Review

Progress on High Voltage PEO-based Polymer Solid Electrolytes in Lithium Batteries

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Polymer electrolytes have attracted great interest for next-generation lithium-based batteries on account of safety and high energy density. In this review, we assess recent progress on the design of poly(ethylene oxide)(PEO)-based solid polymer electrolytes in high voltage lithium batteries and identify possible side reactions between PEO-based electrolytes and existing cathodes. We provide an overview of the ways to enhance high voltage resistance of PEO-based electrolytes. Those include components blend, molecular design and interface modification. With these efforts, we want to present new insights into rational design of PEO-based electrolytes to develop solid-state lithium batteries for advanced performance.

Keywords Poly(ethylene oxide); Lithium battery; High voltage; Molecular design; Interface modification

1 Introduction

With the rapid development of portable electronic devices and stationary energy storage, batteries with a higher gravimetric and volumetric specific energy are of great significance to satisfy these rising industries. As the metal with the smallest relative molecular weight(M=6.94, ρ=0.53 g/cm^3), lithium has an extremely low oxidation potential(–3.04 V *vs.* standard hydrogen electrode)[1] and a high charge-to-mass ratio. The corresponding designed lithium ion batteries has large capacity, high voltage and long cycle life.

However, the employment of organic liquid electrolytes in ithium-ion batteries results in problems, such as effumability, easy leakage and flammability, which pose a serious safety threat to the application of lithium batteries. At present, numerous researches have been conducted to address this issue. Inspired by separators' design, Liu *et al.*[2,3] summarized the rational design ideas and attention points. Dong *et al.*[4] synthesized thermoresponsive separator loaded with core-shell structural paraffin@SiO$_2$ by *in-situ* emulsion interfacial hydrolysis and poly-condensation.

To reduce the flammability of traditional organic electrolyte, Liu *et al.*[5] packaged flame retardant triphenylphosphate ester(TPP) into a heat-sensitive polymer shell. Once thermal runaway occurs, the melted polymer shell would release flame retardants, which greatly suppresses the combustion of the electrolytes. Combined with supramolecular engineering, Chen *et al.*[6] reasonably designed a new supramolecular electrolyte, in which "gaseous-type fire retardant" and "interface improver" can self-assembled by intermolecular interactions. In aspect of suppressing lithium dendrite, Yan *et al.*[7] deposited an ultra-thin(20 nm) layer of Au nanoparticles on separator by evaporation coating. The functional separator could regulate the growth status and orientation of lithium dendrites. Moreover, they proposed that the "solid-liquid" hybrid behavior of a dynamically-cross-linked polymer enables its use as an excellent adaptive interfacial layer for Li metal anodes[8].

Above methods have a significant effect on enhancing the safety of liquid electrolytes, but cannot change the intrinsic flammability and combustibility. In comparison, solid-state electrolytes have greater space for improvement in terms of their thermal stability, energy density, operating temperature range, and mechanical strength. The development of solid-state batteries is recognized as an effective way to settle the safety problems of lithium-based batteries[9,10]. Polymer solid-state electrolytes(SPEs) consist of polymer matrix(typically represented by polyethylene oxide, polyacrylonitrile, polyvinylidene fluoride, etc.) and lithium salts without the addition of liquid organic solvents. Compared with inorganic solid-state electrolytes, SPEs have several advantages, including easily processing, mechanical strength intrinsically in organic polymers, and better flexibility due to the segment movement above glass transition temperature(T_g). What's more, its strong adhesion to the electrode can reduce interfacial impedance.

Polyethylene oxide(PEO) can dissolve different kinds of lithium salts, thus becoming the most widely used system among various polymer matrixes. Li$^+$ dissolves in the PEO and forms a solid solution. As shown in Fig.1(A), under an electric field, Li$^+$ coordinates with the oxygen groups on segments of PEO amorphous regions, and the migration of lithium ions is realized by segment movement, which is the primary Li$^+$ conduction mechanism in PEO[11]. It is also possible for Li$^+$ to

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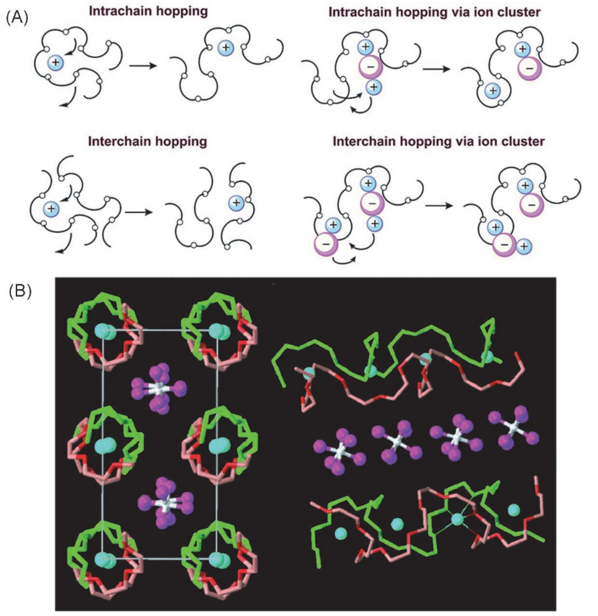

Fig.1 Transmission mechanism of Li^+ in PEO amorphous regions(A) and Li^+ conduction in PEO crystal structure in PEO_6-$LiAsF_6$(B)

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conduct in the crystal regions of PEO, as shown in Fig.1(B). The polymer chains are folded to form a cylindrical tunnel. Li^+ is coordinated with ether-oxygen bonds and transports along the inner space of the cylindrical tunnels, in the meantime, anions are located outside these tunnels[12].

