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Review

Improving ionic conductivity of polymer-based solid electrolytes for lithium metal batteries

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ABSTRACT

Because of its superior safety and excellent processability, solid polymer electrolytes (SPEs) have attracted widespread attention. In lithium based batteries, SPEs have great prospects in replacing leaky and flammable liquid electrolytes. However, the low ionic conductivity of SPEs cannot meet the requirements of high energy density systems, which is also an important obstacle to its practical application. In this respect, escalating charge carriers (*i.e.* Li⁺) and Li⁺ transport paths are two major aspects of improving the ionic conductivity of SPEs. This article reviews recent advances from the two perspectives, and the underlying mechanism of these proposed strategies is discussed, including increasing the Li⁺ number and optimizing the Li⁺ transport paths through increasing the types and shortening the distance of Li⁺ transport path. It is hoped that this article can enlighten profound thinking and open up new ways to improve the ionic conductivity of SPEs.

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1. Introduction

The massive consumption of fossil fuels, rising oil prices and the international community's restrictions on car carbon dioxide emissions have made the discovery of renewable clean energy and technological breakthroughs imminent [1–6]. Lithium metal is considered a holy grail electrode due to its unique theoretical capacity (3860 mA·h·g^{−1}) and lowest redox potential (−3.04 V vs. the standard hydrogen electrode). Compared with lithium ion batteries, lithium metal batteries have higher working voltage and higher energy density, and are considered to be the most promising energy storage system [7–9]. However, carbonates and organic ether-based liquid electrolytes is volatile and flammable, leading to serious safety problems including but not limited to leakage, decomposition, burning or explosion. Therefore, it is necessary to replace the liquid electrolyte with safe solid state electrolytes [6,10–12]. Solid electrolytes can be divided into two categories: inorganic ceramic electrolytes and SPEs. The ionic conductivity of inorganic ceramic electrolytes is close to that of liquid electrolytes at room temperature (10^{−2}–10^{−4} S·cm^{−1}). However, the inorganic

solid electrolyte cannot completely inhibit the growth of lithium dendrites and internal short circuits. The formation of cracks, the diffusion of Li in the grain boundaries and the oriented pores all aggravate dendrite growth and internal short circuits [13–15]. Compared with inorganic ceramic electrolytes, SPEs have the advantages of ductility and flexibility. SPEs are composed of polymer matrix and free lithium salt, and Li⁺ can migrate in the matrix with the segmented movement of the polymer chain.

With outperformed security and processability, SPEs have experienced rapid development for the high energy density battery systems. Narayanan uses polyethylene oxide (PEO) and polydimethylsiloxane (PDMS) as the base polymer and lithium perchlorate (LiClO₄) as the lithium source to synthesize a Li⁺ transport membrane suitable for flexible symmetrical capacitors [16]. Zhao has developed polyacrylonitrile (PAN)-LiClO₄ composite electrolyte modified by a layer of boron nitride nanosheets (BNNF) [17]. PAN-LiClO₄-BNNF has a strong tensile strength (16.0 MPa) and Young's modulus (563.7 MPa). Tang reported a high-performance flexible dual-ion battery based on poly(vinylidene fluoride-hexafluoro propylene) (PVDF-HFP) codoped with PEO and graphene oxide (GO) via weak hydrogen bond interactions [18]. The battery has good flexibility and thermal stability (up to 90 °C), which indicates its potential application in high-performance flex-

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ible energy storage devices. Song used *in-situ* reaction and electrochemical process to prepare stretchable and stable artificial solid electrolyte interface (SEI) layer from polymethyl methacrylate (PMMA)/polyvinylidene fluoride (PVDF) hybrid polymer, which can simultaneously adapt to volume changes and inhibit dendrite growth [19]. However, the low ionic conductivity ($<10^{-6}$ S·cm $^{-1}$) of SPEs at room temperature severely limits its practical application and cannot meet the requirements for fast charging of electronic equipment or electric vehicles [20,21].

To improve the ionic conductivity of SPEs, a lot of efforts have been made. Increasing the content of lithium salt or reducing the crystallinity of the polymer with composite polymers or block copolymers can increase the ionic conductivity by orders of magnitude [22–24]. Adding plasticizers is also one of the most widely used methods. The addition of plasticizers can increase the amorphous regions in the polymer, thereby increasing the ionic conductivity of SPEs [25]. Some solid composite electrolytes composed of SPEs and inorganic fillers inherit the advantages of SPEs and inorganic fillers, and also have high ionic conductivity ($>10^{-4}$ S·cm $^{-1}$) [26–29]. In analogy with daily life, the number of cars (charge carrier) and the quality, species and distance of the roads (Li $^{+}$ transport paths) synergistically determined the final performance.

In this perspective, we reviewed the recent research progress in improving the ion conductivity of SPEs from two critical aspects: charge carriers and Li $^{+}$ transport paths. For the first aspect, strategies mainly focus on increasing the number of charge carriers. Improving the intrinsic ion conduction of the Li $^{+}$ transport paths, increasing the types of Li $^{+}$ transport path and shortening the distance of the Li $^{+}$ transport path is clarified as the three key roads for the second aspect. Meanwhile, the fundamental explanation of mechanism behind these strategies is illustrated. It is hoped that this article will stimulate innovative ideas for the research on improving the ionic conductivity of SPEs for lithium metal batteries.

2. Increase the Number of Charge Carriers

The ionic conductivity can be described by equation, as the sum of the moving charge-carriers through the electrolyte

$$\sigma = \sum c_i q_i \mu_i$$

where q_i is the ionic charge, c_i and μ_i are the concentration and mobility of the charge carriers [30]. According to the equation, the conductivity of ions also depends on the concentration of charge carriers. When the salt concentration is low enough, all Li $^{+}$ are dissolved by the polymer host, and all Li $^{+}$ can be used as charge carriers. However, as the concentration increases, the electrostatic interaction between cations and anions becomes non-negligible, which may reduce the number of charge carriers [31]. Therefore, to improve the Li $^{+}$ conductivity of SPEs, it is necessary to find ways to promote the dissociation of lithium salts.

Anion receptors are a strategy to increase the mobility of Li $^{+}$ by inhibiting the mobility of anions and thereby increase the conductivity. The principle is based on the strong ion dipole interaction between the negative ions and the receptor. The ion–dipole interaction between anion and polymer is basically the driving force for the dissociation of lithium salt, is a key factor in determining the concentration of free ions, and has a significant impact on ion conductivity [31].

Boron-based Lewis acid is one of the most common anion acceptors, which can be polymers or small molecules. Wei and colleagues proposed a SPEs with ethylene carbonate as a rigid polymer backbone and a flexible ether oxygen chain containing anion-trapping boron [32]. The SPE was synthesized *via in situ*

polymerization of a solution precursor obtained by mixing LiTFSI, rigid vinylene carbonate (VC) and exible poly (ethylene glycol) methyl ether methacrylate containing cyclic boroxane groups (BPEGMA). According to calculation, the interaction energy between the boronic ester group and the anion is -36.89 kJ·mol $^{-1}$ with a short B–O distance of 0.465 nm (Fig. 1(a)). The boron of the empty p orbital fixes the anion through electronic interaction. This ingenious design effectively integrates a high ionic conductivity of 9.11×10^{-4} S·cm $^{-1}$ at 25 °C and a high Li $^{+}$ transference number of 0.68 . The combination of hydrogen bonds and calixarene is another strategy for anion acceptor, in which hydrogen bonds is used to interact with anion, and calixarene is applied to enhance the steric effect of anion [31]. Li and his colleagues used aramid nanofibers (ANFs) as multifunctional nano-additives to achieve the purpose of improving the ionic conductivity of polyoxyethylene (PEO)–LiTFSI electrolytes through hydrogen bond interaction [33]. The hydrogen bond interaction between ANF and PEO chain and TFSI $^{-}$ can greatly promote the dissociation of LiTFSI (Fig. 1(b)). The ANF-modified electrolytes show superior room-temperature conductivity of 8.8×10^{-5} S·cm $^{-1}$. Guo and colleagues proposed a new cationic metal–organic framework (CMOF) for immobilizing anions [36]. The CMOF binds the negative ions together through the electrostatic interaction of charge carriers, and the specific surface area is as high as 1082 m 2 ·g $^{-1}$, which further strengthens the adsorption of negative ions on the surface of the CMOF, making the migration number of Li $^{+}$ up to 0.72 . Chen *et al.* proved that the cation part in the framework of covalent organic frameworks can split the ion pair of lithium salt and increase the concentration of freely movable Li $^{+}$ [37]. The cations of the macromolecules can interact with the TFSI $^{-}$ anions through electrostatic force to split the ion pairs in the lithium salt, so that the conductivity of the lithium ions is improved. Peng and co-workers report the use of hydroxypropyl trimethylammonium bis(trifluoromethane) sulfonimide chitosan salt (HACC-TFSI) [38]. In the hybrid SPE, the interaction between the quaternary ammonium salt cation and the TFSI $^{-}$ anion also promotes the dissociation between Li $^{+}$ and TFSI $^{-}$, thereby further improving the ion mobility. The two fitting peaks of the Raman spectrum at 740 and 750 cm $^{-1}$ correspond to free TFSI $^{-}$ and Li(TFSI) $_{2}^{-}$, respectively. Compared with the blank SPE, the hybrid SPEs with 10% HACC-TFSI increased the peak intensity at 740 and weakened at 750 cm $^{-1}$, indicating that the addition of HACC-TFSI promoted the dissociation of ion clusters. And the ionic conductivity of hybrid SPEs with 10% HACC-TFSI increased from 3.8×10^{-6} to 1.78×10^{-5} S·cm $^{-1}$ at 30 °C and from 1.9×10^{-4} to 5.01×10^{-4} S·cm $^{-1}$ at 60 °C.

Moreover, Goodenough has confirmed that some inorganic oxides with oxygen vacancies can decompose lithium salts and release free Li $^{+}$ [39]. Oxygen vacancies are equivalent to being positively charged and can attract negative ion groups to promote the decomposition of lithium salts. Cui and co-workers reported a solid composite polymer electrolyte with Y $_2$ O $_3$ -doped ZrO $_2$ (YSZ) nanowires that are enriched with positive-charged oxygen vacancies, and demonstrated that oxygen-ion conducting YSZ nanowires could effectively enhance the ionic conductivity of the PAN–LiClO $_4$ polymer electrolyte [34]. As shown in Fig. 1(c), the doping of low-valence Y makes the surface of the YSZ nanowires rich in oxygen vacancies. These oxygen vacancies combine with anions to release more Li $^{+}$ and increase conductivity. Incorporation of 7% (mole) of Y $_2$ O $_3$ -doped ZrO $_2$ nanowires results in the highest ionic conductivity of 1.07×10^{-5} S·cm $^{-1}$ at 30 °C. In the work of Chen *et al.*, composite polymer electrolytes (CPEs) are prepared by dispersing oxygen-ion conducting Sm-doped CeO $_2$ (SDC) nanowires into the polyvinylidene fluoride matrix (Fig. 1(d)) [35]. Trivalent Sm $_2$ O $_3$ is doped into CeO $_2$ to form positively charged oxygen

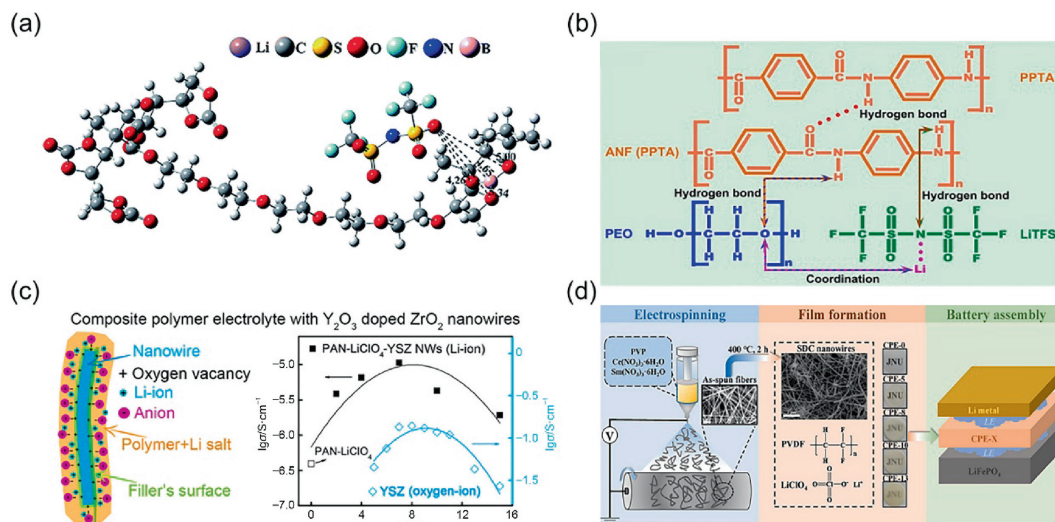


Fig. 1. The number of charge carriers is increased by promoting the dissociation of lithium salts. (a) Geometrical structure of the model unit with binding energy of anions to the boronic ester groups [32]. (b) The interactions between ANFs and PEO chains and LiTFSI [33]. (c) Schematic illustration for Li-ion transport in the CPEs with nanowire fillers [34]. (d) Schematic illustration of the preparation of the SDC nanowires, the formation of CPEs, and the assembly of a lithium-ion battery (LE stands for liquid electrolyte) [35].

