

Polyethylene Oxide-Based Solid-State Composite Polymer Electrolytes for Rechargeable Lithium Batteries

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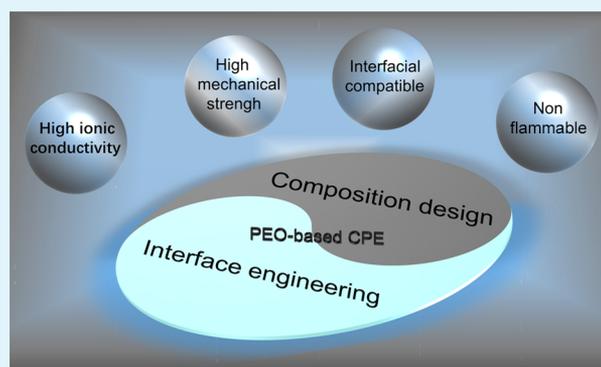
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ABSTRACT: Solid-state polymer electrolytes are considered to be the most promising electrolytes for next-generation high-energy rechargeable lithium batteries due to the advantages of high safety, good mechanical flexibility, and easy film-formation ability. Among all the polymers, polyethylene oxide (PEO) is demonstrated to be a feasible polymer host, based on its high dielectric constant and strong lithium salt dissolving ability. However, the practical application of PEO in the all-solid-state lithium batteries is limited mainly by its low ionic conductivity at room temperature. For decades, researchers dedicate to increase the ion conductivity at room temperature and mechanical properties according to the technology strategy of composite polymer electrolytes. In particular, the electrode/electrolyte interface structure is designed and optimized according to the requirement of different battery systems. Accordingly, in this review, the basic characteristics, ion transport mechanism, composite mechanism of inert/active fillers with polymers, and electrode/electrolyte interface structures are evaluated for the PEO-based composite polymer electrolytes. Finally, the outlook is presented for future development of the solid-state polymer electrolytes and high-energy rechargeable lithium batteries.

KEYWORDS: rechargeable lithium batteries, solid-state electrolyte, composite polymer electrolyte, polyethylene oxide, interface



1. INTRODUCTION

Lithium ion batteries have occupied a dominant position in the field of portable appliances and electric vehicles due to the high energy density and long cycle life. However, traditional lithium ion batteries still have certain hidden troubles in safety, especially the use of volatile organic liquid electrolytes, which easily leads to leaking, burning, and explosion accidents. In order to improve the safety of batteries, replacing traditional liquid electrolytes with solid-state electrolytes (SEs) has become a potential alternative.¹

SEs can be divided into solid-state inorganic electrolytes and solid polymer electrolytes (SPEs) according to their different components. There are two typical systems in solid-state inorganic electrolytes: oxide solid-state electrolytes (O-SEs) and sulfide solid-state electrolytes (S-SEs).² In general, solid-state inorganic electrolytes have a high ion conductivity and lithium ion transference number at room temperature. In particular, the ion conductivity of S-SEs (such as $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ and $\text{Li}_{9.54}\text{Si}_{1.74}\text{P}_{1.44}\text{S}_{11.7}\text{Cl}_{0.3}$) can reach up to $10^{-2} \text{ S cm}^{-1}$ at room temperature, near or even beyond the conductivity of liquid electrolytes.^{3,4} However, there are some disadvantages for such S-SEs, such as large grain boundary resistance, a complex preparation process, and poor interface compatibility between electrolytes and electrodes. The practical application

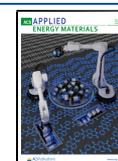
of solid-state inorganic electrolytes is seriously restricted by such poor characteristics.⁵ Compared with solid-state inorganic electrolytes, SPEs have good interface compatibility and mechanical properties, which have emerged in the process of practicalization due to simple preparation technology and easy film-forming properties.⁶ Particularly, polyethylene oxide (PEO) complexed with alkali metal salts shows certain advantages on ion conductivity, which was discovered by Wright et al. in 1973.⁷ Furthermore, Armand proposed complex polymers and lithium salts as solid-state electrolytes for lithium ion batteries.⁸ Subsequently, research and development of SPEs are moved gradually on the fast track.

Gel polymer electrolytes (GPEs) and SPEs are two important types of polymer electrolytes, according to the state of their components. Common polymer hosts are used in GPEs and SPEs together, including poly(ethylene oxide) (PEO),⁹ polyacrylonitrile (PAN),¹⁰ polyvinylidene fluoride

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(PVDF),¹¹ polyvinylidene fluoride-hexafluoropropylene copolymer (PVDF-HFP),¹² poly(methyl methacrylate) (PMMA),¹³ poly(propylene oxide) (PPO),¹⁴ and poly(vinylidene chloride) (PVDC).¹⁵ Usually, GPEs are prepared by swelling polymers in liquid electrolytes. It means that the safety problem is not eliminated completely because flammable organic liquids are still used as the solvent of lithium salts in GPEs.¹⁶ On the contrary, without any organic liquids, lithium salts can be readily dissolved into the polymer matrix through the interaction of lithium ions and ether oxygen bonds to form SPEs. Because of its excellent safety, high mechanical flexibility, good viscoelasticity, and easy film formation, an SPE is considered to be a promising electrolyte system for practical battery applications in the future.¹⁷

More specially, SPEs can be mainly divided into the following three electrolyte systems: polycarbonate-based electrolytes, polysiloxane-based electrolytes, and polyethylene oxide (PEO) electrolytes. Here, PEO demonstrates many excellent characteristics, such as good solubility for lithium salts, high stability to the lithium metal, and low glass transition temperature. Therefore, PEO is widely investigated as an ideal polymer matrix to fabricate SPEs. At present, the ionic conductivity of the PEO-based SPE at room temperature is low (only 10^{-8} to 10^{-4} S cm^{-1}), but it is still the most competitive candidate electrolyte material for building solid-state batteries.¹⁸

Compared with previous review papers of SPEs, here, this review focuses on PEO-based composite polymer electrolytes (CPEs) with various fillers, which are more suitable to probe and discuss the interaction mechanism of PEO and fillers, as well as the ion transport mechanism in depth. Meanwhile, some performance verifications of PEO-based CPEs in different battery systems are introduced, including the interfacial stability and electrochemical performance. In addition, this review summarizes the corresponding strategy and development status of PEO-based CPEs. Moreover, a perspective of the future development and challenges is proposed for PEO-based CPEs, based on the requirements of good safety, high energy density, and long cycling stability for lithium batteries.

2. PEO-BASED SOLID-STATE POLYMER ELECTROLYTE (SPE)

Intrinsically, PEO is a crystalline, thermoplastic, and water-soluble polymer with the chemical formula of $\text{H}-(\text{O}-\text{CH}_2-\text{CH}_2)_n-\text{OH}$. The molecular weight of PEO can vary within a wide range, usually above $20,000 \text{ g mol}^{-1}$; those with a molecular weight of less than $20,000 \text{ g mol}^{-1}$ are called polyethylene glycol (PEG).¹⁹

As mentioned above, lithium salts can be readily dissolved into the PEO matrix to form SPEs. In the framework of SPEs, ethylene oxide (EO) units have a high donor number for Li ions and good chain flexibility, which are helpful to enhance the transport of Li ions. In addition, PEO has a high dielectric constant and strong solubility to lithium salts. PEO is often prepared by ring-opening polymerization of ethylene oxide with the presence of catalysts. At room temperature, the crystallinity of PEO can reach 70–84%, and it has a low glass transition temperature ($-63 \text{ }^\circ\text{C}$).¹⁹

PEO is a semicrystalline polymer at room temperature, and the ion transportation is mainly dominated by the irregular complex chain movement of the amorphous-phase PEO. The transport of Li ions occurs by intrachain or interchain hopping

in the PEO-based SPE, with the processes of breaking/forming lithium–oxygen (Li–O) bonds (Figure 1). The continuous

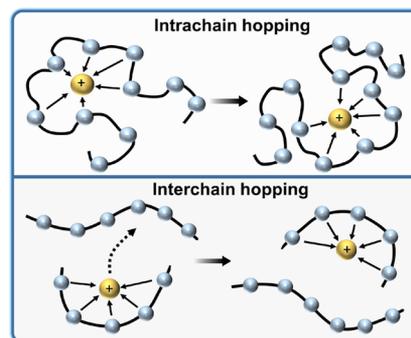


Figure 1. Ion transport mechanism in PEO.

segmenting rearrangement of ligands (EO) leads to long-range displacement of Li ions, thereby achieving rapid transmission of Li ions.¹⁹ In addition, the PEO-based SPE exhibits similar mechanical properties to a true solid because of the chain entanglement of the polymer host. Meanwhile, Li ions seem to remain in a liquid-like state in a microscopic environment, indicating effective ion conduction by the local segmental movement of the polymer.²⁰

At room temperature, the transport of Li ions is limited mainly by low ion conductivity of PEO (high crystallinity), which makes it difficult to meet the charge and discharge requirements of normal Li ion batteries. It was early believed that ion mobility occurred inside crystalline PEO with higher ion conductivity.^{21,22} However, it is generally believed from recent evidence that ion conduction is mainly carried out in the amorphous region of PEO, and the high ion conductivity is usually related to the formation of the amorphous phase in the SPE.²³ Usually, ions can move in the space provided by the free volume of the polymer body, which exhibits good ion conductivity above its melting temperature. However, the polymer presents a molten or amorphous state at this time, resulting in reduced mechanical properties and a limited electrochemical stability window. Thereby, the growth of lithium dendrites is induced correspondingly in the polymer electrolyte, triggering the safety issue of batteries. As the temperature lowers, the ion conductivity decreases rapidly due to the substantial increase in the crystallinity of PEO. Therefore, promoting segment movement and high ion conductivity by adjusting the crystallinity of PEO at room temperature is very important.²⁴

In order to improve the ion conductivity of PEO-based SPEs at room temperature, previous research focused on the adjustment of the amorphous form, such as plasticizing,²⁵ blending,²⁶ copolymerization,²⁷ cross-linking,²⁸ and compounding with fillers to reduce the crystallinity of the system, which can improve electrochemical stability and inhibit the formation of lithium dendrites to a certain extent. Therefore, a composite polymer electrolyte (CPE) is considered to be one of the important technical strategies for the development of PEO-based SPEs in the future because it can combine the merits of both the polymer matrix and fillers.^{29,30}

3. PEO-BASED COMPOSITE POLYMER ELECTROLYTE (CPE)

Improving the ion conductivity and ion transfer rate of SPEs at room temperature can be achieved by adding fillers into the polymer matrix. Compared with a pure SPE, a CPE has a lower melting temperature and glass transition temperature. Introducing fillers into polymers can improve the ion conductivity and mechanical properties of CPEs. A high ion conductivity can promote the rapid transportation of lithium ions in the bulk of CPEs and at the interface between electrodes and CPEs and reduce the interfacial impedance. The enhanced mechanical properties can inhibit the deformation of the interface and the growth of lithium dendrites during the cycle. Furthermore, the electrochemical/chemical stability and structural stability of the electrode/electrolyte interface can be significantly improved. Early research on the fillers is mainly focused on the “inert fillers”, without transferring Li ions. On the one hand, the fillers are added to improve the mechanical properties of SPEs. On the other hand, the fillers can also inhibit the crystallization of polymers and enhance the movement ability of the PEO segment, thereby improving the ion conductivity of CPEs. As shown in Figure 2, there are four types of inert fillers for

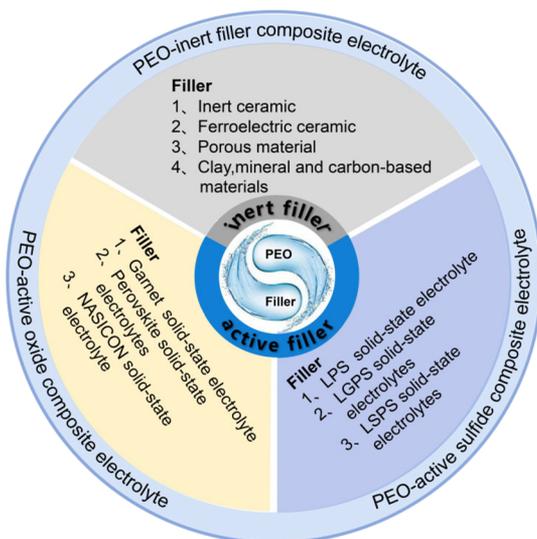


Figure 2. Schematic diagram of the PEO-based CPE with different fillers.

fabricating PEO-based CPEs: (1) inert ceramic, (2) ferroelectric ceramic, (3) porous materials, and (4) clay, mineral, and carbon-based materials. In recent years, with the development of solid inorganic electrolytes, “active fillers” with a good capability of transferring Li ions have also been used to compound with polymers, such as S-SEs and O-SEs (Figure 2).³¹ While reducing the degree of polymer crystallization, the “active fillers” further improve the ion conductivity. Therefore, the “active fillers” could help to construct the CPE with different components and adjustable structures. The increase in the ion conductivity of CPEs is mainly attributed to the decrease in the crystallinity of PEO based on the physical/chemical interactions between the filler particles and PEO chains. Here, as the physical interaction, the addition of fillers can promote the increase in the “free volume” and mobility of polymer segments near the filler

surface, which can significantly increase the formation of the amorphous phase and reduce the crystallinity of PEO. Chemical interaction worked mainly as Lewis acid–base interaction between Lewis acid sites on the filler surface and ionic substances (such as EO segments and lithium salt anions), which can generate additional sites and favorable conduction pathways for ion transport, thus significantly increasing the solubility of lithium salts and reducing the crystallinity of PEO. In addition, there are some other interaction mechanisms for impacting on the crystallinity of PEO, such as osmotic behavior, adsorption, and dielectric polarization.

3.1. Transportation Path of Lithium Ions in the PEO-Based CPE with Different Fillers. According to the morphology and structure for incorporating into the PEO matrix, the inert and active fillers can be divided into four types: zero-dimensional (0D) particle fillers, one-dimensional (1D) linear fillers, two-dimensional (2D) sheet fillers, and three-dimensional (3D) structural fillers. In addition, 3D structural fillers can be further divided into three types: array structure, porous structure, and interpenetrating cross-linked network structure according to their unique morphology (Figure 3).

In general, the 0D particle fillers include metal oxide ceramic particles, ferroelectric ceramic particles, and inorganic solid electrolyte active fillers. The performance of CPEs is affected by the intrinsic characteristics, size, shape, and content of these fillers. In particular, the content of the fillers plays a decisive role in the performance of the CPE and ion transmission paths. The transport of Li ions is mainly through the polymer matrix phase in the CPE with a low filler content, along the permeation network formed by the matrix phase and filler particles in the CPE with a medium filler content, and through the continuous ceramic particle phase in the CPE with a high filler content. Of course, according to the different intrinsic characteristics of different fillers, the definition of the content is also relatively different.^{60,77,88,92,100,107}

The 1D linear fillers, such as nanowires, and nanotubes, are usually prepared from 0D fillers by means of electrospinning. The continuous transport pathways for Li ions and high ion conductivity in CPEs can be provided by these 1D fillers. Usually, Li ions are transferred along the interface between the filler and the polymer based on the consideration of high active sites. Thus, the arrangement of 1D fillers into the polymer matrix has a great influence on the performance of CPEs. The random arrangement of 1D fillers could hinder the continuous transportation of Li ions due to the irregular distribution. Fillers arranged in a straight line could be beneficial to form a continuous path throughout the whole polymer host in order to obtain high ion conductivity.^{52,70,71,95} The 2D sheetlike fillers, such as layered clay, natural mineral vermiculite sheets, g-C₃N₄ nanosheets, and garnet nanosheets, also can be used to construct continuous conducting networks to achieve fast ion transport in the PEO-based CPE.^{60,69,73,89}

The ion transport in the PEO-based CPE with 3D structural fillers is complicated because of their complex structure. For example, in the CPE with 3D array fillers prepared by the template method, lithium ions can rapidly transport through the bulk or the interface of the fillers. In the CPE with some porous fillers, such as MOFs and molecular sieves, lithium ion transportation is usually fast and continuous along the interface of the pore structure. In addition, in the CPE with a filler of 3D interpenetrating cross-linked network structures prepared by

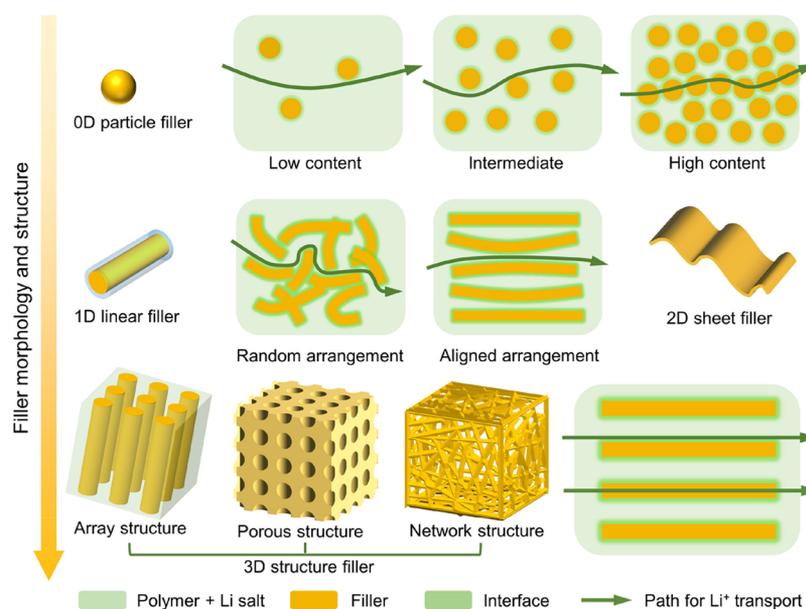


Figure 3. Schematic diagram of the transportation path of Li ions in the PEO-based CPE with different filler morphologies.

