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Solid polymer electrolytes and their role in the development of next generation Li-ion batteries

Abstract. Over the past ten years, lithium-ion batteries (LIBs) have become indispensable for powering wearable technology, smart electronics, and electric cars. However, the use of extremely flammable and volatile liquid electrolytes in typical Li-ion rechargeable batteries raises serious safety issues and prevents future advancements in energy density and dependability. Solid electrolytes have been suggested as viable solutions to these problems. In particular, polymer-based solid electrolytes combine high ionic conductivity with advantages such as low flammability, mechanical flexibility, thermal stability, and improved safety. This review highlights recent advances in solid polymer electrolytes for LIBs, with a focus on their fabrication strategies, structural designs, ionic conductivities, and electrochemical/mechanical stabilities.
Keywords: lithium-ion batteries, solid polymer electrolytes, ionic conductivity, safety, electrochemical stability, fabrication strategies.

Introduction

The development of lithium-ion batteries (LIBs) began in the 1970s with early investigations on Li/TiS_2 systems [1]. In 1991, Sony Corporation and Asahi Kasei commercialized LIBs, which have since become dominant in diverse applications, including mobile electronics, wearable devices, and electric vehicles [2, 3]. LIBs offer high energy density and long cycle life; however, safety concerns remain a critical barrier to their broader deployment.

Lithium hexafluorophosphate ($LiPF_4$) dissolved in organic carbonate liquids is used as a liquid electrolyte in conventional LIBs. Further improvements in energy density and dependability are hampered by these electrolytes' extreme volatility, flammability, and thermal instability. Solid polymer electrolytes (SPEs) have been suggested as viable substitutes to address these issues [4, 5]. However, at room temperature, their comparatively low ionic conductivity and lithium-ion transference numbers have impeded their practical deployment.

Numerous techniques, such as the design of new polymer hosts and the addition of functional additives, have been the subject of extensive research efforts to solve these constraints [6-8]. Crucially, the safety profile of LIBs would be much improved by completely substituting SPEs for liquid electrolytes [9-11]. The development of flexible polymer hosts, such as poly(propylene carbonate), poly(ethylene oxide), and poly(tetrahydrofuran), has been the focus of recent advancements. These hosts exhibit improved ionic conductivity, higher lithium-ion transference numbers, better thermal stability, mechanical robustness, and enhanced interfacial adhesion [12-14]. Although ion conduction mechanisms and lithium-ion transport properties have been examined in a number of papers [8, 15, 16], a thorough summary of recent developments in SPE design is still required.

The goal of this review is to provide an overview of the most recent developments in solid polymer electrolytes, with a focus on synthesis techniques, ionic conductivity enhancement techniques, and assessments of their chemical and thermal durability. Lastly, prospects for the advancement of sophisticated SPEs are examined.

1. Polymer-based solid polymer electrolytes

Among solid polymer electrolytes (SPEs), polyethylene oxide (PEO)- and polyacrylonitrile (PAN)-based systems have been extensively studied [17, 18]. Enhancing Li^+ conductivity in SPEs requires a fundamental understanding of ion transport mechanisms. Polymers containing polar functional groups (–O–, –B–, –N–, C=O, C≡N, C–S–, and C–(O=S=O)–) can effectively dissolve lithium salts through polymer–

salt complexation. Accordingly, polymers such as PEO, PAN, polyethyleneimine (PEI), and polypropylene carbonate (PPC) exhibit good lithium-salt solvation ability [16].

Electrolytes based on PPC are highly transparent due to their predominantly amorphous phase (Figure 1). Unlike many other polymers, PPC exhibits a glass transition temperature (T_g) close to room temperature, which facilitates ionic motion. Its good compatibility with lithium salts and high transparency make PPC a promising candidate for SPE applications. Furthermore, the carbonyl groups in PPC exhibit weaker coordination with lithium ions compared to the stronger coordination of Li^+ with the ether oxygen atoms in polyethers such as PEO [12]. This weaker binding contributes to enhanced ion mobility, and consequently, carbonyl-based PPC exhibits one of the highest room-temperature ionic conductivities among polymer hosts. However, its conductivity (10^{-4}–10^{-5} S·cm^{-1}) remains below the practical requirements for solid polymer electrolytes in lithium-ion batteries.

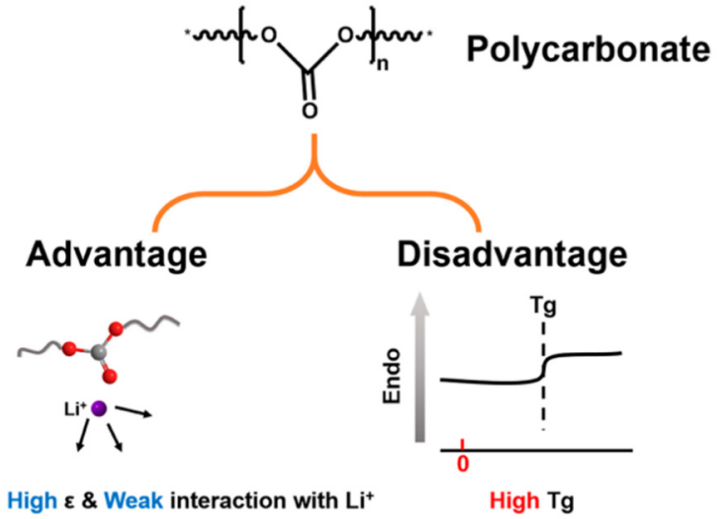


Figure 1 – Schematic diagram illustrating the advantages and disadvantages of polycarbonates [12]