vacancies. The positively charged oxygen vacancies on the surface of the SDC nanowires could serve as Lewis acid sites, which would interact actively with anions of salt, resulting in the release of Li⁺ within CPEs and thus increasing the ionic conductivity. CPE with 10% (mass) of the SDC nanowires reaches the ionic conductivity of $9.09 \times 10^{-5} \text{ S}\cdot\text{cm}^{-1}$ at 30 °C. In the work of Cui *et al.*, a flexible all-solid-state composite electrolyte is synthesized based on oxygen-vacancy-rich Ca-doped CeO₂ (Ca-CeO₂) nanotube, lithium bis(trifluoromethanesulfonyl) imide (LiTFSI), and poly (ethylene oxide) (PEO), namely Ca-CeO₂/LiTFSI/PEO [40]. The as-prepared electrolyte exhibits high ionic conductivity of $1.3 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ at 60 °C.

3. Optimize the Li⁺ Transport Path

In SPEs, the transmission of Li⁺ mainly depends on segment motion of the amorphous region in polymer electrolytes. The conduction mechanism of Li⁺ in the polymer electrolyte is shown in Fig. 2(a) [41]. Li⁺ coordinates with the polar group on the polymer segment that is driven by the electric field, Li⁺ undergoes complexation/dissociation with the polymer segment and migrates from a coordination site to a new site, or at high temperatures, the polymer produces free volume through local segment motion. Li⁺ jumps from one polymer chain to another polymer chain, thereby achieving the Li⁺ transport. In solid inorganic electrolytes, as shown in Fig. 2(b), Li⁺ conduction often depends on defects in the crystal structure [42,43]. This point defect-based mechanism can be divided into vacancy mechanism and non-vacancy mechanism [42–44]. The so-called vacancy mechanism means that Li⁺ exchange their positions with adjacent vacancies to realize the conduction process. The most common non-vacancy mechanism is the gap mechanism. In this case, Li⁺ are conducted in the gaps of the matrix atoms, so Li⁺ are required to be much smaller than the matrix atoms. In addition, by doping nanofillers, the interface between the filler and the polymer will build a fast Li⁺ transport path [45]. Under the interaction of Lewis acid-base, the network of interwoven nanofillers forms a percolating system. In the polymer matrix nearby the nanofillers, a continuous Li⁺ fast conducting percolation network through the SPE is formed, as shown in Fig. 2 (c). These are three forms of Li⁺ transport paths in solid electrolytes.

3.1. Improve the intrinsic Li⁺ conductivity of polymer pathways

In the polymer electrolyte, Li⁺ are transported by segment motion, and this process occurs in the amorphous phase region. Therefore, in order to improve the intrinsic ionic conduction of the polymer, it is necessary to find a way to change the semi-crystallinity of the polymer.

Adding a plastic phase is the most common method to reduce the crystallinity of a polymer. Zhang and co-workers reported poly(ϵ -caprolactone) (PCL)/succinonitrile (SN) blends integrating with PAN-skeleton as solid polymer electrolyte prepared by a facile method [46]. PCL is semicrystalline at room temperature and its ester oxygen is Lewis base, thus limiting its ionic conductivity. SN exhibits a single plastic phase in the temperature range from –35 °C to its melting point. The strategy of their work is to incorporate SN as a plastic additive blending with PCL (PCL/SN) to prepare a biocompatible/biodegradable SPE with a high ionic conductivity of $4 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ at room temperature. LiTFSI is chosen as Li salt because of its large anionic radius and low dissociation energy, leading to a high conductivity. Li and co-workers designed and synthesized a novel single-ion polymer conductor (denoted as P(SSPSILi-alt-MA)), which has no chains with the ability of ionic conduction, with an alternating structure of maleic anhydride (MA) and lithium 4-styrenesulfonyl(phenylsulfonyl)imide (SSPSILi) [47]. Then they prepared a new composited SSPE of polyethylene oxide (PEO) and P(SSPSILi-alt-MA), as shown in Fig. 3(b). P(SSPSILi-alt-MA) shows the good dispersion in PEO due to its completely broken crystalline caused by PEO chains. Here, PEO is equivalent to the plastic phase. The 20% (mass) SSPE membrane presents the highest ion conductivity of $3.08 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ at room temperature.

In polymer matrix, side chains also affect properties of SPE [48]. For example, ether side chains accelerate ionic conduction in polymers. The inter-chain jump efficiency of Li⁺ in the short side chain is higher because it avoids the movement of the center of mass of the long-chain polymer. Grafted polymers have higher ionic conductivity due to lower crystallinity and faster Li⁺ mobility. In the work of He and co-workers, as shown in Fig. 3(c), SPEs based on poly (vinyl alcohol) (PVA) with ureidopyrimidinone (UPy) and poly (ethylene glycol) (PEG) units (PVA-UPy-PEG) were successfully fabricated by the reactions of different chain length epoxide

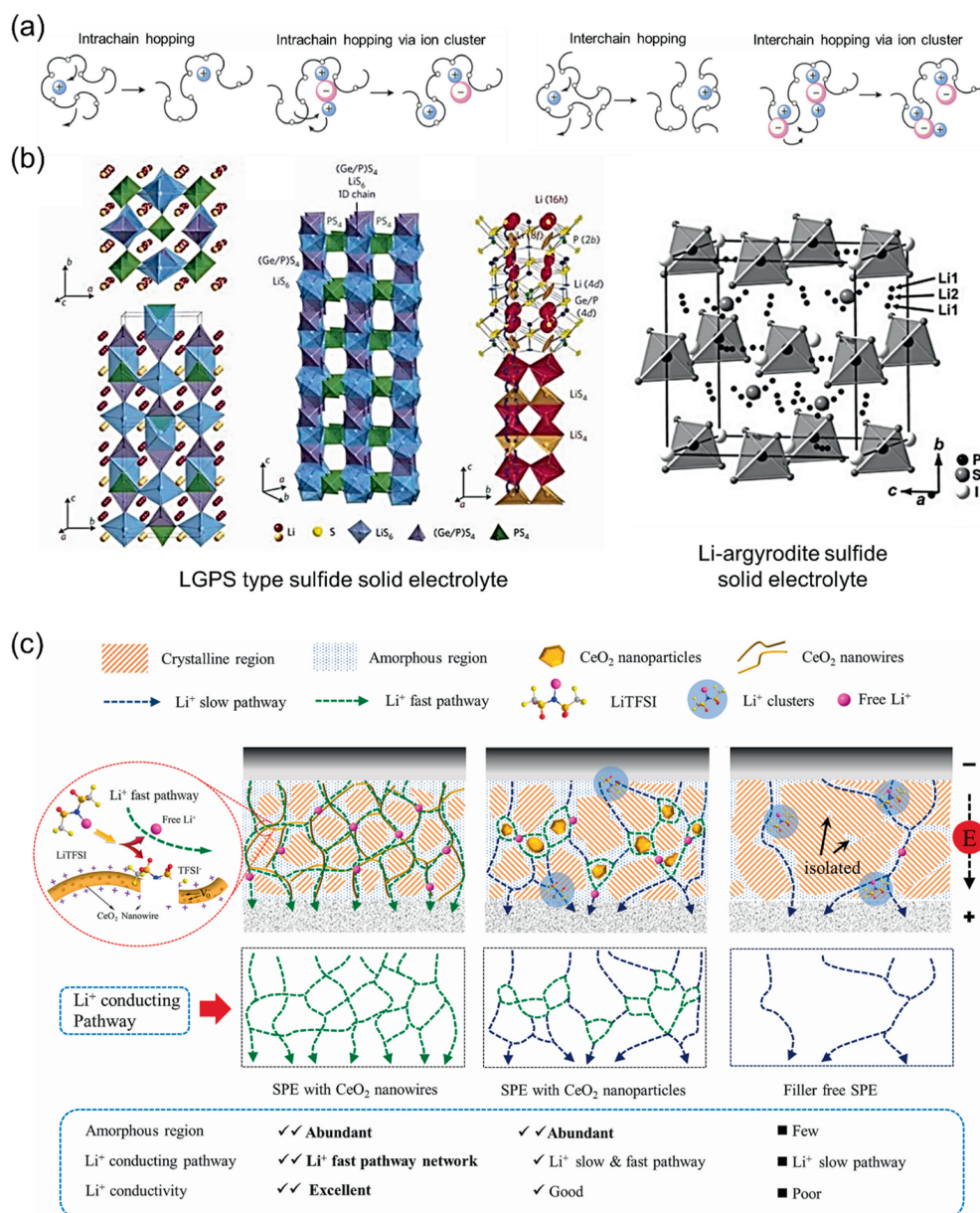


Fig. 2. Types of Li⁺ transport path. (a) Mechanism of ion transport in solid polymer electrolyte [41]. (b) The transport mechanism of Li⁺ in inorganic solid electrolytes [42,43]. (c) Schematic diagram of the interface fast transport path [45].

functionalized-PEG and 2(6-isocyanatohexylaminocarbonylamino)-6-methyl-4[1H]-pyrimidinone (UPy-NCO) with the hydroxyl of PVA [49]. The SPE with the longest PEG side chain (PVA-UPy-PEG750) showed a high ionic conductivity of $1.51 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ at 60 °C. As shown in Fig. 3(d), Zhang and colleagues prepared a solid polymer electrolyte based on polysiloxane by grafting ionic liquid and polyethylene oxide onto a flexible polysiloxane backbone with LiTFSI as the lithium salt [50]. The polymer electrolyte with 10% (mass) 1-vinyl-3-cyanopropylimidazolium bis(trifluoromethylsulfonyl) imide ionic liquid (IN-CN) side chain has the highest ionic conductivity ($3.56 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$), which is 2.7 times that of SPE without side chain ($1.32 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$). The results show that the IN-CN chain group is beneficial to the solid polysiloxane electrolyte to improve the ionic conductivity. Copolymerization promotes the construction of complex polymer matrices by combining different functional groups. Polyethylene glycol oligomers with ether groups, especially polyethylene glycol with allyl groups, are often used as ion-conducting segments in the

copolymerization process. Therefore, it is possible to reduce the crystallinity of the polymer matrix by introducing different fragments to copolymerize with the ether group, while increasing the amorphous domain of the polymer matrix, thereby improving the ionic conductivity of the SPE [47]. Xie and co-workers designed a BAB-type triblock copolymer (TBC) using PCL as the B-block and poly(propylene carbonate) (PPC) as the A-block, as shown in Fig. 3 (e) [51]. PPC has been widely studied and used as a SPE, its amorphous phase leads to a high ionic conductivity. The crystallinity of TBC is tuned through the introduction of PPC block, leading to a high ionic conductivity of $3 \times 10^{-5} \text{ S}\cdot\text{cm}^{-1}$ at 30 °C. In Fan and Chen's research, as shown in Fig. 3(f), a polymer-in-salt polysiloxane SPE was fabricated with bi-grafted polysiloxane copolymer, lithium bis(trifluoromethanesulfonyl)imide and poly(vinylidene fluoride), which shows higher ionic conductivity of $7.8 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ at 25 °C [52]. Therefore, innovations in the design of macromolecules by introducing multiple functional groups and balanced interactions, including copolymerization and grafting, will funda-