However, PEO-based solid electrolytes generally present high crystallinity at room temperature. Its low solubility of lithium salts in crystal regions results in poor ionic conductivity(10^{-7} S/cm)[11]. In addition, the narrow electrochemical stability window(ESW, less than 4 V) restricts its combination with high-voltage cathode[11]. Extending ESW of polymer electrolytes has been a long-term issue，and the high power output, safe energy storage devices renew scientific research interest on this topic[13]. Therefore, integrating desired properties, such as high ionic conductivity, wide electrochemical window, and good mechanical properties concurrently in PEO-based electrolyte is still a challenging task.

In this review, we begin by discussing the possible side reactions between PEO-based polymer solid electrolytes and existing cathode materials. On this basis, we introduced recent advances of high voltage PEO-based solid-state electrolytes. Those include filler doping, molecular design of solid-state electrolyte, and modification of cathode/electrolyte interface. In this way, we aim to offer a perspective on the unresolved challenges and future opportunities for high voltage PEO-based SPEs.

2 Theory Construction

2.1 Reaction on Cathode

In comparison to inorganic solid electrolyte, PEO shows higher stability against reduction on lithium-metal anode. However, it's unstable owing to the oxidation of electron-rich ether oxygen under the high voltage circumstances. Existing researches on PEO-based solid polymer electrolytes mainly focus on improving ionic conductivity, enhancing mechanical strength and suppressing lithium dendrites formation. A small quantity of research has been conducted on its high voltage cathode compatibility. Most studies show that PEO-based solid polymer electrolytes have good compatibility with $LiFePO_4$ cathodes, and its decomosition takes place when voltage is higher than 3.8 V.

Xia *et al.*[14] studied side reactions of PEO with transition metal oxides, such as $LiCoO_2$, $LiNiO_2$, $LiMn_2O_4$, V_2O_5, V_6O_{13} and Li_xMnO_2 by the means of X-ray diffraction(XRD) and differential scanning calorimetry(DSC). The reaction sequence could be confirmable according to released heat, which provided a preliminary direction for the selection of cathode materials. However, the fundamental explanation of mechanism behind these side reactions and enlightening insight are severely lacking.

Zhu *et al.*[15] used first-principles calculations for the interfacial thermodynamics between solid electrolytes and electrode. Calculation results showed that many solid electrolyte-electrode interfaces have limited chemical and electrochemical stability, thus the formation of interfacial layers was thermodynamically favorable. The electrochemical performance of all-solid-state lithium-ion batteries is significantly affected by the interfacial layers with various properties.

Recently, Nie *et al.*[16] captured and analyzed the gas generated at the cathode in $LiCoO_2$|PEO-LiTFSI|Li[LiTFSI: lithium bis(trifluoromethanesulphonyl)imide] system by *in-situ* differential electrochemical mass spectrometry[Fig.2(A, B)]. Combined with density functional theory analysis, it is found that $LiCoO_2$ is the inducement of hydrogen generation at a high potential, and the hydrogen generation process of lithium salts was well explained[as shown in Fig.2(C). This research also suggested that coating $Li_{1.4}Al_{0.4}Ti_{1.6}(PO_4)_3$(LATP) on $LiCoO_2$ can alleviate catalytic effect of $LiCoO_2$ on the hydrogen production reaction[16].

In PEO-based polymer solid electrolytes, lithium salts also participate in the oxidation reaction. What's more, the composite system formed by PEO and different lithium salts may lead to polymer matrix decomposition at a lower oxidation potential. In addition, after assembling full battery

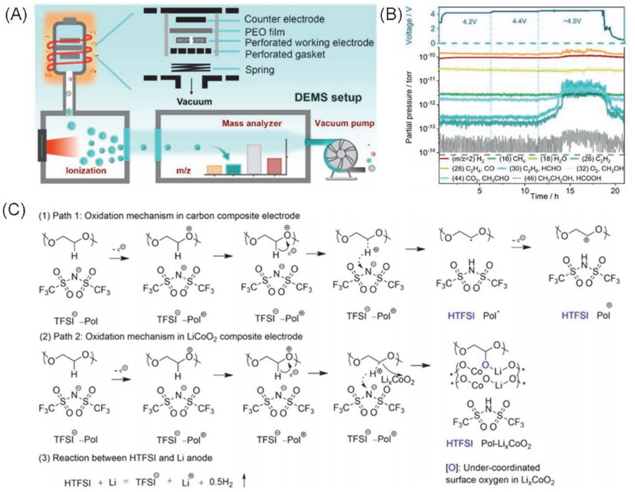

Fig.2 Schematic diagram of the structure of the specially designed DEMS cell(A), voltage profile and corresponding *in situ* DEMS results of mass signal(B), mechanisms of formation of HTFSI and H_2 in a PEO-based solid polymer battery when coupled with an inert carbon composite electrode and a $LiCoO_2$ composite electrode(C)

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with a high-voltage cathode, the volume change during repeated lithiation/delithiation cycles will worsen the interface contact, increase the internal resistance of the battery and further deteriorate the battery performance[17].