Table 1. Performance Parameters of the PEO-Based CPE with Inert Fillers^a

filler	year	electrolyte composition	ionic conductivity (S/cm)	temperature	ref.
inert ceramic	2010	PEO ₁₈ -LiTFSI-10% acid-modified SiO ₂	about 10 ⁻⁵	RT	47
	2011	PEO ₁₈ -LiTFSI-SiO ₂ -PP ₁₃ TFSI	3.6 × 10 ⁻⁵	25 °C	48
	2015	PEO-LiClO ₄ -MUSiO ₂	1.2 × 10 ⁻³	60 °C	50
	2019	PEO-PPO-PEO-LiTFSI-25% nano-SiO ₂	4.58 × 10 ⁻⁵	RT	51
	2018	AAO-PEO-LiTFSI-Al ₂ O ₃	5.82 × 10 ⁻⁴	RT	53
ferroelectric ceramic	2000	PEO ₈ -LiClO ₄ -1.4% BaTiO ₃	1.2 × 10 ⁻³	70 °C	55
	2015	PEO-LiClO ₄ -20% MMT-8% BaTiO ₃ -38% SrTiO ₃	3.46 × 10 ⁻⁵	50 °C	57
	2017	PEO-PVdF-HFP-LiClO ₄ -PC-6% BaTiO ₃	6 × 10 ⁻³	RT	58
	2019	PEO-LiTFSI-8% 5 nm BaTiO ₃	2.2 × 10 ⁻⁵	25 °C	59
porous material			1.9 × 10 ⁻³	80 °C	
	2005	PEO-LiClO ₄ -LiAlSBA	3.4 × 10 ⁻⁵	RT	64
	2013	PEO-LiTFSI-10% MOF-5	3.16 × 10 ⁻⁵	25 °C	61
	2018	PEO-LiTFSI-COF	1.33 × 10 ⁻³	200 °C	66
clay, mineral, and carbon-based materials	2018	PEO-LiTFSI-SSZ-13	1.19 × 10 ⁻³	60 °C	65
	2020	PEO-LiClO ₄ -10% clay-CNT	2.07 × 10 ⁻⁵	25 °C	71
	2019	PEO-LiTFSI-10% HNT-1% LFP	9.23 × 10 ⁻⁵	25 °C	70
	2019	PEO-LiTFSI-5% g-C ₃ N ₄	1.52 × 10 ⁻⁴	60 °C	72
	2019	PEO-LiTFSI-VAVS	1.89 × 10 ⁻⁴	25 °C	69
2019	PEO-LiTFSI-50% ENR	6.45 × 10 ⁻⁵	RT	67	

^aRoom temperature referred to as RT (applicable to all forms in the text).

hot pressing, high temperature annealing, quenching, and hydrogel technology, lithium ions can transport together through the filler phase, the polymer matrix, and the interface between fillers and the polymer host.^{53,54,61,62,65–67,91,98,103,104}

In short, the transport mechanism of lithium ions is very complex in PEO-based CPEs due to the variety of fillers and composite methods. It means that the transport mechanism of lithium ions depends strongly on the composition strategy with fillers and structures of CPEs. Correspondingly, CPEs with high ion conductivity and a stable interface can be achieved by rational composition and structure design.

3.2. PEO-Based CPE with Inert Fillers. In 1982, the inert Al₂O₃ filler was first introduced into the (PEO)₈-LiClO₄ system and was verified to significantly enhance the mechanical properties and ion conductivity of SPEs.³² Subsequently, a large number of inorganic inert fillers were used to improve the

performance of CPEs, including inorganic ceramics, ferroelectric ceramics, porous materials, clays, minerals, and carbon-based materials (Table 1).

Adding ceramic powders into SPEs can not only inhibit the crystallization kinetics but also promote the retention of the amorphous phase below ambient temperature. It is demonstrated that there is no direct interaction between filler particles and polymer chains.³³ The enhancement of conductivity in CPEs may be attributed to indirect specific interactions of the surface groups on filler particles with polymer chains and lithium salt anions, as well as to osmotic behavior or Lewis acid–base interactions. In addition, the main chain dynamics for controlling ion transportation is not significantly affected by adding fillers into polymers. When fillers are added into polymers, the corresponding results are only the increase in the “free volume” and mobility of the

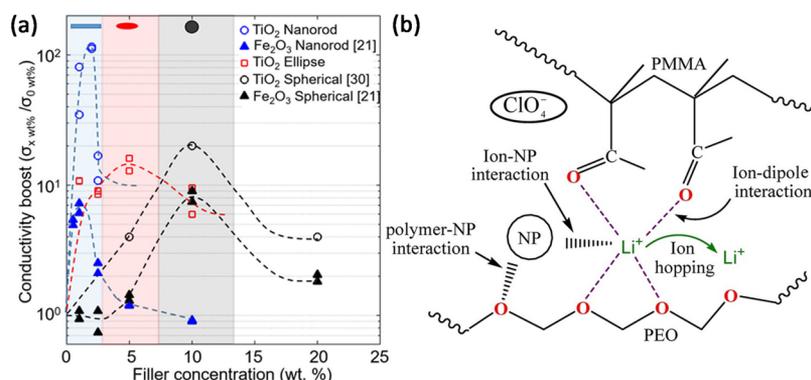


Figure 4. (a) Conductivity boost versus nanofiller concentration at room temperature for (PEO)₁₀:LiClO₄ with variously shaped nanofillers. (b) Lithium ion transport model of the PEO-PMMA-based nanocomposite electrolyte. Reproduced with permission from ref 46. Copyright 2017 Elsevier.

polymer segment near the filler surface, rather than the increase in the number of charge carriers.^{34,35} Therefore, the content and dispersibility of fillers are the key factors affecting the ion conductivity of CPEs.

3.2.1. PEO-Based CPE with Inert Ceramic Fillers. Here, inert ceramic fillers mainly refer to metal oxides, including TiO₂,³⁶ Al₂O₃,³⁷ SiO₂,³⁸ ZrO₂,³⁹ and ZnO.⁴⁰ Moreover, some composite metal oxides and sulfides are also used as fillers to improve the conductivity of the PEO-based CPE, such as MgAl₂O₄, LiAlO₂, and ZnS. Usually, these inert ceramic fillers exist in the form of nano- or micrometer particles, the function of which is to reduce the crystallinity of polymers and enhance mechanical properties.⁴¹ The enhancement of conductivity in the PEO-based CPE is due to the creation of additional sites and favorable conduction pathways for ion transport through Lewis acid–base interactions between filler surface groups (H/OH) and ionic substances.⁴²

Generally, the size of fillers is considered to be a key factor in improving the performance of the PEO-based CPE.⁴³ Compared to the CPE with added nanosized Al₂O₃ fillers, the conductivity of the electrolyte film with added microsized Al₂O₃ fillers is an order of magnitude higher. In addition, it is found from SEM images that the microsized filler can be distributed well on the polymer matrix. Therefore, the conductivity of the CPE is not linearly related to the particle size of fillers. The concentration, surface area, and morphology of inorganic fillers are also crucial factors affecting the conductivity of the PEO-based CPE.⁴⁴ As shown in Figure 4a, the filler concentration, which provides the maximum improvement in ion conductivity, is inversely proportional to the aspect ratio (AR): spherical nanoparticles at the concentration of 10 wt % (AR = 1), ellipse at 5 wt % (AR about 4.4), and nanorods at 1–2 wt % (AR close to 6.6). This shows that in pure metal oxide nanofillers, the performance in terms of ion conductivity cannot be distinguished based on the chemical properties. On the contrary, the shape of the nanofillers has a much more significant effect on the performance.⁴⁵ At the same time, the dielectric properties of the nanofillers are also important factors on the performance of the CPE.⁴⁶ The dielectric and electrical properties of the CPE composed of PEO and polymethyl methacrylate (PMMA) blends, containing different fillers at fixed concentrations, are shown in Figure 4b. The dispersion of nanoparticles interferes with the parallel arrangement of some EO⋯Li⁺, CO⋯Li⁺, and CO⋯Li⁺⋯OE ion–dipole pairs, leading to the decrease in dielectric polarization and hindering the dynamics of

cooperative polymer chains. In other words, the dielectric polarization strength and structural dynamics mask the contribution of the increase in the amount of the amorphous phase to the enhancement of the lithium ion conduction mechanism in this type of nanofiller containing solid ion–dipole complexes. This also verifies that ion conduction is based on the combination of the jumping mechanism and cooperative polymer segment motion.

With further research, the surface modification method of fillers is proposed to increase the dispersion of filler particles in the PEO matrix, which can increase the number of carrier charges and further improve the performance of CPEs.^{47,48} Furthermore, the traditional preparation of CPEs, with ceramic particles directly dispersed into the polymer matrix, could lead to the condensation of nanomaterials. It indicates that there are still large areas of crystallization in the polymer matrix.⁴⁹ Therefore, the in situ synthesis of ceramic filler particles in PEO is proposed, and monodisperse ceramic particles can be formed in the PEO matrix by in situ hydrolysis. There is a stronger chemical/mechanical interaction between the uniformly distributed filler particles and the PEO chain, which significantly suppresses the crystallization of PEO and thus facilitates polymer segmental motion for ion conduction.⁵⁰

The influence of material morphology on conductivity cannot be ignored while considering the filler type and surface characteristics. As shown in Figure 3, constructing a 1D or 2D morphology filler helps to enhance CPE performance. The 1D nanowires can provide more continuous ion conduction pathways, thus increasing ion conductivity.⁵¹ For example, the ZrO₂ nanowires doped with Y₂O₃ can be prepared by electrospinning. The nanowires are rich in positively charged oxygen vacancies on the surface, which could combine with anions and then release more lithium ions, thereby significantly enhancing the ion conductivity of the CPE.⁵² In addition, the CPE with 3D fillers also shows excellent performance. For example, using surface-modified anodic alumina (AAO) as a ceramic scaffold, the AAO-PEO composite electrolyte with densely packed, vertically aligned, and continuous nanoscale ceramic–polymer interface can be prepared. A vertically aligned interface structure enables the CPE to exhibit superior ion conductivity and high mechanical strength.⁵³ Similarly, the 3D cross-linked network PEO@nano-SiO₂ CPE can be also prepared to improve its electrochemical and mechanical stability. Specifically, the PEO@nano-SiO₂ CPE presents a high ion conductivity (4.65×10^{-3} S cm⁻¹) at room temperature, a broad electrochemical stability window with

5.4 V vs Li/Li⁺, a high ion transference number (0.45), and excellent mechanical strength and interfacial stability.⁵⁴ Hence, there are two different modes of lithium ion transport in CPEs. The first one is conventional lithium ion transport by ether oxygen-assisted hopping or polymer chain movement, while the second approach is to enhance lithium ion transport along the ceramic–polymer interface. The ion transport mechanism and conduction characteristics of CPEs can be regulated by adding fillers of different types and morphologies.⁵³

3.2.2. PEO-Based CPE with Ferroelectric Ceramic Fillers.

Because of the spontaneous polarization in the lattice, ferroelectric materials usually have a high dielectric constant. Therefore, introducing ferroelectric materials into the SPE can promote the ionization of lithium salts and thus improve the conductivity of CPEs, including BaTiO₃,⁵⁵ PbTiO₃,⁵⁵ SrBi₄Ti₄O₁₅,⁵⁶ and LiNbO₃.⁵⁵ The conductivity of CPEs with ferroelectric ceramic fillers depends on the combination of lithium salts and ferroelectric materials. The conductivity enhancement in the PEO–LiX CPE with ferroelectric ceramic fillers is rationalized by correlating the combination of anions with lithium cations and the spontaneous polarization of the ferroelectric ceramic materials due to their particular crystal structure.⁵⁵

An electric field has an important influence on the ion conductivity of CPEs with ferroelectric ceramic fillers.⁵⁷ One-order enhancement of conductivity due to the field is observed at 323 K. The electric field (beyond 15 V cm⁻¹) can significantly increase the ion conductivity (by an order of magnitude) in the range of 0–100 V cm⁻¹, further verifying the field dependence of conductivity. In addition, the particle size and content of ferroelectric ceramic fillers are also important factors on the performance of CPEs. For example, the ion conductivity of CPEs gradually increases with increasing the content of BaTiO₃ fillers and reaches a maximum of 6 × 10⁻³ S cm⁻¹ at 6 wt % BaTiO₃ filler.⁵⁸ However, when the content of BaTiO₃ exceeds 6 wt %, the CPE film shows a rather heterogeneous morphology, which is due to the immiscibility caused by excessive addition of BaTiO₃.⁵⁸ The crystallinity of the CPE decreases with the increase in the content of BaTiO₃ and the decrease in average particle size.⁵⁹ Meanwhile, various shapes of ferroelectric ceramic fillers also have a great effect on the performance of CPEs. For example, 5 wt % BaTiO₃ nanowires, nanocubes, and nanospheres are added to SPEs, respectively, and then, the CPE with BaTiO₃ nanospheres shows the highest ionic conductivity (1.8 × 10⁻⁵ S cm⁻¹) at 25 °C.⁶⁰ Therefore, ferroelectric ceramic fillers can effectively improve the ion conductivity of CPEs because of their high dielectric constant. In the future, we should further explore the composite mechanism and expand the composite system.

3.2.3. PEO-Based CPE with Porous Material Fillers. The porous material fillers not only have good compatibility with the polymer matrix but also provide a favorable transmission channel for lithium ions due to the macromolecular pore structures. Therefore, adding porous material fillers into the PEO-based CPE is also an effective way to improve the ion conductivity.

As typical porous material fillers, metal–organic frameworks (MOFs) have attracted attention in various applications due to their high specific surface area and an ordered microporous structure. The addition of MOFs can reduce the crystallinity of PEO and increase the ion conductivity of CPEs to a certain extent and improve the stability of CPEs to the lithium anode.⁶¹ Recently, a Zn₄O(1,4-benzenedicarboxylate)₃ metal–

organic framework (MOF-5) was first incorporated into a PEO-based CPE by an in situ method. The highest ion conductivity of 3.16 × 10⁻⁵ S cm⁻¹ at 25 °C was obtained for the CPE with 10 wt % MOF-5.⁶¹ Usually, it is believed that in such a CPE, the enhancement of conductivity is mainly caused by the interaction of Lewis acid groups on the MOF surface with PEO and lithium salts, which inhibits the crystallization of PEO and facilitates the formation of lithium ion transport channels on the filler surface. Subsequently, some other MOFs as fillers were also demonstrated to be effective to improve the conductivity of PEO-based CPEs, such as the UIO-66 MOF, copper benzene dicarboxylate MOF (Cu-BDC MOF), and magnesium-benzene tricarboxylate MOF (Mg-BTC MOF).

A molecular sieve is a kind of typical 3D porous material with a strong adsorption ability, high selectivity, and high temperature resistance, which can be also used as a new type of porous material filler for fabricating CPEs. In particular, a shape-selective molecular sieve ZSM-5 is added as a filler to a PEO-based CPE, which can effectively reduce the crystallinity of PEO, through the Lewis acid–base interaction between the Lewis acid site on the framework of ZSM-5 and the ether oxygen in the PEO chain.^{62,63} Subsequently, the mesoporous molecular sieve LiAISBA with a pore size of about 7 nm was also added to the PEO/LiClO₄ system to prepare the CPE. The increase in ion conductivity was mainly due to the increase in continuous amorphous domains and the decrease in crystallinity.⁶⁴ Meanwhile, the improvement of ion transport along the LiAISBA surface is beneficial to the improvement of CPE conductivity. Similarly, the highly ordered nanoporous SSZ-13 can be also used as a filler to prepare CPEs. The nanoporous adsorption effect, provided by SSZ-13 in CPEs, is found to significantly improve the lithium ion conductivity (1.91 × 10⁻³ S cm⁻¹ at 91 °C) and widen the electrochemical stability window to 4.7 V vs Li/Li⁺.⁶⁵ The high ion conductivity of such a CPE can be attributed to the following factors: (1) the low crystallinity of the CPE due to the addition of fillers, (2) the surface with opposite charges promoting dissociation of the lithium salt, and (3) a continuous permeation pathway produced by the nanoporous adsorption of the Lewis basic center and lithium ions.

A covalent organic framework (COF) is a new type of organic porous polymer with a periodic structure, adjustable function, and potential as a unique ion conductor or transporter. Using a bottom-up self-assembly approach, dynamic PEO groups with a high concentration can be accumulated into the networks of imine-bonded 2D COFs in a crystalline state. That can solve lithium ions for rapid transport through their segmental motion in rigid 2D COF structures. This also reveals that the conductivity of lithium ions depends on the kinetics and length of the PEO chain in a crystalline state.⁶⁶

In general, this kind of porous material has a stable and fixed pore structure, which can greatly enhance the mechanical strength of CPEs and effectively inhibit the structural change of CPEs during the battery cycle. Therefore, through reasonable regulation, it can provide a good lithium ion transmission channel and has great application potential in batteries.

