

ADVANCES IN POLYMER-IN-SALT ELECTROLYTES FOR LI-BASED BATTERY

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Abstract

Due to their increased safety and energy density, solid-state lithium batteries (SSLBs) are expected to power upcoming electric vehicles and smart grids. However, these batteries face significant challenges due to their relatively low ionic conductivity at room temperature and high electrolyte-electrode interfacial resistance. A practical method for increasing the solid polymer electrolytes' ionic conductivity at room temperature is the preparation of polymer-in-salt solid electrolytes (PISSEs) with lithium salt contents greater than 50% by weight. This method is also suitable for scalable production. In this paper, a broad overview of solid-state polymer electrolytes was presented, along with information on their historical development, optimum polymer needs, and their benefits. Similarly, the structure and ionic conductivity mechanism of polymer-in-salt solid electrolytes were explained by analyzing the interactions between lithium salt and the polymer matrix. The classification of solid-state polymer electrolytes was then discussed, along with the most recent developments in polymer-in-salt solid electrolytes (PISSEs) made from polyacrylonitrile (PAN), polycarbonate derivatives, polyvinylidene fluoride-hexafluoropropylene (PVDF-HFP), and polyethylene oxide (PEO). Finally, a suggestion for potential improvements to the manufacturing of solid polymer Li-ion battery electrolytes that are stable and affordable was made.

Keywords: *Polymer, Salts, Electrolytes, Lithium-batteries, PISSEs, Solid-state.*

1.0 INTRODUCTION

Lithium (Li)-ion batteries have made rapid advancements in recent years in applications such as grid energy storage, portable devices, and electric vehicles (EVs) [1]. This results from using high-performance electrolyte materials, which are critical in ensuring the safety and improving the life cycle of lithium-ion batteries. Lithium-ion battery development is currently hampered by safety concerns, including fires, explosions, and electrolyte leakage from volatile organic solvents (such as carbonates and ethers) in conventional non-aqueous liquid electrolytes [2]. High energy-density post-Li-ion batteries, such as lithium metal, lithium-sulfur (Li-S), and lithium-oxygen (Li-O₂) batteries, are more susceptible to these issues [3–4]. Similarly, ionic liquids (ILs) are not frequently employed as electrolytes for various reasons. First, most ILs lack natural Li-ion. Hence lithium salts must be added to facilitate its conductivity for LIB applications. This makes the electrolyte combination dense, which limits its conductivity and makes it difficult to handle. Moreover, many ILs are expensive, susceptible to oxygen and moisture, and have limited practical applications [5]. The safety issues with lithium batteries can be solved by replacing traditional liquid electrolytes with polymer electrolytes [4]. Solvent-free (solid) polymer electrolyte (SPE), gel polymer electrolyte (GPE), and synthetic polymer electrolyte (CPE) are the three primary categories of polymer electrolytes for Li-based batteries. Nonetheless, this study focused only on SPE.

1.1 Solid Polymer Electrolytes (SPEs)

Salts are incorporated into a polymer matrix to enhance ion conduction in solid polymer electrolytes (SPEs), which can easily be made using solvent casting, hot casting, or extrusion processes [5-6]. Important applications utilizing these materials include dye-sensitized solar cells, fuel cells, and batteries. Because of its processability, low cost, adequate electrical conductivity, as well as the necessary thermal and mechanical qualities to sustain the pressures associated with battery operation, SPE has been widely explored in battery applications. Additionally, due to its excellent thermal stability (fireproof, burn-out, etc.), mechanically robust structure, and leak resistance, SPE is more appealing than currently used liquid electrolytes. Hence, a solid-state battery can be realized with the help of efficient SPEs. SPE has undergone testing for several battery systems (e.g., Li⁺, Na⁺, Mg²⁺, and Zn²⁺) except for Ca²⁺; very few studies have been reported due to its lower transference number [7].

1.2 Historical Development of Solid Polymer Electrolytes (SPEs)

After the discovery of the semi-crystalline structure of poly(ethylene oxide) (PEO) and alkali salts in 1973, research on their electrical characteristics was conducted [8-9]. Armand suggested using these polymer-alkali salt complexes as solid electrolytes in high-energy batteries because of their combined solid-state electrochemistry, flexible structure, and simple processing [10]. A new mechanism that better describes the ionic conductivity in the amorphous phase quickly replaced the original one that initially explained the relationship between the morphology and conductivity of SPE complexes. This new mechanism is similar to inorganic ionic conductors and is based on

ionic transport through polymer helices in crystalline phases [11].

In the early 1980s, studies on the connection between ion transport and polymer segment dynamics heavily influenced the development of SPE. By changing the polymer structure with diverse topologies, such as Comb-like type with short PEO chains and crosslinked network polymers, several methods have been devised to prevent polymer crystallization in SPE. Nevertheless, these methods undermine the mechanical qualities of the polymer by lowering its crystallinity, which goes against the initial justification for adopting strong polymer membranes for safer battery applications. Developing polymer-blend SPEs, block-copolymer SPEs, and ceramic-enhanced SPEs was a major effort in the mid-to-late 1980s to balance fast ion transport and excellent mechanical qualities [12]. Advances were made in the structure of SPEs by Chatani *et al.* in 1987; they first investigated the crystal structure of the PEO:NaI 3:1 crystalline complex using X-ray diffraction [13].

