Topical Review

Ion transport and structural design of lithium-ion conductive solid polymer electrolytes: a perspective

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Abstract
Solid polymer electrolytes (SPEs) possess several merits including no leakage, ease in process, and suppressing lithium dendrites growth. These features are beneficial for improving the cycle life and safety performance of rechargeable lithium metal batteries (LMBs), as compared to conventional non-aqueous liquid electrolytes. Particularly, the superior elasticity of polymeric material enables the employment of SPEs in building ultra-thin and flexible batteries, which could further expand the application scenarios of high-energy rechargeable LMBs. In this perspective, recent progresses on ion transport mechanism of SPEs and structural designs of electrolyte components (e.g. conductive lithium salts, polymer matrices) are scrutinized. In addition, key achievements in the field of single lithium-ion conductive SPEs are also outlined, aiming to provide the status quo in those SPEs with high selectivity in cationic transport. Finally, possible strategies for improving the performance of SPEs and their rechargeable LMBs are also discussed.

Keywords: solid-state lithium metal batteries, solid polymer electrolytes, single lithium-ion conductor, conductive lithium salts, polymer matrices
Future Perspectives
Solid-state lithium metal batteries (SSLMBs) utilizing solid polymer electrolytes (SPEs) are possible solutions to meet the stringent demands in inherent safety and energy densities for next-generation battery technologies. Structural design of lithium salts, polymer matrices, and polyanions are of essential importance in regulating the fundamental properties of SPEs, and thereby enhancing the overall performances of SPE-based SSLMBs.

1. Introduction

Lithium-ion batteries (LIBs) are able to carry electric energy in chemical forms by virtue of the reversible (de)intercalation of Li⁺-ions (Li⁺) into hosting materials, which are known as ‘rocking-chair batteries’ [1]. Amongst existing rechargeable battery technologies, LIBs have achieved widespread applications spanning from portable electronic devices (i.e. computer, communication, and consumer electronics) to electric vehicles, due to their high operating voltage (ca. 4.0 V vs. Li/Li⁺) and energy density (ca. 300 Wh kg⁻¹), relatively long cycle life (>300 cycles), and negligible memory effect [2].

The prevailing LIBs are built with nonaqueous liquid electrolytes comprising lithium hexafluorophosphate (LiPF₆) as conductive salt and organic carbonates (e.g. ethylene carbonate (EC), and methyl ethyl carbonate, etc) as solvents, with the addition of small amounts of functional electrolyte additives (i.e. vinylene carbonate, and fluoroethylene carbonate, etc) [3, 4]. Generally, the as-formulated non-aqueous liquid electrolytes present sufficient ionic conductivities (ca. 10⁻² S cm⁻¹) at room temperature and excellent chemical and electrochemical stabilities (>4.2 V vs. Li/Li⁺) [3], enabling the operation of LIBs with decent power capability. However, the LiPF₆-based nonaqueous liquid electrolytes show poor chemical stability, exacerbating the cycling performance of LIBs during long-term operation, particularly at elevated temperatures (>40 °C) [5]. Effectively, at the industrial level, LiPF₆ is produced via the reaction of lithium fluoride (LiF) and phosphorus pentfluoride (PF₅) in anhydrous hydrogen fluoride solvent [6], in which trace amounts (ppm level) of protic impurities (e.g. hydrogen fluoride) are inevitably inherited from the preparative procedures. It is reported that these protic impurities are responsible for triggering the chemical decompositions of LiPF₆-based electrolyte solutions, generating highly toxic substances, such as phosphorus trifluoride (O=PF₃), and organophosphorus compounds (O=PF₂OR, R=alkyl) (figure 1(a)) [5].

In addition to the chemical instability of LiPF₆, low flash points (e.g. T_flash = 18 °C for DMC [7]) and potential leakage of organic carbonates also impose critical concerns on the inherent safety of electrolyte materials and their rechargeable batteries [7], particularly with the implementation of high-energy electrode materials such as lithium metal and its alloy [8]. Therefore, traditional LIB technologies are unlikely to meet the requirements of the emerging fields with increasing energy density (>400 Wh kg⁻¹) and safety demands, such as power and energy storage and smart grids [9]. Thus, there is an urgent need to develop next-generation battery technologies with low-cost, high-energy density, long cycle lifespan, and high intrinsic safety [10].

With the replacement of organic liquid electrolytes with solid-state electrolytes, solid-state lithium metal batteries (SSLMBs) have been deemed as a feasible solution to enhance the inherent safety and energy density of the contemporary LIBs, due to the elimination of volatile components and the possible utilization of high-capacity electrode materials (e.g. lithium metal electrode: 3860 mAh g⁻¹; figure 1(b)) [11]. Presently, research activities related to SSLMBs have become increasingly important [12].

In 1973, Wright and co-workers [13] reported that the mixtures of poly(ethylene oxide) (PEO) and several alkali metal salts (such as potassium thiocyanate (KSCN) and sodium thiocyanate (NaSCN)) afford ionically conductive plastic materials at higher temperatures (>60 °C) [13]. Later, Armand et al [14] realized the profound significance and potential application of these ionically conductive polymers for developing SSLMB technologies, thus proposing their utilization as solid electrolytes for SSLMBs. Briefly, lithium-ion conductive SPEs possess several intriguing merits, including greatly enhanced safety, ease of processing, simplicity of cell construction and assembly, and so on [15]. Therefore, the research on SPE-based SSLMBs has attracted extensive attention from the academic and industrial sectors (figure 1(c)).

Polymer electrolytes (PEs) are a kind of ionic conductive material utilizing high molecular weight polymer as a matrix. Generally, according to the chemical compositions, PEs can be sorted into four different families, including solid polymer electrolytes (SPEs), composite solid polymer electrolytes (CSPEs), plasticized polymer electrolytes (PPEs, liquid plasticizer content <50 wt%), and gel polymer electrolytes (GPEs, liquid plasticizer content >50 wt%) (figure 1(d)) [16]. Generally, the chemical compositions of SPEs are relatively simple, containing only lithium salts and polymer matrices. For CSPEs, a certain amount of inorganic solid fillers is introduced to improve the transport properties of lithium ions and the mechanical strength of electrolyte membranes [17]. The latest research progresses in this domain have been scrutinized in relevant literature [18, 19]. For PPEs and GPEs, liquid plasticizers are added to promote the segmental motions of polymers and better carry ionic species. Effectively, these two kinds of PEs behave mostly like conventional liquid electrolytes depending on the contents of liquid components [16]. Note that the introduction of small molecule compounds accelerates chemical and electrochemical parasitic reactions at the interphases/interfaces between electrolyte and electrode materials, decreasing the cycle life of corresponding SSLMBs, despite their capability in improving ionic conductivities [20].

In this perspective, recent advances in lithium-ion conductive SPEs are briefly discussed, with main attention paid to the ion transport in SPEs, emerging conductive lithium salts, and polymer matrices utilized. In addition, the status quo of a special type of SPE with lithium-ion transference number (T_Li⁺)
close to unity, single lithium-ion conductive SPEs (SLIC-SPEs), is also reviewed. Design strategies and future directions for developing robust SPEs and their SSLMBs are provided.