2.2 Principles of Thermodynamics

The high-voltage compatibility of electrolyte means its ability to suppress oxidative decomposition. From a thermodynamic point of view, high-voltage SPEs refer to the highest occupied molecular orbital(HOMO) of all components(polymers, lithium salts, and additives) in solid polymer electrolytes is simultaneously lower than the cathode potential. However, because of strong oxidation state and complex valence changes in operation process, the cathode potential may decrease to a lower state than the HOMO of SPEs, thereby further aggravates interfacial side reactions[18]. In order to achieve a stable state for a long cycle, a compact passivation layer must be formed on the cathode/electrolyte interface(CEI).

In general, the HOMO of polymers and lithium salts is determined by their own structures. The frontier orbital energy can be changed or a stable CEI layer can be formed by adjusting electrolytes structure. Morever, intermolecular interactions, such as ion-dipole interactions between lithium salts and polymers, Lewis acid-base interactions(such as hydrogen-bond interaction, positive vacancy-salt interaction, and dipole-dipole interaction) between inorganic additives and polymer electrolytes can also change the chemical environment of polymers and lithium salts, further affecting HOMO energy level. Therefore, in addition to the molecular design of polymer matrix to lower HOMO level, the modulation of intermolecular interactions also plays an important role in high-voltage stability.

As shown in Fig.3, designing high-voltage solid polymer electrolytes essentially requires reducing the HOMO of SPEs or generating a stable CEI[18]. The left parts of this review summarize recent advances on improving the high voltage resistance of PEO-based solid electrolytes from three aspects: filler doping, molecular design of solid electrolytes, and modification of cathode/electrolyte interface. We hope that these contents can generate deeper reflection and pave the way for researching advanced high-voltage PEO-based electrolytes.

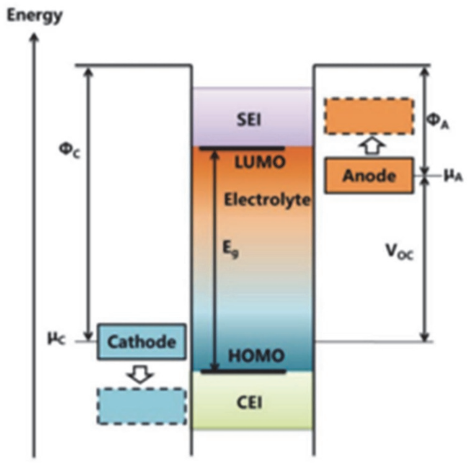

Fig.3 Schematic energy diagram of a polymer electrolyte

E_g is the energy separation of HOMO and LUMO(the lowest unoccupied molecular orbital) of polymer electrolyte. μ_c is the cathode potential.
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3 Filler Doping

3.1 Inorganic Composite Electrolytes

Inorganic fillers possess a wide electrochemical stability window and a high ionic conductivity intrinsically, which are regularly dispersed into PEO matrix to build high-voltage composite solid electrolyte systems.

Guo *et al.*[19] used $Al_4B_2O_9$ nanorods to modify PEO, whose interaction constructed a long-range ordered Li^+ transport channel[Fig.4(A)]. As a result, PEO-based electrolyte exhibited a superior ionic conductivity of 4.35×10^{-1} S/cm at 30 °C. Nano-scale inert ceramic fillers, such as SiO_2[20,21], Al_2O_3, GO, montorites[22], TiO_2[23,24], and ZrO_2 had also been used to modify PEO. These inorganic fillers cannot conduct lithium-ions directly, but the Lewis acid-base interactions between these inert fillers and lithium salts may promote dissociation and provide effective Li^+ pathways.

In addition to inert fillers, inorganic solid electrolytes, such as $Li_7La_3Zr_2O_{12}$[25], $Li_{0.33}La_{0.557}TiO_3$, Li_3PS_4[26,27], $Li_{3/8}Sr_{7/16}Ta_{3/4}Zr_{1/4}O_3$[28], etc., were introduced into the PEO

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composite system to play the role of active fast ion conductors. Active fillers can not only reduce the crystallinity of PEO, but also conduct lithium ions through the inorganic part when pencentage composition is appropriate. Compared with inert fillers, active fillers bring more performance improvement on PEO solid electrolytes due to the insufficient contact between the solid electrolyte and electrode, which results in high interfacial impedance. Chen *et al*.[29] prepared a flexible polymer-garnet solid electrolyte with PEO, $Li_{6.75}La_3Zr_{1.75}Ta_{0.25}O_{12}$(LLZTO), and poly(vinylidene fluoride) (PVDF). A wide electrochemical window of 4.8 V was obtained, benefiting from the interfacial stability of LLZTO and lithium metal[Fig.4(B)].