3.2.4. PEO-Based CPE with Clay, Mineral, and Carbon-Based Materials. Among all the fillers investigated previously, natural clay and minerals are electronically conductive inert materials with adjustable microstructures, which can be introduced into SPEs for improving the performance and reducing costs.⁶⁷ Among them, clay generally has a multi-

layered nanostructure and is often used as an ideal polymer filler. For example, montmorillonite (MMT), as a layered body, can provide a large interfacial contact area. In particular, MMT has high dielectric properties for improving the solubility of lithium salts and a good cation exchange ability for participating in the embedding and swelling process, which makes sure that MMT has a better application prospect in CPEs. In addition, the performance improvement of CPEs is mainly attributed to the high chemical affinity between fillers and PEO, which leads to higher microstructure uniformity for the polymer.⁶⁸ In a similar way, after further treatment, some natural minerals such as vermiculite and elochite can be also used in CPEs with good results. For example, the vertically arranged vermiculite sheets (VAVS) can be added into the PEO matrix to form a continuous and penetrating polymer–filler interface. A high ion conductivity (1.89×10^{-4} S cm⁻¹) is achieved with a lithium ion transference number close to 0.5.⁶⁹ Along with the enhancement of the mechanical strength, LiLi symmetric cells using CPEs are stable over 1300 h with a low overpotential.⁶⁹ In addition, halloysite nanotubes (HNT), with a tubular structure, are also incorporated into PEO because they can provide channels for ion transport. In this PEO-HNT composite electrolyte, adding a small amount of lithium iron phosphate (LFP) greatly improves the stability of the interface between the electrolyte and the LFP electrode, thereby achieving good ion conductivity.⁷⁰ As a result, the introduction of electrode active materials would be helpful for CPE application in practical battery systems.⁷⁰

Generally, conductive carbon-based materials are not suitable fillers for CPEs because they easily cause short circuits between the positive and negative electrodes in the battery. However, it is proven that carbon-based materials can be added to polymers to improve the ion conductivity of the electrolyte after certain modification. In particular, carbon nanotubes (CNTs) are ideal mechanical enhancers for polymer matrices, and ions can be transported with low energy along the interface between fillers and the polymer matrix. In order to avoid the short circuit of electrons, it is necessary to package CNTs in an insulating clay layer to form an effective 3D nanofiller (Figure 5). With the addition of clay-modified CNTs, the free ions in CPEs could be increased, reaching a maximum of 95.7 in the PEO-10% clay-CNT composite electrolyte. This hybrid nanofiller can increase the lithium ion conductivity of the PEO electrolyte by almost two

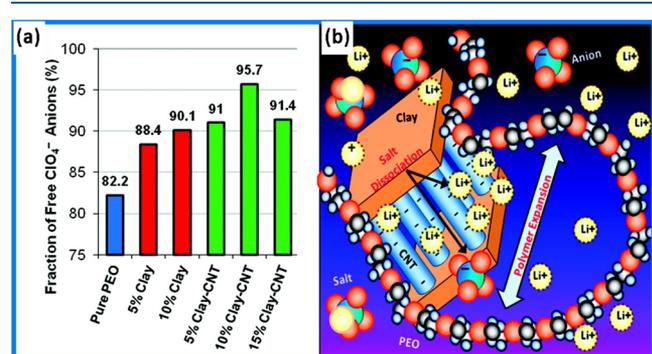


Figure 5. (a) Fraction of dissociated salt ions (ClO₄⁻ anions) based on FTIR analysis of pure and filled PEO electrolytes. (b) Schematics of the interactions between clay, carbon nanotubes, polymer chains, and lithium salts. Reproduced with permission from ref 71. Copyright 2012 American Chemical Society.

orders of magnitude. Furthermore, the mechanical properties of the CPE can be significantly improved, with the increase by 160% in the tensile strength. Importantly, electron conduction in CNTs is blocked by surface clay crystals, eliminating the risk of a short circuit.⁷¹ Similarly, g-C₃N₄ nanosheets as current hot spot materials can be also selected into PEO to prepare CPEs. The improvement of the ion conductivity depends highly on two-dimensional g-C₃N₄ forming an effective ion transport network in the composite electrolyte.⁷² In addition, there is a strong interaction between the surface atoms of g-C₃N₄ and the groups in lithium salts, which promote further dissociation of lithium salts.⁷² Furthermore, adjusting polymer morphology through heat treatment can further improve the compatibility between CPEs and the electrode.⁷³

3.3. PEO-Based CPE with Active Fillers. Since the inert fillers can effectively improve the performance of CPEs, the ion conduction materials should have more effective functions as active fillers to improve the performance of CPEs. Therefore, in recent years, some active fillers, such as S-SEs (such as Li₁₀GeP₂S₁₂) and O-SEs (such as garnet-type Li₇La₃Zr₂O₁₂), and new inorganic solid electrolytes are investigated as candidate fillers for enhancing the performance of PEO-based CPEs. In general, such solid-state electrolytes are demonstrated to have high intrinsic room temperature conductivity and a high number of ion transference. However, the application of solid-state electrolytes as active fillers in CPEs is still limited by some shortcomings, such as large grain boundary resistance and poor electrode–electrolyte interfacial stability.⁷⁴ Therefore, it is necessary to combine the individual advantages of the polymer and inorganic solid-state electrolytes for an effective composite, taking into account both ion transportation and mechanical properties, which provides new design ideas for improving the performance of PEO-based CPEs. Table 2 summarizes the performance parameters of active fillers in PEO-based CPEs.

3.3.1. PEO-Based CPE with Sulfide SEs. Usually, S-SEs has high lithium ion conductivity (about 10⁻² S cm⁻¹), low grain boundary resistance, and a wide potential window.⁷⁵ Two types of S-SE systems are widely studied, including Li₁₀GeP₂S₁₂ (LGPS) (Figure 6a–c)³ and Li₃P₄ (LPS-1) (Figure 6d) or Li₇P₃S₁₁ (LPS-2) (Figure 6e).⁷⁶ In particular, LGPS is shown to be effective to incorporate into the PEO matrix for fabricating CPE membranes.⁷⁷ LGPS particles behave as cross-linking sites between ether oxygen segments and anions, which change the polymer chain structure on the interface and provide a pathway to transport lithium ions in addition to segmental movement. After composition optimization, the PEO-based CPE membrane (Figure 7a) exhibits a maximum ion conductivity (1.21×10^{-3} S cm⁻¹ at 80 °C and 1.18×10^{-5} S cm⁻¹ at 25 °C) (Figure 7b). Meanwhile, compared with the PEO sample (0–4.8 V vs Li/Li⁺), the electrochemical stability of the CPE film with 1% LGPS is significantly improved (0–5.7 V vs Li/Li⁺). When the composite film is used in all-solid-state lithium batteries (Li/LFP and Li/LiCoO₂), the Li/LFP battery exhibits fascinating electrochemical performance, including high capacity retention (92.5% after 50 cycles at 60 °C) and outstanding rate performance (Figure 7c,d). Furthermore, incorporating the solid plasticizer succinonitrile (SN) into the PEO-based electrolyte can further improve battery performance. Usually, an all-solid-state Li/LFP battery with the CPE needs a slow activation process, which may be related to the formation of a

Table 2. Performance Parameters of Active Filler-PEO-Based Composite Electrolytes

filler	year	electrolyte composition	ionic conductivity (S/cm)	temperature	ref.
sulfide solid-state electrolyte	2016	PEO-LiTFSI-1% LGPS	1.21×10^{-3}	80 °C	77
	2016	PEO-LiTFSI-1% LGPS-10% SN	9.1×10^{-5}	25 °C	78
	2018	PEO-LiTFSI-2 vol % LPS	8.01×10^{-4}	60 °C	79
	2019	PEO-LiTFSI-1% LSPS	1.69×10^{-4}	50 °C	81
garnet solid-state electrolyte	2015	PEO-LiClO ₄ -52.5% LLZO	4.42×10^{-4}	55 °C	83
	2016	EPO-LLZTO	5.6×10^{-4}	60 °C	84
	2018	PEO-LiTFSI-60% LLZTO-10% SN	1.22×10^{-4}	30 °C	85
	2019	PEO-16% Ga-LLZO	7.2×10^{-5}	30 °C	86
	2019	PEO-LiClO ₄ -15% LLZO nanosheets	3.6×10^{-4}	RT	89
	2016	PEO-LiTFSI-Al-LLZO	2.5×10^{-4}	RT	90
	2018	PEO-LiTFSI-62% Al-LLZO	8.5×10^{-5}	25 °C	91
perovskite solid-state electrolytes	2018	PEO-LiTFSI-15% LLTO	2.4×10^{-4}	25 °C	95
	2018	PEO-LiClO ₄ -10% LLTO	7.99×10^{-4}	70 °C	92
	2018	PEO-LiTFSI-LLTO	1.8×10^{-4}	25 °C	98
	2018	PEO-LiTFSI-5% LLTO nanowires	3.6×10^{-4}	60 °C	96
	2019	PEO-LiClO ₄ -10% LLTO	2.8×10^{-3}	65 °C	93
NASICON solid-state electrolyte	2016	PEO-LiClO ₄ -70% LAGP-9% SN	1.1×10^{-4}	25 °C	101
	2016	PEO-LiTFSI-20% LAGP	6.67×10^{-4}	60 °C	102
	2019	PEO-LiClO ₄ -vertically aligned LATP	0.52×10^{-4}	RT	103
	2019	PEO-PEG-LiTFSI-vertically aligned LATP	1.1×10^{-3}	60 °C	104

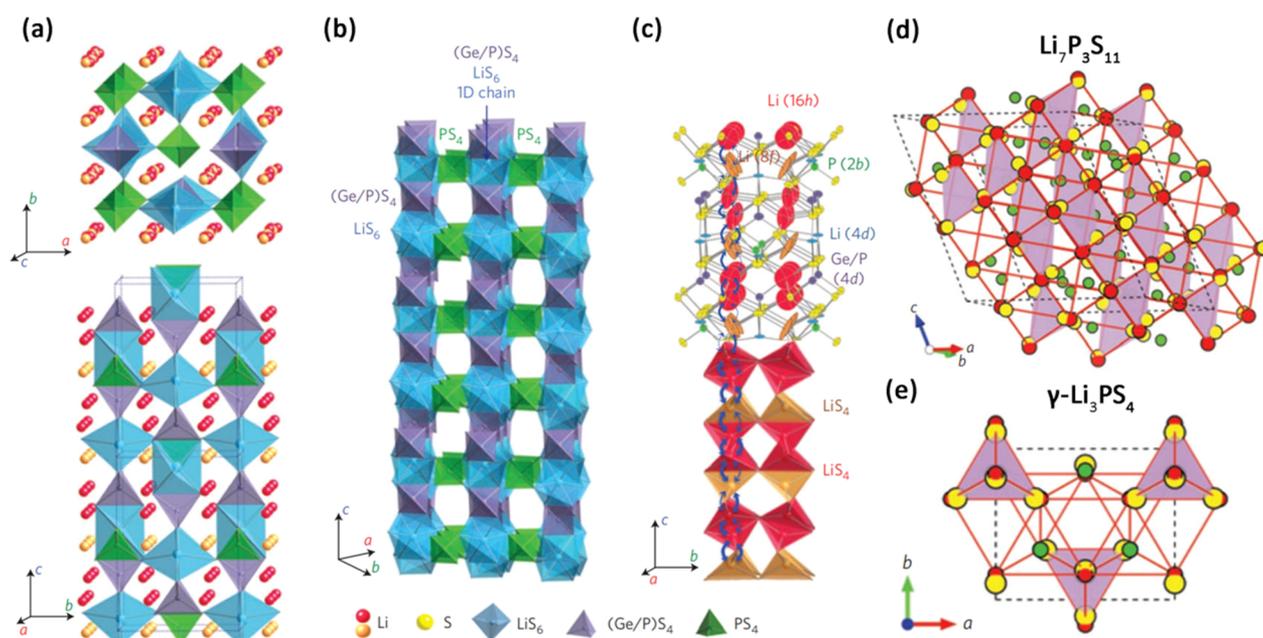


Figure 6. (a) Crystal structure of LGPS. (b) Framework structure of LGPS. (c) Lithium ion conduction pathways in LGPS. (d) Crystal structure of the Li ion conductor $\text{Li}_7\text{P}_3\text{S}_{11}$. (e) Crystal structure of the Li ion conductor $\gamma\text{-Li}_3\text{PS}_4$. Reproduced with permission from ref 76. Copyright 2015 Springer Nature.

new SEI layer and the construction of a new ion diffusion path in the polymer electrolyte.⁷⁸

Correspondingly, the preparation method has a great influence on the performance of PEO-based CPEs with active fillers. Compared with the PEO-LPS-1 composite polymer electrolyte prepared by mechanical mixing, the PEO-2% LPS-1 composite electrolyte prepared by an in situ liquid phase reaction method has a more uniform distribution, which is beneficial to the ion transfer and the formation of a stable electrochemical interface.⁷⁹ In addition, in the in situ prepared PEO-LiClO₄-LPS-2 composite polymer electrolyte, LPS-2 is wrapped by PEO-LiClO₄. Thus, the polymer layer can effectively separate the lithium metal and the LPS-2 solid

electrolyte, inhibit side reactions between the solid electrolyte and lithium, and reduce interfacial resistance.⁸⁰ Similarly, the tin-doped sulfide solid electrolyte $\text{Li}_{10}\text{SnP}_2\text{S}_{12}$ (LSPS) can be also incorporated into the PEO matrix to fabricate CPE films for all-solid-state lithium–sulfur (Li–S) batteries. The optimized PEO-1% LSPS CPE presents a maximum ionic conductivity of $1.69 \times 10^{-4} \text{ S cm}^{-1}$ at 50 °C and the highest mechanical strength.⁸¹ Compared with the PEO/LiTFSI electrolyte, the PEO-1% LSPS CPE also has a high lithium ion transference number, low interfacial resistance, and high interfacial stability with the lithium anode.⁸¹

3.3.2. PEO-Based CPE with Oxide SEs. Compared with sulfide SEs, an oxide solid electrolyte has better chemical

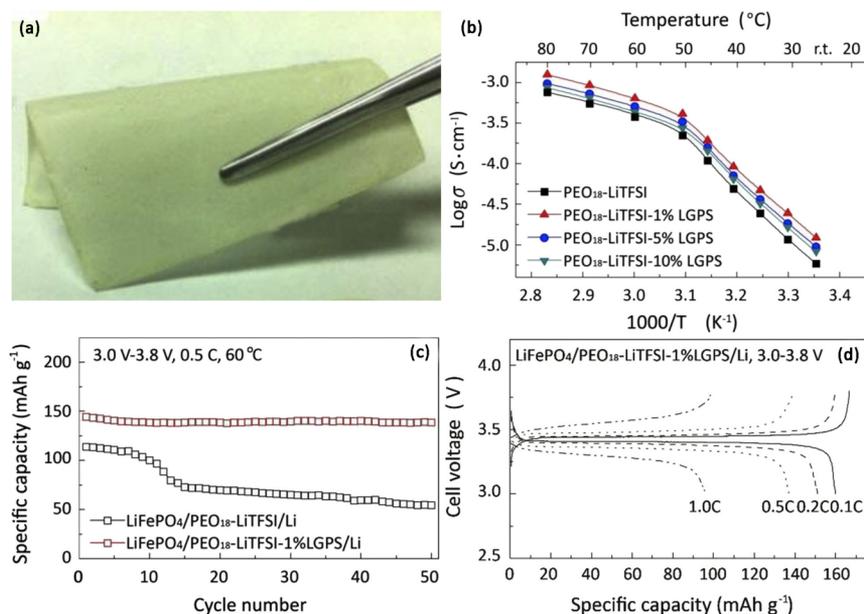


Figure 7. (a) Photo of the SPE membrane. (b) Arrhenius plots for the ionic conductivities of the membranes with various LGPS contents. (c) Capacity retentions of the cell Li/PEO₁₈-LiTFSI-1% LGPS/LFP and the cell Li/PEO₁₈-LiTFSI/LFP at 0.5C. (d) Typical charge/discharge profiles obtained at various rates from 0.1 to 1 C for cell Li/PEO₁₈-LiTFSI-1% LGPS/LFP at 60 °C. Reproduced with permission from ref 77. Copyright 2016 Elsevier.

stability against moisture in air, existing in a crystalline state and a glass (amorphous) state mostly. The typical crystalline electrolyte includes the garnet-type Li₇La₃Zr₂O₁₂ (LLZO) solid electrolyte (Figure 8a), the perovskite-type

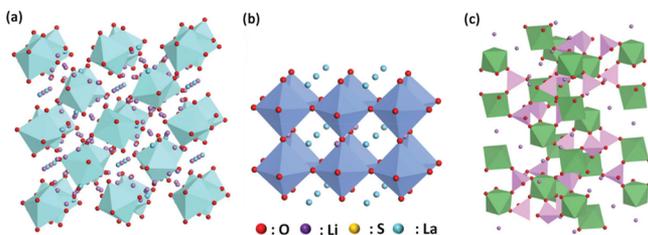


Figure 8. Crystal structures of (a) garnet-type LLZO, (b) perovskite-type LLTO, and (c) NASICON-type LAGP. Reproduced with permission from ref 82. Copyright 2018 Wiley-VCH.

Li_{3-x}La_{2/3-x}TiO₃ (LLTO) solid electrolyte (Figure 8b), the NASICON-type Li_{1+x}Al_xTi_{2-x}(PO₄)₃ (LATP), and the Li_{1+x}Al_xGe_{2-x}(PO₄)₃ (LAGP) solid electrolyte (Figure 8c).⁸² Glass electrolytes include inverse perovskite Li_{3-2x}M_xHalO solid electrolytes and LiPON thin-film solid electrolytes. At present, most of the research studies focus on CPEs with incorporation of garnet SEs, perovskite SEs, and NASICON SEs as fillers.