2. Ion transport in SPEs

A comprehensive understanding of the transport phenomena of ion species is of supreme importance for designing high-performant SPEs. Figure 2(a) outlines several key findings in elucidating the ion transport in SPEs at the microscopic level over the past 40 years. As early as the 1970s, Armand et al [14] anticipated that the segmental motion of polymeric backbones is related to the transport of ion species, particularly for Li$^+$ cations, as shown in figure 2(b). In the 1980s, with solid-state nuclear magnetic resonance techniques, Berthier et al [21] demonstrated that ion transport of a PEO-based SPE system (typically ‘salt in polymer’) occurs primarily in the amorphous region therein. These early studies provide implicit microscopic images of the ion conduction processes in SPEs [22, 23].

From another perspective, Stoeva et al [24] proposed that the crystalline phases of PEO-based SPEs are ionically conductive with well-defined microstructures (figure 2(b)). For the crystalline LiAsF$_6$/PEO electrolytes, relatively rapid diffusion of Li$^+$ ions is realized via the hopping of ionic species without involving the segmental motion of PEO chains (diffusion paths indicated by a pink circle in figure 2(b)), the PEO matrix remains ‘immobilized’ during the ionic conduction processes. In sharp contrast, the ionic conductivities of crystalline LiAsF$_6$/PEO electrolytes are nearly one order of magnitude higher than those of amorphous LiAsF$_6$/PEO electrolytes [24]. Yet, these crystalline SPEs are likely to achieve high ionic conductivities with low molecular weight PEO (< 5000 g mol$^{-1}$), which could hardly afford self-standing films and thereby hinder their practical applications in lithium batteries [24–26].

Since the 1990s, Angell et al [27] systematically studied the ion transport behaviors of the PEO-based electrolyte systems and revealed that the Li$^+$ transport is highly coupled with the movement of polymer chain segments. To quantify the relational degree between the ion transport behavior and the movement of polymer chain segments, the concept of decoupling indices ($R_{\tau}$) was proposed, as mathematically described by equation (1):

$$R_{\tau} = \frac{\tau_s}{\tau_{\sigma}}$$

where $R_{\tau}$ is the decouple indices, $\tau_s$ is the macroscopic structural relaxation time of the matrix glass (in seconds), and $\tau_{\sigma}$ is the conductivity relaxation time (in seconds) [27, 28].

Traditional SPEs comprising polyether-type matrices (e.g. PEO) and common lithium salts (e.g. lithium perchlorate
(LiClO$_4$) are classical ‘coupling’ systems (generally, $R_τ < 1$) [28, 29]. In this scenario, ionic transport is highly correlated with the segmental movement of the polymer chains within the amorphous region (figure 3(c)) [30], and ion mobility is closely related to temperature change, e.g. the ion conductivity decreases rapidly to about $10^{-14}$ S cm$^{-1}$ when lowering the temperature close to glass transition temperature ($T_g$) [28]. In 1993, Angell et al [31] proposed the concept of ‘polymer in salt’ electrolytes, in which a large amount (>50 wt%) of lithium salt with low melting point and high dissociation characteristics is utilized to form ‘decoupled’ SPEs systems. In this scenario, the Li$^{+}$ transportation does not depend on the segmental motions of polymer chains [31].

According to the different transport behaviors of ionic species, SPEs could be generally categorized into ‘coupled’ and ‘decoupled’ systems [32]. For the ‘coupled’ systems, Li$^{+}$ transport is highly correlated with the motion of the polymer chain segments (figure 3(c)). For the ‘decoupled’ systems, the numbers of cation/anion clusters increase with increasing salt concentration, and the aggregated cation/anion clusters are interconnected with each other, favoring the formation of an ionic conductive network which could provide a fast conduction channel for Li$^{+}$ transport [28, 33] (figure 3(c)). In general, the decoupled indices of the ‘decoupled’ system could be as high as $10^{13}$ [27]. Unfortunately, most available lithium salts are unlikely to meet the stringent requirement imposed by ‘decoupled’ SPEs including low melting point and extremely high dissociation. Besides, increasing salt concentration also sacrifices the mechanical properties of the as-formed SPEs [34–36]. Therefore, the development of the ‘coupled’ SPEs systems tend to be more rapid than that of the ‘decoupled’ SPEs ones.

To date, the ‘coupled’ SPEs are the most widely studied attributed to their easy processing and good compatibility with high-energy electrode materials. Among them, PEO and its derivatives are the most thoroughly studied matrices [37–43], which is ascribed to the features below:

(a) the oxygen atom on the repeat unit of ethylene oxide (–CH$_2$CH$_2$O–, EO) owns strong donicity, which can form complexes with metal ions, thus promoting the dissolution of alkali metal salts, and realizing Li$^{+}$ transport via coupling and decoupling of polymer chain segments [30];
(b) traditional PEO-based SPEs own several advantages, including low density (ca. 1.2 g cm$^{-3}$), good chemical stability, and low cost, and can better inhibit lithium dendrites growth in SSLMBs [44, 45].

The neat PEO is a semi-crystalline helical polymer, possessing a certain degree of crystallinity (> 60%), due to
its regular and highly ordered structure [46, 47]. As mentioned above, the ion transport of SPEs relies heavily on the segmental motion and local relaxation of polymeric chains, and Li\(^+\) transport mainly occurs in the amorphous region of SPEs [48–51]. Consequently, the ionic conductivity of PEO-based SPEs is generally lower than 10\(^{-3}\) S cm\(^{-1}\) at room temperature [52], which hinders its large-scale application in SSLMBs. Reducing the crystallinity of traditional PEO-based SPEs has become a hot research topic in the field of SPE-based SSLMBs, and various approaches have been assessed, including structural modifications of PEO, and doping with inorganic materials [44, 53], and so on (see section 4.1 for detailed discussion).

3. Developing robust conductive lithium salts

Generally, the conductive lithium salt not only acts as the source of charge carriers for SPEs, but also participates in the construction of electrode-electrolyte interphases/interfaces via chemical and/or electrochemical reactions [54]. Therefore, the composition and chemical structure of conductive lithium salts have a critical impact on the fundamental properties of SPEs. Generally, ideal conductive lithium salt should contain several traits (figure 3(a)), including solubility, interfacial compatibility, chemical stability, aluminum corrosion, etc.

To form ionic conductors, the breakdown of ionic bonds between Li\(^+\) cation and anions in the presence of electron-donating polymer matrices tend to be of higher priority. Indeed, the dissociation process is determined by the lattice energy of salt, the cohesive energy of polymer, and the solvation energy thereof (figure 3(b)). For polymers, the cohesive energy density (CED) is mathematically expressed as [55]:

\[
CED = \frac{H_{\text{vap}} - RT}{V} = \delta^2
\]

where \(H_{\text{vap}}\) stands for the heat of vaporization, \(R\) and \(T\) represent the respective ideal gas constant and the absolute temperature, \(V\) is the molar volume, and \(\delta\) stands for the solubility parameter, a semi-quantitative measure of the polarity of the repeat units.