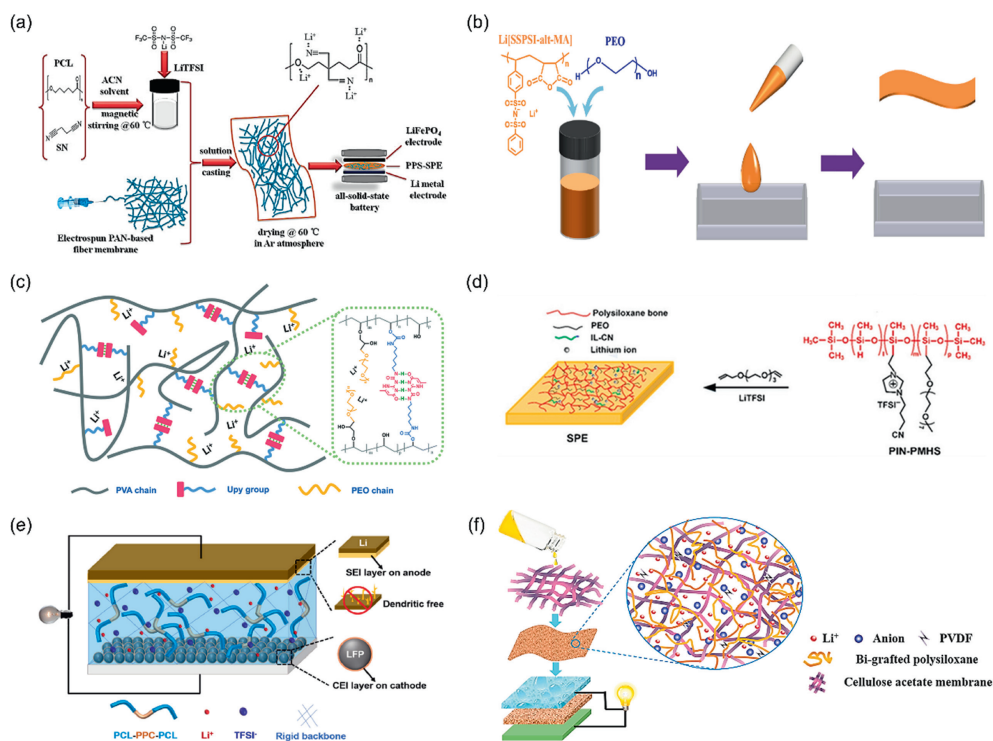


Fig. 3. Altering the semi-crystallinity of the polymer: (a) and (b) adding a plastic phase; (c) and (d) synthesis of grafted polymers; (e) and (f) synthetic copolymers. (a) Schematic illustration for the synthesis route of PPS-SPE [46]. (b) Schematic diagram of preparing the SSPE membranes via the solution-casting method [47]. (c) Schematic illustration for the preparation process of PVA-UPy-PEG [49]. (d) Schematic for the Synthetic Process of SPEs [50]. (e) Schematic illustration of Li metal solid state battery with triblock copolymer electrolyte and stable interfaces [51]. (f) Schematic illustration of fabricating composite polymer electrolyte membrane by solution-casting technique [52].

mentally open up a path for the development of SPEs [48]. In addition, some inorganic nanofillers can also be used as a plastic phase to reduce the crystallinity of the polymer [45].

3.2. Increase the types of Li⁺ transport paths

As discussed above, there are three types of Li⁺ transport paths in SPEs. In addition to the enhancement of intrinsic Li⁺ transport of polymers, we can also increase the other two types of Li⁺ transport path based on SPEs to further improve Li⁺ conductivity.

3.2.1. Doping inactive nano-fillers to construct interfacial channels for rapid Li⁺ transport

Although extensive efforts had been dedicated to the polymer electrolytes, it remains challenging for constructing long-range ordered ion nanochannels owing to their limited chemical and structural flexibility, as well as the complex microphase-separation process [8]. In this occasion, exploration of alternative building blocks that can construct long-range ordered and continuous nanochannels for rapid proton conduction is imperative. Generally speaking, in addition to reducing the crystallinity of the polymer, the filler/polymer interface based on the Lewis acid-base interaction provides a new pathway for Li⁺ transport [53]. The morphology of the filler also has an effect on the interface transport path. Generally speaking, fillers can be divided into zero-dimensional (0D), one-dimensional (1D), two-dimensional (2D). A continuous three-dimensional (3D) Li⁺ transport path can be constructed by adding suitable fillers into the SPE systems.

Add 0D filler to build interface-type Li⁺ transport paths

Xiao and colleagues prepared organic-inorganic hybrid particles poly (methyl methacrylate)-ZrO₂ (PMMA-ZrO₂) by *in-situ* polymerization, and the poly (vinylidene fluoride-

hexafluoropropylene) (P(VDF-HFP))-based composite polymer electrolyte (CPE) membranes doped with different amounts of hybrid particles PMMA-ZrO₂ are prepared by phase inversion [54]. The addition amount of PMMA-ZrO₂ is increased to 5% (mass), and the ion conductivity at room temperature reaches $3.595 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1}$. This is because the addition of PMMA-ZrO₂ can not only reduce the crystallinity of CPE, but also provide continuous interface pathways (Fig. 4(a)). Wei and co-workers demonstrated a facile *in-situ* polymerization/crystallization method to synthesize a homogeneous TiO₂-grafted NHPE with a cross-linked branching structure, comprised of ion-conducting poly (ethylene glycol) methyl ether methacrylate (PEGMEM) and non-polar stearyl methacrylate (SMA) (Fig. 4(b)) [55]. The highly monodispersed TiO₂ nanocrystals enhance the effective interface interaction between the particles and the polymer matrix, and promote the formation of continuous ion conduction channels. The TiO₂-grafted NHPE exhibits superior electrochemical properties with an ionic conductivity of $1.1 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ at 30 °C. Wang proposed a new biotechnology to fabricate novel protein-ceramic hybrid nanofillers for boosting the ionic conductivity [56]. As shown in Fig. 4(c), this hybrid nanofiller is fabricated by coating ion-conductive soy proteins onto TiO₂ nanoparticles via a controlled denaturation process in appropriate solvents and conditions. They developed a new hybrid nanofiller via combining the ion-conductive soy protein (SP) and one classic ceramic nanoparticle, TiO₂, to form a unique protein-ceramic hybrid nanofiller for improving the ion conductivity of SPEs. The matrix of the SPE is an amorphous material based on the complex of ultrahigh molecular-weight PEO and LiClO₄. The ion conductivity is improved by one magnitude from 5×10^{-6} to $6 \times 10^{-5} \text{ S}\cdot\text{cm}^{-1}$ at room temperature.

Add 1D filler to build interface-type Li⁺ transport paths

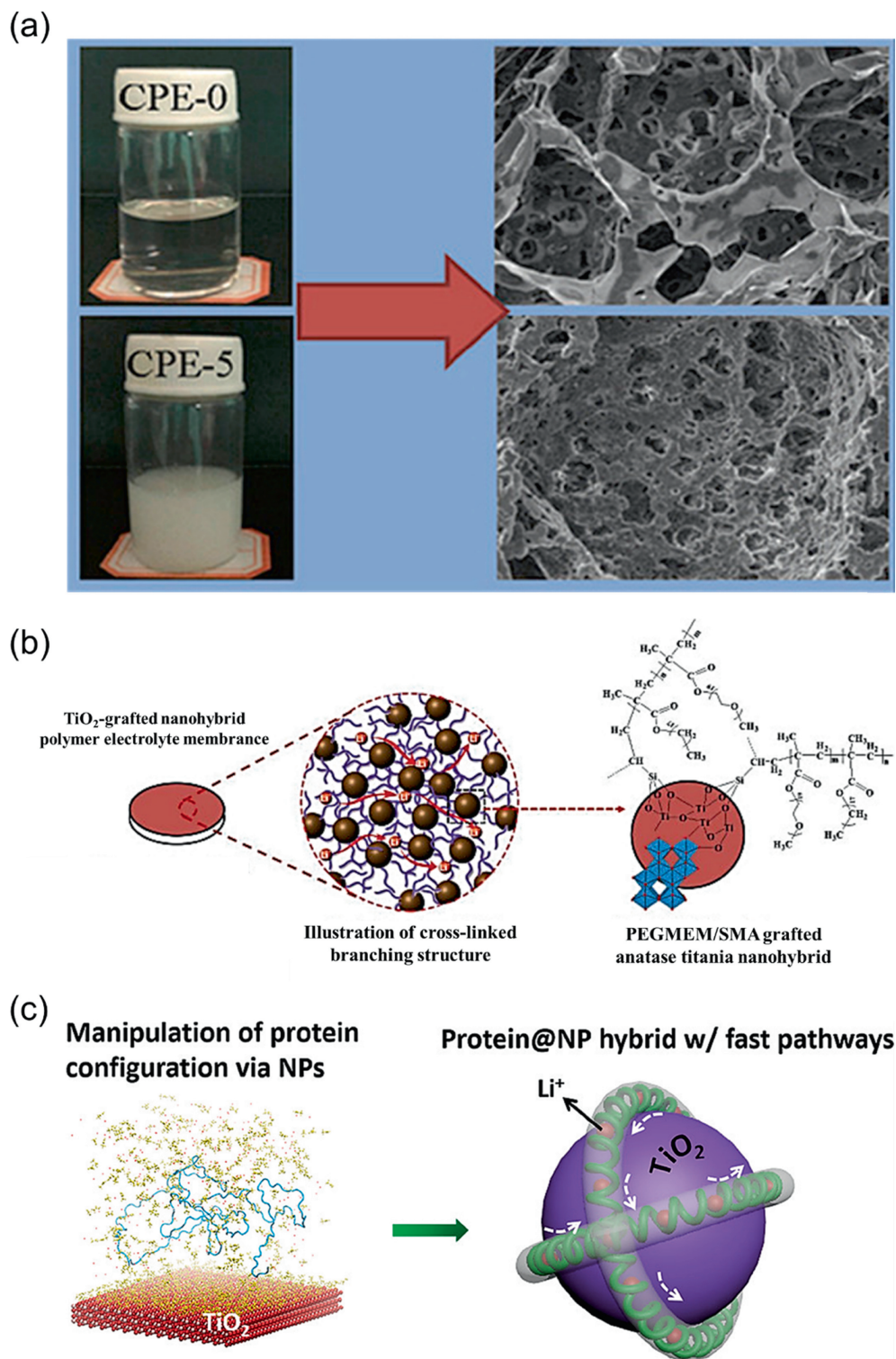


Fig. 4. (a) SEM images of the CPE membranes and the CPE-5 membranes [54]. (b) Schematic illustration of TiO_2 -grafted nanohybrid polymer electrolyte with cross-linked branching structure [55]. (c) Schematic for the preparation of TiO_2 /SP hybrid nanofillers [56].