3.3.2.1. PEO-Based CPEs with Garnet-Type SEs. The garnet-type LLZO and derivatives are ideal solid electrolyte materials with high chemical stability (no reaction with the lithium metal), high lithium ion conductivity (about 10⁻⁴ S cm⁻¹), and a wide potential window (>10 V vs Li/Li⁺). Generally, the ion conductivity of CPEs and the interfacial stability between CPEs and the lithium anode can be significantly improved by adding LLZO particles into PEO.⁸³⁻⁸⁵ For example, the tetragonal LLZO is introduced into the PEO matrix to prepare a CPE. It is found that the CPE containing 52.5% LLZO exhibits the highest ion conductivity

(4.42 × 10⁻⁴ S cm⁻¹ at 55 °C) (Figure 9a). In addition, the charge/discharge performance of the Li/CPE film/NCM₆₂₂ half-cell can be improved obviously, compared to that of half-cells with SPEs and CPEs containing 52.5% Al₂O₃ (Figure 9b).⁸³ The enhancement of CPE ion conductance is mainly attributed to the rapid conduction of ions across the space

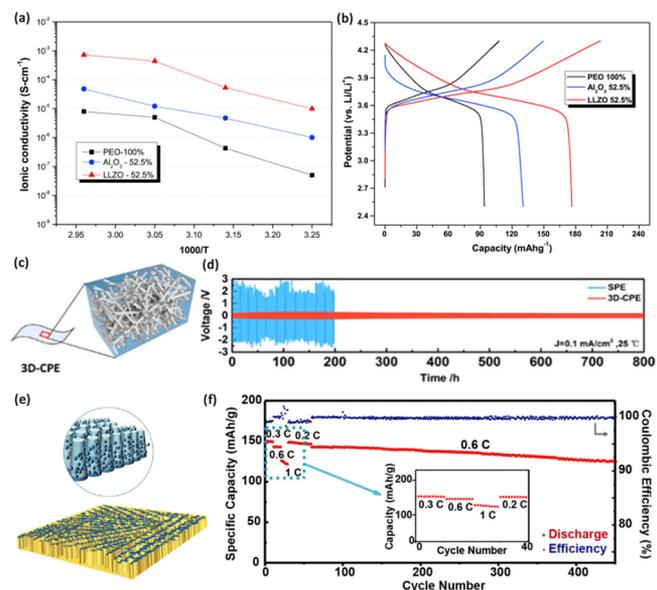


Figure 9. (a) Ion conductivity profiles of the membranes with respect to temperature. (b) Charge-discharge characteristics of coin cells containing various membranes in the 1st cycle at 55 °C. (c) Schematic picture of the structure of 3D-CPEs. (d) Voltage profiles of Li plating and stripping cycling for the SPE and 3D-CPE. (e) Structural model of the ice-templated ceramic/polymer composite electrolyte. (f) Rate capacity of a Li-LAGP/PEO-LFP full cell cycled at 0.3, 0.6, and 1 C followed by 400 cycles at 0.6 C. Reproduced with permission from ref 104. Copyright 2019 Elsevier.

charge region at the interface between the PEO matrix and filler particles. In particular, when the space charge region and phase distribution meet the requirement of forming a percolation threshold, the percolation effect takes place, and continuous fast conduction pathways are then formed.⁸⁶ In addition, the highest contribution to the resistance of CPEs comes from a high activation energy, not from electrostatic repulsion of lithium.⁸⁷

Different from the traditional composite method of introducing inorganic ceramic fillers into the polymer matrix, a new view is proposed, which is changed from “ceramic in polymer” to “polymer in ceramic”. As demonstrated in Figure 3, it is equivalent to changing the content of 0D particle fillers, from “CPE with low filler content” to “CPE with high filler content”. Both types of electrolytes exhibit good performance. The “ceramic in polymer” CPE with a greater flexibility and lower cost is more suitable for small-scale flexible energy storage devices. Meanwhile, the “polymer in ceramic” CPE is more appropriate for a large battery used in electric vehicles due to high mechanical strength and safety.⁸⁸

The ion conductivity and stability of the SPE mixed with nanofillers are significantly enhanced due to the good interaction between nanofillers and the polymer matrix or lithium salts. However, the easy adhesion and agglomeration characteristics of nanoparticles limit their dispersibility and effective concentration in the polymer, thereby preventing further improvement of conductivity and stability of the CPE. Researchers began to consider building a 2D or 3D ion transport network to further improve ion conductivity. For example, 2D garnet nanosheets were synthesized via coprecipitation with a graphene oxide template and incorporated into the PEO matrix to provide an interconnected lithium ion transport path. An optimal ion conductivity ($3.6 \times 10^{-4} \text{ S cm}^{-1}$) at room temperature has been obtained in the CPE with 15 wt % garnet nanosheets.⁸⁹ In addition, 3D garnet nanofibers are prepared by electrospinning and high-temperature annealing, which can provide long-range lithium ion transfer pathways and enhance mechanical properties in PEO-based CPEs.⁹⁰ Similarly, the garnet ($\text{Li}_{6.28}\text{La}_3\text{Zr}_2\text{Al}_{0.24}\text{O}_{12}$) solid electrolyte with a 3D nanostructured framework can also be fabricated via a nanostructured hydrogel for incorporating into PEO. Compared with particle fillers, which exhibit discontinuous conductive paths due to the separation of interface regions, the 3D interconnected fillers can form a continuous ion conductive path. Therefore, the fabricated CPE exhibits good interfacial stability and high ion conductivity.⁹¹

3.3.2.2. PEO-Based CPEs with Perovskite-Type SEs. Perovskite LLTO SEs have the advantages of a stable structure, simple preparation process, and adjustable composition. Thus, LLTO nanoparticles are also used as active fillers in PEO to fabricate CPEs.⁹² Correspondingly, the concentration, morphology, agglomeration, and nanoparticle surface of LLTO fillers have significant effects on the ion transportation of PEO-LLTO-based CPEs. In addition, the transport of lithium ions in CPEs occurs mainly through the polymer phase, not by the conducting LLTO ceramic filler.⁹³ Furthermore, the excellent conductivity of $2.4 \times 10^{-4} \text{ S cm}^{-1}$ at room temperature can be achieved in the CPE with 15% LLTO nanowires.⁹⁴ In a similar way, the 1D LLTO nanofibers prepared by electrospinning are used in the fabrication of PEO-based CPEs, and their good effect on the performance is also verified.^{95,96} Therefore, the CPE with both high ion conductivity and flexibility can be

obtained by preparing the active materials into a 1D structure and compounding with the polymer.

It can be predicted that the influence of filler morphology and dimensions on the performance of CPEs would be the focus of future CPE research. As shown in Figure 3, the arrangement of 1D nanowires has great impact on the ion transport mechanism of the CPE. The preparation of CPEs using linear arrangement nanowires is helpful to obtain high ion conductivity and better mechanical strength. Compared with randomly distributed nanowires, the CPE with such well-aligned nanowires can achieve a ten times increase in conductivity (up to $6.05 \times 10^{-5} \text{ S cm}^{-1}$ at 30°C). Of course, the large improvement on conductivity is mainly attributed to the fast conducting pathway of Li ions without crossing junctions on the surface of the aligned nanowires.⁹⁷ Similarly, a three-dimensional interpenetration CPE with a 3D LLTO nanobackbone can be fabricated by hot pressing and quenching (Figure 9c). At room temperature, an ion conductivity as high as $1.8 \times 10^{-4} \text{ S cm}^{-1}$ is achieved.⁹⁸ Meanwhile, the 3D-CPE membranes can effectively suppress the growth of lithium dendrites, showing excellent stability to the lithium metal; therefore, a symmetric Li/3D-CPE/Li cell with the CPE membranes can keep cycling at a current density of 0.1 mA cm^{-2} for over 800 h (Figure 9d).⁹⁸

3.3.2.3. PEO-Based CPEs with NASICON-Type SEs. The general structure formula of a NASICON-type fast ion conductor is expressed as $\text{LiT}_2(\text{PO}_4)_3$, where T is Ti, Ge, and Zr. Generally, the $\text{Li}_{1+x}\text{M}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ is obtained by using trivalent ions Al, Cr, and Ga, in which the Al-doped material $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ (LATP) has the highest ionic conductivity. Moreover, the stability of Ge with the Li metal is high. Another NASICON structure $\text{Li}_{1+x}\text{Al}_x\text{Ge}_{2-x}(\text{PO}_4)_3$ (LAGP) is obtained by replacing Ti with Ge, which has high chemical stability, ion conductivity, and electrochemical window.⁹⁹

The CPE can be fabricated by adding NASICON LATP and LAGP as fillers into the PEO matrix, which has achieved considerable effects, especially on improving the mechanical properties and ion conductivity of the electrolyte.^{100,101} However, the high conductivity of ceramic fillers is largely affected by the low conductivity of the polymer matrix, especially when nanoparticles are used. Therefore, the particle size and geometry of the ceramic fillers have an important influence on the ion conductivity of the CPE. For example, the CPE can be composed of PEO and four kinds of glass ceramic LAGP of different particle sizes prepared by controlling ball milling conditions. Here, LAGP particles have a positive effect on ion conductivity, the lithium ion migration number, electrochemical stability, and mechanical properties. For the CPE with the same LAGP content, smaller particle sizes are helpful on improving conductivity.¹⁰²

As shown in Figure 3, fabricating a vertically arranged 3D array structure with ceramic fillers can provide a fast and continuous lithium ion transport path in CPEs. In particular, the flexible CPE with LATP nanoparticles of vertical arrangement and connection is fabricated by an ice templating method, and a high ion conductivity ($0.52 \times 10^{-4} \text{ S cm}^{-1}$) at room temperature is obtained.¹⁰³ The conductivity is increased by 3.6 times as compared with the CPE fabricated with LATP nanoparticles.¹⁰³ Similarly, the ideal vertical array of LAGP can also be prepared by using the ice templating method (Figure 9e), and the ion conductivity of this CPE with LAGP of vertically aligned ceramic nanoparticles is $1.11 \times 10^{-3} \text{ S cm}^{-1}$ at 60°C .¹⁰⁴ Meanwhile, the as-prepared CPE shows good

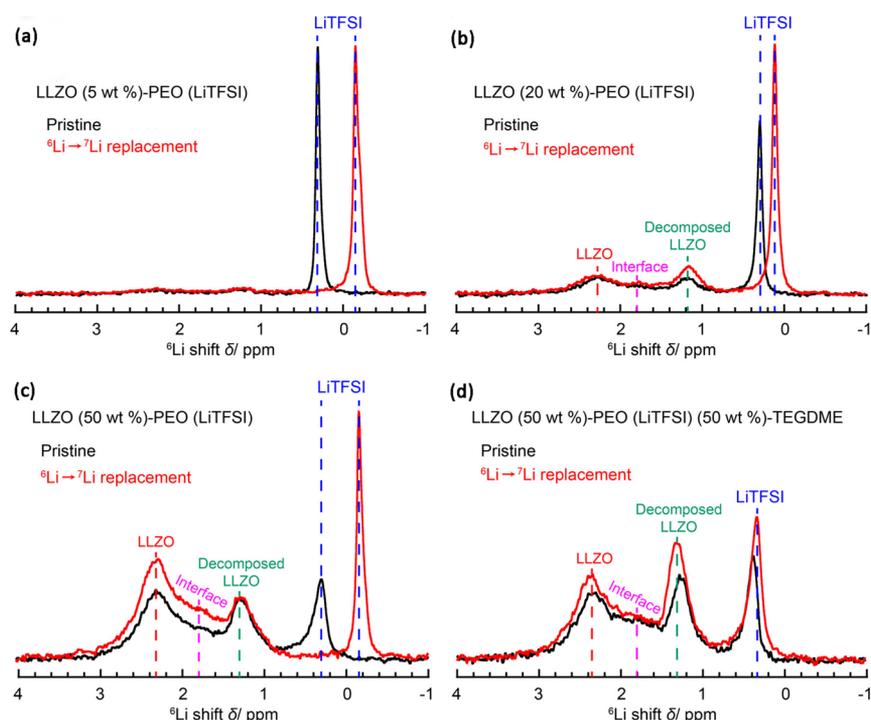


Figure 10. ^6Li NMR comparison of pristine and cycled LLZO (5 wt %)-PEO (LiTFSI) (a), LLZO (20 wt %)-PEO (LiTFSI) (b), LLZO (50 wt %)-PEO (LiTFSI) (c), and LLZO (50 wt %)-PEO (LiTFSI) (50 wt %)-TEGDME (d). Reproduced with permission from ref 107. Copyright 2018 American Chemical Society.

stability in both lithium symmetric batteries and Li/LFP batteries, and the high capacity retention is 87.4% after 400 cycles at 0.6C (Figure 9f).¹⁰⁴

3.4. Ion Transport Mechanism from Nuclear Magnetic Resonance (NMR). Understanding the lithium ion transport path and conduction mechanism is essential for the effective design of high-performance solid electrolytes. However, based on the lithium ion transport mechanism through polymer segment movement in pure PEO-based SPEs, the addition of fillers has a great effect on the transport process of lithium ions, which makes the ion transport mechanism in CPEs more complex. At present, there are several points of view for possible ion transport mechanisms in CPEs: First, the surface groups of the filler particles can change the local structures of the polymer based on the interaction, which may have an impact on the recrystallization of the polymer chains. Increasing the amorphous region of PEO in CPEs is beneficial to the rapid transport of lithium ions. Second, 1D, 2D, and 3D structural fillers can provide continuous and various channels for lithium ions, which further strengthen lithium ion transport.¹⁰⁵ Therefore, this is a great challenge in this area due to the complexity of lithium ion transport and the lack of effective characterization methods. It is noted that nuclear magnetic resonance (NMR) spectroscopy is found to be a powerful tool to probe lithium ion transport in all-solid-state batteries.

The active fillers, such as sulfides SEs and oxides SEs, can lead to higher conductivity of CPEs due to their own characteristics of good lithium ion transport. Therefore, there are more studies on PEO-based CPEs with the addition of active fillers. For example, the local structural environment of lithium ions in the LGPS-PEO (LiTFSI) composite electrolyte can be examined by high-resolution solid-state ^6Li NMR. The ^6Li amount at both the PEO-LGPS interface and LiTFSI

increases nearly threefold, while the ^6Li content of the bulk LGPS decreases relatively. Thus, the conduction of lithium ions is mainly carried out through the PEO-LGPS interface in CPEs. In addition, it is also demonstrated that the ion conductivity of the LGPS-PEO (LiTFSI) composite electrolyte is closely related to the amount of available Li ions at LGPS-PEO interfaces.¹⁰⁶

Similarly, solid-state NMR can also be used to investigate the composition dependence of ion mobility, ion transport pathways, and active ion concentration for ion conductivity of the LLZO-PEO composite electrolyte.¹⁰⁷ As demonstrated in Figure 7, with the increase in the LLZO content, the lithium ion transportation path also varies. When the LLZO content increases from 5 to 20%, ^6Li signal enrichment is distinctively observed for LiTFSI in PEO and decomposed LLZO. Therefore, it is considered that lithium ions are mainly conducted through the PEO matrix, and the decomposed LLZO assists this conduction (Figure 10a,b). However, when the LLZO content exceeds 20%, the main ion transport pathway is varied. Correspondingly, the main ^6Li enrichment occurs mainly in the LLZO peak, some in LiTFSI and interface peaks, and no enrichment in the decomposed LLZO peak (Figure 10c). This suggests that with increasing the LLZO content, the ion transport pathway is gradually transferred from the PEO phase to the percolated network formed by loosely connected LLZO particles. Finally, the conduction mechanism of Li ions in the CPE with the addition of a plasticizer, tetraethylene glycol dimethyl ether (TEGDME), is also studied. The ^6Li NMR spectrum of the PEO-LLZO (50 wt %)-TEGDME sample shows that the lithium ion transport pathway is changed again, returning to the decomposed LLZO and LiTFSI (Figure 10d). This is consistent with the high intrinsic ion conductivity of TEGDME and its ability to reduce

PEO crystallization, resulting in preferential conduction of Li ions through the polymer/TEGDME matrix.

One-dimensional high-resolution ^6Li NMR has also been used to analyze the various Li local structural environments in the LLZO-PEO (LiClO_4) composite electrolyte. Possible Li environments in the CPE are depicted in Figure 11a, including

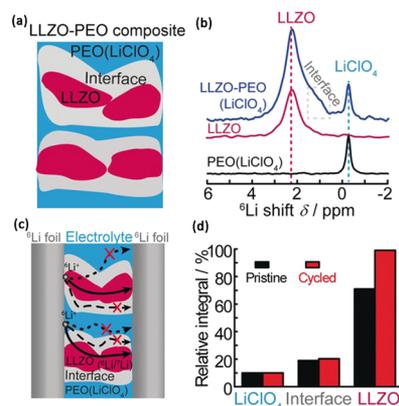


Figure 11. (a) Diagram of local Li environments in LLZO-PEO (LiClO_4) composites. (b) ^6Li NMR of LiClO_4 in PEO, pure cubic LLZO, and the LLZO-PEO (LiClO_4) composite. (c) Illustration of possible ion transport pathways within the composite electrolyte upon cycling the symmetric battery. (d) Quantitative analysis of the ^6Li amount in LiClO_4 , the interface, and LLZO of the LLZO-PEO (LiClO_4) before and after cycling. Reprinted with permission from ref 108. Copyright 2016 Wiley-VCH.

the PEO- LiClO_4 polymer matrix, LLZO grains, and the PEO/LLZO interface. Figure 11b shows the corresponding high-resolution ^6Li NMR spectra of LiClO_4 in PEO, pure cubic LLZO, and the LLZO-PEO (LiClO_4) CPE. Correspondingly, the lithium ion transport pathway is explored in symmetric cells with the ^6Li metal as an electrode (Figure 11c). By comparing the NMR spectra of the CPE before (pristine) and after (cycled) cycling, it is found that the ^6Li peak of the sample after cycling is significantly enhanced, indicating that a large number of ^7Li is replaced by ^6Li in the CPE. The replacement could be further quantified, which shows that the peak intensity of LLZO in the ^6Li spectrum of the CPE increases by 39%, only a 6% increment in the peak of the PEO/LLZO interface, and no increase for LiClO_4 in PEO (Figure 11d). Therefore, it can be inferred that the lithium ion transport in CPE occurs mainly through the LLZO phase, rather than the interface or the PEO matrix.¹⁰⁸ Furthermore, in the LLZO-PEO-TEGDME system, the lithium ion environment in the CPE is changed obviously. The quantitative increase of ^6Li is found in different parts of the CPE after cycling, among which was more in the decomposed LLZO in TEGDME and LiClO_4 in the PEO/TEGDME complex but almost no increase in the PEO/LLZO interface. It means that the pathway of lithium ions is changed in the CPE after adding TEGDME, which is mainly transported through TEGDME-associated phases rather than the ceramic LLZO or PEO/LLZO interface.¹⁰⁹

Based on the above analyses, a conclusion is drawn that lithium ions are transported through low resistance pathways or a phase of high ion conductivity within the CPE. Therefore, improving the total ion conductivity is the key to building high-performance CPEs. As shown in Figure 3, building a 3D structured filler to form a fast and continuous lithium ion

transportation channel is also the key for future research. In addition, the ion transport mechanism in CPEs depends strongly on the composition and structure of CPEs, and there is yet no consensus, which needs further study.