In addition, the microscopic viscosity of the SPEs system plays an important role in dictating the transport properties of ionic species therein [56]. And the viscosity of SPEs is highly correlated with the free volume provided by anions. Therefore, anions with high structural flexibility are necessary for building high-performance SPEs [52]. Presently, various kinds of anions have been introduced into Li-ion conductive SPEs, including halide, carboxylate, sulfonate, and imide anions (figure 3(c) and table 1) [57].

3.1. Sulfonimide-based lithium salts

Sulfonimides, particularly perfluorinated sulfonimide anions, \([(\text{CF}_3\text{SO}_2)\text{N}]^-\text{X}^+\), are one of the most noticeable anions for Li-ion conductive SPEs, attributed to their low affinity toward Li\(^+\) and high structural flexibility [75, 76]. Among which, bis(trifluoromethanesulfonyl)imide anion (\([(\text{CF}_3\text{SO}_2)\text{N}]^-\text{TFSI}^+,\) figure 4(a)) firstly prepared by Meussdorffer and co-workers [77] in the acid form in 1972, appears to be the most investigated candidate representative anions. In the case of TFSI\(^-\) anion, the sulfonimide anion center owns several resonance structures, allowing the delocalization of negative charges on the nitrogen atom to the four oxygen atoms. Additionally, the strong electron-withdrawing ability of CF\(_3\) groups could further lower the Lewis basicity of the anion (Gutmann donor number = 5.4 [75]), affording low dissociation energy of the Li\(^+\) cations. The interconversion between different conformations of TFSI\(^-\) anion occurs with extremely low energy barriers (< 5 kJ mol\(^{-1}\) [78]), which endows its large free volume. These key properties facilitate its dissolution and dissociation in polymer matrices, promoting the rapid transport of ionic species ionic conductivities (e.g. 1 \times 10\(^{-4}\) S cm\(^{-1}\), 80 °C). Presently, LiTFSI has been deemed as a benchmark salt for screening the new anions for Li-ion conductive SPEs [45].

In recent years, other kinds of lithium sulfonimide salts have been employed as conducting salts for SPEs. Lithium fluorosulfonylimide salts containing fluorosulfonyl (FSO\(_2\)−) group have become an interesting family, owing to their unique capability in building stable solid electrolyte interphase/interface (SEI) layer on various kinds of...
Table 1. Ionic conductivities and Li$^+$ transference numbers ($T_{\text{Li}^+}$) of some typical PEO-based electrolytes.

| Lithium salts$^a$     | $\sigma_{\text{bulk}}$ S cm$^{-1}$ (30 °C) | $\sigma_{\text{total}}$ S cm$^{-1}$ (80 °C) | $T_{\text{Li}^+}$ $^c$ | Reference |
|-----------------------|------------------------------------------|------------------------------------------|------------------------|-----------|
| LiBF$_4$              | $6 \times 10^{-7}$                       | $6 \times 10^{-4}$                       | 0.29                   | [58, 59]  |
| LiPF$_6$              | —                                        | $1 \times 10^{-5}$                       | 0.19                   | [59]      |
| LiTFSI                | $1 \times 10^{-5}$                       | $1 \times 10^{-3}$                       | 0.18                   | [52]      |
| LiBETI                | $1 \times 10^{-5}$                       | $9 \times 10^{-4}$                       | 0.33                   | [60]      |
| LiNFSI                | $3 \times 10^{-7}$                       | $3 \times 10^{-4}$                       | 0.25                   | [61]      |
| LiTFNFSI              | $1 \times 10^{-6}$                       | $3 \times 10^{-4}$                       | 0.16                   | [62]      |
| LiFSI                 | $8 \times 10^{-7}$                       | $2 \times 10^{-3}$                       | 0.14                   | [52]      |
| LiFTFSI               | $2 \times 10^{-6}$                       | $1 \times 10^{-3}$                       | 0.17                   | [57]      |
| LiFFPSI               | $3 \times 10^{-6}$                       | $9 \times 10^{-4}$                       | 0.19                   | [57]      |
| LiFNFSI               | $3 \times 10^{-6}$                       | $6 \times 10^{-4}$                       | 0.27                   | [57]      |
| LiHPSI                | $2 \times 10^{-6}$                       | $3 \times 10^{-4}$                       | 0.47                   | [63]      |
| LiDFTFSI              | $1 \times 10^{-5}$                       | $9 \times 10^{-4}$                       | 0.35                   | [64]      |
| LiDFSI                | $2 \times 10^{-6}$                       | $5 \times 10^{-4}$                       | 0.39                   | [65]      |
| LiEFA                 | $3 \times 10^{-6}$                       | $4 \times 10^{-4}$                       | 0.42                   | [66]      |
| LiTFTPSI              | $3 \times 10^{-7}$                       | $3 \times 10^{-3}$                       | 0.69                   | [67]      |
| LiTFEMSISI            | ca. $10^{-5}$                           | $5 \times 10^{-4}$                       | 0.64                   | [68]      |
| LiTFSI                | $6 \times 10^{-6}$                       | $9 \times 10^{-4}$                       | 0.29                   | [69]      |
| LiDOF                 | $2 \times 10^{-6}$                       | ca. $10^{-5}$                           | —                      | [70]      |
| LiBOB                 | $1 \times 10^{-6}$                       | $1 \times 10^{-3}$                       | 0.13                   | [71]      |
| LiTCM                 | $1 \times 10^{-6}$                       | $6 \times 10^{-4}$                       | 0.31                   | [72]      |
| LiDCTA                | —                                        | $6 \times 10^{-4}$                       | 0.25                   | [73]      |
| LiTDI                 | $2 \times 10^{-3}$                       | $1 \times 10^{-3}$                       | 0.15                   | [74]      |

$^a$ The abbreviations are listed as below: lithium bis(pentafluoroethanesulfonyl)imide (LiBETI), lithium bis(oxalato)borate (LiBOB), lithium (benzenesulfonyl)(trifluoromethanesulfonyl)imide (LiBTFSI), lithium difluoro(oxalo)borate (LiDOFB), lithium bis(oxalato)borate (LiDOFB), lithium (difluoromethanesulfonyl)(trifluoromethanesulfonyl)imide (LiDFTFSI), lithium salt with ether-functionalized anion (LiEFA), lithium (fluorosulfonyl) (nonafluorobutanesulfonyl)imide (LiFNFSI), lithium (fluorosulfonyl) (pentafluoroethanesulfonyl)imide (LiFTPSI), lithium bis(fluorosulfonyl)imide (LiFSI), lithium (fluorosulfonyl)(trifluoromethanesulfonyl)imide (LiFTFSI), lithium bis([1,1,3,3,6-hexafluoro-2-propoxy]sulfonyl)imide (LiHPSI), lithium bis(nonafluorobutanesulfonyl)imide (LiNFSI), lithium tricyanomethanide (LiTCM), lithium trifluoromethanesulfonate (LiTFI), lithium bis(trifluoromethanesulfonyl)imide (LiTFPSI), lithium (trifluoromethanesulfonyl)(trifluoromethanesulfonyl)imide (LiTNFSI), lithium (trifluoromethanesulfonyl)iminium (sulfonimide) (LiTNFSI), lithium bis(trifluoromethanesulfonyl)(trifluoromethanesulfonyl)imide (LiTFPSI), lithium bis(trifluoromethanesulfonyl)(trifluoromethanesulfonyl)imide (LiTNFSI), lithium (trifluoromethanesulfonyl)iminium (sulfonimide) (LiTNFSI).

