0000-0002-8811-6336

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