4. INTERFACE BETWEEN THE PEO-BASED CPE AND THE ELECTRODE

In all-solid-state batteries, the biggest challenge is the poor interfacial stability between the SEs and the electrode. Compared with inorganic ceramic electrolytes, SPEs have relatively better interface contact with electrodes, but there are still solid–solid contact characteristics. It is also difficult to achieve sufficient interfacial wettability like liquid electrolytes. Therefore, how to improve the interface contact between the solid electrolyte and the electrode has received more attention in recent years. Interfacial features are crucial to the overall performance of all-solid-state batteries, and some parameters are the key for evaluating the interfacial feature, such as ion conductivity, the ion transference number, interfacial impedance, mechanical properties, chemical/electrochemical stability, effective interface contact area, surface roughness, and surface porosity. Here, the ion conductivity and the ion transference number are involved in the transport process of lithium ions in the bulk and at the interface of CPEs, which are highly related to the interfacial impedance and the power output of batteries. The mechanical properties also have a great impact on inhibiting the deformation of electrodes and CPEs at the interface, as well as preventing the growth of lithium dendrites during battery cycling. The electrochemical/chemical stability of the interface is related mainly to the decomposition and side reactions of both electrodes and CPEs during cycling. In addition, the physical contact at the interface also plays an important role on the interfacial stability. In this section, improving the interfacial stability of CPEs and electrodes is discussed from the following three aspects: the interface between the PEO-based CPE and the cathode, the interface between the PEO-based CPE and the anode, and the layered heterogeneous structure improving the electrolyte/electrode interface.

4.1. Interface between the PEO-Based CPE and the Cathode. At present, in all-solid-state lithium batteries, in order to improve the interfacial stability between the cathode and the CPE, some SPEs are generally added to the cathode to build a composite cathode.^{110,111} For different cathode material systems, the composite strategies are different due to the diversity of cathode systems and characteristics. Generally, it can be divided into low-voltage phosphate cathode materials and high-voltage oxide cathode materials.

4.1.1. Low-Voltage-Type Composite Cathode. The initial decomposition voltage of PEO is 3.9 V (vs Li/Li^+), and its low oxidation window is more compatible with a phosphate cathode. Therefore, PEO is first introduced into an LFP battery system. The composite method can improve the interface compatibility between a cathode and a CPE. In particular, a full composite method is applied to build a composite cathode by adding an SPE to LFP and to form an intimate cathode/CPE interface. The all-solid-state lithium ion battery is prepared by hot pressing of a composite cathode, which consists of LFP with different contents of an SPE (10–30%) or a CPE (filled with 60% AL-LLZTO) and a lithium metal anode. Because of the effective composition and hot pressing between the cathode and the CPE, the pore-free interface between the cathode and the CPE forms, which

greatly improves the performance of the battery.¹¹² The adding of the CPE as a binder to the cathode can significantly improve the interface contact between the CPE and the cathode. Through cross-sectional SEM and element mappings, it can be found that the constituent elements of the CPE are uniformly distributed among the CPE and the cathode, while Fe and P elements of the LFP cathode are only observed in the cathode. Notably, the interface between the cathode and the CPE is very good and dense.¹¹³ In addition, recently, a new concept of a cathode-supported solid electrolyte membrane framework is also proposed. This new type of composite cathode is constructed mainly by casting the solid electrolyte directly on the cathode layer, which can significantly improve the interface contact between the cathode and the CPE, by improving the wetting ability of the electrolyte on the cathode surface and by enhancing the interface adhesion.¹¹⁴ Similarly, the PEO-LITFSI-10 wt % LLZO nanowire (PLLN) composite electrolyte is prepared; then, an integrated all-solid-state battery structure is formed by fusing PEO in both the LFP composite cathode and the CPE at high temperature, which greatly strengthens the interface compatibility and stability between the cathode and the CPE. Therefore, this integrated Li/PLLN/LFP battery exhibits excellent cycling stability at both 60 and 45 °C.¹¹⁵

The introduction of an SPE into a cathode to form a composite cathode can effectively improve the interface wettability and reduce the interfacial resistance. However, the proportion of active materials in the composite cathode could be relatively reduced, which is not beneficial to the improvement of the capacity and energy density of all-solid-state batteries; this is one of the common problems in the development of all-solid-state batteries at present.

4.1.2. High-Voltage-Type Composite Cathode. Due to its low electrochemical oxidation potential window, the conventional PEO-based CPE is difficult to match with high-voltage oxide cathode systems, including commercial LiCoO_2 (LCO), $\text{Li}(\text{Ni}_x\text{Co}_y\text{Mn}_{1-x-y})\text{O}_2$ (NCM) and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. Therefore, further widening the electrochemical stability window of the PEO-based CPE has become a challenge for constructing a high-voltage composite cathode.

It is demonstrated that the reactive terminal $-\text{OH}$ group in the PEO-based SPE has adjustable characteristics, and its electrochemical stability window and electrochemical performance can be effectively adjusted by changing the terminal functional group. For example, replacing $-\text{OH}$ with a more stable $-\text{OCH}_3$ group can expand the electrochemical oxidation window from 4.05 to 4.3 V. Thus, the matching of the PEO-based CPE and the high-voltage cathode material NCM_{523} can be realized.¹¹⁶

Generally, PEO matching with an LCO cathode causes the degradation of all-solid-state battery performance at high-voltage cycles. This is due to the oxidation ability of the lattice oxygen ions in the LCO material at a 4.2 V charging state, which can accelerate the oxidation decomposition of PEO. Meanwhile, the loss of LCO surface oxygen can trigger the formation of spinel or rocksalt phases, as a poor conductor of lithium ions, resulting in a significant increase in the interfacial impedance of the materials. This suggests that if the surface oxidation of the cathode material can be suppressed or if the cathode material with no strong oxidation on the surface is used, then the PEO-based SPE may work stably at a voltage higher than the intrinsic electrochemical oxidation potential.¹¹⁷ In addition, with the introduction of high-voltage cathodes, the

PEO-based SPE has the problem of decomposition and associated gas release, which also seriously affects the safety of all-solid-state batteries.¹¹⁸ It is shown from experiments and theory calculations that the surface catalysis effect of LCO is the root cause of the unexpected H_2 gas release of PEO at 4.2 V. At a voltage higher than 4.5 V, PEO may experience severe dehydrogenation, resulting in the formation of bistrifluoromethanesulfonimide (HTFSI), which will further corrode PEO and react with the lithium metal anode to cause the generation of H_2 gas.¹¹⁸

Therefore, the key to the application of high-voltage composite cathodes in the PEO-based CPE is to improve the stability of the interface between the cathode and the CPE, especially the protection or interface modification of the cathode materials. The conventional cathode protection method is generally to build a coating layer on the active material particles. For example, the LCO surface can be modified by a coating layer of highly ionic conducting and electrochemical oxidation-resistant poly(ethyl cyanoacrylate) (PECA) through an in situ polymerization method. The PECA coating layer significantly inhibits the continuous decomposition of the lithium difluoro(oxalate) borate (LiDFOB) salt in the PEO-based CPE.¹¹⁹ In addition, a thin ALD-derived lithium tantalate is coated on the high-voltage LCO electrode, which shows good compatibility with the PEO-based SPE, thereby enhancing the cycling performance of the battery.¹²⁰ Similarly, covering the LATP coating densely and uniformly on the LCO surface can also effectively suppress the oxidation of the PEO-based CPE under high charging voltage.¹²¹

In general, the addition of high-voltage-resistant components in the PEO-based CPE can also improve the electrochemical stability of the CPE. Taking PEO-LLZTO as a bidirectional lithium ion transport channel, further adding PVDF with high voltage resistance to replace part of the PEO matrix can enhance the electrochemical stability of the PEO-based CPE. Thus, an excellent PEO-LLZTO-PVDF dual conductive network CPE can be obtained, which effectively improves the interfacial stability between the cathode and the CPE.¹²²

The interfacial stability of a high-voltage cathode and a PEO-based CPE can also be improved through the selection and adjusting of lithium salts. For example, the synergy of an LAGP ceramic electrolyte nanocoating and a passivation layer from salt decomposition can improve the interfacial stability between a 4 V cathode and a PEO-based CPE. Usually, the prepared nano-LAGP coating has grain boundaries and pores, which may lead to PEO oxidation. By optimizing the type and content of lithium salt, the lithium salts decompose in situ on the surface of LAGP-LCO during cycling to form a passive protective layer. This synergy allows lithium ions to pass through the interface layer but hinders the oxidative decomposition of the PEO-based SPE, thereby preventing the further oxidation of the PEO-based CPE above 4 V.¹²³ In addition, the addition of three lithium salts of LiBOB , LiNO_3 , and LiTFSI into the PEO-based CPE can also facilitate the stable cycling of Li/CPE/NCM_{111} cells.¹²⁴ The high-voltage stability of a trinal-salt CPE is significantly higher than that of a single-salt CPE and a dual-salt CPE. The typical failure mechanism of a single-salt CPE and a dual-salt CPE in Li/NMC batteries is also explored. For a single-salt CPE, failure is usually triggered by the decomposition of PEO, which further leads to high charging capacity of Li/NMC batteries and finally failure of the cells (usually less than 5 cycles). Although the dual-salt CPE helps to improve the interfacial stability with the

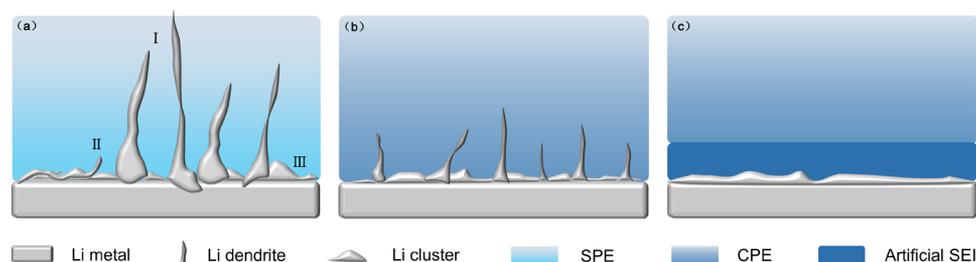


Figure 12. (a–c) Schematic diagram of the growth of lithium dendrites in the SPE, the CPE, and the CPE with an artificial SEI.

high-voltage cathode, failure and short circuit may still occur due to the unstable anode interface. In comparison, the trinal-salt CPE has higher oxidation stability at potentials as high as 4.6 V, which shows a much more extended cycle life in Li/NMC cells. This indicates that the composition of salts also changes the glass transition temperature and crystallinity, which has a great impact on the ionic transport and mechanical properties of the PEO-based CPE.¹²⁴

The high-voltage composite cathode is one of the crucial directions for achieving a high energy density of all-solid-state lithium batteries. It is necessary to comprehensively consider and regulate the interface compatibility and stability of the cathode and the PEO-based CPE.

4.2. Interface between the PEO-Based CPE and the Li Metal Anode. The uncontrollable growth of lithium dendrites and low Coulombic efficiency (CE) impede further application of lithium metal electrodes in next-generation high-energy rechargeable batteries. For a long time, SEs are regarded as a potential solution to solve the dendrite issues in lithium-based batteries due to their high mechanical strength. However, in recent years, it is revealed from numerous works that the lithium dendrite issues in all-solid-state Li-metal batteries are still serious, and the interaction mechanism is complex.¹²⁵ In a word, an SPE cannot completely block the growth of dendrites in theory due to its relatively low shear modulus. Furthermore, most of the PEO-based CPEs need to operate at high temperatures, which simultaneously reduces their mechanical strength and increases the tendency of dendrites penetrating SEs. As shown in Figure 12a, the possible mechanism of lithium dendrite nucleation and growth in SPEs is presented as follows: (I) Lithium dendrites grow at the tip in an SPE, (II) lithium dendrites grow laterally and extends from the SPE/anode interface, and (III) lithium dendrite growth caused by the charge redistribution at the lithium/SPE interface. Based on the lithium dendrite growth mechanism and intrinsic characteristics of SPEs, there are various strategies to alleviate dendrite growth in PEO-based SPEs, such as, the PEO-based CPE with various fillers to suppress Li dendrites due to its reinforced mechanical strength (Figure 12b), introducing an artificial solid electrolyte interface (SEI) film into the Li/CPE interface to avoid the dendrite problem (Figure 12c).

Solid-state electrolytes bear a mission of suppressing Li dendrites and improving the safety of all-solid-state lithium metal batteries. However, individual inorganic solid-state electrolytes have some problems, when coupled with the lithium metal anode. For example, a chemical reaction occurs at the interface when S-SEs (LGPS) contact the lithium metal. The O-SE (LLZO) particles could react with the lithium metal to form a LiCO_3 layer, resulting in the increase in interfacial impedance. In addition, there are many voids at the interface of the lithium metal and microsized inorganic solid-state

electrolyte particles, which is beneficial for the growth of lithium dendrites. The ion conductivity and mechanical flexibility of CPEs can be effectively improved with the addition of fillers. In particular, high interfacial stability with low interfacial impedance between the CPE and the lithium metal can be obtained, thus achieving a uniform lithium deposition and inhibiting the growth of lithium dendrites to some extent. For example, adding an acid-modified nano- SiO_2 filler to a PEO-based SPE can effectively reduce the interfacial resistance between the lithium metal anode and the CPE and thus suppress the formation of lithium dendrites.⁴⁷ Furthermore, adding *N*-methyl-*N*-propylpiperidinium bis-(trifluoromethanesulfonyl)imide (PP13TFSI) to the PEO-LiTFSI- SiO_2 system can also inhibit the growth of lithium dendrites, which may be attributed to the synergy of nano- SiO_2 and PP13TFSI, and the addition of PP13TFSI plays a positive role in the formation of the passivation film on the CPE.⁴⁸ The large interfacial resistance between the lithium metal anode and the electrolyte is caused mainly by the Li deficiency at the interface. Three-dimensional ^7Li magnetic resonance imaging (MRI) is introduced to study the Li distribution in SEs. It is found that lithium ions have a large depletion at the interface of a Li/LGPS/Li symmetric battery, and the uniformity of Li distribution in the electrolyte is also significantly reduced. Adding an appropriate amount of PEO-LiTFSI to prepare a CPE can greatly improve the uniformity of Li distribution at the interface and in the electrolyte and reduce the Li depletion at the interface, thereby significantly improving the long-term cycling stability of the all-solid-state batteries.¹²⁶ Moreover, compared with the zero-dimensional fillers, the high-dimensional fillers are helpful to enhance the mechanical strength of CPEs, improve the ionic conductivity, and inhibit the growth and penetration of lithium dendrites.^{53,98,104} For example, CPEs filled with 3D garnet nanofibers can effectively block the growth of lithium dendrites in a symmetric lithium cell during repeated lithium stripping/plating at room temperature, with a current density of 0.2 mA cm^{-2} around 500 h and a current density of 0.5 mA cm^{-2} over 300 h.⁹⁰

Although the strategy of introducing various fillers into SPEs can prevent the growth of lithium dendrites to some extent, some filamentous lithium dendrites are still produced during long cycling, resulting in a micro short circuit, further leading to overcharge (low CE), capacity degradation, and recovery after the short circuit of the cells (Figure 12b).

Building an artificial SEI protection layer at the interface between the Li anode and the PEO-based CPE to achieve uniform lithium deposition is an ideal strategy.¹²⁷ This artificial SEI layer should have uniform coverage, good wettability with both Li and the PEO-based CPE, high ionic conductivity, poor electronic conductivity, and good mechanical strength. Generally, polymers are ideal materials for constructing

artificial SEI films because of their high ion transportation capability, better flexibility, and the characteristics of conducting ions only and not conducting electrons (Figure 12c).¹²⁸ For example, an ultrathin (approximately 70 nm) PEO-ureido-pyrimidinone (UPy) artificial SEI layer can be constructed in situ on the lithium anode to enhance the stability of the anode/SEs interface.¹²⁹ In addition, lithium fluoride (LiF) is a good stable material for incorporating into the poly(vinylidene-*co*-hexafluoropropylene) (PVDF-HFP) matrix to construct a composite artificial SEI layer, which could combine the merits of the high flexibility of the polymer and the embedded hard LiF particles to achieve uniform lithium deposition.¹³⁰ Similarly, a LiF-Li₃N-rich SEI layer can be also prepared to improve interface compatibility and to prevent the formation of lithium dendrites.¹³¹ The symmetrical Li/LAGP-PEO/Li cells with an SEI protection layer can cycle stably with low polarization for nearly 400 h at a current density of 0.05 mA cm⁻².

PEO exhibits good compatibility for the lithium metal, which can usually be used as a protective layer of the lithium anode, but the conventional CPE structure design is not effective for the protection of the lithium metal anode; thus, it is necessary to design a new CPE structure. In particular, a CPE of a double-layer structure is designed, in which the LAGP-PEO (LiTFSI) layer provides high ionic conductivity and the PEO (LiTFSI) layer is responsible for protecting the lithium metal anode. The PEO (LiTFSI) coating layer can form a bridge connecting the LAGP SEs and the lithium anode, furthermore preventing the direct contact between LAGP and the lithium metal and thus avoiding side reactions between LAGP and the Li anode. Therefore, this double-layer structure design can effectively inhibit the growth of lithium dendrites.¹³² Similarly, in a sandwich structure PEO/PEO-LLTO/PEO CPE, the LLZO nanofiber frameworks are used to improve the mechanical strength, ion conductivity, and electrochemical stability of the CPE, while the PEO layers on both sides enable superb electrolyte/electrode interfacial contact, reducing the interfacial resistance and ensuring excellent cycling stability. As a result, the Li symmetrical cell can operate stably for 400 h without short circuiting.¹³³

All-solid-state lithium batteries with solid-state electrolytes bear an important mission to achieve both high energy density and good safety. However, the growth mechanism of lithium dendrites on the interface of the lithium anode and a solid electrolyte is not very clear at present, which is still the biggest problem for the application of lithium metal batteries. Therefore, realizing the uniform deposition of dendrite-free lithium at the interface of the lithium anode and the solid-state electrolyte is the main direction in future research.