Adding 20%(mass fraction) $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$(LATP) to the PEO matrix significantly improved the electrochemical performance. The ionic conductivity at 30 °C was an order of magnitude higher than that of pure PEO, and the electrochemical window reached 4.84 V, making the electrolyte system compatible with $LiNi_{0.85}Co_{0.1}Al_{0.05}O_2$, and the Ti-Mg-Al coated and doped $LiCoO_2$ high voltage cathode operate stably[30]. Liu *et al*.[31] fully immersed nylon fiber skeleton in the $Li_{0.33}La_{0.557}TiO_3$(LLTO) precursor solution, and after drying and calcination, a three-dimensional LLTO inorganic solid electrolyte was obtained. Then added PEO solution dropwise onto it so as to obtain a vertical bicontinuous phase structure inside. The voids inside were helpful for the rapid conduction of lithium ions. The corresponding $LiFePO_4$/Li half-cell exhibited a discharge capacity of 154.7 mA·h/g after 150 cycles at 1 C, which maximized the conductive function of ceramic framework and improved the polymer electrochemical stability[Fig.4(C)].

Combined with inorganic fillers, the experiment results prove that the electrochemical window of PEO-based electrolytes is greatly widened and the ionic conductivity is also improved. However, inorganic fillers also face harsh preparation process, and under some circumstances, high temperature and air isolation conditions are necessary. These fillers often present an optimal concentration when used in PEO-based polymer electrolytes, and it is necessary to find the best proportion to achieve better modification effect and control the cost in practical application.

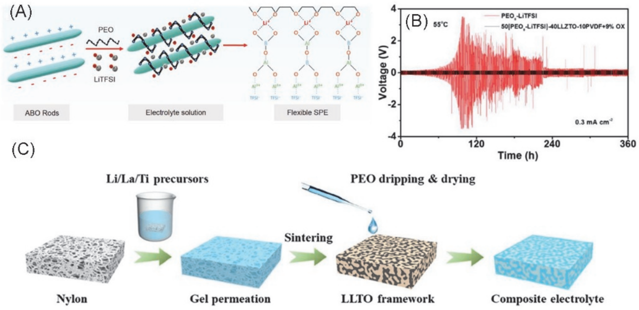

Fig.4 Mechanism of ion conductivity enhanced by PEO-based electrolyte with ABO(A), voltage-time curves of Li|Li symmetric battery for lithium deposition/stripping at 0.3 mA/cm^2 using PEO-LiTFSI and composite electrolyte, respectively(B), and schematic synthesis of the LLTO frame and PLLF electrolyte(C)

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3.2 Organic Composite Electrolytes

It is difficult to simultaneously achieve low impedance, high ionic mobility, and wide electrochemical window with just one kind of polymer matrix as electrolyte for lithium-based batteries. The chain structure of PEO polymer matrix is highly ordered and presents a semi-crystalline state at 60 °C. To some extent, the transport rate of lithium-ions is limited by the decrease of segment movement. In lately progress for PEO modification, it's feasible to combine PEO with organic compounds possessing strong antioxidant ability, such as ionic liquids[32—37], polymers[29,38—45], short-chain nitriles, esters, etc. In this way, the crystallinity of PEO segment can be effectively reduced to promote the ion transport while broaden the electrochemical window. The lone pairs of electrons in polymer matrix and anions in many high-concentration electrolytes can be stabilized by strengthening the coordination bond between them.

Carbon nanotubes(CNTs) are considered as ideal mechanical reinforcements for polymer matrix due to their high aspect ratio and outstanding modulus. However, its high electrical conductivity may cause short-circuits when directly used in SPEs. Tang *et al*.[22] successfully grew one-dimensional carbon nanotubes on two-dimensional montmorillonite sheets. The electron conduction between carbon nanotubes was blocked by insulating clay sheets, which increased the ionic conductivity of PEO electrolyte by nearly two magnitude [Fig.5(A)].

Since the transport of lithium-ions in PEO solid electrolytes mainly depends on their coordination with the polar groups on segments and movement of polymer amorphous segment, hence reducing the crystallinity of PEO is the key to improve the ionic conductivity at room temperature. Some scholars add plasticizers, such as ethylene carbonate and dimethyl carbonate to PEO to construct gel polymer electrolytes(GPEs). It is possible to achieve an ionic conductivity and an interfacial impedance close to liquid electrolytes.