As shown in Fig. 5(a), Tao and co-workers fabricated $\text{Mg}_2\text{B}_2\text{O}_5$ nanowire enabled poly (ethylene oxide) (PEO)-based solid-state electrolytes (SSEs) [57]. The SSEs including 10% (mass) $\text{Mg}_2\text{B}_2\text{O}_5$ nanowires has the highest ionic conductivity of $1.53 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ at 40°C and $3.7 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ at 50°C . The elevated ionic conductivity is attributed to the improved motion of PEO chains and the increased Li^+ migrating pathway on the interface between $\text{Mg}_2\text{B}_2\text{O}_5$

O_5 and PEO-LiTFSI. In the work of Wang and Zhong *et al.*, core-shell protein-ceramic nanowires for more efficiently building fast ion-conduction networks in SPEs are reported [58]. As shown in Fig. 5(b), Li^+ conducts at high speed along the 1D nanowires at the polymer-filler interface. Yang and co-workers introduced palygorskite ($(\text{Mg},\text{Al})_2\text{Si}_4\text{O}_{10}(\text{OH})$) nanowires as a new ceramic filler to form composite solid electrolytes (CPE), which can improve the

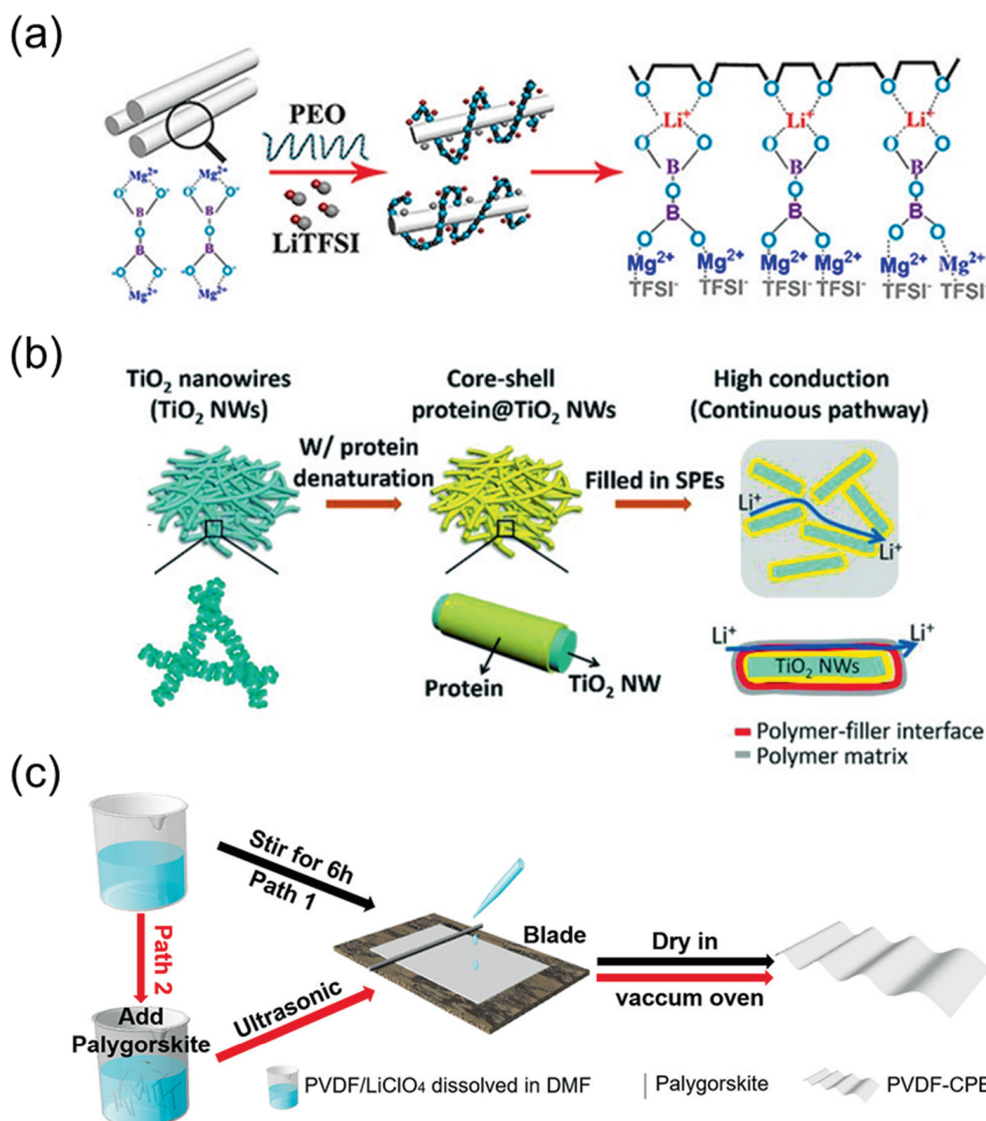


Fig. 5. (a) Schematic illustration of the synthetic route of $\text{Mg}_2\text{B}_2\text{O}_5$ nanowires [57]. (b) The advantages of protein@ TiO_2 NWs for building faster ion-conduction pathways in SPEs [58]. (c) A Schematic diagram of the synthesis of PVDF-based polymer electrolytes and PVDF/palygorskite nanowires/CPE [59].

ionic conductivity of PVDF-based polymer electrolyte (Fig. 5(c)) [59]. The ionic conductivities of 3% (mass) PVDF/palygorskite CPEs reaches $1.7 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ at 60°C .

Add 2D filler to build interface-type Li^+ transport paths

Yang and colleagues prepared a unique solid-state polymerization of MXene-based mesoporous silica nanosheets with a sandwich structure, which are fabricated *via* controllable hydrolysis of tetraethyl orthosilicate around the surface of MXene- Ti_3C_2 under the direction of cationic surfactants [60]. As shown in Fig. 6(a), the mesopores and surface of the nanosheets have abundant functional groups, which is conducive to the formation of Lewis acid-base interactions, and allows Li^+ to quickly migrate at the mesoporous nanosheet/polymer interface. Luo Group, for the first time, introduced 2D additives using few-layer vermiculite clay sheets (VS) as an example to comprehensively upgrade poly (ethylene oxide)-based solid polymer electrolyte (Fig. 6(b)) [61]. 2D fillers have higher surface area than 0D and 1D fillers and thus higher active interface with polymers in SPE, which is beneficial to the interface conduction of Li^+ . The 10% (mass) VS composite SPE has the highest ionic conductivity. The ionic conductivity of VS com-

posite SPE is $2.9 \times 10^{-5} \text{ S}\cdot\text{cm}^{-1}$ at 25°C . Gao and co-workers synthesized MnO_2 nanosheets by ultrasonic-assisted simple redox reaction between KMnO_4 and 2-(*N*-morpholino) ethanesulfonic acid, and introduced MnO_2 nanosheets into PEO-LiTFSI polymer electrolyte (Fig. 6(c)) [62]. Because MnO_2 can be combined with PEO chains, Li^+ can carry out long-range migration on MnO_2 nanosheets. Density functional theory calculations reflect that the binding energy between PEO/Li complex and MnO_2 is small, and Li^+ is easily desorbed from PEO and migrates to MnO_2 nanosheets, realizing conduction at the MnO_2 -polymer interface. The ionic conductivity of the MnO_2 composite solid polymer electrolyte is $1.95 \times 10^{-5} \text{ S}\cdot\text{cm}^{-1}$ at 30°C . Wu and co-workers used the method of expansion and filtration to embed PEO-LiTFSI into the middle layer of vermiculite nanosheets to prepare a thin laminar composite solid electrolyte (LCSE), namely Vr/PEO-LCSE [63]. As shown in Fig. 6(d), continuous interlayer interface pathways result in a high ionic conductivity of $1.22 \times 10^{-5} \text{ S}\cdot\text{cm}^{-1}$ at 25°C .

Adding fillers to build a 3D Li^+ transmission network

As shown in Fig. 7(a), traditional nanofiller polymer composite electrolytes often have discontinuous transport paths and parallel

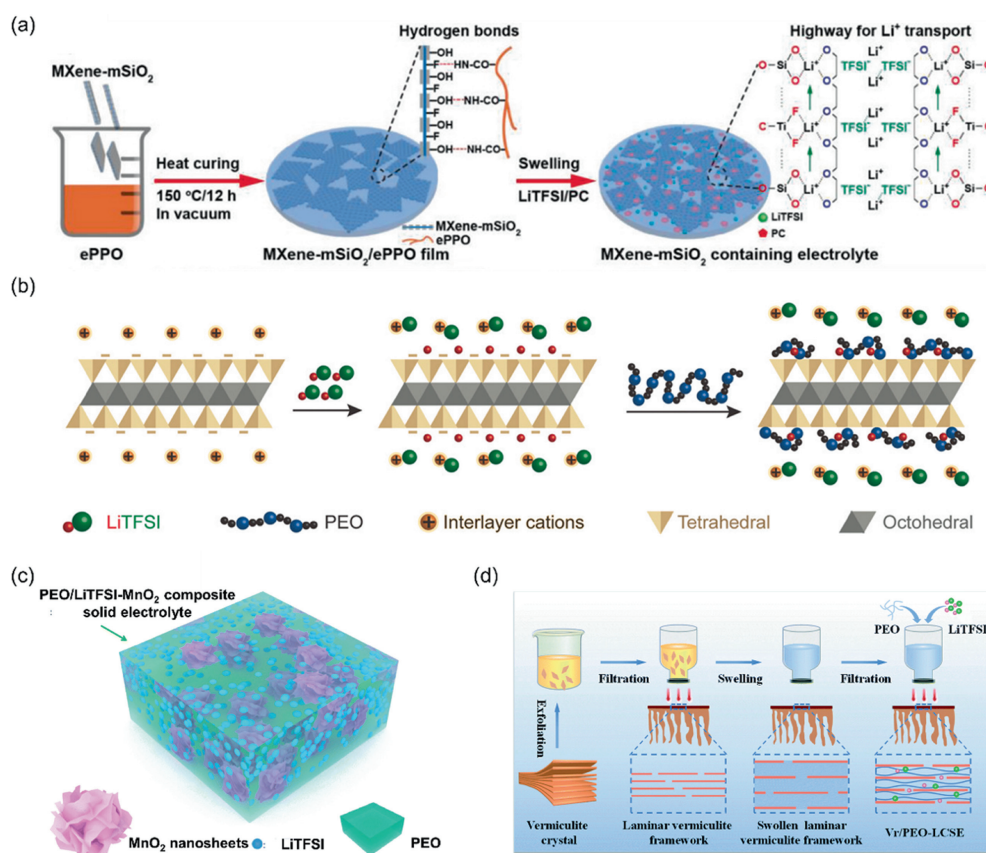


Fig. 6. (a) Schematic illustrating the fabrication of the MXene-mSiO₂ containing solid polymer electrolyte [60]. (b) Schematic showing the mechanism for VS enhanced ionic conductivity in SPE [61]. (c) A schematic diagram showing the composition of a PEO/LiTFSI/MnO₂ solid polymer electrolyte membrane [62]. (d) Schematic illustration of the preparation procedure of Vr/PEO-LCSE [63].

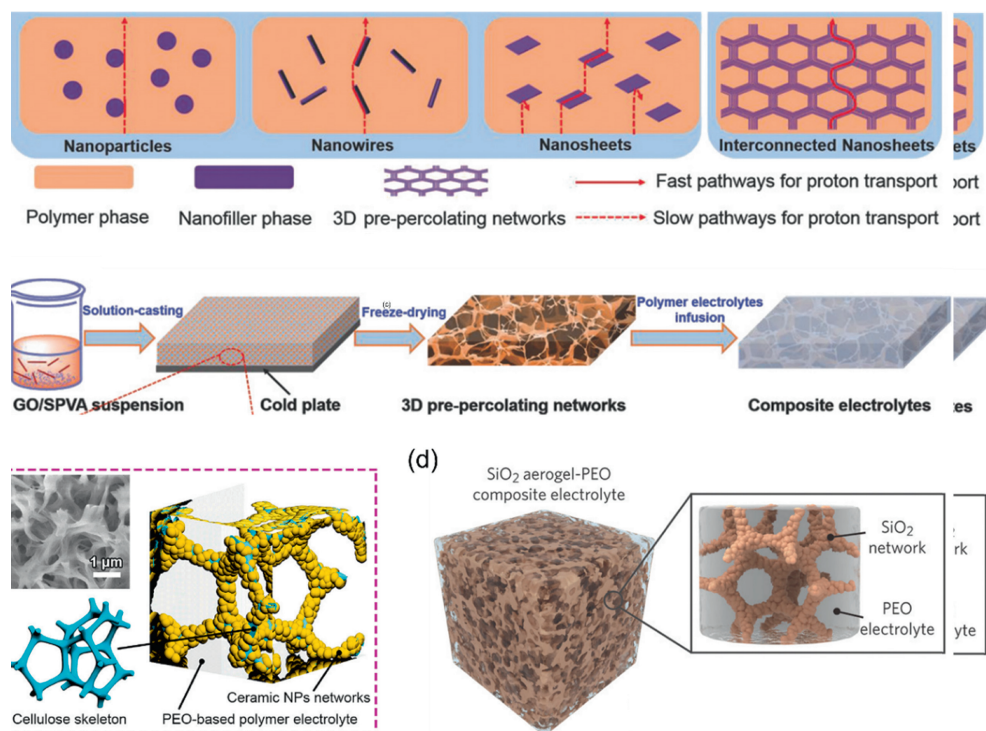


Fig. 7. (a) Schematics of composite electrolytes with two status of nanofillers inside polymer matrix [64]. (b) Schematic illustration of the synthesis procedure of 3D sGO prepercolating networks and composite electrolytes by the infusion of polymer electrolytes [64]. (c) Three-dimensional schematic showing the network structures of the cellulose-based CPE. Inset is the typical SEM image showing the cellulose networks structure [65]. (d) Schematic of the SiO₂-aerogel-reinforced CPE [53].

orientation of 2D nanofillers in the polymer matrix, while 3D networks can provide a continuous path through the entire bulk composite [64]. Wu and co-workers designed 3D percolating networks using sulfonated graphene oxide (sGO) nanosheets as building blocks for high-performance solid electrolytes via a freeze-casting method (Fig. 7(b)) [64]. Composite electrolytes were further fabricated by infusing polymer electrolytes (Nafion and sulfonated poly(ether-ether-ketone) (SPEEK)) into the 3D sGO networks. The conductive path of the 3D network is continuous, which greatly improves the conductivity of the composite electrolyte. Liu and colleagues used natural cellulose fibers and ceramic nanoparticles to successfully develop a 3D cellulose/ceramic network composite polymer electrolyte [65]. Monodisperse ceramic nanofillers are first driven by the self-assembly of hybrid cellulose fibers to form an interconnected network, and then polymer electrolytes are injected into it (Fig. 7(c)). The synthesized composite electrolyte not only provides a 3D continuous Li^+ path, but also the Li^+ conductivity is high. Cui and colleagues prepared a high-conductivity CPE ($6 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ at 30°C) by introducing rigid mesoporous SiO_2 aerogel as the 3D skeleton of the polymer-based electrolyte [53]. The interconnected SiO_2 aerogels provide a large and continuous surface for strong anion adsorption, thereby creating a highly conductive path in the composite material (Fig. 7(d)).