2. Fundamental Characteristics of Solid Polymer Electrolytes (SPEs)

a) Ionic Conductivity

It is well established that electronic conductivity in polymers is higher in spatially ordered systems, while greater ionic conductivity can be achieved in disordered or amorphous polymer domains. Complexes formed between lithium salts and solvating polymers exhibit varying degrees of ionic conductivity [19]. Polymers can be fully amorphous or semicrystalline, depending on chain regularity. In amorphous polymers, segmental motion of the chains occurs above the glass transition temperature (T_g), while crystalline regions melt at the melting point (T_f). A key feature of polymer electrolytes is that ionic transport is confined to the amorphous phase above T_g, where Li^+ mobility is strongly coupled with the segmental motion of polymer chains [20].

Extensive research has focused on enhancing the ionic conductivity of polymer–Li salt systems over the past decades [21-23]. Nevertheless, the ionic conductivity of state-of-the-art SPEs (10^{-4}–10^{-5} S·cm^{-1}) still falls short of liquid electrolytes (10^{-2} S·cm^{-1}), highlighting the need for further development to enable practical replacement of flammable organic electrolytes.

b) Electrochemical, Chemical, and Thermal Stability

The practical applicability of SPEs is largely determined by their electrochemical stability window. The charge–discharge potentials of electrode materials must lie within this window; otherwise, side reactions may occur, leading to capacity fading and reduced safety. Current lithium-ion battery technology relies on intercalation-type cathodes and anodes with operating voltages close to Li/Li^+. Most com-

mercial cathodes operate below 4.3 V [24], therefore, an ideal SPE should maintain stability within 0–5 V versus Li/Li^+.

Chemical stability is equally critical, particularly at the interface with the lithium-metal anode. Unstable interactions can result in dendrite formation, grain boundary opening, and the development of isolated "islands" at the interface, all of which compromise battery safety and performance [25].

Thermal stability is another essential parameter, as polymer electrolytes must withstand elevated operating temperatures without degradation. To replace conventional liquid electrolytes and separators, SPEs must resist shrinkage or dimensional changes at temperatures around 150–165°C [26]. Such thermal robustness is a prerequisite for improving the intrinsic safety of LIBs.

c) Mechanical Properties

In addition to high ionic conductivity and chemical/thermal stability, SPEs must possess adequate mechanical strength to ensure reliable battery operation. Electrolytes that are too brittle or excessively rigid exhibit poor interfacial contact with electrodes, impeding charge transfer and increasing internal resistance [27, 28]. Thus, intimate electrode–electrolyte interactions and steady long-term cycling performance depend on striking a balance between mechanical integrity and flexibility.

3. Innovative Methods for Solid Polymer Electrolyte Synthesis

a) Techniques to Boost SPEs' Ionic Conductivity

Polymer-based solid electrolytes have been thoroughly studied in recent years due to their potential to replace liquid electrolytes in lithium-ion batteries as well as their inherent safety. Improving SPEs' ionic conductivity has been the subject of extensive research.

The creation of ultrathin polymer electrolyte sheets is one successful tactic. Improved conductivity is achieved by decreasing the electrolyte thickness, which also shortens the ion migration path and lowers the ionic resistance. It is still difficult to prepare ultrathin solid polymer electrolytes without sacrificing their mechanical integrity. Excessive thinning can increase the risk of internal short circuits, particularly in electrolytes with low mechanical strength and toughness [29].

Recently, ultrathin solid polymer electrolytes (UTPEs) based on grafted agarose with polyethylene oxide (PEO) were reported, demonstrating an ionic conductivity of 1.2×10^{-4} $S \cdot cm^{-1}$ at room temperature [30]. In this work, UTPEs were synthesized via a reaction between single-helical agarose and PEO in the presence of isophorone diisocyanate (IPDI). Electrochemical impedance spectroscopy (EIS) of UTPEs with varying thicknesses was conducted using $LiFePO_4$ (LFP) || Li cells to assess interfacial stability. The cell employing a 32 μm UTPE exhibited lower interfacial impedance during cycling, while the one with a 72 μm UTPE showed progressively increasing impedance. Moreover, the solid-state LFP||Li cell with UTPE demonstrated superior cycling and rate performance compared to cells using an electrolyte mixture of agarose/PEO/LiTFSI (Figure 2).

The unique helical structure of ultrathin polymer electrolytes (UTPEs) not only enhances their mechanical properties but also increases free volume and facilitates segmental motion, both of which are crucial for lithium-ion hopping. As a result, the UTPE demonstrated an ionic conductivity of 1.2×10^{-4} $S \cdot cm^{-1}$ at room temperature.

In another approach, a polymer–polymer solid-state electrolyte was designed using an 8.6 μm-thick nanoporous polyimide (PI) film filled with polyethylene oxide/lithium bis(trifluoromethanesulfonyl) imide (PEO/LiTFSI) [31]. This composite electrolyte combines a nonflammable PI host containing vertically aligned nanochannels with Li-ion conducting PEO/LiTFSI fillers. The high modulus of the PI framework effectively suppresses lithium dendrite penetration, while the vertical nanochannels promote uniform infiltration of the polymer electrolyte and improve ionic transport. The resulting ultrathin polymer–polymer composite electrolyte exhibits excellent flexibility, low resistance, and high energy density in full-cell configurations.