Another significant discovery was made in 1988. The PEO-LiCF₃SO₃ matrix was filled with fast ionic conductor particles Li₃N by Skraup *et al.*, which had a high ionic conductivity of 10⁻³ S/cm at ambient temperature [14]. Compared to the empty PEO-based polymer electrolyte, the resulting composite polymer electrolyte had a significantly greater ionic conductivity. More interestingly, Wieczorek *et al.* discovered that nonionic fillers like Al₂O₃ increased the ionic conductivity of PEO-based polymer electrolytes by at least one order of magnitude [15]. The growth of the amorphous phase with high ion mobility is mostly responsible for this. Polymer electrolytes have had major benefits since this groundbreaking study, including flame retardancy, ease of workability, higher resilience to vibration, shock, and mechanical deformation than liquid electrolytes, and improved electrode/electrolyte interface contact. It has also been shown to be more compatible with solid inorganic electrolytes [16].

The development of traditional PEO-based SPEs continued throughout the 1990s with efforts to boost charge carrier density and decouple ion transport from mechanical support. In addition to the traditional SPE methods, Angell *et al.* demonstrated the benefit of utilizing a new polymer in salt electrolyte with exceptional performance [17]. Last, Scrosati *et al.* created a class of nanocomposite SPEs with improved mechanical, thermal, and electrochemical stability and room temperature conductivity, which are interesting candidates for high-performance lithium battery applications [18]. A reconsideration of the foundations of the ion conduction process in polymer electrolytes has resulted from Bruce *et al.* discover's of several P(EO)₆LiX crystalline complexes with rapid ion carriers [19].

1.3 Fundamentals of SPEs (polymer-lithium salt complex)

The Gibbs free energy, $\Delta G = \Delta H - T \Delta S$, must decrease after the dissolution of salt in any solvent, whether liquid or polymer, at a specific temperature and pressure. The lattice energy of the salt, which is high for ions with high charges and small radii, and the need to create coordination sites in the polymer are the important factors that lead to positive ΔH , making the dissolution less favorable. The interaction between the polymer's coordinating group and

the cation, and the electrostatic interaction between the dissolved ions, which both result in exothermic processes favoring the dissolution, are also among the factors that affect the change in enthalpy. Due to competition between two components, the entropy changes. As the salt crystal lattice is shattered and ions are dissolved in the polymer, the entropy rises. As the polymer chains stiffen due to coordination with ions, the entropy drops. The polymer's segmental motion is reduced as a result. The loss in entropy caused by the pinning of polymer chains is higher than the rise in entropy caused by lattice breaking, and the resulting change in entropy is often negative, favoring salt precipitation, especially at high temperatures [20-22].

Remarkably, the polymer moiety should have a very low glass transition temperature (T_g) for higher room temperature conductivity. If $T > T_g$, then more amorphous regions should be available at room temperature for segmental mobility of the polymer chain, which may favor lithium cation transport. However, when $T < T_g$, then segmental mobility would be suppressed, and thus, no conductivity would occur. Similarly, a lower melting point (T_m) may result in higher ionic conductivity. Moreover, the polymer hosts should be capable of dissolving lithium ions; This is even more noticeable in polymers with a higher dielectric constant; those with longer repeating units [8].

In summary, the host polymers must satisfy the following vital requirements to effectively solvate the salt and create a polymer-lithium complex: (I) High electron-donor properties; the best candidates for complex formation are polymers with a greater concentration of sequential polar groups on their backbone, such as ether (-O-), sulfide (-S-), amine (-N-), phosphine (-P-), carbonyl (C=O), and cyano (C=N); (II) high dielectric constant: a dielectric constant of the polymer host will lead to effective charge separation of the salts, which further leads to the high concentration of charge carriers; (iii) a suitable separation between the coordinating centers, best exemplified by crown ethers; (iv) ease of synthesis and processing; (v) High molecular weight of the polymer moiety is also desirable to achieve SPEs with better mechanical strength and flexible backbone and low steric hindrance for bond rotation; (VI) High backbone flexibility is needed to lower the energy barrier for bond rotation; (vii) The type of cation solvation: To promote salt dissociation, polymer-cation interactions must result in a compromise between sufficient strength to assure the solubility of the salt via cation solvation and sufficient lability to promote ionic hopping between coordinating sites [23, 24].

1.4 Advantages and Disadvantages SPEs

SPEs have several advantages over other solid electrolytes that make them superior in various applications. SPEs are easily processible as they can be solution cast [25] or fabricated using a solvent-free hot pressing approach [26-28]. Such a system can be adaptable and compliant depending on the type of SPE, which gives rise to certain unusual device applications like wearable power. The non-flammability and lack of vapor pressure of SPEs make them excellent candidates for battery applications where safety is crucial, such as in electric vehicles or implantable medical devices. The major issues facing the SPEs are conductivity and interfacial resistance, which can be remedied by adding plasticizer and electrode support integrated membrane, respectively.