3.2.2. Doping active fillers to further increase the type of Li^+ transport path

Active ceramic fillers intrinsically have Li^+ conductive capability, which can be directly used as solid electrolytes for lithium batteries [66]. Generally speaking, these ceramic fillers include oxide type and sulfide type materials. There are three types of Li^+ transport paths in the composite solid electrolyte composed of active fillers and polymers, that are, the chain transport of the polymer itself, the defect transport of the active filler and the filler-polymer interface transport.

Add oxide-type active fillers to SSEs

The common oxide type active fillers are perovskite-type ceramics and garnet-structure ceramics. Perovskite-type ceramics have a typical structure of ABO_3 ($\text{A} = \text{La}$, Sr , or Ca ; $\text{B} = \text{Al}$ or Ti). Garnet-structured ceramic electrolytes are in the structure of $\text{A}_3\text{B}_2(\text{XO}_4)_3$ ($\text{A} = \text{Ca}$, Mg , Y , or La ; $\text{B} = \text{Al}$, Fe , Ga , Ge , Mn , Ni , or V , and $\text{X} = \text{Si}$, Ge , or Al) [67].

Wang *et al.* designed a ceramic composite electrolyte polymer by a template method and solution method (Fig. 8(a)) [67]. The polymer combines $\text{Li}_{6.4}\text{La}_3\text{Zr}_2\text{Al}_{0.2}\text{O}_{12}$ (LLZAO) frame with polyethylene oxide (PEO)/LiTFSI (T-LAPL). The T-LAPL composite electrolyte has a significant increase in Li^+ conductivity at room temperature ($2.51 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$). Scheiba and co-workers prepared cross-linked polyethylene glycol by polymerization of terminal active groups and added garnet filler $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZ) to study its electrical conductivity [68]. As shown in Fig. 8(b), the cross-linked polymer body is a polyethylene glycol block of O, O-bis(2-aminopropyl) polypropylene glycol block at 908°C , the terminal amine of polypropylene glycol and bisphenol A is synthesized by the polymerization of the terminal epoxy group of diglycidyl ether, and LiTFSI is used as the lithium salt. Ionic conductivities higher than $5.0 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ above 45°C were obtained. Dirican and co-workers developed a new type of CSE composed of silane-modified $\text{Li}_{6.28}\text{La}_3\text{Al}_{0.24}\text{Zr}_2\text{O}_{12}$ (s@LLAZO) nanofibers and poly(ethylene glycol) diacrylate (PEGDA) [69]. 3-(trimethoxysilyl) propyl methacrylate enables the incorporation of a high content of LLAZO nanofibers with the polymer matrix and results in a well-percolated, three-dimensional LLAZO network fully embedded in

the PEGDA matrix (Fig. 8(c)). When the filler content is appropriate, Li^+ can conduct high-speed conduction along the interface and also with the help of active fillers, which is the maximum ion conductivity. Chang and co-workers have synthesized a highly ion conductive stable composite solid polymer electrolyte (CSPE) composed of a poly(ethylene oxide)-LiTFSI matrix, $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ ceramic filler, and poly(ethylene glycol) dimethyl ether (PEGDME) plasticizer [70]. As shown in Fig. 8(d), Li^+ can not only conduct along the filler-polymer interface, but also conduct high-speed conduction along the active filler. The CSPE containing 10% (mass) PEGDME (CSPE10) shows the highest ionic conductivity of $4.7 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ at 60°C . Zhao developed a CSE with a novel PEO|PEO-perovskite|PEO structure [71]. This composite electrolyte structure is composed of PEO-LiTFSI on both sides and a network of perovskite $\text{Li}_{0.33}\text{La}_{0.557}\text{TiO}_3$ (LLTO) nanofibers filled in the middle. The ionic conductivities are calculated to be $1.6 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ at 24°C .

Add sulfide-based active fillers to SSEs

Kamaya *et al.* first reported a new lithium superionic conductor- $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ (LGPS) with a 3D framework structure [72]. However, one of the raw materials for LGPS is GeS_2 , which is expensive, so some low-cost sulfide-type ceramics are needed. In recent years, it has been discovered that lithium yttrium ore with the general structure of $\text{Li}_6\text{PS}_5\text{X}$ ($\text{X} = \text{Cl}$, Br , or I) as an electrolyte has high ionic conductivity [73]. Xu *et al.* prepared a polyethylene oxide (PEO)/ Li_3PS_4 hybrid polymer electrolyte by *in-situ* method, as shown in Fig. 9(a) [74]. Li_3PS_4 nanoparticles have a good distribution and have a positive effect on the transfer of Li^+ . The results show that the optimal electrolyte of PEO-2% (volume) Li_3PS_4 has an ionic conductivity of $8.01 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ at 60°C . Chen added $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ (LGPS) to a polyethylene oxide-LiTFSI (PEO-LiTFSI) matrix to prepare a composite solid polymer electrolyte (SPE) membrane (Fig. 9(b)) [75]. The maximum ion conductivity can reach $1.21 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1}$ at 80°C . Compared with inactive fillers, LGPS is a super-ionic conductor with ultra-high Li^+ conductivity. In addition to reducing polymer crystallinity and building a transmission interface, it can also directly participate in ion transport by providing ions. Janek and colleagues reported on the composite solid electrolyte of SPE | $\text{Li}_6\text{PS}_5\text{Cl}$ | SPE (PEO10: LiTFSI), as shown in Fig. 9(c) [76]. The conductivities of the SPE and $\text{Li}_6\text{PS}_5\text{Cl}$ were determined by blocking electrode measurements, achieving conductivities of $1.01 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1}$ and $15.7 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1}$ at 80°C . With the addition of $\text{Li}_6\text{PS}_5\text{Cl}$, the ionic conductivity of the composite electrolyte is excellent.

In conclusion, the improvement of Li^+ conductivity is mainly due to the following three reasons: (1) The addition of active filler reduces the crystallinity of polymer, which increases the ionic conductivity of polymer electrolyte; (2) The polymer-active filler interface provides Li^+ conductivity; (3) Active filler provides a fast and continuous Li^+ transport path. It just corresponds to the three types of Li^+ transport path.

3.3. Shorten the distance of the Li^+ transport path

As we all know, the straight-line distance is the shortest path between two points. Thus, it is reasonable to design a vertical channel to shorten the Li^+ transport distance within less time. Yang and co-workers used an ice template-based method to prepare $\text{Li}_{1-x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ (LATP) nanoparticles (NPs) arranged vertically in polyethylene oxide (PEO) matrix, as shown in Fig. 10(a), with a conductivity of $5.2 \times 10^{-5} \text{ S}\cdot\text{cm}^{-1}$, which is 3.6 times of the compound electrolyte with randomly dispersed LATP NPs [77]. Cui group reported a composite polymer electrolyte with well-

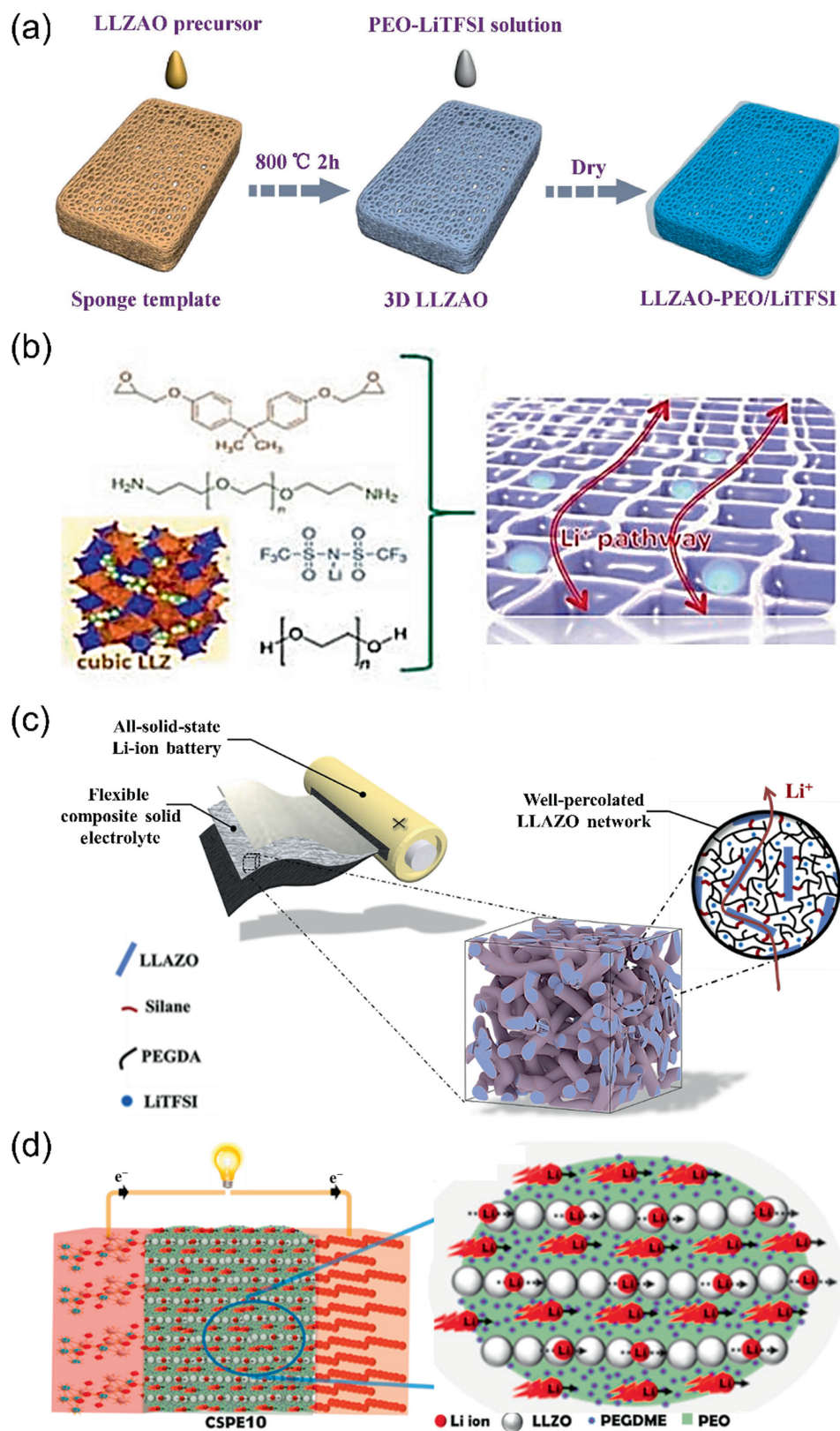


Fig. 8. (a) Schematic illustration for the synthesis of the T-LAPL composite electrolyte [67]. (b) Schematic diagram of garnet-type composite electrolyte synthesis and lithium ion transmission [68]. (c) Schematic of s@LLAZO-PEGDA CSE, providing fast and nontortuous Li⁺ conductive pathways [69]. (d) Schematic diagram of Li⁺ conduction path [70].