Electrochemical performance and morphological studies (Figure 3) revealed that approximately 11% of the PI surface area was occupied by PEO/LiTFSI fillers. Cross-sectional SEM images confirmed that the fillers fully infiltrated the vertical nanochannels of the PI framework. Interestingly, the PEO/LiTFSI confined within aligned PI pores exhibited a higher ionic conductivity (2.3×10^{-4} $S \cdot cm^{-1}$) compared to a conventional PEO/LiTFSI thin film (5.4×10^{-5} $S \cdot cm^{-1}$), highlighting the beneficial effect of nanoscale confinement.

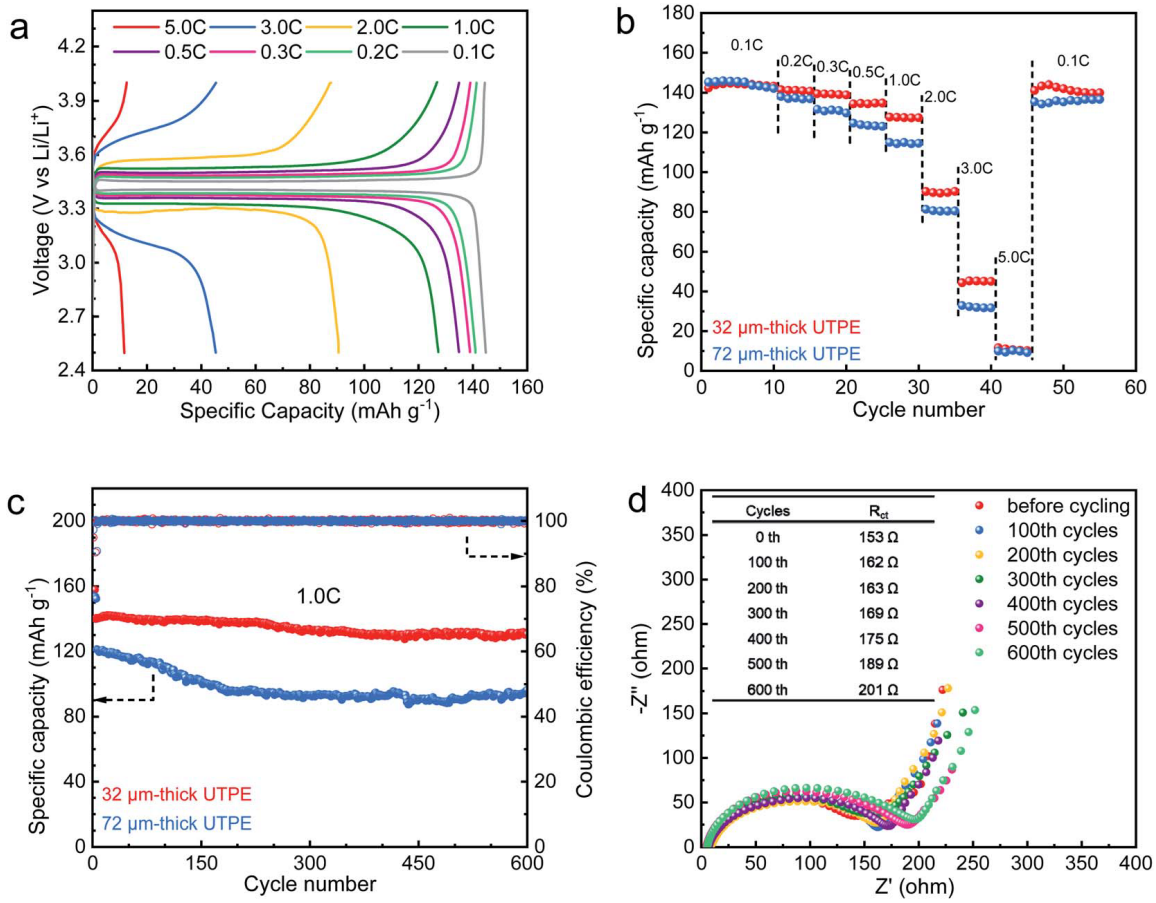


Figure 2 – (a) Voltage profiles of Li|LFP cells with a 32 μm UTPE at various C-rates at room temperature; (b) rate performance of Li|LFP cells with UTPEs of different thicknesses; (c) discharge capacity and coulombic efficiency at 1.0C; (d) EIS of Li|LFP cells with a 32 μm UTPE after different cycles [30]

Sun et al. [32] proposed another strategy to enhance ionic conductivity by employing an *in situ* solidification method based on the ring-opening polymerization of ε-caprolactone (ε-CL). This approach enabled the fabrication of ultrathin (~11 μm) poly(ε-caprolactone) (PCL)-based polymer electrolytes. The *in situ* polymerization not only simplified electrolyte preparation but also yielded mechanically stable films with improved interfacial compatibility and ionic transport, making them promising candidates for next-generation solid-state batteries.