In order to maximize the capacity of the $LiCoO_2$ cathode, Xu *et al*.[40] used a gel polymer separator composited with PEO and PVDF-HFP to enhance the oxidative stability of the liquid component in polymer matrix. By taking the advantage of oxidation behaviour of succinonitrile rather than that of carbonate solvent, they constructed a high quality CEI film to

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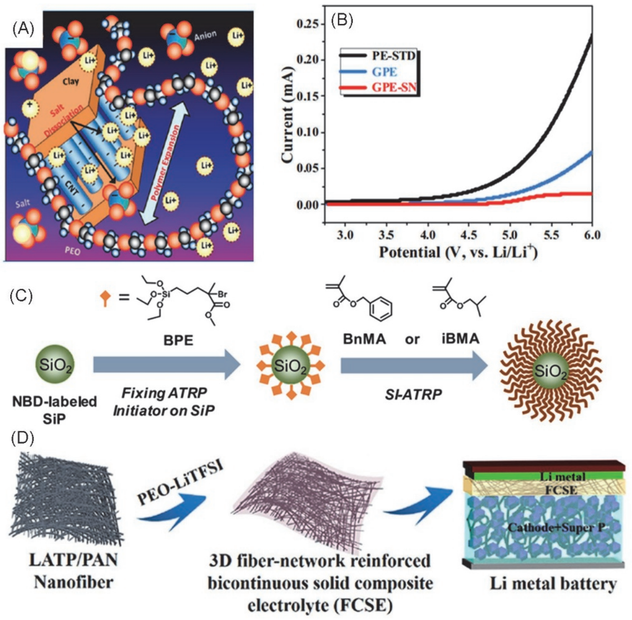

Fig.5 Schematic diagram of interactions between clay, carbon nanotubes, polymer chains, and lithium ions(A), linear scanning votammegram of Li/Pt cells using PE-STD, GPE, and GPE-SN electrolytes at a scanning rate of 1 mV/s(B), schematic diagram of composite electrolyte synthesis(C), and schematic diagram of fiber-reinforced composite electrolyte preparation(D)

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protect the structural integrity of cathode[46]. The resulting GPE decomposition voltage was as high as 5.2 V. At 55 °C, corresponding $LiCoO_2$|GPE|Li coin cell retained 82% of capacity after 350 cycles at 1 C[Fig.5(B)].

Yahata *et al.*[47] prepared quasi-solid electrolytes by thermally induced phase separation of polymer and ionic liquid mixtures. Furthermore, they found that the polymer/ionic liquid mixtures underwent solution phase separation at a lower critical temperature, while the addition of silica particles with surface-grafted polymer chains could avoid this problem and form a continuous ionically conductive phase[Fig.5(C)].

Replacing organic liquid electrolytes with solid lithium ion conductors is a promising approach to achieving the superior performance of lithium metal batteries. Nevertheless, because lithium dendrites may penetrate ceramic electrolyte through grain boundaries, neat PEO also faces the drawback of interface instability. Li *et al.*[38] suggested an LATP/PAN/PEO 3D fibrous network-enhanced bicontinuous solid-state electrolyte with a flexible Li^+ conductive network. By casting PEO-LiTFSI solution on LATP/PAN nanofibers, a higher mechanical strength was obtained. It was worth noting that the composite electrolyte exhibited excellent electrochemical stability after being in contact with Li metal for 15 d, and the tensile strength reached 10.72 MPa[Fig.5(D)].

In addition, new lithium salts, such as lithium difluoro(oxalato) borate(LiDFOB)[48], lithium bis(1,3-dibutyl-4,5-imidazoledicarboxylate-tetrafluroborate) borate(LiBIB)[49], etc., have also been used in the research of high voltage modification of PEO. There is an ion-dipole interaction between polymer matrix and lithium salt, which can not only change the Li^+ conductivity, but also affect the electrochemical stability window of the "salt-in-polymer" electrolytes.

Yuan *et al.*[50] used a fluorinated lithium bis(malonato) borate(LiBMB) in the PEO system, which is an imidazole-modified thermotropic ionic liquid crystal with a high ionic conductivity. It was obversed that the thickness of folded chain in crystal region was decreased after blending. When LiBMB accounted for 34%—75%(mass fraction), the electrochemical window of the composite electrolyte could be broden to 6.8 V.

At present, the most typical organic solid electrolyte is a "lithium salts-in-polymer" system, which contains a variety of ions that transfer between anode and cathode to form a dual-ions conductor. The migration and accumulation of anions at the electrolyte/electrode interface can lead to concentration polarization and even trigger side reactions. In order to limit the migration of irrelevant anions, the concept of single-ion conductors was proposed. By grafting anions on polymer chains through intermolecular interaction or confining them to the inorganic skeleton, it's effective to restrict anion movement and alleviate concentration polarization.

A novel single-ion conductor solid electrolyte was obtained by mixing aluminate complex-polyethylene glycol (LiAl-PEG) with PEO[51]. As a result, it exhibited a superior oxidative decomposition voltage of 4.8 V and a relatively high ionic conductivity of 4.0×10^{-5} S/cm at 30 °C.

After blending with organics, which mainly composed of plasticizer, polymer matrices, and new lithium salts, PEO-based electrolytes reach a wide electrochemical window over 5 V. The ionic conductivity at room temperature is slightly inferior to that of the inorganic fillers due to viscosity.