aligned inorganic Li⁺-conductive nanowires [78]. The well-aligned Li_{0.33}La_{0.557}TiO₃ (LLTO) nanowires were obtained by electrospinning, and then cast into dimethylformamide (DMF) solution con-

taining PAN and LiClO₄, and vacuum dried to obtain a solid composite electrolyte. As shown in Fig. 10(b), compared to random nanowires, the aligned nanowires greatly shorten the distance of

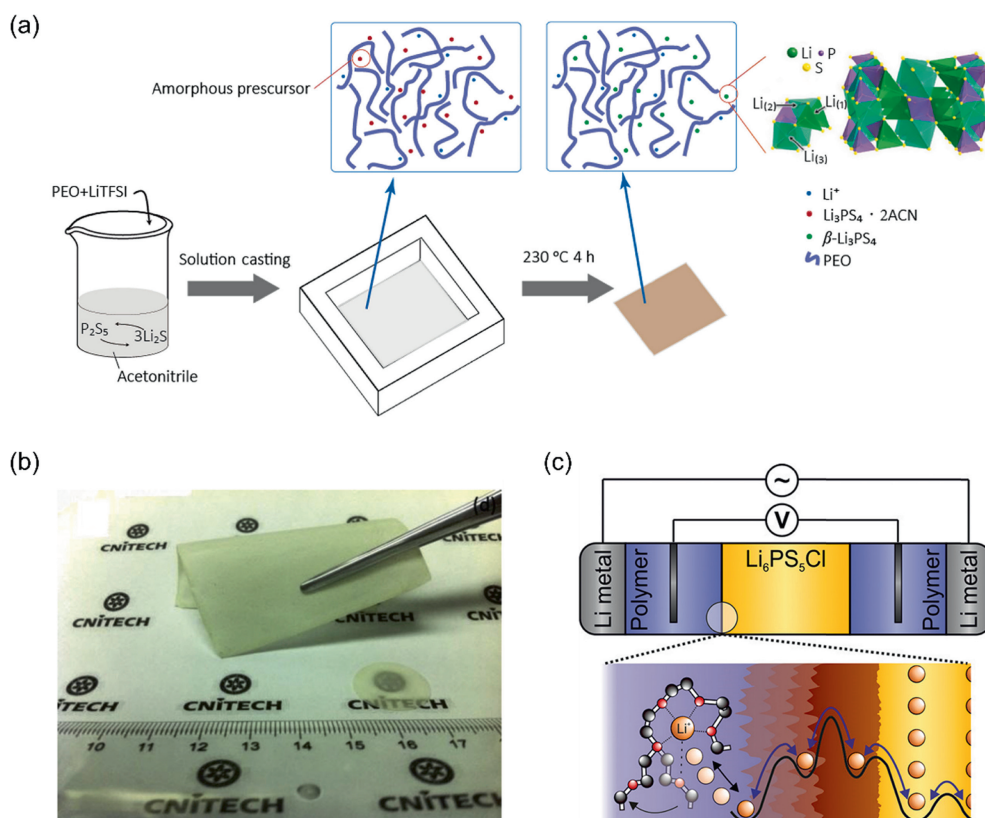


Fig. 9. (a) The process flow diagram of *in-situ* preparation of PEO/Li₃PS₄ hybrid polymer electrolytes [74]. (b) A photo of SPE membrane [75]. (c) Schematic of SPE | Li₆PS₅Cl | SPE [76].

the transport path due to their orientation. Well-aligned inorganic Li⁺-conductive nanowires exhibit an ionic conductivity of $6.05 \times 10^{-5} \text{ S}\cdot\text{cm}^{-1}$ at 30 °C, which is one order of magnitude higher than previous polymer electrolytes with randomly aligned nanowires. Luo group demonstrated that vertically aligned 2D vermiculite flakes are used as fillers for SPEs [79]. The preparation method of this vertical arrangement of vermiculite flakes (VAVS) is the vertical temperature gradient freezing of vermiculite dispersion, as shown in Fig. 10(c). After infiltration with PEO-LiTFSI-based SPE, the VAVS composite SPE (VAVS-CSPE) has vertically aligned continuous and penetrating polymer-filler interfaces. Cui *et al.* filled 8.6-μm-thick nanoporous polyimide (PI) with polyethylene oxide/lithium bis(trifluoromethanesulfonyl) imide (PEO/LiTFSI) to obtain a composite solid electrolyte (Fig. 10(d)) [80]. The vertical channel greatly shortens the transmission distance of Li⁺. The ionic conductivity of the prepared polymer electrolyte can reach $2.3 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ at 30 °C. Therefore, the orderly arrangement structure of the fillers in SPEs provides a fast, continuous and shortest path for the transmission of Li⁺. Cui and colleagues prepared a nano-ceramic-polymer composite electrolyte with surface-modified alumina as the ceramic scaffold and polyethylene oxide as the polymer matrix [81]. The electrolyte has a vertically arranged and continuous nano-ceramic-polymer interface. Using the method of melt infiltration, the polymer electrolyte is vertically arranged through the channels of the anodized aluminum oxide discs. Moreover, they demonstrated for the first time the rapid transport of Li⁺ along with the ceramic-polymer interface (Fig. 10(e)). The vertically arranged interface structure in the composite electrolyte enables the composite solid electrolyte to have superior ionic conductivity. The ionic conductivity of the composite solid electrolyte is as high as $5.82 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ at the electrode level.

According to the above different strategies, we summarize the work on improving the ionic conductivity of SPEs in recent years, as shown in Table 1.

4. Conclusions and Outlook

SPEs have always been considered the best choice to replace liquid electrolytes in lithium batteries due to their ductility and flexibility. However, the problem of low ionic conductivity at room temperature severely limits its practical application. Ion conduction is also a charge transfer process, Li⁺ acts as a charge carrier, and the polymer matrix provides a Li⁺ transport path for it. Therefore, the ionic conductivity of SPEs can be improved by increasing the number of charge carriers and optimizing the transport path, as discussed in this article. The idea of charge transfer through the interaction between the charge carrier and the transport path greatly simplifies the complex conduction mechanism of Li⁺ in SPEs. It is expected that this idea can provide a new direction for future research on improving the ionic conductivity of SPEs.

Although the above methods can improve the ionic conductivity of SPEs to a certain extent, it is still far lower than that of liquid electrolytes at room temperature. Before the practical application of SPEs to all-solid-state lithium metal batteries, it is necessary to further improve the ion conductivity. In future research, the following points can be considered: (1) The ion conductivity is closely related to the free carrier concentration. To increase the carrier concentration, it is necessary to find a way to promote the dissociation of lithium salt. Therefore, it is very important to further study the dissociation mechanism of lithium salt, which is also conducive to the design and development of lithium salt suitable for SPEs; (2) Develop some new polymerization methods, such as electrochemical polymerization and controllable free radical polymerization,

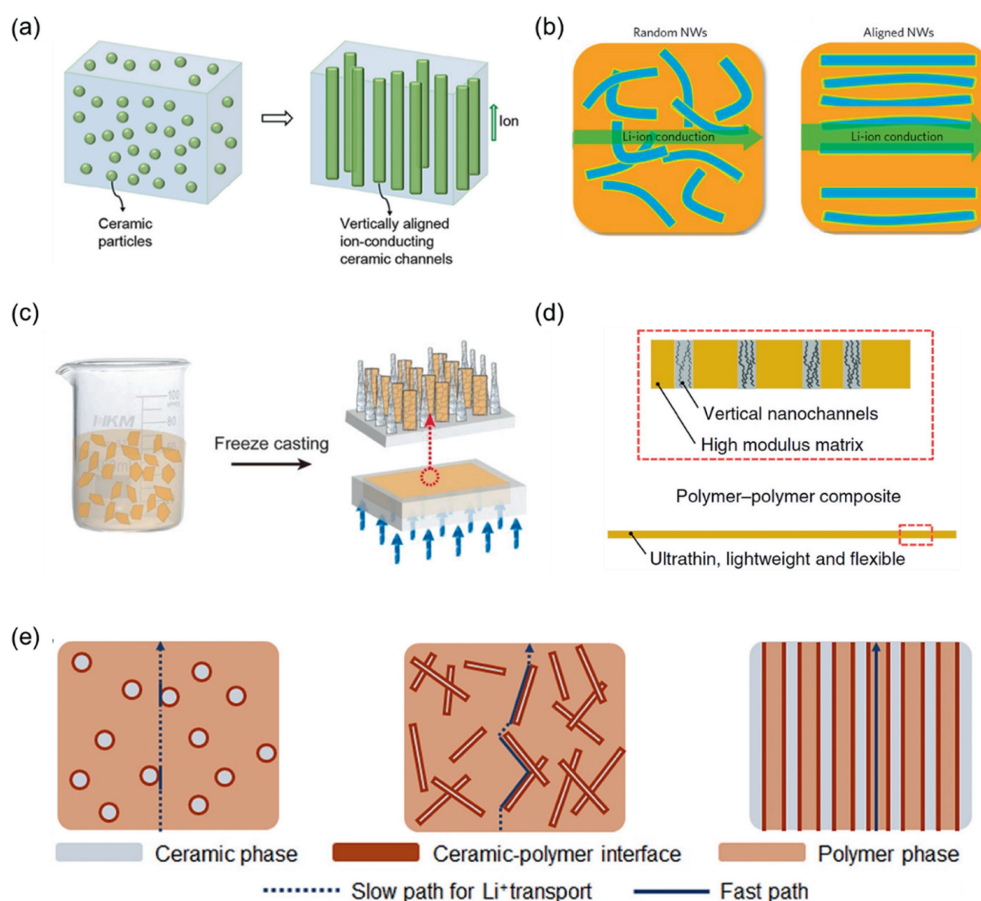


Fig. 10. (a) Schematic of vertically aligned and connected ceramic channels for enhancing ionic conduction [77]. (b) Random nanowires and arranged nanowires in the composite polymer electrolyte Li^+ transport path [78]. (c) Schematic of vertical temperature gradient freezing of VS dispersion in a Teflon mold, which is placed on top of liquid N_2 to induce the directional freezing casting [79]. (d) Schematic showing the design principles of our polymer-polymer composite SSE [80]. (e) Schematics of composite solid polymer electrolyte with three types of geometrical structures of the ceramic-polymer interface [81].

Table 1
Reported ionic conductivity of polymer-based solid electrolytes

Strategy	Materials	Ionic conductivity/ $\text{S}\cdot\text{cm}^{-1}$	Year	Ref.
Promote dissociation of lithium salt	P(V-B)/LiTFSI	9.11×10^{-4} (25 °C)	2019	[32]
	PEO/ANFs/LiTFSI	8.8×10^{-5} (RT)	2020	[33]
	PVDF/Sm-doped $\text{CeO}_2/\text{LiClO}_4$	9.09×10^{-5} (30 °C)	2019	[39]
	PEO/Ca-doped $\text{CeO}_2/\text{LiTFSI}$	1.3×10^{-4} (60 °C)	2020	[40]
Reduce polymer crystallinity	PCL/SN/LiTFSI (plastic phase)	4×10^{-4} (RT)	2017	[46]
	PVA-UPy-PEG/LiClO ₄ (grafted)	1.51×10^{-4} (60 °C)	2019	[49]
	PCL-PPC-PCL/LiTFSI (copolymers)	3×10^{-5} (30 °C)	2020	[51]
Add filler	P(VDF-HFP)/PMMA-ZrO ₂ /LiPF ₆ (0D)	5.6×10^{-3} (RT)	2018	[54]
	PEO/LiClO ₄ /TiO ₂ (0D)	6×10^{-5} (RT)	2018	[56]
	PEO/Mg ₂ B ₂ O ₅ /LiTFSI (1D)	1.53×10^{-4} (40 °C)	2018	[57]
	PVDF/palygorskite (1D)	1.7×10^{-4} (60 °C)	2018	[59]
	PEO/VS/LiTFSI (2D)	2.9×10^{-5} (25 °C)	2018	[61]
	Vr/PEO-LCSE (2D)	1.22×10^{-5} (25 °C)	2020	[63]
	PEO/LAGP/LiTFSI (3D)	1.1×10^{-4} (60 °C)	2020	[65]
	PEO/LiTFSI/SiO ₃ (3D)	6×10^{-4} (30 °C)	2018	[53]
	PEO/LLZAO/LiTFSI	2.51×10^{-4} (RT)	2020	[67]
Active filler	PEG/LiTFSI/LLZ	5×10^{-4} (above 45 °C)	2019	[68]
	PEGDME/LiTFSI/LLZ	4.7×10^{-4} (60 °C)	2020	[70]
	PEO/LLTO/LiTFSI	1.6×10^{-4} (24 °C)	2019	[71]
	PEO/Li ₃ PS ₄ /LiTFSI	8.01×10^{-4} (60 °C)	2018	[74]
	PEO/LGPS/LiTFSI	1.21×10^{-3} (80 °C)	2015	[75]
	PEO/LATP/LiClO ₄	5.2×10^{-5} (RT)	2017	[77]
Shorten Li^+ transmission distance	PAN/LLTO/LiClO ₄	6.05×10^{-5} (30 °C)	2017	[78]
	PEO/LiTFSI/PI	2.3×10^{-4} (30 °C)	2019	[80]

etc. These emerging polymerization methods provide prospects for the design of low crystallinity polymers; (3) Focus on the construction and control of the filler-polymer interface. The Li^+ transport paths can be stabilized by designing the filler structure and optimizing the compatibility of the filler-polymer interface; (4) While improving the ionic conductivity, other issues that may exist should also be considered. For example, there is an interface stability problem between SPEs and electrodes like traditional lithium-ion batteries. In addition to designing the electrode, we can also try to solve it in terms of electrolytes, such as increasing the viscoelasticity of polymer to improve the interface stability.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