Promising solid polymer electrolytes have been described from the polymerization of ε-caprolactone (ε-CL) monomers catalyzed by $Sn(Oct)_2$. According to the authors, when $Sn(Oct)_2$ is utilized as a catalyst during synthesis, it not only successfully stimulates the ring-opening polymerization of ε-CL but also changes into a layer of Li–Sn alloy when it comes into contact with the lithium metal anode. This alloy layer is essential for inhibiting the formation of dendrites. The study found that the in situ produced poly(ε-caprolactone) (PCL)-based polymer electrolyte (in situ PCL SPE) operated for up to 900 hours with a low polarization potential of 45 mV, exhibiting excellent stability in symmetric Li|Li cells. A tiny quantity of propylene carbonate (PC) was added to further enhance ionic conductivity and cell performance. The addition of the commercial liquid electrolyte mainly served to enhance ionic conductivity at room temperature, reaching 2.1×10^{-5} S·cm^{-1} at 27°C – approximately 30 times higher than that of the pristine in situ PCL SPE (6.7×10^{-7} S·cm^{-1}). Moreover, the polymer electrolyte exhibited favorable electrochemical properties, including a suitable lithium-ion transference number and broad electrochemical stability (–0.5 to 4.3 V), making it a viable candidate for high-performance solid-state lithium metal batteries (LMBs).

In general, the ionic conductivity of solid polymer electrolytes can also be improved by reducing

the electrolyte thickness to the ultrathin scale. To address conductivity and interfacial issues, Jian-Fang Wu and Xin Guo investigated the incorporation of nanostructured metal–organic frameworks (MOFs) [33]. Due to their multifunctional properties, MOFs were found to enhance ionic conductivity, suppress polymer crystallinity, and improve interfacial stability with the lithium electrode. Specifically, the PEO-n-UIO composite polymer electrolytes, prepared by dispersing nanoporous UIO/Li-IL fillers in PEO, exhibited an increased lithium-ion conductivity of 1.3 $\times 10^{-4}$ S·cm^{-1} at 30°C. This improvement was attributed to the inherently high ionic conductivity of UIO/Li-IL and the suppression of PEO crystallinity.

Other researchers optimized the balance between crystallinity and ionic conductivity by incorporating well-established functional units into polymer electrolytes, such as ethylene oxide, carbonate, and lithium sulfonamide groups [17]. By tailoring the monomer stoichiometry, the resulting copolymer achieved an ionic conductivity of 1.2 $\times 10^{-4}$ S·cm^{-1} at 70°C. In this study, the polymers were synthesized via a two-step melt polycondensation process using poly(ethylene glycol) (M_n = 1500), dimethyl carbonate, and a functional diol containing sulfonimide groups (Figure 3).

Using this synthetic route, three different copolymer compositions were targeted to optimize performance: PEO_{34}:bis-MPTFSI (lithium ((3-((3-hydroxy-2-(hydroxymethyl)-2-methylpropanoyl)oxy) propyl)sulfonyl)(trifluoromethyl)sulfonyl)amide) at 75:25 mol% (SIPC-1), 50:50 mol% (SIPC-2), and 25:75 mol% (SIPC-3). The ionic conductivity at room temperature was as follows: SIPC-3 > SIPC-2 > SIPC-1.

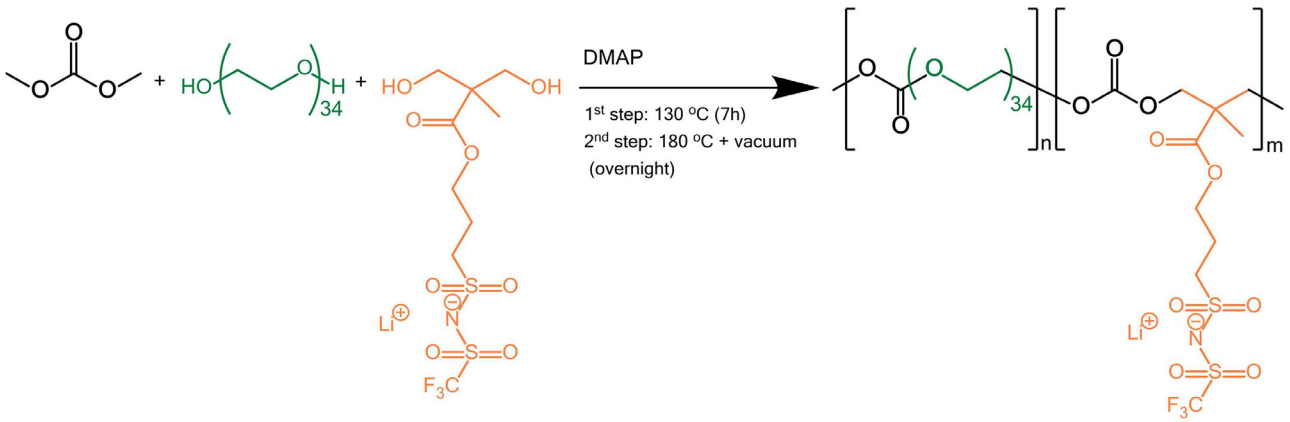


Figure 3 – Polycondensation route of poly(ethylene oxide carbonate) polymer electrolytes [17]

When both carbonate and ether oxygens were taken into account, the O/Li molar ratio had a significant impact on Li^+ conduction above the melting temperature of the crystalline EO phase (T > 50°C). SIPC-2 showed the best balance between coordinating oxygen atoms and lithium ions, with O/Li = 35. On the other hand, SIPC-3 (O/Li = 6) showed decreased conductivity because there were not enough carbonate/EO units to properly coordinate and dissociate lithium ions, whereas SIPC-1 (O/Li = 110) had too little lithium to support effective ionic conduction. SIPC-2 attained an ionic conductivity of 1.2 $\times 10^{-1}$ S·cm^{-1} at 70°C.