4 Molecular Design of Solid Electrolyte

There is a balance between mechanical strength and conductivity of lithium ion in polymer electrolyte. Reducing the crystallinity by adding fillers or organic plasticizers can improve the ionic conductivity of PEO polymer electrolyte, but it will greatly damage mechanical properties. On account of inevitable volume expansion of cathode, the CEI obtained in these two composite systems would suffer from breakage during lithiation/delithiation process under high voltage, which leads to re-exposing polymer to active cathode and

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failing to achieve ideal thermodynamic stability. In order to fundamentally realize the compatibility between PEO and high-voltage cathode materials, the intrinsic high-voltage tolerance of PEO-based polymer, namely a low HOMO state, is decisive by customized design from molecular structure perspective.

Primary molecular designs of PEO solid electrolyte include modification to end groups or side groups of PEO[51—57], construction of single-ion conductor[58,59], graft copolymerization[60,61], block copolymerization[62—69], and molecular chain crosslinking[70—76]. The HOMO energy level and kinetic characteristics of PEO molecules can be adjusted to improve the high-voltage compatibility. This displays great potential in alleviating the conflict between ionic conductivity and mechanical properties.

Villaluenga *et al.*[77] replaced the hydrogen atoms on the main chain of PEO with fluorine atoms with stronger electron-absorbing ability, and changed the end group into —OH to obtain PFPE-diol. Followed by ball milling, covalent bonding was realized with inorganic sulfide Li_3PS_4(75Li_2S-25P_2S_5) and LiTFSI to obtain a flexible and non-combustible composite single-ion conductive electrolyte[Fig.6(A)]. The ionic conductivity at room temperature was 10^{-4} S/cm and the electrochemical stability window was 5 V. Yang *et al.*[78] used poly(ethylene glycol)(PEG) and poly(ethylene glycol)dimethyl ether(PEGDME), with a similar structure to PEO, to explore the influence of main chain and end groups on oxidation resistance. The result showed that the oxidation potential of —C—O—C was above 4.3 V, while hydroxyl was oxidized above 4.05 V, indicating that the instability of —OH was one of the factors limiting the voltage window of PEO. The terminal groups of PEO, hydroxyl and hydrogen, were replaced by —OCH_3 and —CH_3, respectively, to obtain PEGDME[Fig.6(B)]. When it was used as solid electrolyte in $LiFePO_4$-PEGDME-Li battery, the surface remained intact after continuous deposition and exfoliation for 1000 h and the capacity remained 97% after 210 cycles at 0.53 mA/cm^2.

Wang *et al.*[79] obtained poly(ethylene glycol) diacrylate by changing the two end groups of PEO, and the high flexibility further promoted lithium ion conductivity. Then crosslinked metal organic frameworks(MOFs) were introduced into the system to design a PEO solid electrolyte branched by mercaptan. There was a large number of branched —C—S—C— bonds in the polymer chain to provide super toughness and the electrochemical stability window was achieved up to 5.4 V[Fig.6(C)].

Due to the different electrochemical potential of Li^+ in cathode and electrolyte, the P-N junction similar to that in electronic conductor will appear, forming a space charge layer, which leads to a high interfacial resistance and further inhibits the transference of Li^+. Bouchet *et al.*[80] synthesized a polystyrene-PEO-polystyrene triblock copolymer and grafted the anionic group of LiTFSI onto the benzene ring to obtain a single-ion conductor polymer electrolyte. Compared with the neutral block copolymer, higher degree of lithium salt dissociation and a stable potential of more than 5 V were achieved[Fig.6(D)]. Zhan *et al.*[60] grafted imidazole ionic liquids with nitrile groups and PEO to the main chain of flexible polysiloxane. Since nitrile groups are strong electron-absorbing groups with low HOMO energy levels, nitrile polymer solid electrolyte has high oxidation potential, high dielectric constant and strong coordination ability. The interaction between lithium ion and cyano group can effectively improve the ionic conductivity of electrolyte[81].

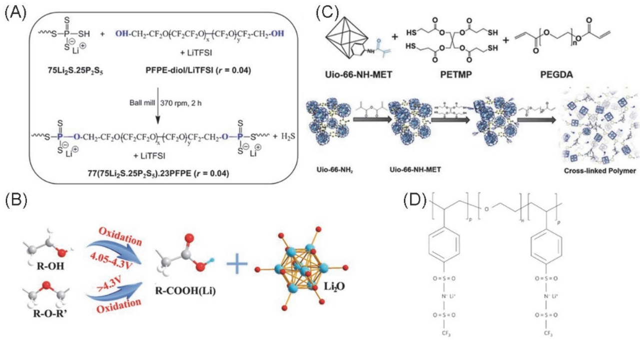

Fig.6 Synthesis of hybrid electrolyte 77(75Li_2S-25P_2S_5 by mechanochemical reaction)·23PFPE(*r*=0.04)(A), possible oxidation mechanism of ether polymers at high pressure(B), the path of cross-linked polymer synthesis(C), and the chemical structure of the single-ion conductor triblock copolymer P(STFSILi)-b-PEO-b-P(STFSILi)(D)

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Chemical cross-linking can effectively improve mechanical strength, but in fact the resulting rigid polymer usually forms a chain segment region with an increased crystallinity and a low ionic conductivity. Linear PEO solid electrolyte may be penetrated by lithium dendrites to cause short circuit and unstable voltage operation. Homann *et al.*[70] used azo-iso-butyronitrile(AIBN) as initiator to induce linear PEO crosslinking to form a semi-interpenetrating network, which could maintain elastic deformation within 0.28 MPa, with electrochemical window value up to 4.6 V.