$^b$ Ionic conductivity.

$^c$ Li$^+$ transference number.

The anode materials (Li$^+$ anode and graphite electrode). Lithium bis(fluorosulfonyl)imide ([(FSO$_2$)$_2$N$^-$], FSI$^-$, figure 4(a)), one representative example of lithium fluorosulfonimide salts, was synthesized in acid form by Appel in the early 1960s [79]. The anion was proposed as a candidate for battery application by Armand in the 1990s [80]. In the past years, our group has systematically investigated the properties of various kinds of LiFSE-based SPEs, including a wide array of polymeric matrices (e.g. PEO [52] and poly(ionic liquids) (PILs) [81]), which show much higher ionic conductivities and better chemical and electrochemical stabilities on electrode materials than those of the LiTFPSI-based ones [69].

It has been demonstrated that the rotation barriers of fluorosulfonimide anions are lower than the symmetric perfluorinated sulfonimide anions (e.g. 0.9 kJ mol$^{-1}$ for (fluorosulfonyl)(pentafluoroethanesulfonyl)imide ((FSO$_2$)$_2$N$^-$), FNSI$^-$) vs. 6.3 kJ mol$^{-1}$ for bis(perfluoroethanesulfonyl)imide ((C$_2$F$_5$SO$_2$)$_2$N$^-$), BETI$^-$) [82], endowing the formers with better structural flexibility and stronger plasticizing ability [82]. Besides, the S–F bond in the fluorosulfonimide anions tends to be more electrochemically active compared to the C–F bonds in the symmetric perfluorinated sulfonimide anions, which may undergo electrochemical degradations prior to the reductions of polymer matrices (ca. 1.0 V vs. Li/Li$^+$, figure 4(b)) [54]. The as-formed decomposition products (especially LiF) of the fluorosulfonimide anions favor the formation of dense and electronic insulating SEI layers, thus preventing continuous depositions of electrolyte components [54, 83].

With the extension of the perfluorocarbon side chain, lithium fluorosulfonimide salts show enhanced compatibility with Li$^+$ anode significantly improved stability toward (electro-)chemical oxidation, which is related to the decomposed products of the longer perfluoroalkyl chains which may improve the stability of electrode–electrolyte interfaces [57]. As a result, a prototype Li$^+$-lithium iron phosphate (LiFePO$_4$, LFP) cell with LiFNFSI/PEO at a molar ratio of EO unit to Li$^+$ (hereafter abbreviated as [EO]/[Li$^+$]), by mole) of 20 showed excellent cyclability (capacity retention: > 80% at cycle 500) [57]. However, the SPEs based on lithium perfluorinated sulfonimide salts suffer from rapid anionic migrations due to the negligible interactions between anion and polymer matrices (compared with the Li$^+$ dipole interactions). Typical $T_{\text{Li}^+}$ values for these electrolytes are close to 0.2. The rapid transport of anionic species induces concentration gradients, which causes undesired concentration polarizations and leads to inferior utilization of active materials of composite electrodes [84, 85].

Through the attachment of anionic moieties onto the polymer matrices (or inorganic macromolecules), the transport of anionic species could be nearly eliminated, as extensively discussed in section 4. Alternatively, enhancing the interactions between anions and polymer matrices via non-covalent bonds could also slow down the migration of anions. Researchers also focus on other ingenious and effective approaches to capture anion by introducing hydrogen-bond in conductive lithium salt structure. Oteo et al [86] reported the utilization of a non-perfluorinated sulfonimide anion, lithium (difluoromethanesulfonyl)(trifluoromethanesulfonyl)imide ([HC$_2$F$_2$SO$_2$](CF$_3$SO$_2$)N)Li, LiDFTFSI) for Li-ion conductive SPEs. LiDFTFSI/PEO shows a high $T_{\text{Li}^+}$ value compared with the LiTFISI-based one (e.g. 0.35 (LiDFTFSI/PEO) vs. 0.20 (LiTFISI/PEO), 70 °C). It is anticipated that the suppressed anion transport is highly related to the enhanced interaction between the H atom with positive charge in DFTFSI$^-$ anion and dipole in PEO (i.e. hydrogen bonds). Afterwards, this hypothetical structure (i.e. [EO···H–)] was captured by molecular dynamics simulations of similar systems carried out by Qiao et al [65]. Besides, one could also count on other interactions between anion and polymer matrices, e.g. dipole–dipole interaction, dipole–dipole interaction [68], π–π stacking [67], etc (see the schematic diagram in figure 4(c))
By replacing an oxygen atom in TFSI\(^{-}\) anion with strong electron-withdrawing group CF\(_3\)SO\(_2\)N=, the interactions between Li\(^{+}\) cations and sulfonimide anions could be further reduced. The as-obtained anion, (trifluoromethane(S-trifluoromethanesulfonylimino)sulfonyl) (trifluoromethanesulfonyl) imide ([CF\(_3\)SO(=NSO\(_2\)CF\(_3\))]\(^{-}\), figure 4(a)), shows extremely low affinity toward Li\(^{+}\) cations, and high ionic conductivity for its PEO-based SPEs compared to the LiBETI-based ones \[^{69}\]. This result clearly suggests the important role of negative charge delocalization in achieving highly Li\(^{+}\)-ion conductive SPEs \[^{69}\].

3.2. Other emerging conductive lithium salts

In addition to the sulfonimide-based conductive lithium salts, several other kinds of conductive lithium salts have also received extensive attention in the domain of SPE-based SSLMBs. For example, lithium bis(oxalate)borate (LiBOB) and lithium difluoro(oxalate)borate (LiDFOB) have been investigated by several research groups (figure 5(a)), owing to their ability in forming robust SEI layers on Li\(^{0}\) anode to suppress the continuous reductive decompositions of polymer matrices \[^{87}\].

In another example, Zhang et al systematically characterized the effect of lithium tricyanomethanide (LiC(CN\(_3\)), LiTCM, figure 5(b)), as a fluorine-free conductive salt, on the properties of PEO-based electrolytes \[^{72}\]. LiTCM/PEO provides lower polarizations for Li\(^{0}\)||Li\(^{0}\) symmetrical cell as compared to the LiTFSI/PEO reference system, despite its slightly lower ionic conductivities resulting from higher glass transitions \((T\(_{g}\): –27 °C (LiTCM/PEO) vs. –30 °C (LiTFSI/PEO)). The improved interfacial compatibility would be attributed to the reductive polymerizations of the TCM\(^{-}\) anion, generating a highly Li\(^{+}\)-conductive graphene-contained SEI layer therein \[^{72}\].