1.5 Requirements of Polymer Electrolytes for Solid-State Lithium-based Batteries

The major requirements of polymer electrolytes for Solid-State Lithium-based Batteries are briefly discussed as follows [29]:

(1) The ionic conductivity is the major parameter for polymer electrolyte, which should be up to the level of 10^{-4} - 10^{-3} S/cm at room temperature, and are crucial for the fast ions transport and can enable the stable operation of high-performance SSLMBs with reasonable rate capacities.

(2) The electrochemical stability window should be wide enough (4.5-5.0 V vs.Li+/Li), by which the polymer electrolytes with strong anti-oxidation powers can be used for the high-voltage and high-capacity cathode materials to contribute the higher energy density for SSLMBs, especially the Ni-rich and Li-rich transition metal oxides.

(3) The ions transference number of polymer electrolyte should tend to be ~ 1 , then the concentration of mobile anions can be lessened largely, which is advantageous for fast cations transport and suppression of concentration polarization of polymer electrolyte, and reduction of potential polarization as well as side reactions at the electrolyte/electrode interfaces in the solid-state batteries.

(4) As reported by Monroe and Newman, the lithium dendrite generation and growth can be inhibited when the high shear modulus of the polymer electrolyte is 1.8 times higher than that of the Li (~ 6 GPa) [30]. The mechanical strength of polymer electrolytes should be reasonable; then, the electrolyte membrane is suitable for the facile assembling of batteries and favorable for suppressing lithium dendrite growth in SSLMBs.

(5) The thermal stability of polymer electrolytes is significant for the stable operation of SSLMBs at wide temperatures, especially for the batteries that need to be placed at high temperatures when the ionic conductivity is low at room temperature.

(6) The chemical stability of polymer electrolyte also needs to be considered for SSLMBs, which involves the chemical reaction between polymer electrolyte and electrode, like the reduction by Li metal anode at the interface. Besides, the electrode/electrolyte interface, primarily the close interface contact with compatibility and stability during the long cycling of SSLMBs, is also vital for improving the battery performance.

2.0 Classification Solid Polymer Electrolytes Based on Lithium Salt Content

Since their discovery, solid polymer electrolytes have garnered much research interest. They exhibit a good combination of flexibility, Li-ion conductivity, and compatibility with the cathode and the lithium metal anode [31, 32]. At any given temperature, the conductivity of a polymer electrolyte is often lower than that of a corresponding liquid electrolyte. To increase conductivity, a variety of novel polymer electrolyte types have been developed with desired functionalities, and therefore diverse classifications are proposed. The polymer electrolytes are divided into

different types based on the various functional groups of the polymer matrix, and the properties can be improved by changing the functional unit [29]. The novel class of solid polymer electrolytes is divided into two categories based on the amount of lithium salt in the polymer matrices: salt-in-polymer electrolytes and polymer-in-salt electrolytes. The main distinction between the two is the lithium salt content, which is less than 50% in the former and greater than 50% in the latter, respectively [32].

2.1 Salt-in-polymer” Electrolytes

Salt-in-polymer electrolytes are the earlier investigated class of polymer electrolytes in which the lithium salt content is always less than 50% by weight, and the polymer matrix is the major component. The ions transported in these polymer electrolytes are connected with polymer chain segments with certain functional groups [29,31].

2.2 “Polymer-in-Salt” Electrolytes (PISSEs)

For the “salt-in-polymer” electrolytes, the content of lithium salt in the polymer matrix is relatively low, which induces low ionic conductivity [33]. Comparatively, by raising the lithium salt content over 50% wt., also known as a polymer-in-salt electrolyte, the ion transport of polymer electrolytes can be improved [34]. The high concentration of lithium salt may also improve the transference number of Li-ion. The battery's potential for polarization can then be reduced, and the side reaction between the electrolyte and electrode can be eliminated due to the polymer electrolyte's low concentration of mobile anions. Interestingly, the ion transport in the polymer-in-salt electrolyte can be accomplished via decoupling with polymer segmental relaxation across the channel structure [35]. The percolation path of the molten salt region exists in the high salt content as opposed to isolated clusters in the lower concentration zone. When the desired concentration of clusters is reached, all individual clusters interact to form an infinite cluster, which speeds up the cationic carrier process throughout the electrolyte [36].

The polymer again induces mechanical stability of the conducting composite and suppresses the salt crystallization due to the interaction with the lithium cations. Thus, PISSE is promising as it combines the merits of polymer electrolytes (elastic properties) and superionic glasses (high lithium transport number). Such an electrolyte might have conductivities that are significantly higher than those of conventional polymer electrolytes [37]. The energy density of a battery based on a polymer-in-salt electrolyte may not be noticeably lower than that of a salt-in-polymer electrolyte, even though lithium salt has a higher density than polymer. Also, the thickness of the polymer-in-salt electrolyte sheet can be drastically lowered, resulting in an extremely lightweight and high energy density for the battery. For instance, Angell *et al.* described a polymer-in-salt electrolyte with a high content of lithium salts than 50% wt. in a small amount of polymer matrix, which sufficiently reduced the T_g and retained the rubber state at 25 °C and then offered the high ionic conductivity and wide electrochemical stability window. With a salt level of 70% wt., the highest ionic conductivity can be achieved [17].