4.3. Improving All-Solid-State Battery Performance via the PEO-Based CPE with a Layered Heterogeneous Structure. The interface performance of the CPE with both a cathode and an anode has a decisive influence on the performance of the all-solid-state batteries. Improving the stability of both interfaces and reducing the interfacial resistance are the key to the construction of high-performance all-solid-state lithium batteries. Here, the layered heterogeneous structure is a new design philosophy, which can modify the cathode and the anode at the same time and improve the overall performance of the all-solid-state lithium batteries.¹³⁴ As demonstrated in Figure 13, this layered heterogeneous structure CPE is usually composed of two or more components, in which each component is independent, or

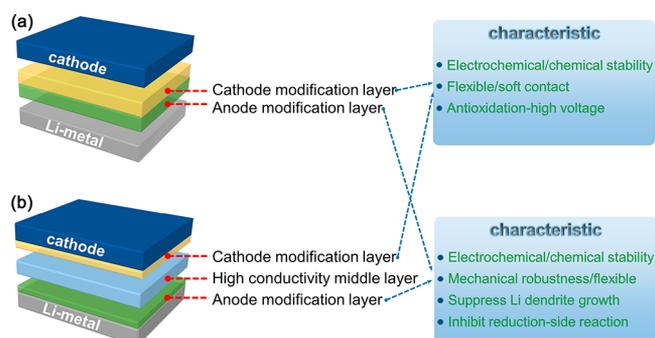


Figure 13. (a,b) Schematic diagram of the layered heterogeneous structure and modified layer characteristics.

two different components are closely combined, even permeating into each other. Usually, the layered heterogeneous structure in the CPE can be divided into double-layer and three-layer structures, as shown in Figure 13a. Here, the double-layer heterogeneous structure is consisted of the cathode-modified layer and the anode-modified layer, while the three-layer heterogeneous structure is composed of the high-conductivity intermediate layer and the double-layer heterogeneous structure (Figure 13b). The cathode-modified layer should exhibit the following characteristics: (1) high electrochemical/chemical stability, (2) reliable flexibility and soft contact with the cathode, and (3) a good antioxidation ability at high voltage. For the anode-modified layer, the following features are of necessity: (1) high electrochemical/chemical stability, (2) good mechanical robustness/flexibility, (3) effective suppressing of the growth of lithium dendrites, and (4) a good antireduction ability at low voltage. In the layered heterogeneous structure, different components could have different functions, and the synergy of all components can help to build a high-performance CPE and improve the performance of the all-solid-state lithium batteries.

In particular, in order to satisfy the application requirements of a high-voltage LCO cathode and a lithium metal anode, a three-layer PEO-based CPE based on different lithium salts is constructed and presented excellent electrochemical performance. The initial interlayer provides high ionic conductivity for the whole CPE, while the PEO-SN-LiTFPFB and PEO-LiTFSI-5% LiTFPFB electrolyte layers are introduced into the cathode and anode sides as coating layers, respectively, which can remarkably improve the interface contact between the electrolyte and electrodes and accelerate the formation of a stable cathode electrolyte interface (CEI) and SEI film. This three-layer PEO-based CPE exhibits extremely excellent performance in high-voltage Li/LCO batteries.¹³⁵

Furthermore, in the design of multifunctional modified ceramic electrolytes, a compatible SE is designed by inversely coating LAMP with PAN and PEO, thus constructing a stable electrode/solid electrolyte Janus interface. The upper PAN layer is helpful to construct a soft contact with the NCM₆₂₂ cathode, and the lower PEO layer is effective to protect LAMP from being reduced by the lithium metal, which ensures the high-voltage tolerance of the CPE and enhances the interfacial stability of the lithium anode. This dual-functional modified ceramic electrolyte combines the advantages of different components to ensure excellent cycling stability (89% after 120 cycles) and high Coulombic efficiency (over 99.5% per cycle) in the all-solid-state lithium batteries.¹³⁶

In addition, a double-layer PEO-based CPE can also be designed with different polymer matrices. Wherein, the poly(*N*-methyl-malonic amide) (PMA)-LiTFSI high-voltage stable layer is used to contact the cathode, and the PEO-LiTFSI low-voltage stable layer is used to contact the lithium anode. A long charge/discharge cycle life can be achieved in the 4 V rechargeable Li/LCO cell by fully utilizing each layer, with dendrite-free, low-impedance plating of a Li metal anode and no oxidation of the CPE on the cathode side during cycling. Meanwhile, there is no obvious gap across three interfaces, and an intimate and uniform contact between the Li anode and the CPE is also achieved. After cycling 100 times at 65 °C, a dense passivating layer with good conduction of Li ions can be formed at the lithium anode/CPE interface without obvious formation of lithium dendrites. The above features indicate that this specific design of a double-layer structure CPE not only significantly improves the stability at a high voltage but also successfully suppresses the formation of lithium dendrites.¹³⁷

Similarly, the layered structure CPE can also be used for improving the performance of Li–S batteries.^{138–141} Typically, a PEO-based CPE is coated on both sides of LATP, which can prevent the lithium metal anode from directly contacting LATP and enhance the stability of the interface between LATP and the sulfurized polyacrylonitrile (SPAN) cathode. Correspondingly, the solid-state Li–S battery delivers the ultrahigh initial discharge capacity of 1793 mA h g⁻¹ at 75 °C and excellent cycling stability.¹³⁸ In addition, various active fillers (Li_xPON, Li_xSiPHN, and Li_xSiPON) can also be used to prepare PEO-based composite membranes with good ion transport. At room temperature, the maximum ion conductivity of the 60PEO/Li₃SiPON film is 2.8 × 10⁻³ S cm⁻¹. The solid-state Li–S battery shows a high discharge capacity of 1000 mA h g⁻¹ (sulfur) at 0.25 C with high Coulombic efficiency over 100 cycles.¹⁴⁰ The interesting point in the solid-state Li–S battery is that the reaction mechanism could be altered. For example, by coating the S/C cathode with a layer of PVDF, the reaction mechanism of the solid-state Li–S battery with the PEO-based CPE changes obviously. Low-solvent PVDF not only inhibits the formation of soluble polysulfides but also alters the reaction mechanism of sulfur from a multistep “solid–liquid–solid” reaction to a one-step “solid–solid” reaction, thus greatly improving the cycling performance of solid-state Li–S batteries. Long-chain polysulfides are insoluble in the PVDF polymer, which facilitates the direct transformation of elemental sulfur to solid Li₂S₂/Li₂S during cycling without forming intermediate products. Therefore, the introduction of polymers with low solvent properties into the sulfur cathode is promising for the development of solid-state Li–S batteries with long cycle life.¹⁴¹

Based on the above analyses, the layered heterogeneous structure design could be a feasible strategy to solve the interface issue of the all-solid-state batteries. However, more interfaces could be produced with introducing the layered structure design, which requires better structural design to reduce the interfacial resistance. In addition, the multilayer structure design may lead to an increase in the CPE thickness, which also has a negative effect on the ion conductivity and energy density of the all-solid-state batteries. Therefore, further research is needed to coordinate these issues.

5. CONCLUSIONS AND OUTLOOKS

The solid-state polymer electrolyte is one of the ideal choices for the next-generation high-energy and high-safety rechargeable lithium batteries. PEO is the most widely studied polymer matrix based on its high dielectric constant and strong lithium salt dissolving ability. However, the application of pure PEO in batteries is restricted mainly by the low ion conductivity and narrow electrochemical window. The most effective technical strategy is to construct a PEO-based CPE in view of ion conductivity, mechanical properties, and interfacial stability.

The introduction of inorganic fillers into the polymer matrix can balance the issues of ion conductivity and mechanical properties, which not only improves the ion conductivity but also guarantees that the CPE has good mechanical properties and a stable electrode/electrolyte interface. In the past decades, “inert fillers” such as metal oxides, ferroelectric materials, porous materials, and natural clays are introduced to fabricate the PEO-based CPE. These inert fillers are effective to suppress the crystallization of PEO, promote their segment motion, and significantly improve conductivity and mechanical properties of the CPE. In recent years, sulfide and oxide inorganic SEs are also used as “active fillers” to form composite structures with PEO. While reducing the crystallization degree, the advantages of high ion conductivity are expected to fuse into CPEs to further improve their ion conductivity. In addition, multidimensional structural fillers can help to construct new ion transportation networks and thus to realize the rapid transmission pathway of Li ions.

The interface between a CPE and an electrode is the key issue to construct high-performance all-solid-state lithium batteries, especially the interfacial stability of the high-voltage cathode side and the growth of lithium dendrites on the lithium anode side. On the cathode side, the strategies of a composite cathode and cathode surface modification are generally adopted to improve the compatibility of CPEs with the low-voltage cathode and the interfacial stability of the high-voltage cathode. Meanwhile, on the lithium anode side, it is quite difficult for a simple CPE to inhibit the growth of lithium dendrites; thus, constructing an artificial SEI layer becomes an effective technical strategy for the modification of the anode/CPE interface. Furthermore, the construction of the layered heterogeneous structure CPE exerts the synergy of different parts, which can simultaneously modify both the cathode and the anode, thereby synergistically improving the overall performance of the all-solid-state lithium batteries.

At present, significant progress is achieved for the PEO-based CPE, but there are still many challenges in practical application. Looking forward to future development, we need to focus on the following requirements and trends:

Further improve the ion conductivity at room temperature: At present, most of the research studies are to improve the ion conductivity of the PEO-based CPE, and it is difficult to achieve high ion conductivity similar to that of liquid electrolytes at room temperature. In order to compete with traditional liquid lithium ion batteries, a PEO-based CPE with further improved room-temperature conductivity has become the core goal.

Exploration and construction of the new conduction mechanisms of Li ions: The ionic conductivity of the PEO-based CPE is directly restricted by the conduction mechanism. The improvement of ion conductivity is

mainly based on the microregulation of the crystallization characteristics of PEO and the introduction of active fillers. In order to achieve a breakthrough on high ion conductivity, it is necessary to construct new conduction mechanisms of Li ions, which could combine the introduction of high intrinsic conductivity material systems and the design of new composite mechanisms.

Exploring new materials and composite mechanisms: Among various PEO-based CPEs, the traditional composite technology of PEO and fillers and the conventional interface design between a CPE and the anode/cathode are gradually improved in the past decades. The construction of new conduction mechanisms of Li ions naturally requires the introduction of new materials and composite mechanisms, especially the introduction of interdisciplinary concepts and technologies to support the realization of the new mechanism.

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Janek, J.; Zeier, W. G. A solid future for battery development. *Nat. Energy* **2016**, *1*, 16141.
- (2) Lian, P. J.; Zhao, B. S.; Zhang, L. Q.; Xu, N.; Wu, M. T.; Gao, X. P. Inorganic sulfide solid electrolytes for all-solid-state lithium secondary batteries. *J. Mater. Chem. A* **2019**, *7*, 20540–20557.
- (3) Kamaya, N.; Homma, K.; Yamakawa, Y.; Hirayama, M.; Kanno, R.; Yonemura, M.; Kamiyama, T.; Kato, Y.; Hama, S.; Kawamoto, K.; Mitsui, A. A lithium superionic conductor. *Nat. Mater.* **2011**, *10*, 682–686.

- (4) Kato, Y.; Hori, S.; Saito, T.; Suzuki, K.; Hirayama, M.; Mitsui, A.; Yonemura, M.; Iba, H.; Kanno, R. High-power all-solid-state batteries using sulfide superionic conductors. *Nat. Energy* **2016**, *1*, 16030.

- (5) Bachman, J. C.; Muy, S.; Grimaud, A.; Chang, H. H.; Pour, N.; Lux, S. F.; Paschos, O.; Maglia, F.; Lupart, S.; Lamp, P.; Giordano, L.; Shao-Horn, Y. Inorganic solid-state electrolytes for lithium batteries: mechanisms and properties governing ion conduction. *Chem. Rev.* **2016**, *116*, 140–162.

- (6) Meyer, W. H. Polymer Electrolytes for Lithium-Ion Batteries. *Adv. Mater.* **1998**, *10*, 439–448.

- (7) Fenton, D. E.; Parker, J. M.; Wright, P. V. Complexes of alkali metal ions with poly(ethylene oxide). *Polymer* **1973**, *14*, 589–580.

- (8) Armand, M. Polymer solid electrolytes—an overview. *Solid State Ionics* **1983**, *9-10*, 745–754.

- (9) Pan, K.; Zhang, L.; Qian, W.; Wu, X.; Dong, K.; Zhang, H.; Zhang, S. A Flexible Ceramic/Polymer Hybrid Solid Electrolyte for Solid-State Lithium Metal Batteries. *Adv. Mater.* **2020**, *32*, 2000399.

- (10) Duan, H.; Fan, M.; Chen, W. P.; Li, J. Y.; Wang, P. F.; Wang, W. P.; Shi, J. L.; Yin, Y. X.; Wan, L. J.; Guo, Y. G. Extended Electrochemical Window of Solid Electrolytes via Heterogeneous Multilayered Structure for High-Voltage Lithium Metal Batteries. *Adv. Mater.* **2019**, *31*, 1807789.

- (11) Bag, S.; Zhou, C.; Kim, P. J.; Pol, V. G.; Thangadurai, V. LiF modified stable flexible PVDF-garnet hybrid electrolyte for high performance all-solid-state Li-S batteries. *Energy Storage Mater.* **2020**, *24*, 198–207.

- (12) Xia, Y.; Liang, Y. F.; Xie, D.; Wang, X. L.; Zhang, S. Z.; Xia, X. H.; Gu, C. D.; Tu, J. P. A poly(vinylidene fluoride-hexafluoropropylene) based three-dimensional network gel polymer electrolyte for solid-state lithium-sulfur batteries. *Chem. Eng. J.* **2019**, *358*, 1047–1053.

- (13) Guan, S.; Wang, W.; Zheng, J.; Xu, C. A method to achieve full incorporation of PMMA-based gel electrolyte in fiber-structured PVB for solid-state electrochromic device fabrication. *Electrochim. Acta* **2020**, *354*, 136702.

- (14) Wang, S.; Zhang, L.; Li, J.; Zeng, Q.; Liu, X.; Chen, P.; Lai, W.-Y.; Zhao, T.; Zhang, L. A nanowire-nanoparticle double composite polymer electrolyte for high performance ambient temperature solid-state lithium batteries. *Electrochim. Acta* **2019**, *320*, 134560.

- (15) Hambali, D.; Osman, Z.; Othman, L.; Isa, K. B. M.; Harudin, N. Magnesium (II) bis(trifluoromethanesulfonimide) doped PvdC-co-AN gel polymer electrolytes for rechargeable batteries. *J. Polym. Res.* **2020**, *27*, 159.

- (16) Song, J. Y.; Wang, Y. Y.; Wan, C. C. Review of gel-type polymer electrolytes for lithium-ion batteries. *J. Power Sources* **1999**, *77*, 183–197.

- (17) Neburchilov, V.; Martin, J.; Wang, H.; Zhang, J. A review of polymer electrolyte membranes for direct methanol fuel cells. *J. Power Sources* **2007**, *169*, 221–238.

- (18) Yang, L. Y.; Wei, D. X.; Xu, M.; Yao, Y. F.; Chen, Q. Transferring lithium ions in nanochannels: a PEO/Li⁺ solid polymer electrolyte design. *Angew. Chem., Int. Ed.* **2014**, *53*, 3631–3635.

- (19) Xue, Z.; He, D.; Xie, X. Poly(ethylene oxide)-based electrolytes for lithium-ion batteries. *J. Mater. Chem. A* **2015**, *3*, 19218–19253.

- (20) Zhou, D.; Shanmukaraj, D.; Tkacheva, A.; Armand, M.; Wang, G. Polymer electrolytes for lithium-based batteries: advances and prospects. *Chem* **2019**, *5*, 2326–2352.

- (21) Gadjourova, Z.; Andreev, Y. G.; Tunstall, D. P.; Bruce, P. G. Ionic conductivity in crystalline polymer electrolytes. *Nature* **2001**, *412*, 520–523.

- (22) Fullerton-Shirey, S. K.; Maranas, J. K. Effect of LiClO₄ on the Structure and Mobility of PEO-Based Solid Polymer Electrolytes. *Macromolecules* **2009**, *42*, 2142–2156.

- (23) Tan, S.-J.; Zeng, X.-X.; Ma, Q.; Wu, X.-W.; Guo, Y.-G. Recent Advancements in Polymer-Based Composite Electrolytes for Rechargeable Lithium Batteries. *Electrochem. Energy Rev.* **2018**, *1*, 113–138.

- (24) Zhang, D.; Xu, X.; Qin, Y.; Ji, S.; Huo, Y.; Wang, Z.; Liu, Z.; Shen, J.; Liu, J. Recent Progress in Organic-Inorganic Composite

Solid Electrolytes for All-Solid-State Lithium Batteries. *Chemistry* **2020**, *26*, 1720–1736.

(25) Ma, Q.; Chakrabarti, A.; Mei, X.; Yue, Z.; Dunya, H.; Filler, R.; Mandal, B. K. New oligoether plasticizers for poly(ethylene oxide)-based solid polymer electrolytes. *Ionics* **2018**, *25*, 1633–1643.

(26) Sundaramahalingam, K.; Vanitha, D.; Nallamuthu, N.; Manikandan, A.; Muthuvinayagam, M. Electrical properties of lithium bromide poly ethylene oxide/poly vinyl pyrrolidone polymer blend electrolyte. *Phys. B* **2019**, *553*, 120–126.

(27) Devaux, D.; Glé, D.; Phan, T. N. T.; Gigmes, D.; Giroud, E.; Deschamps, M.; Denoyel, R.; Bouchet, R. Optimization of Block Copolymer Electrolytes for Lithium Metal Batteries. *Chem. Mater.* **2015**, *27*, 4682–4692.

(28) Sakakibara, T.; Kitamura, M.; Honma, T.; Kohno, H.; Uno, T.; Kubo, M.; Imanishi, N.; Takeda, Y.; Itoh, T. Cross-linked polymer electrolyte and its application to lithium polymer battery. *Electrochim. Acta* **2019**, *296*, 1018–1026.

(29) Fan, L.; Wei, S.; Li, S.; Li, Q.; Lu, Y. Recent progress of the solid-state electrolytes for high-energy metal-based batteries. *Adv. Energy Mater.* **2018**, *8*, 1702657.

(30) Liang, J.; Luo, J.; Sun, Q.; Yang, X.; Li, R.; Sun, X. Recent progress on solid-state hybrid electrolytes for solid-state lithium batteries. *Energy Storage Mater.* **2019**, *21*, 308–334.