In addition, Hückel-type salts are another emerging candidate for SPEs attributed to highly delocalized negative charges by conjugated \(\pi\) bonds \[^{45}\]. Egashira et al reported the physicochemical properties of SPEs with a Hückel-type salt, lithium dicyanotriazolate (LiDCTA, figure 5(c)) \[^{73}\]. LiDCTA/PEO exhibits a decent ionic conductivity value of \(4 \times 10^{-4} \text{ S cm}^{-1}\) at 80 °C. Besides, another Hückel-type salt,
lithium 2-trifluoromethyl-4, 5-dicyanoimidazolate (LiTDI, figure 5(c)), could form a low-melting phase in PEO, thereby inhibiting the crystallization of the electrolyte and improving the ionic conductivities of SPEs [74].

Overall, since the initial utilization of SPEs for SSLMBs, the sulfonimide-based lithium salts have become a research hotspot due to their unique properties such as highly flexible structure, low charge density, ease in structural modifications, etc. Remarkable achievements have been made in terms of the design of innovative lithium salts for SPEs; yet, mechanistic understandings of the role of certain functional groups in SSLMBs, especially the interphases formed between electrode and SPEs with different kinds of anions, are still needed.

4. Developing advanced polymer matrices

The characteristics of polymer matrices have a profound influence on the performances of SPEs [88–90], and the fundamental physical properties of some popular polymer matrices are summarized in table 2. As a reference polymer, the \( T_g \) of PEO is relatively low (\( T_g = -64 ^\circ C \)), a sign of rapid segmental motion of EO units above room temperature [89]. By replacing the C–O linkage with Si–O bond, one may further decrease the \( T_g \) value. For example, poly(dimethylsiloxane) (–(Si(CH\(_3\))\(_2\))O–, PDMS) shows an extremely low glass transition behavior at \(-127 ^\circ C \); yet, the practical application of PDMS-based SPEs is hindered by its high cost, difficulty in process, and adverse side effects (i.e. the hydrolysis of Si–O–Si to silanol, and the spontaneous condensation at room temperature) [90, 91]. Through the incorporation of polar groups (e.g. nitrile, carbonyl), one may promote the dissolution of metal salts; however, the strong van der Waals interactions between these groups drastically increase the CED of the neat polymer and the \( T_g \) values. In a typical example, high-molecular-weight poly(acrylonitrile) (PAN) shows a high glass transition at 125 °C (table 2) and CED (620–900 J cm\(^{-3}\) mol\(^{-1}\)), which could barely solvate common lithium salts in the absence of small molecular solvents [92, 93]. Therefore, with commercially available polymers, it is rather difficult to obtain highly conductive and self-standing SPEs membranes.

The design of the molecular structures of polymer matrices is one of the most effective methods to boost the ionic conductivity at room temperature and anti-oxidation properties of PEO-based SPEs [53, 87, 94–97]. Here, the research progress related to some emerging polymer matrices is discussed in the following section, including (a) Jeffamine-based amorphous polymers, and (b) polycarbonate and its derivatives. Note that, except for neutral polymers without any ionic groups, there has been a growing interest in utilizing polymerized ionic liquids as matrices for SPEs [81, 98–101]. The progress in this domain has been scrutinized in recent review articles [101] and will not be discussed in the present work.

4.1. Amorphous polyethers

Jeffamine® is a kind of commercial polyether amines, terminated with primary amino groups and containing ethylene oxide (EO), propylene oxide (–CH(CH\(_2\))CH\(_2\)O–, PO), or a mixture of EO/PO [102]. Utilizing Jeffamine moiety in building SPEs delivers several advantages, including (a) the repeat unit of EO/PO could effectively dissolve and dissociate lithium salt due to the strong donicity of EO/PO units, (b) the structural disorder of EO/PO could efficiently inhibit the crystallization processes; and (c) the primary amino group at the end could undergo condensation polymerizations with anhydride, thus allowing facile regulation on the topological structure of the polymer matrices. Consequently, Jeffamine® compounds provide a simple and effective approach for the efficient preparation of novel polymer matrices (figure 6(a)) [102]. The basic physical properties of some Jeffamine-based SPEs are collected in table 3.
and Jeffamine M-2070, table
ine compounds (i.e. Jeffamine M-600, Jeffamine M-1000,
and scalable. Combining the high degree of configurational
noteworthy that the synthesis route of the matrices is simple
poly(ethylene propylene maleic anhydride) backbone. It is
amine oligomer side chains (i.e. Jeffamine compounds) and
class of comb-like polymer matrices comprising polyether
points of PEO [109].

In 1992, Benrabah et al [103] synthesized a series of
polyamide compounds through the polycondensation reaction
between Jeffamine (e.g. Jeffamine ED-600, ED-900, terep- 
thaloyl chloride (TAT), etc) and acyl chloride, aiming to lower
the crystallinity of polyether-based SPEs (figure 4). It is
reported that the PO units in Jeffamine-type polymers could
effectively restrain the crystallization of SPEs, allowing the
LiTFSI-based SPEs to achieve improved ionic conductivities
(ca. 10^{-6} S cm^{-1} at 30 ^\circ C) at temperatures below the melting
points of PEO [103].

Subsequently, Aldalur et al [104] reported a novel
class of comb-like polymer matrices comprising polyether
amine oligomer side chains (i.e. Jeffamine compounds) and
poly(ethylene propylene maleic anhydride) backbone. It is
noteworthy that the synthesis route of the matrices is simple
and scalable. Combining the high degree of configurational
freedom and flexibility of the PO/OE units in Jeffa-
mire compounds (i.e. Jeffamine M-600, Jeffamine M-1000,
and Jeffamine M-2070, table 3), a series of new polymer
matrices with good elastic and amorphous properties have
been obtained [104]. Differing from linear PEO-based ones,
the comb-like SPEs containing Jeffamine show high ionic
cconductivity (LiTFSI/Jeffamine, 4.5 \times 10^{-5} S cm^{-1} at
room temperature) and excellent electrochemical stability
(figure 6(b)). Furthermore, the cycling stabilities of Li^{\text{II}}/LiF
and Li^{\text{II}}/LiS cells are remarkably enhanced, proving the feas-
ibility of utilizing Jeffamine compounds as a building block for
high-performance SPEs [104].

Based on the previous synthesis and screening of
Jeffamine-type polymers, Aldalur et al [105] combined
LiFSI with the amorphous PMA-Jeffamine polymer matrices,
attempting to improve ionic conductivities under room
temperature and the interfacial stability between electro-
yte and lithium metal anode. The electrolyte comprising
of LiFSI/Jeffamine-poly(ethylene-alt-maleic anhydride),
(PeMA) shows high ionic conductivities at ambient tem-
perature (e.g. 1.8 \times 10^{-5} S cm^{-1} at 30 ^\circ C, table 3, entry 7), and
enabled long-term cycling of Li symmetric cells (exceeding