Molecular design significantly brodens electrochemical stability window(ESW) from the structure perspective. Copolymerization and cross-linking methods are commonly used. In comparison, modification of PEO functional group is a recreational method. For example, hydrogen atoms on main chains are replaced by fluorine atoms, and the end group —OH is replaced by —OCH_3 or other stable groups so as to obtain high voltage derivatives.

5 Interface Modification

5.1 Surface Coating

Surface coating of high-voltage cathode can restrain the side reactions between electrode and PEO-based polymer and reduce the interface impedance. It's the earliest strategy used in solid state lithium battery to solve the interfacial problem between $LiCoO_2$ composite cathode and PEO-based polymer electrolyte[48]. Yang *et al.*[82] first used Al_2O_3, MgO or $AlPO_4$ as cladding material to improve the capacity retention rate and structure stability of $LiCoO_2$. Taking Al_2O_3-coated $LiCoO_2$ as an example, $LiAlO_2$ produced by the lithiation from Al_2O_3 can shrink the contact surface between Co^{4+} and PEO and reduce the occurrence of side reactions. However, the generation of new surface will also increase the diffusion resistance of lithium ions and reduce ionic conductivity. In order to refrain from descending lithium ion conductivity after the coating of inert oxide, a large number of studies have employed fast ionic conductors, such as $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$(LATP) for coating to prevent the oxidation of polymer solid electrolyte while maintaining high ionic conductivity.

The present coating methods include solid-phase mixing method, precursor method, solution method, atomic layer deposition method, and so on. Wang *et al.*[83] prepared an LATP-coated NCM622 cathode by solid-phase mixing method. Under heat treatment at 600 °C, LATP-coated NCM622 was cycled 100 times under the condition of 4.5 V cut-off voltage and 1 C. Its capacity retention rate was 90.9%, which was better than that of uncoated modified materials. Morimoto *et al.*[84] coated $LiCoO_2$ with 5%(mass fraction) $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ (c-LATP) by solid-phase mixing method and achieved an outstanding cycle stability at 4.5 V[Fig.7(A)]. Shim *et al.*[85] prepared $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ with a smaller particle size by using the precursor method, as shown in Fig.7(B). In the circumstances, $LiCoO_2$ was covered more evenly and better electrochemical performance was auquired than that of the solid-phase coating. Li *et al.*[86] coated 0.5%(mass fraction) LATP on the surface of $LiCoO_2$ by solution method, as shown in Fig.7(C). The surface of the material was smooth without large particle deposition.

Sun *et al.*[87] deposited lithium niobate(LNO) on the surface of NCM811 by the atomic layer deposition technology, and the coating thickness can be controlled by adjusting the cycle number. Experimental results showed that 10 nm ALD-LNO coating can prevent the destruction of layered structure and inhibit the loss of lattice oxygen[Fig.7(D)]. After cladding LNO, the NCM811|PEO|Li solid-state batteries have an average Coulombic efficiency up to 99.2% after 200 cycles at 60 °C and 0.2 C[Fig.7(E)]. Although the best coating effect and ideal electrochemical performance can be obtained by the layer deposition method, limited by high cost of the preparation process, this kind of technology is not widely applicable, and more economical *in-situ* coating method needs to be explored.

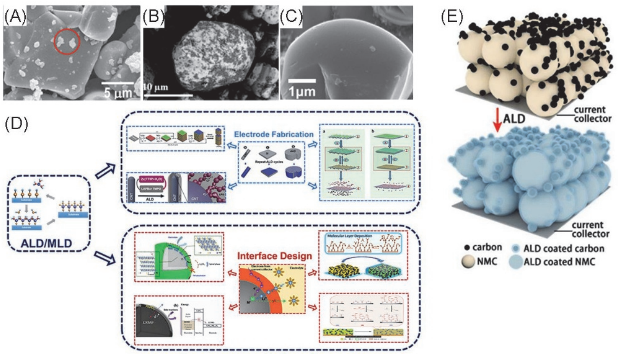

Fig.7 SEM image of 5% c-LATP coated $LiCoO_2$(A), SEM image of LATP precursor coated $LiCoO_2$(B), SEM image of 0.5% LATP coated $LiCoO_2$ by solution method(C), the development of ALD/MLD for electrode fabrication and interface modification in Li battery liquid cells(D) and schematical diagram of the ALD-LNO coating on NMC811 electrode(E)

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5.2 Structure Design of Solid Polymer

In the charge transfer process of solid state lithium batteries, the electrochemical window of a single polymer substrate is limited to be compatible with both electrodes. The common solution is to choose coupling solvent of high-voltage resistance and low-voltage resistance, respectively, to possess the bifunctional effect. In liquid electrolyte system, the free diffusion of two electrolyte solvent molecules will impair its electrochemical performance. For solid state lithium batteries, a double-layered polymer electrolyte can be designed to inhibit lithium dendrites formation at anode and a stable charge-discharge cycle at high-voltage cathode can be achieved.