- [1] J.-M. Tarascon, M. Armand, Issues and challenges facing rechargeable lithium batteries, *Nature* 414 (6861) (2001) 359–367.
- [2] Y. Meesala, A. Jena, H. Chang, R.S. Liu, Recent advancements in Li-ion conductors for all-solid-state Li-ion batteries, *ACS Energy Lett.* 2 (12) (2017) 2734–2751.
- [3] A. Arya, A.L. Sharma, Insights into the use of polyethylene oxide in energy storage/conversion devices: A critical review, *J. Phys. D Appl. Phys.* 50 (44) (2017) 443002.
- [4] X. Cheng, J. Pan, Y. Zhao, M. Liao, H. Peng, Gel polymer electrolytes for electrochemical energy storage, *Adv. Energy Mater.* 8 (7) (2018) 1702184.
- [5] D. Lin, Y. Liu, Y. Cui, Reviving the lithium metal anode for high-energy batteries, *Nat. Nanotechnol.* 12 (3) (2017) 194–206.
- [6] H. Wang, L. Sheng, G. Yasin, L. Wang, H. Xu, X. He, Reviewing the current status and development of polymer electrolytes for solid-state lithium batteries, *Energy Storage Mater.* 33 (2020) 188–215.
- [7] H. Lee, M. Yanilmaz, O. Toprakci, K. Fu, X. Zhang, A review of recent developments in membrane separators for rechargeable lithium-ion batteries, *Energy Environ. Sci.* 7 (12) (2014) 3857–3886.
- [8] D.W. Shin, M.D. Guiver, Y.M. Lee, Hydrocarbon-based polymer electrolyte membranes: importance of morphology on ion transport and membrane stability, *Chem. Rev.* 117 (6) (2017) 4759–4805.
- [9] S. Zhang, K. Ueno, K. Dokko, M. Watanabe, Recent advances in electrolytes for lithium-sulfur batteries, *Adv. Energy Mater.* 5 (16) (2015) 1500117.
- [10] M.R. Palacin, Recent advances in rechargeable battery materials: a chemist's perspective, *Chem. Soc. Rev.* 38 (9) (2009) 2565.
- [11] J. Janek, W.G. Zeier, A solid future for battery development, *Nat. Energy* 1 (2016) 16141.
- [12] Y.S. Hu, Batteries: Getting solid, *Nat. Energy* 1 (2016) 16042.
- [13] Y. Ren, Y. Shen, Y. Lin, C. Nan, Direct observation of lithium dendrites inside garnet-type lithium-ion solid electrolyte, *Electrochem. Commun.* 57 (2015) 27–30.
- [14] S. Zekoll, C. Marriner-Edwards, A. Hekselman, J. Kasemchainan, C. Kuss, D. Armstrong, D. Cai, R.J. Wallace, F.H. Richter, J. Thijssen, P.G. Bruce, Hybrid electrolytes with 3D bicontinuous ordered ceramic and polymer microchannels for all-solid-state batteries, *Energy Environ. Sci.* 11 (2018) 185–201.
- [15] C. Wang, Y. Gong, B. Liu, K. Fu, Y. Yao, E. Hitz, Y. Li, J. Dai, S. Xu, W. Luo, E.D. Wachsman, L. Hu, Conformal nanoscale ZnO surface modification of garnet-based solid-state electrolyte for lithium metal anodes, *Nano Lett.* 17 (2017) 565–571.
- [16] A.B. Puthirath, S. Patra, S. Pal, M. Manoj, A.P. Balan, J. Sankaran, T.N. Narayanan, Transparent flexible lithium ion conducting solid polymer electrolyte, *J. Mater. Chem. A* 5 (22) (2017) 11152–11162.
- [17] K. Liu, M. Wu, H. Jiang, Y. Lin, T. Zhao, An ultrathin, strong, flexible composite solid electrolyte for high-voltage lithium metal batteries, *J. Mater. Chem. A* 8 (36) (2020) 18802–18809.
- [18] G. Chen, F. Zhang, Z. Zhou, J. Li, Y. Tang, A flexible dual-ion battery based on PVDF-HFP-Modified gel polymer electrolyte with excellent cycling performance and superior rate capability, *Adv. Energy Mater.* 8 (25) (2018) 1801219.
- [19] Z. Zhou, Y. Feng, J. Wang, B. Liang, Y. Li, Z. Song, D.M. Itkis, J. Song, A robust, highly stretchable ion-conductive skin for stable lithium metal batteries, *Chem. Eng. J.* 396 (2020) 125254.
- [20] W. Liu, S.W. Lee, D. Lin, F. Shi, S. Wang, A.D. Sendek, Y. Cui, Enhancing ionic conductivity in composite polymer electrolytes with well-aligned ceramic nanowires, *Nat. Energy* 2 (5) (2017) 17035.
- [21] J. Zhang, J. Zhao, L. Yue, Q. Wang, J. Chai, Z. Liu, X. Zhou, H. Li, Y. Guo, G. Cui, L. Chen, Safety-reinforced poly(propylene carbonate)-based all-solid-state polymer electrolyte for ambient-temperature solid polymer lithium batteries, *Adv. Energy Mater.* 5 (24) (2015) 1501082.
- [22] A.C. Balazs, T. Emrick, T.P. Russell, Nanoparticle polymer composites: Where two small worlds meet, *Science* 314 (5802) (2006) 1107–1110.
- [23] J. Janek, W.G. Zeier, A solid future for battery development, *Nat. Energy* 1 (9) (2016) 16141.
- [24] A. Manthiram, X. Yu, S. Wang, Lithium battery chemistries enabled by solid-state electrolytes, *Nat. Rev. Mater.* 2 (3) (2017) 16103.
- [25] D.K. Pradhan, R.N.P. Choudhary, B.K. Samantaray, Studies of dielectric and electrical properties of plasticized polymer nanocomposite electrolytes, Studies of dielectric and electrical properties of plasticized polymer nanocomposite electrolytes, *Mater. Chem. Phys.* 115 (2–3) (2009) 557–561.
- [26] M. Dirican, C. Yan, P. Zhu, X. Zhang, Composite solid electrolytes for all-solid-state lithium batteries, *Mater. Sci. Eng. R Rep.* 136 (2019) 27–46.
- [27] X. Liu, X. Li, H. Li, H.B. Wu, Recent progress of hybrid solid-state electrolytes for lithium batteries, *Chem.-Eur. J.* 24 (69) (2018) 18293–18306.
- [28] M. Keller, A. Varzi, S. Passerini, Hybrid electrolytes for lithium metal batteries, *J. Power Sources* 392 (2018) 206–225.
- [29] X.-B. Cheng, C.-Z. Zhao, Y.-X. Yao, H. Liu, Q. Zhang, Recent advances in energy chemistry between solid-state electrolyte and safe lithium-metal anodes, *Chem* 5 (1) (2019) 74–96.
- [30] D. Chen, M.A. Mahmoud, J.-H. Wang, G.H. Waller, B. Zhao, C. Qu, M.A. El-Sayed, M. Liu, Operando investigation into dynamic evolution of cathode-electrolyte interfaces in a Li-ion battery, *Nano Lett.* 19 (3) (2019) 2037–2043.
- [31] Q. Zhou, J. Ma, S. Dong, X. Li, G. Cui, Intermolecular chemistry in solid polymer electrolytes for high-energy-density lithium batteries, *Adv. Mater.* 31 (50) (2019) 1902029.
- [32] C. Ma, Y. Feng, F. Xing, L. Zhou, Borate decorated anion-immobilized solid polymer electrolyte for dendrite-free, long-life Li metal batteries, *J. Mater. Chem. A* 7 (34) (2019) 19970–19976.
- [33] L. Liu, J.D. Lyu, J.S. Mo, H. Yan, Comprehensively-upgraded polymer electrolytes by multifunctional aramid nanofibers for stable all-solid-state Li-ion batteries, *Nano Energy* 69 (2020) 104398.
- [34] W. Liu, D. Lin, J. Sun, G. Zhou, Y. Cui, Improved lithium ionic conductivity in composite polymer electrolytes with oxide-ion conducting nanowires, *ACS Nano* 10 (12) (2016) 11407–11413.
- [35] P. Lun, P. Liu, H. Lin, Z. Dai, Z. Zhang, D. Chen, Ionic conductivity promotion of polymer membranes with oxygen-ion conducting nanowires for rechargeable lithium batteries, *J. Membr. Sci.* 580 (2019) 92–100.
- [36] H. Hou, B. Wu, T. Zhang, X. Zheng, Anion-immobilized polymer electrolyte achieved by cationic metal-organic framework filler for dendrite-free solid-state batteries, *Energy Storage Mater.* 18 (2019) 59–67.
- [37] H. Chen, H. Tu, C. Hu, Y. Liu, D. Dong, Y. Sun, Y. Dai, S. Wang, H. Qian, Z. Lin, L. Chen, Cationic covalent organic framework nanosheets for fast Li-ion conduction, *J. Am. Chem. Soc.* 140 (3) (2018) 896–899.
- [38] J. Tan, X. Ao, A. Dai, Y. Yuan, J. Lu, Polycation ionic liquid tailored PEO-based solid polymer electrolytes for high temperature lithium metal batteries, *Energy Storage Mater.* 33 (2020) 173–180.
- [39] N. Wu, P.-H. Chien, Y. Qian, Y. Li, H. Xu, N.S. Grundish, B. Xu, H. Jin, Y.-Y. Hu, G. Yu, J.B. Goodenough, Enhanced surface interactions enable fast Li^+ conduction in oxide/polymer composite electrolyte, *Angew. Chem. Int. Ed.* 59 (10) (2020) 4131–4137.
- [40] H. Chen, D. Adekoya, L. Hencz, J. Ma, S. Chen, C. Yan, H. Zhao, G. Cui, S. Zhang, Stable seamless interfaces and rapid ionic conductivity of Ca-CeO₂/LiTFSI/PEO composite electrolyte for high-rate and high-voltage all-solid-state battery, *Adv. Energy Mater.* 10 (21) (2020) 2000049.
- [41] Z. Xue, D. He, X. Xie, Poly(ethylene oxide)-based electrolytes for lithium-ion batteries, *J. Mater. Chem. A* 3 (38) (2015) 19218–19253.
- [42] N. Kamaya, K. Homma, Y. Yamakawa, M. Hirayama, R. Kanno, M. Yonemura, T. Kamiyama, Y. Kato, S. Hama, K. Kawamoto, A. Mitsui, A lithium superionic conductor, *Nat. Mater.* 10 (9) (2011) 682–686.
- [43] H.-J. Deiseroth, S.-T. Kong, H. Eckert, J. Vannahme, C. Reiner, T. Zaiß, M. Schlosser, Li₆PS₅X: A class of crystalline Li-rich solids with an unusually high Li^+ mobility, *Angew. Chem. Int. Ed.* 47 (4) (2008) 755–758.
- [44] H. Lee, P. Oh, J. Kim, H. Cha, S. Chae, S. Lee, J. Cho, Advances and prospects of sulfide all-solid-state lithium batteries via one-to-one comparison with conventional liquid lithium ion batteries, *Adv. Mater.* 31 (29) (2019) 1900376.
- [45] X. Ao, X. Wang, J. Tan, S. Zhang, C. Su, L. Dong, M. Tang, Z. Wang, B. Tian, H. Wang, Nanocomposite with fast Li^+ conducting percolation network: Solid polymer electrolyte with Li^+ non-conducting filler, *Nano Energy* 79 (2021) 105475.
- [46] D. Zhang, L. Zhang, K. Yang, H. Wang, C. Yu, D. Xu, B. Xu, L.-M. Wang, superior blends solid polymer electrolyte with integrated hierarchical architectures for all-solid-state lithium ion batteries, *ACS Appl. Mater. Interfaces* 9 (42) (2017) 36886–36896.
- [47] C. Cao, Y. Li, Y. Feng, C. Peng, Z. Li, W. Feng, A solid-state single-ion polymer electrolyte with ultrahigh ionic conductivity for dendrite-free lithium metal batteries, *Energy Storage Mater.* 19 (2019) 401–407.