Despite their promising conductivity, SIPC-based electrolytes exhibited low glass transition temperatures (~ –40°C) and linear chain structures, leading to poor mechanical stability above the melting point of the EO crystalline phase. To address this, PEG diacrylate (PEGDA, M_n = 575) was incorporated as a cross-linker, with SIPC-2 selected for optimization due to its superior ionic conductivity above room temperature. Upon ultraviolet irradiation, freestanding films of single-ion conducting poly(ethylene oxide carbonate) were obtained with small amounts of networked PEGDA. The addition of 5 wt% PEGDA did not significantly affect ionic conductivity: at 70°C, SIPC-2 with 5 wt% PEGDA reached 3.2 $\times 10^{-5}$ S·cm^{-1}, compared to 1.2 $\times 10^{-4}$ S·cm^{-1} for the uncrosslinked SIPC-2. However, increasing the PEGDA content to 10 wt% caused a sharp decline in conductivity (9.6 $\times 10^{-7}$ S·cm^{-1}). Because this decrease was observed even above the EO crys-

talline melting point, it was attributed more to altered crystallinity and reduced chain mobility than to the semi-interpenetrated PEGDA network itself.

In a related approach, Meabe et al. [34] synthesized various aliphatic polycarbonates for use as solid polymer electrolytes via traditional polycondensation of diols with dimethyl carbonate. Recently, aliphatic polycarbonates have been proposed as promising alternatives to PEO-based matrices, offering excellent room-temperature ionic conductivity, broad electrochemical stability, and high lithium-ion transference numbers [35]. In this study, the authors fabricated a series of aliphatic polycarbonates containing between 4 and 12 methylene groups between carbonate units. The ionic conductivity of these polycarbonate-based SPEs was slightly improved by optimizing the Li^+/polymer ratio, reaching ~1×10^{-4} S·cm^{-1}. Interestingly, polymers with longer methylene spacers showed higher conductivities. Furthermore, the P10C and P12C samples, which exhibited the lowest molecular weights, delivered the highest conductivities due to reduced chain entanglement and improved segmental mobility.

Other authors have synthesized aliphatic carbonate-based solid polymer electrolytes through ring-opening polymerization of cyclic carbonates as well as copolymerization of CO_2 with epoxides [35, 36]. Mindemark and co-workers suppressed the crystallinity of poly(ε-caprolactone) (PCL) by copolymerizing it with trimethylene carbonate (TMC), which enhanced the ionic conductivity to 4.1×10^{-5} S·cm^{-1} at 25°C. In this work, carbonate repeating units were incorporated into the PCL backbone, enabling the material to act as a more effective solid polymer electrolyte host. The authors demonstrated that introducing carbonate units not only reduced the crystallinity of the polyester but also broadened the temperature range over which higher ionic conductivity was maintained. They proposed that the improved Li^+ transport originated either from the weaker coordination of carbonate groups with Li^+ compared to ester groups, or from the disruption of the regular sequence of the PCL backbone, which enhanced chain mobility.

Morioka et al. [37] reported an alternative strategy by fabricating polycarbonates with oxyethylene (OE) end groups via alternating copolymerization of CO_2 and glycidyl ether monomers. In this study, three types of polycarbonates derived from CO_2 and glycidyl ether monomers were synthesized. These polymers combined the benefits of polycarbonates (low T_g, amorphous structure, wide electrochemical window) with the Li^+ coordination ability of oxyethylene segments, offering a promising design pathway for advanced solid polymer electrolytes.

They subsequently employed lithium bis(fluorosulfonyl)imide (LiFSI) to investigate the influence of oxyethylene (OE) chain length on the ion-conductive properties of the polycarbonate-based electrolytes. According to their findings, polycarbonates with ether end groups exhibited relatively high Li^+ transference numbers, often exceeding 0.4. The authors suggested that such elevated values indicate weaker interactions between the polymer main chains and cations compared to conventional polyethers. At a salt concentration of 188 mol%, most Li^+ ions were found to interact with carbonate groups, yet the polycarbonate electrolytes still maintained high Li^+ transference values. Notably, the polycarbonate with ethoxy side groups combined with LiTFSI achieved a Li^+ transference number above 0.7, comparable to those of single-ion conducting polymers [17].

Morioka and co-workers attributed this behavior to the fact that polycarbonates with ethoxy side groups contain only a single ether oxygen atom in the terminal group, making it difficult to form stable coordination structures as typically observed in the PEO system. Instead, the short ether side chains likely promote faster Li^+ migration, thereby contributing to both the enhanced ionic conductivity and the high transference values.

Yi Cui and co-workers reported the in-situ preparation method of polymer electrolytes containing ceramic SiO_2 particles (composite polymer electrolytes) (Figure 4) [38].

According to the research, the *in situ* CPE shows a dissociation ratio of 98.1%, which is significantly higher than those of the ceramic-free SPE (85.0%), PEO–fumed SiO_2 CPE (87.4%), and *ex situ* CPE (92.8%). This demonstrates that the *in situ* hydrolysis method markedly enhances the ability of the PEO matrix to dissociate $LiClO_4$. The high dissociation is mainly attributed to the small, highly monodisperse SiO_2 particles that provide a large surface area. Consequently, the *in situ* PEO–MUSiO_2 CPE exhibits ionic conductivity in the range of 10^{-4}–10^{-5} S cm^{-1} at room temperature and reaches 1.2×10^{-3} S cm^{-1} at 60°C, approaching that of liquid electrolytes. Its ionic conductivity at 30 and 60°C was also compared with literature values for similar systems prepared by mechanical mixing.