Polymer-in-salt electrolytes can produce high ionic conductivity, but as salt concentration increased, poor

mechanical strength was unavoidable. To improve the mechanical properties of polymer electrolytes, rigid support must be added. The fact that the cation-coordinating macromolecule is the main constituent in typical salt-in-polymer electrolytes is one of the key distinctions between the two electrolytic systems. As a result, mobile ion migration occurs in amorphous areas and is assisted by the movements of the macromolecule host [38]. Only at temperatures higher than the glass transition temperature of such electrolytes can high ionic conductivities be attained [39]. The related system of polymer-in-salt electrolyte with lithium salt as the major component exhibits much higher ionic conductivities than the salt-in-polymer scheme by creating a rubbery version of a glass-like polymer electrolyte [28]. Therefore, provide a standard platform to combine the desirable mechanical properties of rubbery polymers with the fast-ionic conduction of glassy electrolytes. The polymer-in-salt electrolytes' very high salt content encourages the formation of an ionic conducting network of aggregated cation/anion clusters linked to create percolation pathways for fast ion migration as a promising strategy to increase the ionic conductivity of the [40].

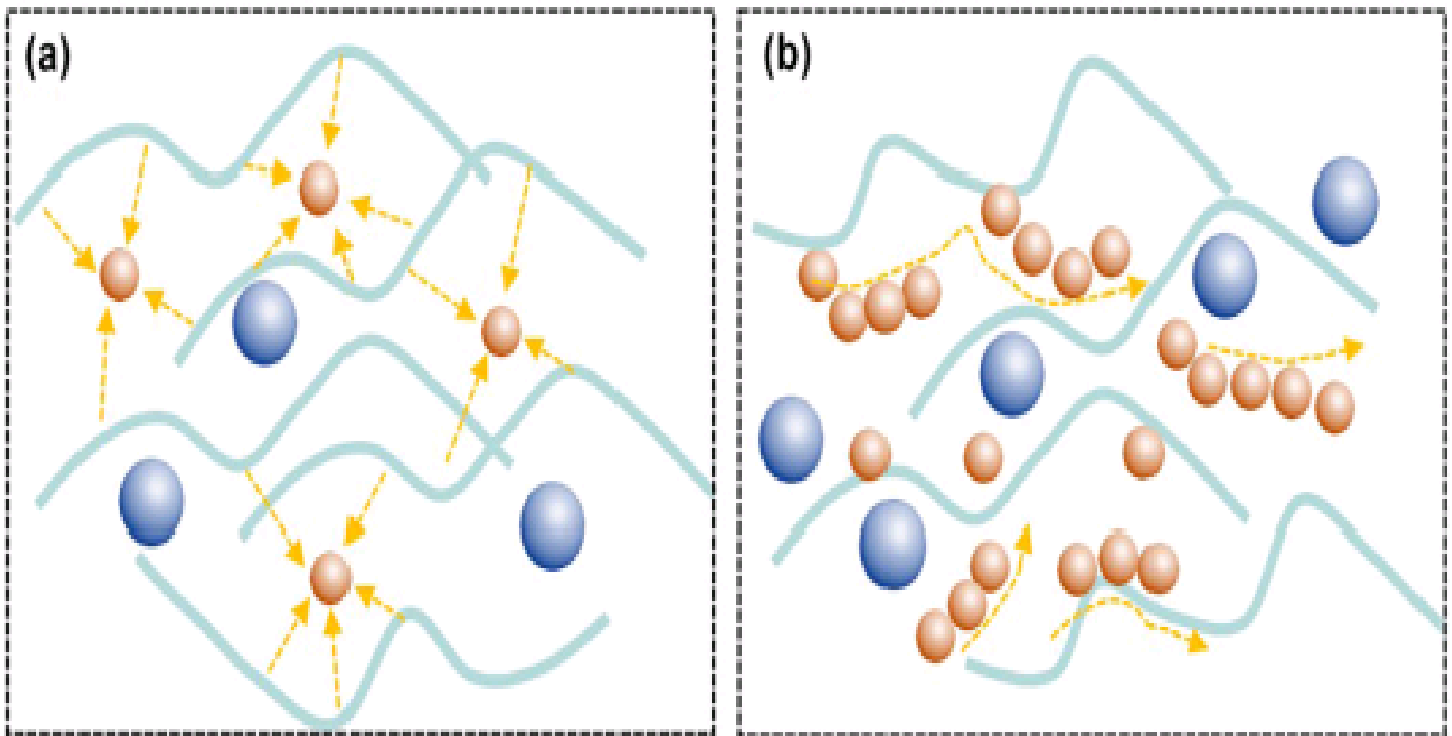


FIGURE 1: The schematic diagrams with ion migration mechanisms in various polymer electrolytes: (bluish - Anions; brownish - Lithium-ion; and Grey-polymer chains)(a) "Salt-in-polymer," and (b) "Polymer-in-Salt." (adapted from [29])

3.0 Recent Advances on Polymer-in-Salt Electrolytes (PISSEs)

To form high-concentration salt PISSEs, the dissociation energy of the lithium salt must be low. Lithium bis(trifluoromethane sulfone)imide (LiTFSI) and Lithium bis(fluorosulfonyl)imide (LiFSI) are usually used as lithium salts for PISSEs system because they readily dissolve in the polymer owing to high delocalization of charge in the anions. As another important component, the polymer matrix not only enables the dissolution of a considerable amount of lithium salt but also works as the framework of the electrolyte membrane. Thus, the polymer backbone should have a high dielectric constant and mechanical strength. According to the polymer host, current PISSEs can be divided into polyacrylonitrile(PAN)-based and polycarbonate derivative-based [35].