Goodenough *et al.*[88] designed a double-layer polymer solid electrolyte(DLPSE) with poly(*N*-methylpropylene amide)(PMA)-LiTFSI contacting with cathode and PEO-LiTFSI in contact with anode. PMA contains a repeating unit of dimethyl acetamide(DMAc), which has a high dielectric constant and is commonly used as an additive to protect electrolyte from oxidation by high-voltage cathode[Fig.8(A, B)]. Meanwhile, DMAc is easily reduced by lithium metal anode, so the PMA-LiTFSI layer only contacts between the high-voltage cathode and PEO-LiTFSI layer. PEO-LiTFSI has good flexibility and plasticity, which can suppress the formation of lithium dendrite to a certain extent. The system

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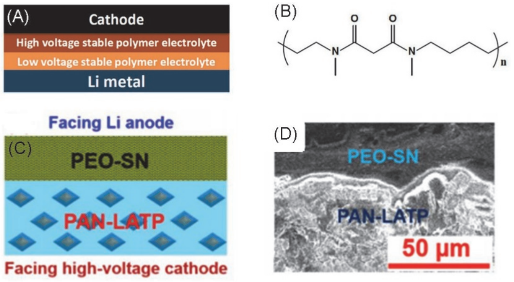

Fig.8 Stacking model of DLPSE in an all-solid-state cell(A) and molecular structure of PMA(B), schematic of the laminated dualpolymer/polymer-ceramic composite electrolyte (LDPPCCE)(C), and cross-section SEM image of the PEO-SN-LiTFSI | PAN-LATP-LiTFSI LDPPCCE(D)

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delivered high electrochemical stability of 4.75 V. Manthiram *et al.*[89] selected PEO as the matrix on the anode side and added succinonitrile(SN) to improve Li^+ conductivity at room temperature. An oxidation resistant polyacrylonitrile(PAN) matrix was used in the cathode side, and an LATP powder was added to improve the ionic conductivity and inhibit the penetration by the lithium dendrite. The ion conductivity of the composite electrolyte is 1.31×10^{-4} S/cm and the electrochemical window is 5 V. The full battery consists of NCM811|PEO-SN-LiTFSI|PAN-LATP-LiTFSI|Li displaying high capacity and stable cycle performance. In addition to directly designing multilayer electrolytes, chemical or electrochemical processes can also be used to construct *in-situ* interface layers with better contact on the electrode surface [Fig.8(C, D)].

Li *et al.*[83] believed that $Li_{1.5}Al_{0.5}Ge_{1.5}P_3O_{12}$(LAGP) was similar to LATP, which had good electronic conductivity and excellent high voltage stability. However, when LAGP was used as coating material, the grain boundary and pores inside nanocoating layer would lead to the oxidative decomposition of PEO. Lithium bis(oxalate)borate(LiBOB) can regulate the chemical composition of CEI, therefore, they were proposed to combine LiBOB with LAGP coating modification strategy to improve the interfacial stability between cathode and polymer. The *in-situ* decomposition product of LiBOB around electrode can fill the gaps of LAGP coating layer, which further reduced the possibility of oxidative decomposition of PEO. In addition, Fu *et al.*[90] directly introduced PEO-LiBOB polymer into cathode to construct a composite cathode. PEO-LiBOB can not only be used as an ideal binder, but also conduct ions, which could be contributed to the stable CEI formation to inhibit the oxidation decomposition of polymer and avoid the corrosion to aluminum current collector caused by $TFSI^-$.

The CEI membrane constructed by *in-situ* initiation polymerization is one of the most effective solutions to improve the compatibility between high-voltage cathode and PEO-based electrolyte. However, there are still many problems to be settled, such as optimization of *in-situ* preparation method, screening principle of polymerization precursor, lithium-ions conductivity of CEI membrane, and advanced characterization technology.

6 Conclusions and Outlook

Possible side reactions between PEO solid electrolyte and common cathode materials are addressed in this review. We also highlight recent progress about the PEO solid polymer electrolyte matched with the high-voltage cathode in lithium-based batteries from three aspects of filler doping, molecular design and interface construction. In this way, we expect to offer new insights for improving energy density and enhancing the interfacial contact. As for high-voltage compatibility, current PEO-based electrolytes with an electrochemical stability window of 4.5—5 V seem to be quite outstanding. For example, it is difficult to achieve both mechanical strength and electrochemical performance, and there still lack of systematic theoretical understanding of the SPEs degradation mechanism and evolution at cathode interface. In the future, more extensive and in-depth research can be carried out on the interface between high voltage cathode and solid electrolyte with novel characterization approaches, so as to further monitor solid-state battery operation and accelerate commercialization of high-voltage PEO-based solid electrolyte in lithium batteries.

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Conflicts of Interest

The authors declare no conflicts of interest.

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