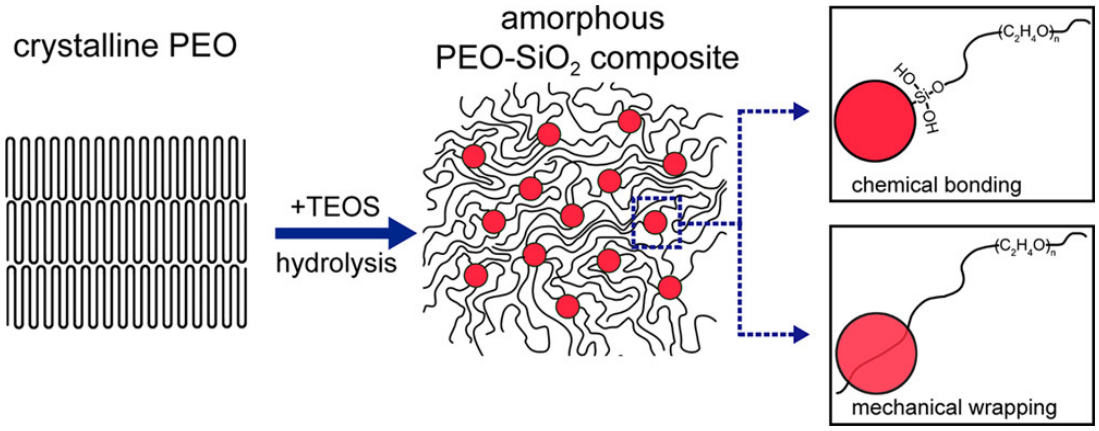


Figure 4 – Schematic illustration of in-situ preparation of PEO-based composite polymer electrolyte

Lin et al. developed a homogeneous solid composite polymer electrolyte based on $LiClO_4$-doped PEO plasticized with meso-tetra(carboxyphenyl) porphyrin (TCPP), a porphyrin-based COF, using a simple and scalable solution-casting method [39]. The TCPP incorporation significantly enhances the thermal stability of PEO electrolytes to above 330°C and improves Li^+ ionic conductivity to 2.34×10^{-5} S cm^{-1} at room temperature, enabling safer and more stable lithium-ion battery operation. The authors also explained the interactions between the TCPP filler and the $LiClO_4$-doped PEO polymer electrolyte. They reported that complexation among PEO, $LiClO_4$, and TCPP disrupts the crystallinity of PEO, which in turn enhances the ionic conductivity of the PEO-based electrolyte (Figure 5).

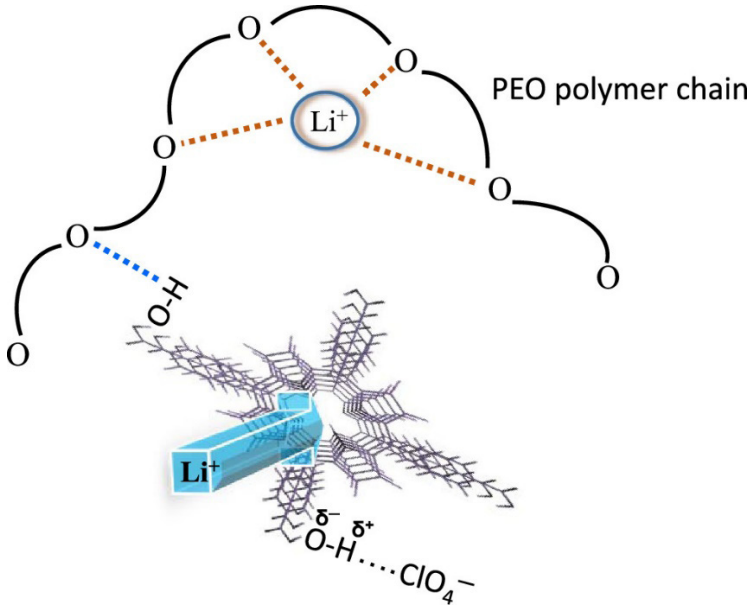


Figure 5 – Schematic illustration of the interaction between filler, Li salt and PEO [39]

Another strategy to improve the ionic conductivity of solid polymer electrolytes involves the incorporation of ionic liquids (ILs). For instance, Anji Reddy Polu and Hee-Woo Rhee studied the effect of adding the ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMImTFSI) into a PEO–lithium difluoro(oxalato)borate (LiDFOB) polymer matrix. In this work, solid polymer elec-

trolytes were prepared using a solution-casting technique [40].

The ionic conductivity of PEO-based solid polymer electrolytes can also be enhanced through phase modification induced by the incorporation of ionic liquids. To examine the influence of lithium salt and the ionic liquid EMImTFSI on the semi-crystalline nature of PEO, the authors performed X-ray diffraction (XRD) analysis.