(31) Li, L.; Deng, Y.; Chen, G. Status and prospect of garnet/polymer solid composite electrolytes for all-solid-state lithium batteries. *J. Energy Chem.* **2020**, *50*, 154–177.

(32) Weston, J. E.; Steele, B. C. H. Effects of inert fillers on the mechanical and electrochemical properties of lithium salt-poly(ethylene oxide) polymer electrolytes. *Solid State Ionics* **1982**, *7*, 75–79.

(33) Croce, F.; Curini, R.; Martinelli, A.; Persi, L.; Ronci, F.; Scrosati, B.; Caminiti, R. Physical and chemical properties of nanocomposite polymer electrolytes. *J. Phys. Chem. B* **1999**, *103*, 10632–10638.

(34) Jayathilaka, P. A. R. D.; Dissanayake, M. A. K. L.; Albinsson, I.; Mellander, B. E. Effect of nano-porous Al₂O₃ on thermal, dielectric and transport properties of the (PEO)₉LiTFSI polymer electrolyte system. *Electrochim. Acta* **2002**, *47*, 3257–3268.

(35) Money, B. K.; Hariharan, K.; Swenson, J. Glass transition and relaxation processes of nanocomposite polymer electrolytes. *J. Phys. Chem. B* **2012**, *116*, 7762–7770.

(36) Polu, A. R.; Rhee, H. W. Effect of TiO₂ nanoparticles on structural, thermal, mechanical and ionic conductivity studies of PEO₁₂-LiTDI solid polymer electrolyte. *J. Ind. Eng. Chem.* **2016**, *37*, 347–353.

(37) Fullerton-Shirey, S. K.; Maranas, J. K. Structure and Mobility of PEO/LiClO₄ Solid Polymer Electrolytes Filled with Al₂O₃ Nanoparticles. *J. Phys. Chem. C* **2010**, *114*, 9196–9206.

(38) Ketabi, S.; Lian, K. The effects of SiO₂ and TiO₂ nanofillers on structural and electrochemical properties of poly(ethylene oxide)-EMIHSO₄ electrolytes. *Electrochim. Acta* **2015**, *154*, 404–412.

(39) Croce, F.; Sacchetti, S.; Scrosati, B. Advanced, high-performance composite polymer electrolytes for lithium batteries. *J. Power Sources* **2006**, *161*, 560–564.

(40) ElBellhi, A. A.; Bayoumy, W. A.; Masoud, E. M.; Mousa, M. A. Preparation, Characterizations and Conductivity of Composite Polymer Electrolytes Based on PEO-LiClO₄ and Nano ZnO Filler. *Bull. Korean Chem. Soc.* **2012**, *33*, 2949–2954.

(41) Kim, Y. W.; Lee, W.; Choi, B. K. Relation between glass transition and melting of PEO-salt complexes. *Electrochim. Acta* **2000**, *45*, 1473–1477.

(42) Dissanayake, M. A. K. L. Nano-composite solid polymer electrolytes for solid state ionic devices. *Ionics* **2004**, *10*, 221–225.

(43) Yap, Y. L.; You, A. H.; Teo, L. L.; Hanapei, H. Inorganic filler sizes effect on ionic conductivity in polyethylene oxide (PEO) composite polymer electrolyte. *Int J. Electrochem. Sc.* **2013**, *8*, 2154–2163.

(44) Dissanayake, M. A. K. L.; Jayathilaka, P. A. R. D.; Bokalawala, R. S. P.; Albinsson, I.; Mellander, B. E. Effect of concentration and

grain size of alumina filler on the ionic conductivity enhancement of the (PEO)₉LiCF₃SO₃: Al₂O₃ composite polymer electrolyte. *J. Power Sources* **2003**, *119-121*, 409–414.

(45) Vasudevan, S.; Fullerton-Shirey, S. K. Effect of nanoparticle shape on the electrical and thermal properties of solid polymer electrolytes. *J. Phys. Chem. C* **2019**, *123*, 10720–10726.

(46) Choudhary, S.; Sengwa, R. J. Effects of different inorganic nanoparticles on the structural, dielectric and ion transportation properties of polymers blend based nanocomposite solid polymer electrolytes. *Electrochim. Acta* **2017**, *247*, 924–941.

(47) Liu, S.; Imanishi, N.; Zhang, T.; Hirano, A.; Takeda, Y.; Yamamoto, O.; Yang, J. Effect of nano-silica filler in polymer electrolyte on Li dendrite formation in Li/poly(ethylene oxide)-Li(CF₃SO₂)₂N/Li. *J. Power Sources* **2010**, *195*, 6847–6853.

(48) Liu, S.; Wang, H.; Imanishi, N.; Zhang, T.; Hirano, A.; Takeda, Y.; Yamamoto, O.; Yang, J. Effect of co-doping nano-silica filler and N-methyl-N-propylpiperidinium bis (trifluoromethanesulfonyl)imide into polymer electrolyte on Li dendrite formation in Li/poly(ethylene oxide)-Li(CF₃SO₂)₂N/Li. *J. Power Sources* **2011**, *196*, 7681–7686.

(49) Liu, Y.; Lee, J. Y.; Hong, L. Morphology, crystallinity, and electrochemical properties of in situ formed poly(ethylene oxide)/TiO₂ nanocomposite polymer electrolytes. *J. Appl. Polym. Sci.* **2003**, *89*, 2815–2822.

(50) Lin, D.; Liu, W.; Liu, Y.; Lee, H. R.; Hsu, P. C.; Liu, K.; Cui, Y. High ionic conductivity of composite solid polymer electrolyte via in situ synthesis of monodispersed SiO₂ nanospheres in poly(ethylene oxide). *Nano Lett.* **2016**, *16*, 459–465.

(51) Wang, S.; Zhang, L.; Li, J.; Zeng, Q.; Liu, X.; Chen, P.; Lai, W.-Y.; Zhao, T.; Zhang, L. A nanowire-nanoparticle double composite polymer electrolyte for high performance ambient temperature solid-state lithium batteries. *Electrochim. Acta* **2019**, *320*, 134560.

(52) Liu, W.; Lin, D.; Sun, J.; Zhou, G.; Cui, Y. Improved lithium ionic conductivity in composite polymer electrolytes with oxide-ion conducting nanowires. *ACS Nano* **2016**, *10*, 11407–11413.

(53) Zhang, X.; Xie, J.; Shi, F.; Lin, D.; Liu, Y.; Liu, W.; Pei, A.; Gong, Y.; Wang, H.; Liu, K.; Xiang, Y.; Cui, Y. Vertically aligned and continuous nanoscale ceramic-polymer interfaces in composite solid polymer electrolytes for enhanced ionic conductivity. *Nano Lett.* **2018**, *18*, 3829–3838.

(54) Zhu, Y.; Cao, J.; Chen, H.; Yu, Q.; Li, B. High electrochemical stability of a 3D cross-linked network PEO@nano-SiO₂ composite polymer electrolyte for lithium metal batteries. *J. Mater. Chem. A* **2019**, *7*, 6832–6839.

(55) Sun, H. Y.; Takeda, Y.; Imanishi, N.; Yamamoto, O.; Sohn, H.-J. Ferroelectric materials as a ceramic filler in solid composite polyethylene oxide-based electrolytes. *J. Electrochem. Soc.* **2000**, *147*, 2462.

(56) Shanmukaraj, D.; Wang, G. X.; Liu, H. K.; Murugan, R. Synthesis and characterization of SrBi₄Ti₄O₁₅ ferroelectric filler based composite polymer electrolytes for lithium ion batteries. *Polym. Bull.* **2007**, *60*, 351–361.

(57) Sunitha, V. R.; Radhakrishnan, S. Field enhanced Li ion conduction in nanoferroelectric modified polymer electrolyte systems. *Ionics* **2014**, *21*, 949–954.

(58) Prabhakaran, P.; Manimuthu, R. P.; Gurusamy, S. Influence of barium titanate nanofiller on PEO/PVdF-HFP blend-based polymer electrolyte membrane for Li-battery applications. *J. Solid State Electrochem.* **2016**, *21*, 1273–1285.

(59) Zhang, Y.; Wang, X.; Feng, W.; Zhen, Y.; Zhao, P.; Li, L.; Cai, Z. The effects of the size and content of BaTiO₃ nanoparticles on solid polymer electrolytes for all-solid-state lithium-ion batteries. *J. Solid State Electrochem.* **2019**, *23*, 749–758.

(60) Zhang, Y.; Wang, X.; Feng, W.; Zhen, Y.; Zhao, P.; Cai, Z.; Li, L. Effects of the shapes of BaTiO₃ nanofillers on PEO-based electrolytes for all-solid-state lithium-ion batteries. *Ionics* **2018**, *25*, 1471–1480.

(61) Yuan, C.; Li, J.; Han, P.; Lai, Y.; Zhang, Z.; Liu, J. Enhanced electrochemical performance of poly(ethylene oxide) based compo-

site polymer electrolyte by incorporation of nano-sized metal-organic framework. *J. Power Sources* **2013**, *240*, 653–658.

(62) Xi, J.; Qiu, X.; Cui, M.; Tang, X.; Zhu, W.; Chen, L. Enhanced electrochemical properties of PEO-based composite polymer electrolyte with shape-selective molecular sieves. *J. Power Sources* **2006**, *156*, 581–588.

(63) Xi, J.; Miao, S.; Tang, X. Selective transporting of lithium ion by shape selective molecular sieves ZSM-5 in PEO-based composite polymer electrolyte. *Macromolecules* **2004**, *37*, 8592–8598.

(64) Li, X.; Zhao, Y.; Cheng, L.; Yan, M.; Zheng, X.; Gao, Z.; Jiang, Z. Enhanced ionic conductivity of poly(ethylene oxide) (PEO) electrolyte by adding mesoporous molecular sieve LiAlSBA. *J. Solid State Electrochem.* **2005**, *9*, 609–615.

(65) Li, W.; Zhang, S.; Wang, B.; Gu, S.; Xu, D.; Wang, J.; Chen, C.; Wen, Z. Nanoporous adsorption effect on alteration of the Li⁺ diffusion pathway by a highly ordered porous electrolyte additive for high-rate all-solid-state lithium metal batteries. *ACS Appl. Mater. Interfaces* **2018**, *10*, 23874–23882.

(66) Zhang, G.; Hong, Y. L.; Nishiyama, Y.; Bai, S.; Kitagawa, S.; Horike, S. Accumulation of glassy poly(ethylene oxide) anchored in a covalent organic framework as a solid-state Li⁺ electrolyte. *J. Am. Chem. Soc.* **2019**, *141*, 1227–1234.

(67) Lee, T. K.; Zaini, N. F. M.; Mobarak, N. N.; Hassan, N. H.; Noor, S. A. M.; Mamat, S.; Loh, K. S.; KuBulat, K. H.; Su'ait, M. S.; Ahmad, A. PEO based polymer electrolyte comprised of epoxidized natural rubber material (ENR₅₀) for Li-Ion polymer battery application. *Electrochim. Acta* **2019**, *316*, 283–291.

(68) Moreno, M.; Quijada, R.; Santa Ana, M. A.; Benavente, E.; Gomez-Romero, P.; González, G. Electrical and mechanical properties of poly(ethylene oxide)/intercalated clay polymer electrolyte. *Electrochim. Acta* **2011**, *58*, 112–118.

(69) Tang, W.; Tang, S.; Guan, X.; Zhang, X.; Xiang, Q.; Luo, J. High-performance solid polymer electrolytes filled with vertically aligned 2D materials. *Adv. Funct. Mater.* **2019**, *29*, 1900648.

(70) Zhu, Q.; Wang, X.; Miller, J. D. Advanced nanoclay-based nanocomposite solid polymer electrolyte for lithium iron phosphate batteries. *ACS Appl. Mater. Interfaces* **2019**, *11*, 8954–8960.

(71) Tang, C.; Hackenberg, K.; Fu, Q.; Ajayan, P. M.; Ardebili, H. High ion conducting polymer nanocomposite electrolytes using hybrid nanofillers. *Nano Lett.* **2012**, *12*, 1152–1156.

(72) Sun, Z.; Li, Y.; Zhang, S.; Shi, L.; Wu, H.; Bu, H.; Ding, S. g-C₃N₄ nanosheets enhanced solid polymer electrolytes with excellent electrochemical performance, mechanical properties, and thermal stability. *J. Mater. Chem. A* **2019**, *7*, 11069–11076.

(73) Yang, J.; Wang, X.; Zhang, G.; Ma, A.; Chen, W.; Shao, L.; Shen, C.; Xie, K. High-performance solid composite polymer electrolyte for all solid-state lithium battery through facile microstructure regulation. *Front Chem* **2019**, *7*, 388.

(74) Riphaut, N.; Stiasny, B.; Beyer, H.; Indris, S.; Gasteiger, H. A.; Sedlmaier, S. J. Editors' Choice—Understanding Chemical Stability Issues between Different Solid Electrolytes in All-Solid-State Batteries. *J. Electrochem. Soc.* **2019**, *166*, A975–A983.

(75) Yue, L.; Ma, J.; Zhang, J.; Zhao, J.; Dong, S.; Liu, Z.; Cui, G.; Chen, L. All solid-state polymer electrolytes for high-performance lithium ion batteries. *Energy Storage Mater.* **2016**, *5*, 139–164.

(76) Wang, Y.; Richards, W. D.; Ong, S. P.; Miara, L. J.; Kim, J. C.; Mo, Y.; Ceder, G. Design principles for solid-state lithium superionic conductors. *Nat. Mater.* **2015**, *14*, 1026–1031.

(77) Zhao, Y.; Wu, C.; Peng, G.; Chen, X.; Yao, X.; Bai, Y.; Wu, F.; Chen, S.; Xu, X. A new solid polymer electrolyte incorporating Li₁₀GeP₂S₁₂ into a polyethylene oxide matrix for all-solid-state lithium batteries. *J. Power Sources* **2016**, *301*, 47–53.

(78) Chen, B.; Huang, Z.; Chen, X.; Zhao, Y.; Xu, Q.; Long, P.; Chen, S.; Xu, X. A new composite solid electrolyte PEO/Li₁₀GeP₂S₁₂/SN for all-solid-state lithium battery. *Electrochim. Acta* **2016**, *210*, 905–914.

(79) Chen, S.; Wang, J.; Zhang, Z.; Wu, L.; Yao, L.; Wei, Z.; Deng, Y.; Xie, D.; Yao, X.; Xu, X. In-situ preparation of poly(ethylene oxide)/Li₃PS₄ hybrid polymer electrolyte with good nanofiller

distribution for rechargeable solid-state lithium batteries. *J. Power Sources* **2018**, *387*, 72–80.

(80) Xu, X.; Hou, G.; Nie, X.; Ai, Q.; Liu, Y.; Feng, J.; Zhang, L.; Si, P.; Guo, S.; Ci, L. Li₃P₃S₁₁/poly(ethylene oxide) hybrid solid electrolytes with excellent interfacial compatibility for all-solid-state batteries. *J. Power Sources* **2018**, *400*, 212–217.

(81) Li, X.; Wang, D.; Wang, H.; Yan, H.; Gong, Z.; Yang, Y. Poly(ethylene oxide)-Li₁₀SnP₂S₁₂ composite polymer electrolyte enables high-performance all-solid-state lithium sulfur battery. *ACS Appl. Mater. Interfaces* **2019**, *11*, 22745–22753.

(82) Liu, Y.; He, P.; Zhou, H. Rechargeable Solid-State Li-Air and Li-S Batteries: Materials, Construction, and Challenges. *Adv. Energy Mater.* **2018**, *8*, 1701602.

(83) Choi, J. H.; Lee, C. H.; Yu, J. H.; Doh, C. H.; Lee, S. M. Enhancement of ionic conductivity of composite membranes for all-solid-state lithium rechargeable batteries incorporating tetragonal Li₇La₃Zr₂O₁₂ into a polyethylene oxide matrix. *J. Power Sources* **2015**, *274*, 458–463.

(84) Zhang, J.; Zhao, N.; Zhang, M.; Li, Y.; Chu, P. K.; Guo, X.; Di, Z.; Wang, X.; Li, H. Flexible and ion-conducting membrane electrolytes for solid-state lithium batteries: dispersion of garnet nanoparticles in insulating polyethylene oxide. *Nano Energy* **2016**, *28*, 447–454.

(85) Zha, W.; Chen, F.; Yang, D.; Shen, Q.; Zhang, L. High-performance Li_{6.4}La₃Zr_{1.4}Ta_{0.6}O₁₂/poly(ethylene oxide)/succinonitrile composite electrolyte for solid-state lithium batteries. *J. Power Sources* **2018**, *397*, 87–94.

(86) Li, Z.; Huang, H. M.; Zhu, J. K.; Wu, J. F.; Yang, H.; Wei, L.; Guo, X. Ionic conduction in composite polymer electrolytes: case of PEO:Ga-LLZO composites. *ACS Appl. Mater. Interfaces* **2019**, *11*, 784–791.

(87) Brogioli, D.; Langer, F.; Kun, R.; La Mantia, F. Space-charge effects at the Li₇La₃Zr₂O₁₂/poly(ethylene oxide) interface. *ACS Appl. Mater. Interfaces* **2019**, *11*, 11999–12007.

(88) Chen, L.; Li, Y.; Li, S.-P.; Fan, L.-Z.; Nan, C.-W.; Goodenough, J. B. PEO/garnet composite electrolytes for solid-state lithium batteries: From “ceramic-in-polymer” to “polymer-in-ceramic”. *Nano Energy* **2018**, *46*, 176–184.

(89) Song, S.; Wu, Y.; Tang, W.; Deng, F.; Yao, J.; Liu, Z.; Hu, R.; Alamus; Wen, Z.; Lu, L.; Hu, N. Composite solid polymer electrolyte with garnet nanosheets in poly(ethylene oxide). *ACS Sustainable Chem. Eng.* **2019**, *7*, 7163–7170.