3.1 Polyacrylonitrile(PAN)-based PISSEs

Among PAN-based PISSEs systems, the PAN-LiTFSI PISSE is the most prominent [41]. Nevertheless, the system exhibits weak electrochemical stability and limited ionic conductivity, though. This is due to the PAN's strong CN groups, which give the chains a high thermodynamic but low kinetic flexibility. It is advantageous to incorporate inorganic functional elements into PISSEs to increase ionic conductivity further and enhance electrochemical stability. To achieve more flexible chains and improve the interaction between the polymer and Li-ion, some inorganic elements with inherent stability can prevent polymer crystallization [42]. Moreover, they can improve the mechanical strength, stability, and other properties of PISSEs.

Wu *et al.* reported a PAN-LiTFSI SPE (84 wt. % LiTFSI in 16 wt. % PAN) integrated with graphene oxide (GO) nanosheets, which improved the ionic conductivity, electrochemical stability, thermal stability, and chemical stability of the SPE—the SPE with 0.9 wt. % GO nanosheets demonstrate the ionic conductivity of 1.1×10^{-4} S/cm at 30 °C, which is almost one order of magnitude greater than the filler-free one [43]. This is because these oxygen-containing groups (e.g., COOH, -CO, -OH, and -COC-) in laminated GO nanosheets interact with Li-ion, leading to the decoupling of the ionic transport from segmental motion in the electrolyte and building up a conductive framework on the surface of GO nanosheets. Furthermore, the electrochemical window is extended by 0.5 V to approximately 5 V (vs. Li⁺/Li); and the thermal stability is also better than pristine SPE attributed to an isolating effect between PAN and GO nanosheets. Wu *et al.* again discovered that by preventing the metaphase that may have resulted from high-concentration LiTFSI crystallization and precipitation from PAN, GO nanosheets could maintain the bulk conductivity of the PAN-LiTFSI SPE [43].

Hongcai *et al.* prepared a membrane with a solution-casting method which dramatically showed that a polymer-in-salt electrolyte based on polyacrylonitrile with a lithium salt as the major component exhibits a wide electrochemically stable window, a high ionic conductivity, and an increased lithium-ion transference number [44]. The growth of dendrites from the lithium-metal anode was suppressed effectively by the polymer-in-salt electrolyte

to increase the safety features of the batteries; it was found that stable interphase was formed between the lithium-metal anode and the polymer-in-salt electrolyte to restrain the wild parasitic reactions, and thus demonstrated an all-solid-state battery configuration with a LiFePO_4 cathode and the polymer-in-salt electrolyte, which exhibited superior cycling stability and rate capability.

Wang's group researched a polymer electrolyte composed of PAN, propylene carbonate (PC), and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) by Raman and AC impedance spectroscopy [45]. In the polymer electrolyte with a relatively low salt proportion, the cations of the dissolved salt were associated with the polymer and transported by the segmental motion of the polymer, corresponding to the splitting of the 2270 cm^{-1} component from the 2245 cm^{-1} band of the nitrile stretching. As more salt was added, ionic associates such as $[\text{Li}^m\text{TFSI}^n]$ ($m>n$) were formed. In the Raman spectrum, a new peak at 2280 cm^{-1} depicting the interaction between the polymer and ionic cluster $[\text{Li}^m\text{TFSI}^n]$ ($m>n$), as well as the 2270 cm^{-1} peak related to the nitrile- Li^+ interaction was observed. When the salt content was extremely high, efficient percolation paths were formed and contributed the most to the ionic conductivity of the electrolyte. A transition from "salt-in-polymer" to "polymer-in-salt" electrolyte was observed at this moment, and conductivities of $10^{-3} \sim 10^{-4}\text{ S/cm}$ were acquired at room temperature, which agreed with Bushkova's results that a conductivity of $2.1 \times 10^{-3}\text{ S/cm}$ could be obtained at $[\text{CN}]/[\text{Li}]=2$ for PAN copolymer/ LiClO_4 electrolyte. Nonetheless, both polymers were scarcely soluble in organic solvents, making preparing a solvent-free thin electrolyte film difficult [46].

To overcome this problem, Florjanczyk and his coworkers prepared random acrylonitrile copolymers with butyl acrylate [poly(AN-r-BuA)] [36]. Due to the presence of the BuA monomeric units, these copolymers readily dissolved in acetonitrile, which enabled the preparation of electrolytes by the standard solvent casting technique. They found that as the content of lithium bis(trifluoromethanesulfone)imide increased, the polymer/lithium salt complexes became by far more flexible. On the other hand, when the salt content increased, the PEO systems became less adaptable. This appeared to be caused by the ether groups' significantly superior donor characteristics to the nitrile groups. The conductivities, however (10^{-5} S/cm at RT), were lower than those of pure PAN ionic rubbers. It was clear from the temperature dependence of conductivity in these systems that ion mobility and the segmental polymer matrix obeyed the VTF equation.