| Entry | Electrolytes | Jeffamine-type | [EO]/[Li^{+}] | T_{g}/^\circ C | T_{m}/^\circ C | σ/S cm^{-1} | Reference |
|-------|-------------|----------------|--------------|--------------|--------------|-------------|-----------|
| 1     | LiTFSI/TAT/Jeffamine/NMAA | J-600 | 8 | -63 | 3.0 \times 10^{-7} (30 ^\circ C) | [103] |
| 2     | LiTFSI/TAT/Jeffamine/NMAA | J-900 | 8 | -52 | 8.0 \times 10^{-6} (30 ^\circ C) | [103] |
| 3     | LiTFSI/Jeffamine/PeMA | M-600 | 20 | -47 | 3.5 \times 10^{-5} (25 ^\circ C) | [104] |
| 4     | LiTFSI/Jeffamine/PeMA | M-1000 | 20 | -44 | 3.2 \times 10^{-5} (25 ^\circ C) | [104] |
| 5     | LiTFSI/Jeffamine/PeMA | M-2070 | 20 | -49 | 4.0 \times 10^{-5} (25 ^\circ C) | [104] |
| 6     | LiFSI/Jeffamine/PeMA | M-2070 | 20 | -50 | 7.9 \times 10^{-5} (25 ^\circ C) | [105] |
| 7     | LiFSI/Jeffamine/PeMA | M-2070 | 20 | -57 | 1.8 \times 10^{-4} (30 ^\circ C) | [106] |
| 8     | LiTFSI/Jeffamine-co-PS/PeMA | M-2070 | 8 | -51 | 1.6 \times 10^{-5} (30 ^\circ C) | [107] |
| 9     | LiTFSI/Jeffamine/PPGDA | T-3000 | 20 | -68 | 7.7 \times 10^{-6} (RT) | [108] |
| 10    | LiTFSI/Jeffamine/PPD-OA | T-3000 | 20 | -51 | 5.7 \times 10^{-5} (60 ^\circ C) | [109] |

The abbreviations are listed as below: trimesic acid trichloride (TAT), N-methylallylamine (NMAA), lithium bis(trifluoromethanesulfonylimide (LiTFSI), methacrylic anhydride (MAA), poly(propylene oxide)diacrylate (PPO-DA), poly(propylene glycol)diacrylate (PPGDA), poly(ethylene-alt-maleic anhydride) (PeMA), lithium bis(fluorosulfonylimide (LiFSI), polystyrene (PS).

The Jeffamine type being used to synthesize SPEs.
Molar ratio of EO unit to lithium ion.
Glass transition temperature.
Decomposition temperature.
Ionic conductivity.
Figure 6. Jeffamine-based polymer matrices for solid polymer electrolytes (SPEs). (a), (b) Ionic conductivities of Jeffamine-based SPEs (a) and cycling performance of Li$^+$ symmetrical cells using Jeffamine-based SPEs. (a), (b) Reprinted from [105], Copyright (2018), with permission from Elsevier. (c) Schematic illustration of the chain ordering in solid and flowable Jeffamine-based polymer matrices. (d), (e) Charge/discharge profiles (d) and (e) cycling performance of Li$^+$/LiFePO$_4$ (LFP) cells using Jeffamine-based SPEs. (c), (d), (e) Reprinted from [106], Copyright (2019), with permission from Elsevier.

800 h, figure 6(c)). As a result, the corresponding Li$^+$/LFP battery can operate with decent cycling stability under ambient temperatures.

In addition, the synthesis procedures have a remarkable effect on the properties of Jeffamine-type polymers [106]. Usually, for the solvents with low dielectric constants (e.g. trifluorotoluene), the as-obtained Jeffamine-type polymers are highly entangled, behaving like rubber. However, for the solvents with a high dielectric constant (e.g. N,N-dimethylformamide), the starting material PEAaMA could be well dissolved and the as-obtained polymers are somehow flowable, as shown in figure 6. The flowable polymer electrolytes (FPEs) own several advantages: (a) high ionic conductivities at room temperatures (e.g. $1.4 \times 10^{-4}$ S cm$^{-1}$ under 30 °C) owing to the low $T_g$ and highly amorphous characteristics, and (b) improved chemical and electrochemical compatibility towards lithium anode due to the better adhesion properties (figure 6(b)). It has been demonstrated that, with Jeffamine
Figure 7. Proposed ionic transport mechanism in polyether and polyester blended electrolytes. Reprinted with permission from [114]. Copyright (2020) American Chemical Society.

FPEs as an artificial layer, the cycle life of the Li$^{+}$|LiFePO$_4$ cell is extended in comparison with its counterparts containing PEO (figure 6(e)) [106].

Besides high ionic conductivity, the high-strength property is also essential for the processing of SPEs in SSLMBs. Grafting PS onto a Jeffamine backbone to prepare copolymers (Jeffamine-PS) [107], or blending the PEMa-Jeffamine matrices with PVDF nanofibers [110], can effectively improve film-forming ability with little expense at ionic conductivities, e.g. 7.9 x 10$^{-5}$ S cm$^{-1}$ for Jeffamine-PS copolymers under 40 °C, and ca. 10$^{-4}$ S cm$^{-1}$ for the PEMa-Jeffamine/PVDF blended electrolyte under 30 °C [110]. Compared with semi-crystalline PEO-based ones, Jeffamine-based self-standing SPEs display relatively high ionic conductivities even under room temperature and enhance chemical and electrochemical properties, which are promising alternatives to PEO-based SPEs for SSLMBs.

Additionally, the Jeffamine-based compounds can be used as other components of batteries, such as polymer adhesives, oxidized active materials, and interface coatings, thus improving the mobility of Li$^{+}$ ions, electrochemical performance, and chemical and electrochemical compatibility toward lithium electrodes [102].

4.2. Polycarbonate and its derivatives

Compared to polyether matrices, polycarbonates have attracted extensive attention from the battery community, due to their stronger oxidation resistances than polyether-type polymer matrices [111]. Commonly, polycarbonate-type polymers utilized for SPEs include poly(ethylene carbonate) (PEC), poly(propylene carbonate) (PPC), and poly(trimethylene carbonate) (PTMC). Interestingly to note that the values of $T_g$ for these three kinds of polycarbonate matrices are much higher than that of PEO, i.e. $T_g = 18$ °C (PEC) vs. $T_g = 25$ °C–45 °C (PPC) vs. $T_g = -9.6$ °C (PTMC) vs. $T_g = -64$ °C (PEO) (table 2), indicating that the segmental motions in these polymers are rather difficult [111–113]. Meabe et al [114] comparatively investigated the ion transport mechanism of SPEs based on polyether and polyesters comprising LiTFSI as the lithium salt and the blend of poly($\varepsilon$-caprolactone) (PCL) and PEO as the polymer matrices. It is reported that LiTFSI is inclined to coordinate with the carbonyl group (–OC=O–) in PCL backbone in the case of PCL content >50 mol%, and there are plenty of compact ion pairs. Lithium salt can be effectively dissolved, and Li$^{+}$ cation is preferentially coordinated with oxyethylene units in the PEO structure, in case of PCL content <50 mol%. Based on these understandings of coordination and phase separation, the ionic conduction mechanism of polyether/polyester hybrid systems is elucidated (figure 7) [114].

In addition, the polycarbonate-based SPEs show high ionic conductivity compared with polyether-based ones even at room temperature [111, 115, 116], for example, 3.0 x 10$^{-4}$ S cm$^{-1}$ under 20 °C for cellulose nonwoven/PPC reported by Cui and co-workers [115], and 10$^{-4}$ S cm$^{-1}$ for LiFSI/PEC under 30 °C reported by Tominaga et al [117]. Further investigations suggest that low molecular weight components (e.g. PC and EC), originating from the chemical decompositions of PPC and PEC, are responsible for the unexpectedly high ionic conductivities observed for the polycarbonate-based SPEs (figure 8) [118, 119].