According to the study, the intensity and crystallinity of the XRD peaks of pure PEO were noticeably reduced after incorporating LiDFOB into the PEO matrix. The complete dissolution of the lithium salt in the PEO matrix was demonstrated by the absence of LiDFOB diffraction peaks in any of the polymer electrolyte membranes. The peak intensities further dropped as the IL concentration increased when the ionic liquid was added to the PEO20–LiDFOB polymer electrolyte. This indicates that the polymer electrolytes' crystallinity was significantly reduced as a result of coordination contacts between Li^+ and EMIm cations with the ether oxygen atoms of PEO. Consequently, the energy barrier for segmental motion of polymers was reduced. According to conductivity experiments, adding LiDFOB enhanced the ionic conductivity to 1.2×10^{-1} S·cm^{-1}, which is three orders of magnitude higher than that of pure PEO. The PEO20–LiDFOB polymer electrolyte's ionic conductivity was further improved by the addition of ionic liquid, reaching 9.44×10^{-1} S·cm^{-1} at ambient temperature and 1.85×10^{-1} S·cm^{-1} at 30°C.

Polu and co-authors achieved a maximum ionic conductivity of 1.85×10^{-4} S·cm^{-1} at 30°C for a 40 wt% IL content, demonstrating that ionic-liquid-incorporated PEO–LiDFOB polymer electrolytes are among the most promising candidates for lithium-ion batteries.

Lu et al. constructed a free-standing and flexible polymer electrolyte film based on a lithium-containing zwitterionic poly(ionic liquid) (PIL), with and without propylene carbonate (PC), via in-situ photopolymerization [41]. In this work, a polymerizable ionic liquid, [VIPS][LiTFSI], was synthesized by equimolar neutralization of the imidazolium-type zwitterion 3-(1-vinyl-3-imidazolio)propanesulfonate (VIPS) with lithium bis(trifluoromethylsulfonyl)imide (LiTFSI), driven by intermolecular electrostatic interactions. Upon UV cross-linking, the lithium-containing IL was polymerized into a flexible, free-standing electrolyte film.

The ionic conductivities of the pure PIL film and gel polymer electrolyte films containing different PC contents were measured using the alternating current (AC) impedance method. As shown in Figure 6, all electrolyte films demonstrated a progressive increase in ionic conductivity with increasing temperature. Specifically, in the range of 30-150°C, the pure PIL film without PC exhibited an increase in ionic conductivity from 2.4×10^{-5} to 2.9×10^{-3} S·cm^{-1}.

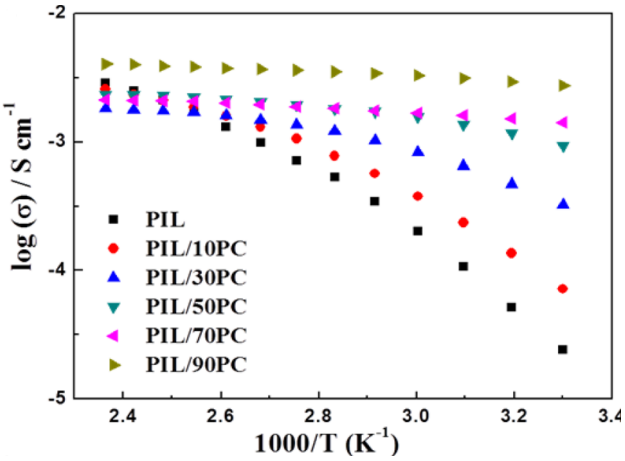


Figure 6 – Temperature-dependent ionic conductivity of PIL/χPC polymer electrolytes (χ denotes the weight fraction of PC) [41]

The authors revealed that with the addition of PC, the ionic conductivities significantly increased to ~10^{-3} at room temperature because of the further ion–dipole interaction between Li^+ and PC.

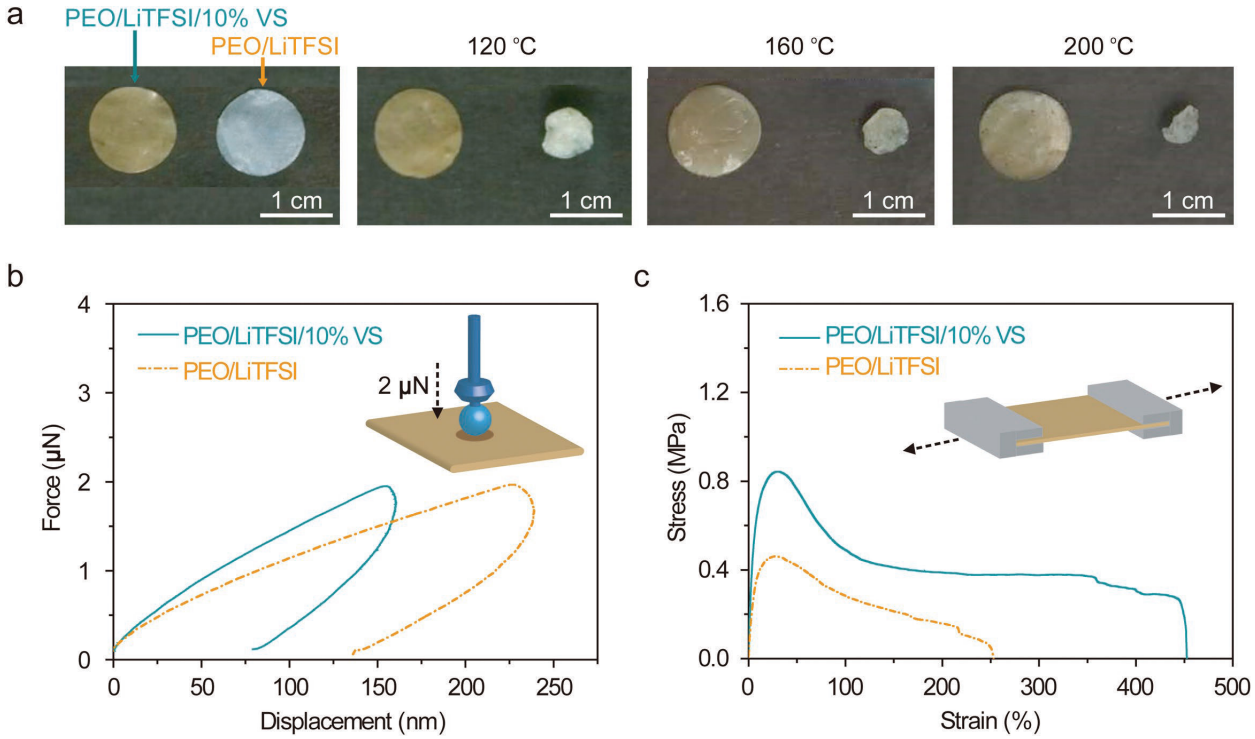
b) Strategies to Improve the Thermal and Chemical Stability of SPEs