3.2 Polycarbonate Derivative-based PISSEs

Recently, polycarbonates have been found to have high solubility and good dissociation for lithium salts and are reasonable as the polymer matrix for solid-state Li-ion batteries, unusually as the polymer host of PISSEs [47]. Nonetheless, polycarbonate-based PISSEs are subjected to a profound deterioration of mechanical properties, which probably causes failure to form a self-standing film. To increase mechanical properties, adding materials with excellent strength is a simple and efficient method. Tominaga's group first synthesized poly(ethylene carbonate) (PEC)-based PISSE with 80 wt. % LiFSI using a 3D-ordered macroporous polyimide matrix to improve its mechanical

properties [48]. Nevertheless, the hybrid membrane sacrifices parts of the ionic conductivity of PEC. Whereafter, Zhao, *et al.* put poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) into PECLi80 electrolyte (80 wt. % LiTFSI in 20 wt. % PEC) with the polymer-in-salt structure to maintain the conductivity of PEC and enhance the mechanical performance of the polymer electrolyte using the better mechanical strength of PVDF-HFP [33]. The unique hybrid polymer electrolyte FPEC80/50 (50 wt. % PEC80 in 50 wt. % PVDF-HFP) shows a high ionic conductivity of 1.08×10^{-4} S/cm at 30 °C but also a stable electrochemical window around 4.5 V (vs. Li⁺/Li) due to the combined effect between PEC and PVDF-HFP. As a result, The Li/FPEC80/50/LiFePO₄ cell exhibits excellent rate capacity and cycling stability.

Zhao *et al.* developed a high-concentration lithium-salt polymer electrolyte consisting of poly(ethylene carbonate) (PEC), poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP), and lithium bis (trifluoromethane sulfonimide) (LiTFSI) [33]. This polymer electrolyte has two transport pathways for lithium ions. One emanated from the PECLi phase, in which lithium salt can be dissolved and dissociated in PEC, forming a “polymer in salt” in a PVDF-HFP substrate. The other is that PVDF-HFP and PEC synergistically promote the Li-ion movement. As a result, the high-concentration lithium-salt polymer electrolyte illustrates a high ionic conductivity (1.08×10^{-4} S/cm). It demonstrates a wide and stable electrochemical window at around 4.5 V (vs. Li⁺/Li). It is also capable of quelling the growth of lithium dendrite. After that, He *et al.* fabricated a polymer electrolyte consisting of 80 wt % bis(trifluoromethanesulfonyl) imide (LiTFSI), 20% polyethylene carbonate (PEC), and polyamide (PA) fiber membrane skeleton [49]. The polymer electrolyte shows good mechanical strength and high ionic conductivity as well as good wettability to porous electrodes.

Fan *et al.* have introduced the polyamide (PA) fiber membrane to strengthen the mechanical strength of PEC-LiTFSI-based “polymer-in-salt” electrolyte [50]. The ionic conductivity of PEC-LiTFSI (80 wt.%)/PA can reach 4.05×10^{-4} S/cm at 55 °C. After that, the PVDF-HFP was added to enhance the mechanical strength further and maintain high ionic conductivity. Again, the biphasic polymer electrolyte with high content of lithium salt can deliver good mechanical strength by adjusting the ratio of PEC and PVDF-HFP. Similarly, the dual path of ion transport exist in polymer electrolyte: one is offered by the coordination and dissociation of lithium salt in a PEC-LiTFSI “polymer-in-salt” electrolyte that is surrounded by PVDF-HFP porous matrix; the other is induced by a synergistic effect of PVDF-HFP and PEC that can speed up the movement of the ions. The as-prepared polymer electrolyte exhibited high ionic conductivity of 1.08×10^{-4} S/cm at 30 °C, wide electrochemical stability window above 4.5 V (vs. Li⁺ /Li), and suppression of lithium dendrite growth. Thus, among the many polymer electrolytes, the polymer-in-salt electrolyte with good ionic conductivity appears promising. Yet, issues, including the stability, expense, and interfacial resistance between the polymer electrolyte and electrode, as well as others, should be fixed for large-scale applications.

Chen *et al.* proposed a polymer-in-salt bi-grafted polysiloxane (BPSO) copolymer electrolyte (the mass ratio of

LiTFSI to BPSO is 150 %) with super high ionic conductivity at room temperature and further set the composite polymer electrolyte membrane with high-ionic-candidate acetate (CA) membranes as the backbone and polymer-in-salt bi-grafted polysiloxane copolymers as the ion-conducting materials [51]. After introducing CA, although the ionic conductivity of BPSO copolymer electrolyte is sacrificed, its mechanical strength is extremely improved; thus, the lithium dendrites growth is obstructed. A viable method to improve the mechanical and ionic conductivity of polycarbonate derivative-based PISSEs is to add active ceramic fillers. Active ceramic fillers with inherent hardness can transmit Li-ion and prevent crystallization.