Note that the high interfacial reactivity occurred between polycarbonate and lithium electrode, which affects their chemical and electrochemical stability to some extent. Wang et al [120] revealed that significant side reactions between PPC electrolyte and lithium electrode at the elevated temperature
(80 °C) generate liquid components such as PC (as shown in figure 8), which brings great safety risks. Therefore, to date, polycarbonate-based SPEs are still under basic research in the laboratory, which cannot meet the application requirements of SSLMBs at current stage.

5. Single lithium-ion conductive SPEs

Typically, the classic SPEs obtained with discrete anions are typical dual-ion conductors \((T_{Li}^+ < 0.4)\), in which both negative and positive charges could migrate under the electric field \([84, 121]\). During charge/discharge cycles, the migration of anionic species (in opposite directions vs. cationic species) gradually causes concentration gradient and internal polarizations of redox reactions, which finally accelerates dendrite growth and parasitic reactions at electrode-electrolyte interphases/interfaces \([122, 123]\). Therefore, the selectivity of cation transport is of vital importance for the stable operation of SSLMBs \([124]\).

To suppress or even eliminate the migration of the negative charges in SPEs, a new type of SPEs has been suggested, which is known as single-ion conductive SPEs (SLIC-SPEs). Generally, SLIC-SPEs with the values of \(T_{Li}^+\) close to unity are majorly obtained by three approaches (figure 9) \([17, 122, 124, 125]\): (a) chemically grafting the anions on polymeric backbones (figure 9(a)); (b) covalently bonding the anions of lithium salts on the inorganic backbone (figure 9(b)), and (c) incorporating anion acceptors to cage the anions in dual-ion conductive SPEs (figure 9(c)). Currently, several excellent reviews have systemically discussed the SLIC-SPEs built from the latter two approaches (utilizing inorganic backbones and anion acceptors \([126, 127]\)), and we will mainly focus on the SLIC-SPEs made from the first method, i.e. attaching anions to polymeric backbones in chemical means (figure 9(a)).

For typical dual-ion SPEs, lithium salt and polymer matrices are indispensable. Inheriting the same concept, the research activities in the polymer backbone-based SLIC-SPEs could be briefly presented in two aspects: (a) rational design of the anionic center, aiming to improve the dissociation of lithium ions and thereby provide higher concentrations of active ions; and (b) regulating the topological structures of polymer backbones, with the objective of facilitating rapid ion transport through ionic sites \([124]\). Some representative SLIC-SPEs and their basic properties are also summarized in table 4. The key achievements in both aspects are presented in the following sections.

5.1. Rational design of anionic center

Since the 1980s, the effect of anionic structures on \(Li^+\) conductivities of SLIC-SPEs has been continuously investigated by various research groups \([124]\). Early attempts carried out by Tsuchida et al \([128]\) focused on a polymeric lithium salt based on carboxylate anions \((-CO_2^-)\). These carboxylate-based SLIC-SPEs presented extremely low ionic conductivities even at high temperatures (ca. \(10^{-8}\) S cm\(^{-1}\) under 60 °C), owing to the strong affinity of carboxylate anions towards \(Li^+\) cations \([124]\). Afterward, Bannister et al \([129]\) suggested the incorporation of perfluoroalkyl chains, and the as-obtained SLIC-SPEs showed nearly two orders of magnitudes improvement in ionic conductivities \((10^{-6}\) S cm\(^{-1}\) under 60 °C), as compared to those based simple alkyl carboxylate groups. This suggests that replacing hydrocarbon alkyl groups with perfluoroalkyl groups can facilitate lithium-ion dissociation of carboxylate anions, thus improving the ionic conductivities of SLIC-SPEs.

To further improve the dissociation of \(Li^+\) cations, sulfonate anions \((-SO_3^-)\) with better negative charge delocalization as compared to carboxylate anions have been studied in the 1990s. Zhang and co-workers \([132]\) reported several kinds of sulfonate-based SLIC-SPEs, which effectively show slightly higher ionic conductivities than those of carboxylate-based ones, e.g. \(1.8 \times 10^{-7}\) S cm\(^{-1}\) for poly(lithium sulfaoalkyl methacrylate) (LiPSAM/PEO ([EO]/[Li\(^+\)] = 18, by mole)) vs. \(4.3 \times 10^{-10}\) S cm\(^{-1}\) for poly(lithium(\(\omega\)-carboxy)oligo(oxyethylene) methacrylate) (LiPCME7) at room temperature. Inspired by the great success of LiTFSI in SPEs, the delocalized sulfonimide structure was also suggested to construct highly \(Li^+\)-conductive SLIC-SPEs. In 2011, Meziane et al \([138]\) reported the first example of sulfonimide-based polysalt, lithium poly ((4-styrenesulfonyl)(trifluoromethanesulfonyl)imide) (LiPSTFSI), for building highly conductive SLIC-SPEs.
Effectively, the LiPSTFSI/PEO exhibited much higher ionic conductivities in comparison with poly(lithium 4-styrenesulfonyl) (LiPSTFSI/PEO) at the same temperatures, e.g., 9.5 × 10^{-6} S cm^{-1} (LiPSTFSI/PEO) vs. 7.2 × 10^{-7} S cm^{-1} (LiPSS/PEO) at [EO]/[Li^{+}] = 20 (by mole) and 70 °C. The remarkable improvement in ionic conductivities evidences the determining role of negative charge delocalization on the transport properties of SLIC-SPEs.

Stemming from our continuous effort on the design of robust anions for battery use and the previous results related to the sulfonimide-based SLIC-SPEs, we proposed a new family of ‘super-delocalized polyanions’ [69, 122, 123, 137, 139], in which the anionic center was obtained by substituting an =O group of typical sulfonimides (i.e., –SO_{2}–N^{(−)}–SO_{2}–CF_{3}) with a strong electro-withdrawing group, –N–SO_{2}CF_{3}. The SLIC-SPEs containing the super polysalt, poly[(4-styrenesulfonyl) (trifluoromethyl)S-trifluoromethylsulfonylimino) sulfonylimide], LiPSsTFSI, showed surprisingly high Li-only ionic conductivities (ca. 10^{-4} S cm^{-1} at 70 °C). These results suggest that

![Figure 9. Three strategies for building SLIC-SPEs based on (a) organic and (b) inorganic backbones, (c) and anion acceptor.](image)

Table 4. Physicochemical properties of some representative single Li-ion conductive solid polymer electrolytes (SLIC-SPEs).