Safety remains one of the major challenges limiting the widespread application of LIBs in the electric vehicle market. A critical strategy for enhancing thermal safety lies in tailoring the battery chemistry. Thermal failure of solid electrolytes and cathode–electrolyte interfaces (CEIs), as well as the underlying mechanisms, have been comprehensively discussed by Zu *et al.* [42]. The authors emphasized that the electrolyte composition, electrode type, and processing technique have a significant impact on the SEI/CEI's thermal stability.

Using chemicals to strengthen the SEI/CEI and improve its thermal robustness through precursor processes is one intriguing strategy. Tang *et al.* [43] demonstrated this by introducing two-dimensional (2D) additives, specifically few-layer vermiculite (VS) clay sheets, into PEO-based solid polymer electrolytes. With the incorporation of VS, the polymer

electrolyte exhibited significant improvements in thermal stability, mechanical modulus, ionic conductivity, electrochemical stability, reduced flammability, and lower interfacial resistance.

The composite SPE was prepared by solution casting of a homogeneous mixture of PEO, LiTFSI, and VS in acetonitrile, and its thermal properties were compared with those of pristine PEO/LiTFSI SPE (Figure 7). As expected, the pristine SPE film underwent severe shrinkage at temperatures above 120°C, which could potentially lead to catastrophic short-circuiting between electrodes. In contrast, the VS-containing composite SPE maintained dimensional stability even above 200°C. The 2D VS effectively suppressed the melting-induced shrinkage of PEO and preserved the structural integrity of the composite, confirming its role in improving the high-temperature stability of SPEs.



(a) photographs of VS composite and pristine SPEs before and after 30 min heat treatment at different temperatures; (b) nanoindentation load–displacement curves; (c) tensile stress–strain curves of VS composite and pristine SPEs

Figure 7 – Enhanced thermal and mechanical stability of SPEs with VS [43]

In addition to 2D filler approaches, certain functional components–including C=C, N≡C, halogen, phosphorus, sulfur, phenol, organic borates, boranes, and silanes–have been shown to promote the formation of thermally stable SEI/CEI layers [12, 44]. Another effective method is in situ polymerization/solidification, which can simultaneously enhance electrochemical, chemical, and thermal stability of polymer electrolytes [45]. Furthermore, a carefully designed fabrication procedure can help minimize interfacial resistance, a critical requirement for the ideal SEI/CEI.

Recent advances suggest that SPEs modified with inorganic fillers, vertically aligned channels, or layered sheet structures represent some of the most promising designs, offering a balance of thermal stability, high ionic conductivity, and long-term electrochemical stability [46-49].

Conclusion

Solid polymer electrolytes have emerged as one of the most promising alternatives to liquid electrolytes for next-generation lithium-ion batteries due to their potential for enhanced safety, mechanical flexibility, and wide electrochemical stability windows. However, their practical deployment is still challenged by issues of relatively low ionic conductivity

at room temperature, limited Li^+ transference numbers, and interfacial instability with electrodes.

Recent developments have shown that structural changes, including side-chain engineering, copolymerization, and the addition of aliphatic carbonate units, can successfully reduce polymer crystallinity and promote Li^+ transport. In the meantime, by weakening Li^+ coordination and improving ion dissociation, the development of ionic liquids, zwitterionic groups, and quaternary ammonium salts has opened up new ways to boost conductivity and transference numbers.

Strategies to deal with chemical and thermal stability are equally significant. The mechanical robustness, flame retardancy, and thermal endurance of polymer electrolytes have been greatly enhanced by the addition of 2D fillers (such as vermiculite sheets), inorganic nanoparticles, vertically oriented channels, and functional chemical groups. The simultaneous improvement of interfacial compatibility, electrochemical performance, and structural integrity is further made possible by in situ polymerization processes.

Overall, the ongoing development of SPEs necessitates a synergistic strategy that combines sophisticated processing techniques, functional additives, and polymer chemistry design. SPEs are anticipated to be crucial in enabling solid-state lithium-ion batteries with high energy density, safety, and durability for electric vehicles and large-scale energy storage as long as they continue to advance.

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Conflict of interest

No conflicts of interest are disclosed by the authors.

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