(90) Fu, K. K.; Gong, Y.; Dai, J.; Gong, A.; Han, X.; Yao, Y.; Wang, C.; Wang, Y.; Chen, Y.; Yan, C.; Li, Y.; Wachsmann, E. D.; Hu, L. Flexible, solid-state, ion-conducting membrane with 3D garnet nanofiber networks for lithium batteries. *Proc. Natl. Acad. Sci.* **2016**, *113*, 7094–7099.

(91) Bae, J.; Li, Y.; Zhao, F.; Zhou, X.; Ding, Y.; Yu, G. Designing 3D nanostructured garnet frameworks for enhancing ionic conductivity and flexibility in composite polymer electrolytes for lithium batteries. *Energy Storage Mater.* **2018**, *15*, 46–52.

(92) Wei, W.; Li, L.; Zhang, L.; Hong, J.; He, G. An all-solid-state Li-organic battery with quinone-based polymer cathode and composite polymer electrolyte. *Electrochem. Commun.* **2018**, *90*, 21–25.

(93) Milian Pila, C. R.; Cappe, E. P.; Mohallem, N. D. S.; Alves, O. L.; Aguilar Frutis, M. A.; Sánchez-Ramírez, N.; Torresi, R. M.; León Ramírez, H.; Laffita, Y. M. Effect of the LLTO nanoparticles on the conducting properties of PEO-based solid electrolyte. *Solid State Sci.* **2019**, *88*, 41–47.

(94) Liu, W.; Liu, N.; Sun, J.; Hsu, P. C.; Li, Y.; Lee, H. W.; Cui, Y. Ionic conductivity enhancement of polymer electrolytes with ceramic nanowire fillers. *Nano Lett.* **2015**, *15*, 2740–2745.

(95) Zhu, P.; Yan, C.; Dirican, M.; Zhu, J.; Zang, J.; Selvan, R. K.; Chung, C.-C.; Jia, H.; Li, Y.; Kiyak, Y.; Wu, N.; Zhang, X. Li_{0.33}La_{0.557}TiO₃ ceramic nanofiber-enhanced polyethylene oxide-based composite polymer electrolytes for all-solid-state lithium batteries. *J. Mater. Chem. A* **2018**, *6*, 4279–4285.

- (96) Zhu, L.; Zhu, P.; Fang, Q.; Jing, M.; Shen, X.; Yang, L. A novel solid PEO/LLTO-nanowires polymer composite electrolyte for solid-state lithium-ion battery. *Electrochim. Acta* **2018**, *292*, 718–726.
- (97) Liu, W.; Lee, S. W.; Lin, D.; Shi, F.; Wang, S.; Sendek, A. D.; Cui, Y. Enhancing ionic conductivity in composite polymer electrolytes with well-aligned ceramic nanowires. *Nat. Energy* **2017**, *2*, 17053.
- (98) Wang, X.; Zhang, Y.; Zhang, X.; Liu, T.; Lin, Y. H.; Li, L.; Shen, Y.; Nan, C. W. Lithium-salt-rich PEO/Li_{0.3}La_{0.55}7TiO₃interpenetrating composite electrolyte with three-dimensional ceramic nano-backbone for all-solid-state lithium-ion batteries. *ACS Appl. Mater. Interfaces* **2018**, *10*, 24791–24798.
- (99) Thokchom, J. S.; Kumar, B. Composite effect in superionically conducting lithium aluminium germanium phosphate based glass-ceramic. *J. Power Sources* **2008**, *185*, 480–485.
- (100) Cheng, Q.; Li, A.; Li, N.; Li, S.; Zangiabadi, A.; Li, T.-D.; Huang, W.; Li, A. C.; Jin, T.; Song, Q.; Xu, W.; Ni, N.; Zhai, H.; Dontigny, M.; Zaghbi, K.; Chuan, X.; Su, D.; Yan, K.; Yang, Y. Stabilizing solid electrolyte-anode interface in Li-metal batteries by boron nitride-based nanocomposite coating. *Joule* **2019**, *3*, 1510–1522.
- (101) Jung, Y.-C.; Park, M.-S.; Doh, C.-H.; Kim, D.-W. Organic-inorganic hybrid solid electrolytes for solid-state lithium cells operating at room temperature. *Electrochim. Acta* **2016**, *218*, 271–277.
- (102) Zhao, Y.; Huang, Z.; Chen, S.; Chen, B.; Yang, J.; Zhang, Q.; Ding, F.; Chen, Y.; Xu, X. A promising PEO/LAGP hybrid electrolyte prepared by a simple method for all-solid-state lithium batteries. *Solid State Ionics* **2016**, *295*, 65–71.
- (103) Zhai, H.; Xu, P.; Ning, M.; Cheng, Q.; Mandal, J.; Yang, Y. A flexible solid composite electrolyte with vertically aligned and connected ion-conducting nanoparticles for lithium batteries. *Nano Lett.* **2017**, *17*, 3182–3187.
- (104) Wang, X.; Zhai, H.; Qie, B.; Cheng, Q.; Li, A.; Borovilas, J.; Xu, B.; Shi, C.; Jin, T.; Liao, X.; Li, Y.; He, X.; Du, S.; Fu, Y.; Dontigny, M.; Zaghbi, K.; Yang, Y. Rechargeable solid-state lithium metal batteries with vertically aligned ceramic nanoparticle/polymer composite electrolyte. *Nano Energy* **2019**, *60*, 205–212.
- (105) Munoz, S.; Greenbaum, S. Review of Recent Nuclear Magnetic Resonance Studies of Ion Transport in Polymer Electrolytes. *Membranes* **2018**, *8*, 120.
- (106) Zheng, J.; Wang, P.; Liu, H.; Hu, Y. Y. Interface-enabled ion conduction in Li₁₀GeP₂S₁₂-Poly(ethylene Oxide) Hybrid Electrolytes. *ACS Appl. Energy Mater.* **2019**, *2*, 1452–1459.
- (107) Zheng, J.; Hu, Y. Y. New insights into the compositional dependence of Li-ion transport in polymer-ceramic composite electrolytes. *ACS Appl. Mater. Interfaces* **2018**, *10*, 4113–4120.
- (108) Zheng, J.; Tang, M.; Hu, Y.-Y. Lithium ion pathway within Li₇La₃Zr₂O₁₂-polyethylene oxide composite electrolytes. *Am. Ethnol.* **2016**, *128*, 12726–12730.
- (109) Zheng, J.; Dang, H.; Feng, X.; Chien, P. H.; Hu, Y. Y. Li-ion transport in a representative ceramic-polymer-plasticizer composite electrolyte: Li₇La₃Zr₂O₁₂-polyethylene oxide-tetraethylene glycol dimethyl ether. *J. Mater. Chem. A* **2017**, *5*, 18457–18463.
- (110) Zhou, W.; Wang, S.; Li, Y.; Xin, S.; Manthiram, A.; Goodenough, J. B. Plating a dendrite-free lithium anode with a polymer/ceramic/polymer sandwich electrolyte. *J. Am. Chem. Soc.* **2016**, *138*, 9385–9388.
- (111) Sun, J.; Huang, Y.; Wang, W.; Yu, Z.; Wang, A.; Yuan, K. Application of gelatin as a binder for the sulfur cathode in lithium-sulfur batteries. *Electrochim. Acta* **2008**, *53*, 7084–7088.
- (112) Chen, R. J.; Zhang, Y. B.; Liu, T.; Xu, B. Q.; Lin, Y. H.; Nan, C. W.; Shen, Y. Addressing the interface issues in all-solid-state bulk-type lithium ion battery via an all-composite approach. *ACS Appl. Mater. Interfaces* **2017**, *9*, 9654–9661.
- (113) Sheng, O.; Jin, C.; Luo, J.; Yuan, H.; Huang, H.; Gan, Y.; Zhang, J.; Xia, Y.; Liang, C.; Zhang, W.; Tao, X. Mg₃B₂O₅ Nanowire Enabled Multifunctional Solid-State Electrolytes with High Ionic Conductivity, Excellent Mechanical Properties, and Flame-Retardant Performance. *Nano Lett.* **2018**, *18*, 3104–3112.
- (114) Chen, X.; He, W.; Ding, L.-X.; Wang, S.; Wang, H. Enhancing interfacial contact in all solid state batteries with a cathode-supported solid electrolyte membrane framework. *Energy Environ. Sci.* **2019**, *12*, 938–944.
- (115) Wan, Z.; Lei, D.; Yang, W.; Liu, C.; Shi, K.; Hao, X.; Shen, L.; Lv, W.; Li, B.; Yang, Q.-H.; Kang, F.; He, Y.-B. Low resistance-integrated all-solid-state battery achieved by Li₇La₃Zr₂O₁₂nanowire upgrading polyethylene oxide (PEO) composite electrolyte and PEO cathode binder. *Adv. Funct. Mater.* **2019**, *29*, 1805301.
- (116) Yang, X.; Jiang, M.; Gao, X.; Bao, D.; Sun, Q.; Holmes, N.; Duan, H.; Mukherjee, S.; Adair, K.; Zhao, C.; Liang, J.; Li, W.; Li, J.; Liu, Y.; Huang, H.; Zhang, L.; Lu, S.; Lu, Q.; Li, R.; Singh, C. V.; Sun, X. Determining the limiting factor of the electrochemical stability window for PEO-based solid polymer electrolytes: main chain or terminal –OH group? *Energy Environ. Sci.* **2020**, *13*, 1318–1325.
- (117) Qiu, J.; Liu, X.; Chen, R.; Li, Q.; Wang, Y.; Chen, P.; Gan, L.; Lee, S.-J.; Nordlund, D.; Liu, Y.; Yu, X.; Bai, X.; Li, H.; Chen, L. Enabling stable cycling of 4.2 V high-voltage all-solid-state batteries with PEO-based solid electrolyte. *Adv. Funct. Mater.* **2020**, *30*, 1909392.
- (118) Nie, K.; Wang, X.; Qiu, J.; Wang, Y.; Yang, Q.; Xu, J.; Yu, X.; Li, H.; Huang, X.; Chen, L. Increasing poly(ethylene oxide) stability to 4.5 V by surface coating of the cathode. *ACS Energy Lett.* **2020**, *5*, 826–832.
- (119) Ma, J.; Liu, Z.; Chen, B.; Wang, L.; Yue, L.; Liu, H.; Zhang, J.; Liu, Z.; Cui, G. A strategy to make high voltage LiCoO₂ compatible with polyethylene oxide electrolyte in all-solid-state lithium ion batteries. *J. Electrochem. Soc.* **2017**, *164*, A3454–A3461.
- (120) Liang, J.; Sun, Y.; Zhao, Y.; Sun, Q.; Luo, J.; Zhao, F.; Lin, X.; Li, X.; Li, R.; Zhang, L.; Lu, S.; Huang, H.; Sun, X. Engineering the conductive carbon/PEO interface to stabilize solid polymer electrolytes for all-solid-state high voltage LiCoO₂ batteries. *J. Mater. Chem. A* **2020**, *8*, 2769–2776.
- (121) Yang, Q.; Huang, J.; Li, Y.; Wang, Y.; Qiu, J.; Zhang, J.; Yu, H.; Yu, X.; Li, H.; Chen, L. Surface-protected LiCoO₂ with ultrathin solid oxide electrolyte film for high-voltage lithium ion batteries and lithium polymer batteries. *J. Power Sources* **2018**, *388*, 65–70.
- (122) Chen, L.; Qiu, X.; Bai, Z.; Fan, L. Z. Enhancing interfacial stability in solid-state lithium batteries with polymer/garnet solid electrolyte and composite cathode framework. *J. Energy Chem.* **2021**, *52*, 210–217.
- (123) Li, Z.; Li, A.; Zhang, H.; Lin, R.; Jin, T.; Cheng, Q.; Xiao, X.; Lee, W.-K.; Ge, M.; Zhang, H.; Zangiabadi, A.; Waluyo, I.; Hunt, A.; Zhai, H.; Borovilas, J.; Wang, P.; Yang, X.-Q.; Chuan, X.; Yang, Y. Interfacial engineering for stabilizing polymer electrolytes with 4V cathodes in lithium metal batteries at elevated temperature. *Nano Energy* **2020**, *72*, 104655.
- (124) Zhao, Q.; Chen, P.; Li, S.; Liu, X.; Archer, L. A. Solid-state polymer electrolytes stabilized by task-specific salt additives. *J. Mater. Chem. A* **2019**, *7*, 7823–7830.
- (125) Cao, D.; Sun, X.; Li, Q.; Natan, A.; Xiang, P.; Zhu, H. Lithium dendrite in all-solid-state batteries: growth mechanisms, suppression strategies, and characterizations. *Matter* **2020**, *3*, 57–94.
- (126) Chien, P.-H.; Feng, X.; Tang, M.; Rosenberg, J. T.; O'Neill, S.; Zheng, J.; Grant, S. C.; Hu, Y.-Y. Li Distribution Heterogeneity in Solid Electrolyte Li₁₀GeP₂S₁₂ upon Electrochemical Cycling Probed by ⁷Li MRI. *J. Phys. Chem. Lett.* **2018**, *9*, 1990–1998.
- (127) Zhu, J.; Li, P.; Chen, X.; Legut, D.; Fan, Y.; Zhang, R.; Lu, Y.; Cheng, X.; Zhang, Q. Rational design of graphitic-inorganic Bi-layer artificial SEI for stable lithium metal anode. *Energy Storage Mater.* **2019**, *16*, 426–433.
- (128) Wang, C.; Bai, G.; Yang, Y.; Liu, X.; Shao, H. Dendrite-free all-solid-state lithium batteries with lithium phosphorous oxynitride-modified lithium metal anode and composite solid electrolytes. *Nano Res.* **2018**, *12*, 217–223.
- (129) Wang, G.; Chen, C.; Chen, Y.; Kang, X.; Yang, C.; Wang, F.; Liu, Y.; Xiong, X. Self-stabilized and strongly adhesive supramolecular

polymer protective layer enables ultrahigh-rate and large-capacity lithium-metal anode. *Am. Ethnol.* **2019**, *132*, 2071–2076.

(130) Xu, R.; Zhang, X. Q.; Cheng, X. B.; Peng, H. J.; Zhao, C. Z.; Yan, C.; Huang, J. Q. Artificial soft-rigid protective layer for dendrite-free lithium metal anode. *Adv. Funct. Mater.* **2018**, *28*, 1705838.

(131) Hou, G.; Ma, X.; Sun, Q.; Ai, Q.; Xu, X.; Chen, L.; Li, D.; Chen, J.; Zhong, H.; Li, Y.; Xu, Z.; Si, P.; Feng, J.; Zhang, L.; Ding, F.; Ci, L. Lithium dendrite suppression and enhanced interfacial compatibility enabled by an ex situ SEI on Li anode for LAGP-based all-solid-state batteries. *ACS Appl. Mater. Interfaces* **2018**, *10*, 18610–18618.

(132) Wang, C.; Yang, Y.; Liu, X.; Zhong, H.; Xu, H.; Xu, Z.; Shao, H.; Ding, F. Suppression of lithium dendrite formation by using LAGP-PEO (LiTFSI) composite solid electrolyte and lithium metal anode modified by PEO (LiTFSI) in all-solid-state lithium batteries. *ACS Appl. Mater. Interfaces* **2017**, *9*, 13694–13702.

(133) Liu, K.; Zhang, R.; Sun, J.; Wu, M.; Zhao, T. Polyoxyethylene (PEO)|PEO-Perovskite|PEO composite electrolyte for all-solid-state lithium metal batteries. *ACS Appl. Mater. Interfaces* **2019**, *11*, 46930–46937.

(134) Zhang, Z.; Chen, S.; Yao, X.; Cui, P.; Duan, J.; Luo, W.; Huang, Y.; Xu, X. Enabling high-areal-capacity all-solid-state lithium-metal batteries by tri-layer electrolyte architectures. *Energy Storage Mater.* **2020**, *24*, 714–718.

(135) Wang, C.; Wang, T.; Wang, L.; Hu, Z.; Cui, Z.; Li, J.; Dong, S.; Zhou, X.; Cui, G. Differentiated lithium salt design for multilayered PEO electrolyte enables a high-voltage solid-state lithium metal battery. *Adv. Sci.* **2019**, *6*, 1901036.

(136) Liang, J. Y.; Zeng, X. X.; Zhang, X. D.; Zuo, T. T.; Yan, M.; Yin, Y. X.; Shi, J. L.; Wu, X. W.; Guo, Y. G.; Wan, L. J. Engineering janus interfaces of ceramic electrolyte via distinct functional polymers for stable high-voltage Li-metal batteries. *J. Am. Chem. Soc.* **2019**, *141*, 9165–9169.

(137) Zhou, W.; Wang, Z.; Pu, Y.; Li, Y.; Xin, S.; Li, X.; Chen, J.; Goodenough, J. B. Double-layer polymer electrolyte for high-voltage all-solid-state rechargeable batteries. *Adv. Mater.* **2019**, *31*, 1805574.

(138) Wang, Y.; Wang, G.; He, P.; Hu, J.; Jiang, J.; Fan, L.-Z. Sandwich structured NASICON-type electrolyte matched with sulfurized polyacrylonitrile cathode for high performance solid-state lithium-sulfur batteries. *Chem. Eng. J.* **2020**, *393*, 124705.

(139) Zhang, Y.; Chen, R.; Wang, S.; Liu, T.; Xu, B.; Zhang, X.; Wang, X.; Shen, Y.; Lin, Y.-H.; Li, M.; Fan, L.-Z.; Li, L.; Nan, C.-W. Free-standing sulfide/polymer composite solid electrolyte membranes with high conductance for all-solid-state lithium batteries. *Energy Storage Mater.* **2020**, *25*, 145–153.

(140) Temeche, E.; Zhang, X.; Laine, R. M. Solid Electrolytes for Li-S Batteries: Solid Solutions of Poly(ethylene oxide) with Li_xPON- and Li_xSiPON-Based Polymers. *ACS Appl. Mater. Interfaces* **2020**, *12*, 30353–30364.

(141) Fang, R.; Xu, H.; Xu, B.; Li, X.; Li, Y.; Goodenough, J. B. Reaction Mechanism Optimization of Solid-State Li–S Batteries with a PEO-Based Electrolyte. *Adv. Funct. Mater.* **2020**, *31*, 2001812.