| Entry | Polyanionic lithium salts⁶ | Method | \( T_{p}^{°C} \) | \( \sigma_{total} / S \ cm^{-1} \) | \( T_{Li^{+}} \) | Reference |
|-------|----------------------------|--------|----------------|-----------------|-------------|-----------|
| 1     | LiPCME₂                    | Homopolymerization | -23            | 4.3 × 10^{-10} (30 °C) | —           | [128]     |
| 2     | LiPCHFEM/PEO                | Homopolymerization | —              | 3.0 × 10^{-6} (25 °C) | —           | [129]     |
| 3     | P (MEO-co-MALi)            | Copolymerization | -62            | 1.6 × 10^{-5} (25 °C) | —           | [130]     |
| 4     | P (MEO-co-AALi)            | Copolymerization | -42            | 1.5 × 10^{-5} (25 °C) | —           | [131]     |
| 5     | LiPSAM/PEO                 | Homopolymerization | —              | 1.8 × 10^{-5} (25 °C) | —           | [132]     |
| 6     | LiPSS/PEO                  | Homopolymerization | -66            | 7.0 × 10^{-5} (25 °C) | —           | [133]     |
| 7     | LiPNS/PNE                  | Homopolymerization | 9               | 4.0 × 10^{-5} (30 °C) | —           | [134]     |
| 8     | P (AE₁₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋_-…

⁶ The abbreviations are listed as below: LiPCME₂ (poly(lithium(ω-carboxy) oligo(oxyethylene)methacrylate)), LiPCHFEM (poly(lithium 2-(4-carboxyhexafluoro-butanol)-oxy) ethyl methacrylate)), PEO (poly(ethylene oxide)), P(MEO-co-MALi) (poly(lithium methacrylate-co-oligo(oxyethylene) methacrylate)), P(MEO-co-AALi) (poly(lithium oligo-oxyethylene methacrylate-co-acyrlamidocaproate)), LiPSAM (poly(lithium sulfoalkyl methacrylate)), LiPSS (poly(lithium 4-styrenesulfonate)), LiPNS (poly(lithium N-propylsulfonate ethylenimine)), PNE (poly(4-oligo-oxyethylene ethylenimine)), P(AE₁₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋_-…

*b Glass transition temperature.

*² Ionic conductivity of electrolytes.

*² Li-ion transference number.
introducing a stronger electro-withdrawing group in sulfonimide anions can efficiently promote the Li-ion transport in SLIC-SPEs (figure 10).

5.2. Regulating the topological structure of polymer backbones

For polymer backbone-based SLIC-SPEs, PEO is utilized as a polymer matrix to facilitate Li\(^+\) transportation for those polysalts without solvating units for lithium ions; yet, the high degree of crystallinity of PEO greatly slows down the migrations of ionic species under ambient temperatures (<60 °C) [123]. Therefore, the topological structures of polymer backbones are also key factors determining the ionic conductivities of SLIC-SPEs [122, 123]. Polymerizing salt monomers with soft monomers is an effective pathway to decrease the degree of crystallinity and \(T_g\), and accelerate Li\(^+\) transport [122, 135, 136]. Besides, copolymerization could also circumvent the possible phase separation of the blended SLIC-SPEs, and improve not only the long-term durability of electrolyte membranes but also interphase contact between electrodes and electrolytes [122, 137].

The common copolymerization methods are random copolymerization, block copolymerization, and homopolymerization and so on (figure 11) [124]. Random copolymerization can decrease the degree of crystallinity of SLIC-SPEs and \(T_g\), thus, promoting Li\(^+\) transport among chain segments. In addition, the performance of polyanion conductors, the SLIC-SPEs are the typical single-ion conductors, and show several traits: (a) relatively high ionic conductivity reaches up to ca. 10\(^{-7}\) S cm\(^{-1}\). That is, for the sulfonate anion based SLIC-SPEs, the ionic conductivity could also be elevated by copolymerizing with the oligomeric EO segments. Actually, two orders of magnitude higher conductivities can be obtained in case fluorinated polymer monomers are applied [135, 136].

Our group [120] reported several kinds of amorphous SLIC-SPEs (Li[PSTFSI-co-MPEGA]) via copolymerizing with different LiTFSI with methoxy polyethylene glycol acrylate (MPEGA) ratios. The ionic conductivity of the Li[PSTFSI-co-MPEGA] copolymer electrolytes are higher by 1–3 orders of magnitude than these of LiPSTFSI/PEO blended electrolytes (7.6 × 10\(^{-6}\) S cm\(^{-1}\) for Li[PSTFSI-co-MPEGA] ([EO]/[Li\(^+\)] = 20.5, by mole) and 2.2 × 10\(^{-10}\) S cm\(^{-1}\) for LiPSTFSI/PEO ([EO]/[Li\(^+\)] = 20, by mole) at room temperature). In addition, Bouchet et al [137] reported ABA triblock copolymer SLIC-SPEs, LiPSTFSI-b-PEO-b-LiPSTFSI (figures 11(d) and (e)), which exhibited decent ionic conductivities (e.g. 1.3 × 10\(^{-5}\) S cm\(^{-1}\) under 60 °C, [EO]/[Li\(^+\)] = 12.1, by mole) and sufficient mechanical strength, allowing the Li/LiFePO\(_4\) cells to be operated with good rate capabilities (138 mAh g\(^{-1}\) at 2 C operated under 80 °C).

In short, compared to the traditional double-ion conductors, the SLIC-SPEs are the typical single-ion conductors, and show several traits: (a) relatively high \(T_L\); (c) impressing parasitic reactions b/w electrolytes and electrodes, particularly with lithium electrode, thereof, reducing the accumulation of SEI film products (i.e. produces a thin, dense and stable SEI interphase) and (d) robust chemical and electrochemical stability under high voltage region as well as the improved capacity of SSLMBs.
6. Conclusion

Compared to the commercialized liquid electrolyte, SPEs have several advantages, including ease of process, and intrinsic safety. Although the SSLMBs have been exemplarily applied, continuous efforts are still needed to further improve intrinsic safety and compatibility with electrode materials, as detailed below:

(a) For current LiTFSI/PEO systems, conductive lithium salt structure, $R_1^+SO_2^−N^−SO_2^−R_2^2$ ($R_1^+$, $R_2^2$; $R_1^+$ = n-C$_{1-x}$F$_{2x+1}$, $R_2^2$ = n-C$_{1-x}$F$_{2x+1}$), could be further modified to extend the degree of negative charge delocalization, in the hope of lowering the crystallinity degree of PEO and promoting the transport of Li$^+$ ions [141].

(b) Compared with the linear PEO matrix, the comb polymers with multi-branch chain structure show lower $T_g$ and degree of crystallinity, which is contributed to amorphous SPEs at ambient temperature. Note that overcoming polymer crystallization can not only improve the conductivity of SPEs under ambient temperature but also enhance the stability of the electrode and electrolyte interface.

(c) For SLIC-SPEs systems, improving the dielectric constant of the polymer matrices seems to be an effective strategy to promote the dissociation of Li$^+$, and thereby improve the Li$^+$ transport capability therein. In addition, one may also attain high $T_{Li^+}$ values by grafting anions to polymer nanoparticles via semi-batch emulsion polymerization [142].

In short, by the structure design of conductive lithium salt and polymer matrices, the ion transport characteristics and physical and electrochemical properties of SPEs could be significantly enhanced. Bridging the research activities between academia and industrial sectors could certainly promote the pragmatic development of SPEs.

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