Li *et al.* fabricated a ceramic/polymer composite electrolyte by dissolving $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$ (LAGP) into poly(propylene carbonate) (PPC)-LiFSI 80 wt. % PISSE solution [52]. This PPC-based electrolyte was considered an adequate alternative to PEO-based composed polymer electrolyte. Compared with LAGP/PEO-SPE-80/20 electrolyte, LAGP/LiFSI80-80/20 concert 1-2 orders of magnitude higher ionic conductivity beneficial from the synergistic effect between LAGP and PPC-LiFSI 80 wt. % PISSE. Consequently, the Li/LAGP/LiFSI80-80/20/LiFePO₄ cell displays better cycling properties than the Li/LAGP/PEO-SPE-80/20/LiFePO₄ cell, which is also due to the improved interfacial behavior during cycling between the electrode and composite electrolyte.

3.3 Polyvinylidene fluoride-hexafluoropropylene (PVDF-HFP) based PISSEs

Liu *et al.* used polyvinylidene fluoride-hexafluoropropylene (PVDF-HFP) and excessive LiTFSI to formulate polymers-in-salt electrolytes (PVHLi-1.1) [53]. This electrolyte enhances the stability of the electrode/electrolyte interface and delivers more channels and sites for lithium-ions transportation, and the side effect of the 3D structure can inhibit the irregular growth of lithium dendrites. The SEM image of PVHLi-1.1 film reveals that PVHLi-1.1 fully infiltrated the 3D porous TiO₂/Li, exhibiting high ionic conductivity (1.24×10^{-4} S/cm) and a high Li-ion transference number. Ultimately, the capacity retention rate of polymers-in-salt electrolytes was as high as 86.8% after 800 cycles.

Furthermore, a poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP)-based polymer-in-salt solid electrolyte (PISSE) with high room-temperature ionic conductivity (1.24×10^{-4} S/cm) was designed and constructed a model integrated TiO₂/Li SSLB with 3D full infiltration of the solid electrolyte. By forming aggregated ion clusters, unique ionic channels are generated in the PISSE, delivering much faster Li-ion transport than common polymer electrolytes. Moreover, the integrated device simultaneously achieves maximized interfacial contact and electrochemical and mechanical stability, presenting a high performance near that of liquid electrolytes. A pouch cell made of 2 SSLB units in series exhibits a high voltage plateau (3.7 V) and volumetric energy density comparable to many commercial thin-film batteries (microbatteries), which also exhibit strong flexibility and brilliant safety under abuse tests [53].

Chen *et al.* prepared a salt polymer composed of lithium bis (trifluoromethane sulfone-imide) (LiTFSI), polyvinylidene fluoride (PVDF), and double-grafted polysiloxane copolymer by the solution-casting method, and then

compounded it with cellulose acetate to prepare polymer electrolyte [54]. The solid electrolyte exhibits interesting mechanical properties delivered by cellulose acetate. Polysiloxane, LiTFSI, and the PVDF-prepared polymer salt solid-phase extracts offer high ionic conductivity. Hence, lithium-sulfur batteries assembled with this polymer electrolyte present good cycling performance at 1C.

Hao *et al.* developed a novel polymer-in-salt solid electrolyte via a supramolecular strategy based on poly(methyl vinyl ether-alt-maleic anhydride) (PME) and novel single-ion lithiated polyvinyl formal (LiPVFM)/lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) composite salts (Dual-Li) [55]. Hydroxyl of LiPVFM in Dual-Li forms a strong hydrogen bond with the carboxylic acid group induced by the partial ring-opening reaction of maleic anhydride in PME. Meanwhile, PME with abundant carbonyl enables enhanced LiTFSI coordination in the polymer/salt composites. As a result, the greatly enhanced mutual solubility of PME and Dual-Li is of importance to build a “polymer-in-salt” solid electrolyte (PISE), which exhibits high ionic conductivity of 3.57×10^{-4} S/cm, wide electrochemical window beyond 5 V, and superior lithium-ion transference number of 0.62 at 25 °C as well as excellent interfacial compatibility with electrodes— assembled LiCoO₂||Li solid batteries present prominent high-voltage cyclability with 89.2% capacity retention in 225 cycles. Similarly, LiNi_{0.7}Mn_{0.2}Co_{0.1}O₂||Li pouch cells exhibit excellent safety even under harsh conditions. The study offers a promising method to handle the high voltage compatibility and interfacial issues using PISE in solid-state batteries [55].

3.4 Polyethylene oxide (PEO)-based PISSEs

One example is the ionic rubber based on the ternary LiClO₄-LiNO₃-LiOAc and high molecular weight PEO (MW ~8x10⁶) reported by Angel's group [17]. They found that an ambient conductivity as high as 10⁻³ S/cm could be obtained from this ionic rubber, with a large rubbery temperature range (~20 °C to ~130°C). The current challenge is to find salt or salt mixtures with wider electrochemical windows (>4.5 V) which are compatible with PEO polymer or new high molecular weight polymers which are stable in more aggressive melts. Once this problem is solved, the practical application of this new ionic rubber in lithium batteries is very favorable. Based on this assumption, they formulated a series of lithium sulfonates, which are known to exhibit electrochemical stability. One special material was formed by complexing the anion of lithium chlorosulfonic, ClSO₃⁻, with aluminum chloride to give the chloroaluminate-chlorosulfonic anion, [AlCl₃-SO₃Cl]⁻. Combining the high decoupling index (6x10⁷) and a low T_g (-30.4°C) gave an ionic conductivity of 1.6x10⁻³ S/cm at room temperature, with a 4.0 V electrochemical window.