- [48] N. Meng, F. Lian, G. Cui, Macromolecular design of lithium conductive polymer as electrolyte for solid-state lithium batteries, *Small* 17 (3) (2021) 2005762, <https://doi.org/10.1002/sml.17.310.1002/sml.202005762>.
- [49] Y.H. Jo, B. Zhou, K. Jiang, S. Li, C. Zuo, H. Gan, D. He, X. Zhou, Z. Xue, Self-healing and shape-memory solid polymer electrolytes with high mechanical strength facilitated by a poly(vinyl alcohol) matrix, *Polym. Chem.* 10 (2019) 6561–6569.
- [50] X. Zhan, J. Zhang, M. Liu, J. Lu, Q. Zhang, F. Chen, Advanced polymer electrolyte with enhanced electrochemical performance for lithium-ion batteries: The effect of nitrile-functionalized ionic liquid, *ACS Appl. Energy Mater.* 2 (3) (2019) 1685–1694.
- [51] B. Zhang, Y. Liu, X. Pan, J. Liu, K. Doyle-Davis, L. Sun, J. Liu, X. Jiao, J. Jie, H. Xie, X. Sun, Dendrite-free lithium metal solid battery with a novel polyester based triblock copolymer solid-state electrolyte, *Nano Energy* 72 (2020) 104690.
- [52] L. Chen, L. Fan, Dendrite-free Li metal deposition in all-solid-state lithium sulfur batteries with polymer-in-salt polysiloxane electrolyte, *Energy Storage Mater.* 15 (2018) 37–45.
- [53] D. Lin, P.Y. Yuen, Y. Liu, W. Liu, N. Liu, R.H. Dauskardt, Y. Cui, A silica-aerogel-reinforced composite polymer electrolyte with high ionic conductivity and high modulus, *Adv. Mater.* 30 (32) (2018) 1802661.
- [54] Z. Wang, C. Miao, W. Xiao, Y. Zhang, P. Mei, X. Yan, Y. Jiang, Effect of different contents of organic-inorganic hybrid particles poly (methyl methacrylate) ZrO_2 on the properties of poly (vinylidene fluoride-hexafluoropropylene)-based composite gel polymer electrolytes, *Electrochim. Acta* 272 (2018) 127–134.
- [55] C. Ma, J. Zhang, M. Xu, Q. Xia, J. Liu, S. Zhao, L. Chen, A. Pan, D.G. Levy, W. Wei, Cross-linked branching nanohybrid polymer electrolyte with monodispersed TiO_2 nanoparticles for high performance lithium-ion batteries, *J. Power Sources* 317 (2016) 103–111.
- [56] X. Fu, C. Li, W. Yu, L.P. Kovatch, W. Zhong, Building ion-conduction highways in polymeric electrolytes by manipulating protein configuration, *ACS Appl. Mater. Interfaces* 10 (5) (2018) 4726–4736.
- [57] O. Sheng, C. Jin, J. Luo, H. Yuan, H. Huang, Y. Gan, J. Zhang, Y. Xia, C. Liang, W. Zhang, $Mg_2B_2O_5$ nanowire enabled multifunctional solid-state electrolytes with high ionic conductivity, excellent mechanical properties, and flame-retardant performance, *Nano Lett.* 18 (2018) 3104–3112.
- [58] X. Fu, W. Yu, F. Xin, L. Scudiero, W. Zhong, Core-shell hybrid nanowires with protein enabling fast ion conduction for high-performance composite polymer electrolytes, *Small* 14 (2018) 1803564.
- [59] P. Yao, B. Zhu, H. Zhai, X. Liao, Y. Zhu, W. Xu, C. Qian, J. Charles, L. Zheng, Z. Jia, PVDF/polygorskite nanowire composite electrolyte for 4V rechargeable lithium batteries with high energy density, *Nano Lett.* 18 (10) (2018) 6113–6120.
- [60] Y. Shi, B. Li, Q. Zhu, K. Shen, W. Tang, Q. Xiang, W. Chen, C. Liu, J. Luo, S. Yang, MXene-based mesoporous nanosheets toward superior lithium ion conductors, *Adv. Energy Mater.* 10 (9) (2020) 1903534.
- [61] W. Tang, T. Shan, C. Zhang, Q. Ma, X. Qian, Y.W. Yang, J. Luo, Simultaneously enhancing the thermal stability, mechanical modulus, and electrochemical performance of solid polymer electrolytes by incorporating 2D sheets, *Adv. Energy Mater.* 8 (24) (2018) 1800866.
- [62] Y. Li, Z. Sun, D. Liu, Y. Gao, Y. Wang, H. Bu, M. Li, Y. Zhang, G. Gao, S. Ding, A composite solid polymer electrolyte incorporating MnO_2 nanosheets with reinforced mechanical properties and electrochemical stability for lithium metal batteries, *J. Mater. Chem. A* 8 (4) (2020) 2021–2032.
- [63] P. Zhai, N. Peng, Z. Sun, W. Wu, W. Kou, G. Cui, K. Zhao, J. Wang, Thin laminar composite solid electrolyte with high ionic conductivity and mechanical strength towards advanced all-solid-state lithium-sulfur battery, *J. Mater. Chem. A* 8 (44) (2020) 23344–23353.
- [64] L. Cao, H. Wu, P. Yang, X. He, J. Li, Y. Li, M. Xu, M. Qiu, Z. Jiang, Graphene oxide-based solid electrolytes with 3D prepercolating pathways for efficient proton transport, *Adv. Funct. Mater.* 28 (50) (2018) 1804944.
- [65] C. Wang, D. Huang, S. Li, J. Yu, M. Zhu, N. Liu, Z. Lu, Three-dimensional-percolated ceramic nanoparticles along natural-cellulose-derived hierarchical networks for high Li^+ conductivity and mechanical strength, *Nano Lett.* 20 (10) (2020) 7397–7404.
- [66] Y. Liu, B. Xu, W. Zhang, L. Li, Y. Lin, C.W. Nan, Composition modulation and structure design of inorganic-in-polymer composite solid electrolytes for advanced lithium batteries, *Small* 16 (15) (2019) 1902813.
- [67] D. Cai, D. Wang, Y. Chen, S. Zhang, X. Wang, X. Xia, J. Yu, A highly ion-conductive three-dimensional LLZO-PEO/LiTFSI solid electrolyte for high-performance solid-state batteries, *Chem. Eng. J.* 394 (2020) 124993.
- [68] G. Tian, Z. Zhao, T. Zinkevich, K. Elies, F. Scheiba, H. Ehrenberg, A crosslinked polyethyleneglycol solid electrolyte dissolving lithium bis (trifluoromethylsulfonyle)imide for rechargeable lithium batteries, *ChemSusChem* 12 (20) (2019) 4708–4718.
- [69] C. Yan, P. Zhu, H. Jia, Z. Du, J. Zhu, R. Orenstein, H. Cheng, N. Wu, M. Dirican, X. Zhang, Garnet-rich composite solid electrolytes for dendrite-free, high-rate, solid-state lithium-metal batteries, *Energy Storage Mater.* 26 (2020) 448–456.
- [70] J. Cha, P.N. Didwal, J.M. Kim, D. Chang, C. Park, Poly(ethylene oxide)-based composite solid polymer electrolyte containing $Li_7La_3Zr_2O_{12}$ and poly (ethylene glycol) dimethyl ether, *J. Membr. Sci.* 595 (2020) 117538.
- [71] K. Liu, R. Zhang, J. Sun, M. Wu, T. Zhao, Polyoxethylene (PEO)/PEO-perovskite/PEO composite electrolyte for all-solid-state lithium metal batteries, *ACS Appl. Mater. Interfaces* 11 (50) (2019) 46930–46937.
- [72] N. Kamaya, K. Homma, Y. Yamakawa, M. Hirayama, R. Kanno, M. Yonemura, T. Kamiyama, Y. Kato, S. Hama, K. Kawamoto, A. Mitsui, A lithium superionic conductor, *Nat. Mater.* 10 (2011) 682–686.
- [73] S. Wang, Y. Zhang, X. Zhang, T. Liu, Y. Lin, Y. Shen, L. Li, C. Nan, High-conductivity argyrodite Li_6PS_5Cl solid electrolytes prepared via optimized sintering processes for all-solid-state lithium-sulfur batteries, *ACS Appl. Mater. Interfaces* 10 (49) (2018) 42279–42285.
- [74] S. Chen, J. Wang, Z. Zhang, L. Wu, L. Yao, Z. Wei, Y. Deng, D. Xie, X. Yao, X. Xu, In-situ preparation of poly(ethylene oxide)/ Li_3PS_4 hybrid polymer electrolyte with good nanofiller distribution for rechargeable solid-state lithium batteries, *J. Power Sources* 387 (2018) 72–80.
- [75] Y. Zhao, C. Wu, G. Peng, X. Chen, X. Yao, Y. Bai, F. Wu, S. Chen, X. Xu, A new solid polymer electrolyte incorporating $Li_{10}GeP_2S_{12}$ into a polyethylene oxide matrix for all-solid-state lithium batteries, *J. Power Sources* 301 (2015) 47–53.
- [76] F.J. Simon, M. Hanauer, A. Henss, F.H. Richter, Jürgen Janek, Properties of the interphase formed between argyrodite-type Li_6PS_5Cl and polymer-based PEO10:LiTFSI, *ACS Appl. Mater. Interfaces* 11 (45) (2019) 42186–42196.
- [77] H. Zhai, P. Xu, M. Ning, Q. Cheng, J. Mandal, Y. Yang, A flexible solid composite electrolyte with vertically aligned and connected ion-conducting nanoparticles for lithium batteries, *Nano Lett.* 17 (2017) 3182–3187.
- [78] W. Liu, S.W. Lee, D. Lin, F. Shi, S. Wang, A.D. Sendek, Y. Cui, Enhancing ionic conductivity in composite polymer electrolytes with well-aligned ceramic nanowires, *Nat. Energy* 2 (2017) 17035.
- [79] W. Tang, S. Tang, X. Guan, X. Zhang, Q. Xiang, J. Luo, High-performance solid polymer electrolytes filled with vertically aligned 2D materials, *Adv. Funct. Mater.* 29 (2019) 1900648.
- [80] J. Wan, J. Xie, X. Kong, Z. Liu, K. Liu, F. Shi, A. Pei, H. Chen, W. Chen, J. Chen, X. Zhang, L. Zong, J. Wang, L. Chen, J. Qin, Y. Cui, Ultrathin, flexible, solid polymer composite electrolyte enabled with aligned nanoporous host for lithium batteries, *Nat. Nanotechnol.* 14 (2019) 705–711.
- [81] X. Zhang, J. Xie, F. Shi, D. Lin, Y. Liu, W. Liu, A. Pei, Y. Gong, H. Wang, K. Liu, Y. Xiang, Y. Cui, Vertically aligned and continuous nanoscale ceramic-polymer interfaces in composite solid polymer electrolytes for enhanced ionic conductivity, *Nano Lett.* 18 (6) (2018) 3829–3838.