Wu *et al.* prepared a polymer-in-salt electrolyte with enhanced oxidative stability by combining polyethylene oxide (PEO) and lithium bis(fluorosulfonyl)imide (LiFSI) with a dry ball milling [56]. The high voltage stability and ionic conductivity of PEO-based polymer electrolyte systems change with the content of LiFSI. The polymer electrolyte with EO/Li = 1 has high ionic conductivity and oxidative stability. The first principles exhibit that the coordination of EO with Li-ion in the electrolyte with EO/Li = 1 reduces the HOMO energy level, thereby boosting the oxidation voltage. Consequently, the lithium metal batteries with the polymer-in-salt electrolyte produced a high capacity

retention of 74.4% over 186 cycles at a high voltage of 4.3 V.

4.0 Perspective

To manufacture higher energy density batteries, solid-state lithium metal batteries like Li-S [57] and Li-O₂ [58] cells must complement those made from SPEs. This is due to the lithium metal bond, which has the greatest negative electrochemical potential and an extremely large specific capacity (3860 mAh/g) (-3.04 V vs. standard hydrogen electrode). While cycling, particularly at high current densities, the development of lithium dendrites will pierce the electrolyte membrane and result in a short circuit. To prevent lithium dendrites in such situations, the PISSE requires relatively high mechanical stiffness. As a result of this, I made the following recommendations:

4.1 Development of Novel Lithium Salts with Desired Functionalities

The cost of lithium salt must be considered due to its massive use in PISSEs. Lithium salts used for PISSEs systems are either LiFSI or LiTFSI, which are expensive. Likewise, the high lithium salt concentration is unstable and leads to easy crystallization. Therefore, it is vital to develop new lithium salts with low cost and high stability.

4.2 Synthesize new Polymer Matrices via Functional Units Adjustments

To further decrease the cost of PISSEs, it is critical to find some new polymer matrix. In addition to being cheap, the polymer host should also have the following aspects: (1) high dielectric constant to boost the dissolution of lithium salts; (2) superior mechanical strength; (3) excellent stability, including thermal stability, chemical stability, and electrochemical stability; (4) ability to immobilize the anion of the lithium salt to form single-ion conductivity, as Rolland *et al.* reported [59]. These properties can be enhanced by the strategy of functional unit adjustment, including copolymerizing, cross-linking, and grafting from monomer functional units are the most common methods. Considering the cheap abundance and the mature industries, natural polymers and modified natural polymers are possible candidates.

4.3 Use Electrode-Supported PISSE Integrated Membrane

Although the properties of PISSEs can be enhanced by adding functional inorganic or organic materials, the performances of PISSE-based LIBs still have to be improved. This is because of the inferior interfacial contact between the polymer electrolyte and the electrode, which leads to huge interfacial resistance [60,61]. It is hard for the rigid solid electrolyte membrane to effectively wet interface like liquid electrolytes. This problem can be addressed by casting the polymer electrolyte solution on the electrode to situ form the polymer electrolyte membrane and constructing an electrode-supported PISSE integrated membrane [62-64]. By reducing the thickness of the polymer electrolyte, this integrated structural design can increase the battery's energy density while simultaneously improving the performance of the electrode by expanding the contact area between the electrode and the solid electrolyte. The fact that such a solid-state battery does not increase the interfacial impedance

between the electrode and the polymer electrolyte even before deforming means that it can power flexible devices. The 3D electrode structure, particularly the 3D nanoarray structure grown directly on a current collector, will be suitably advantageous to further enhance the performances of the flexible battery with the electrode-supported PISSE integrated membrane [65,66]. Because of sufficient interspacing between the various nanostructures, the electrode with a 3D nanoarray structure may achieve not only the quick passage of electrons but also complete contact between the active materials and PISSEs.

Conclusion

Solid polymer Li-ion batteries with reassuring safety, high energy density, and arbitrary structure show great potential for future energy storage. SPEs with outstanding capabilities, such as strong ionic conductivity at room temperature, large electrochemical windows, and good mechanical qualities, are essential to developing commercially viable solid polymer lithium-ion batteries. Among various SPEs, PISSEs are promising due to superior ionic conductivity at room temperature. In this review, the historical development, requirements for ideal SPEs, the challenges of conventional salt-in-polymer electrolytes, the ion-conduction mechanism of PISSEs, and recent advances in improving PISSEs were discussed. Some challenges, including stability, cost, and interfacial resistance between PISSEs and electrodes, have also been put forward. In future studies, searching for optimal PISSEs and optimizing the interface with electrodes are indispensable for advancing the performance of related solid-state Li-ion batteries. In addition to paving the way for the widespread use of solid-state lithium-ion batteries, the development of PISSEs offers new insight into how to address solid electrolyte design and interfacial problems in high voltage SLMBs, advancing the creation of polymer electrolyte-based solid batteries with high energy density, performance, and safety. It is foreseen that significant progress will be made soon.

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