Review

Challenges and Development of Composite Solid Electrolytes for All-solid-state Lithium Batteries

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All-solid-state lithium batteries are considered to be a new battery system with great development potential and application prospects due to the advantages of high energy density and high security. As a key component of all-solid-state lithium batteries, the development of solid-state electrolytes has received extensive attention in recent years, but most solid electrolytes still exhibit problems, such as low ion conductivity and poor interface compatibility. The design of composite solid-state electrolyte materials with both excellent electrochemical and mechanical properties is an effective way to develop all-solid-state lithium batteries. This review introduces different types of pure component solid electrolytes and analyzes their respective advantages and characteristics firstly. Furthermore, the research progress of composite electrolytes in preparation method, ionic conduction, suppression of lithium dendrites, and the improvement of electrochemical performances are reviewed from the perspective of composite electrolyte structure design, which is to meet different performance requirements. And the future development direction and trend of composite electrolytes are prospected.

Keywords All-solid-state lithium battery; Solid electrolyte; Composite solid electrolyte

1 Introduction

Lithium-ion batteries have gradually become an important energy storage device in modern life since the commercialization of them in the 1990s. Lithium-ion batteries are widely used in various fields, such as daily life and production from rail transit to electronic products due to the advantages of high energy density, high output power, low self-discharge, no memory effect and environmental friendliness[1,2]. However, traditional lithium-ion batteries use the organic liquid electrolyte as the ion transmission medium. These organic liquid electrolytes have various safety hazards, such as leakage, volatilization, and combustion. Side-reactions with the electrode during the charge and discharge process will lead to the degradation of battery capacity and service life[3,4]. In addition, electrolytes and diaphragm occupy a large part of the volume and mass in the traditional lithium-ion batteries, which limits the increase of battery energy density[5]. When the liquid electrolyte is replaced with the solid electrolyte, the safety problem caused by the electrolyte will be solved[6]. Electrodes and electrolyte membranes can be stacked in the same mold to form the internal series of the battery with special assembly technology, which is of great significance for improving the energy density of the entire battery module[7,8]. In addition, the energy density of traditional lithium-ion batteries using graphite anodes has approached its upper limit[9]. The next generation of high energy density batteries represented by the lithium metal systems is difficult to adapt to the electrolyte environment[10], because the uneven lithium deposition on the surface of the lithium anode during the working process can easily lead to the growth of lithium dendrites, that will pierce the diaphragm and cause short-circuit or explosion[11,12]. In addition, the use of solid electrolyte can alleviate the above problems, and it brings the possibility for the development and the use of solid-state lithium metal batteries[13].

The solid electrolytes have high mechanical strength and wide electrochemical window, that can match the application requirements of high voltage cathode and lithium metal anode at the same time, which is of great significance for improving the energy density of the lithium batteries[14,15]. All-solid-state lithium batteries are considered to be the next generation lithium battery technology with great development potential due to the advantages of high energy density and high safety. As the core component of solid-state lithium batteries, solid-state electrolyte affects the batteries performance, such as the energy density, cycle stability, and work safety in a direct way. Recently, various strategies have been carried out to improve the electrolyte performance. However, the research and application of electrolytes still face many problems[16,17]. The primary problems are the basic electrochemical performance of electrolytes, such as ion conductivity and Li-ions transference number. Higher ion conductivity and Li-ions transference number can reduce battery polarization and guide lithium ions to deposit uniformly. These are the basic requirements of the ability to work with high current and stable circulation for battery[18]. Unfortunately, most polymer

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electrolytes show a low ionic conductivity(10^{-8}—10^{-5} S/cm) and a low Li-ions transference number(t_{Li^+}<0.5) at room temperature[19]. Although oxide and a sulfide electrolytes exhibit a higher ionic conductivity(10^{-4}—10^{-3} S/cm) and a higher lithium Li-ions transference number(t_{Li^+} close 0.5), the serious interface impedance of oxide electrolytes[20] and the poor air stability of sulfide electrolytes limit the feasibility of their application[1]. Thus, many attentions should be paid to the stability of the interface between the electrolyte and the electrode. The interface problems are mainly manifested in the electrochemical window of the electrolyte and the ability to inhibit lithium dendrites[21]. The polymer solid electrolytes have low interface impedance, because of their better wettability and flexibility in contact with the electrodes. But the ability of polymer electrolytes to inhibit lithium dendrites is not as good as those of other rigid ceramic solid electrolytes. In addition, the electro-chemical window of most polymer electrolytes is narrow relatively, so the improvement of the energy density of solid-state batteries is relatively limited since it is difficult to match high-voltage cathode materials[22]. Generally, oxide solid electrolytes have a wide electrochemical window, and their ability to inhibit the rigidity of lithium dendrites is also excellent. But the latest research shows that lithium dendrites can even grow by the internal grain boundaries of ceramics, which indicates that to resist the growth of lithium dendrites through the mechanical strength of the solid electrolyte is not feasible[23,24]. Generally, oxide solid electrolytes are prepared through a series of cumbersome technological processes, such as hydrothermal, ball milling, and high-temperature sintering, which make the production more expensive[25]. Although the preparation of the sulfide electrolytes is simple, the preparation and storage processes are strict for the environment and equipment due to their poor air stability, which is also not suitable for large-scale production. The preparation process of polymer solid electrolytes is simple, which requires some processes, such as mixing, dissolving, and forming. Unfortunately, polymer electrolytes are almost difficult to work normally at room temperature when matching with electrodes[26]. Thus, the preparation methods and their suitable application fields of solid electrolytes are of great significance to the study of the large-scale commercialization of solid electrolytes.

Obviously, the existing single-component solid electrolyte system cannot meet all the performance requirements of solid lithium batteries. Composite solid electrolytes combine different types of solid electrolytes together through regulating component and designing structural, which is also an effective way to study new solid electrolytes[27]. However, composite solid electrolytes also face many problems. In order to solve these problems, the characteristics and advantages of the various components of the composite electrolytes need to be fully understood firstly. Secondly, the research should focus on how to improve the preparation, ionic conduction, lithium dendrites, and electrochemical window of the composite electrolyte. Finally, the development trend and the prospect of composite electrolytes in the future are also worthy of attention.

2 Solid Electrolytes

Generally, solid electrolytes can be divided into three categories: inorganic solid electrolytes, polymer solid electrolytes and composite solid electrolytes[28]. This review will focus on composite solid electrolytes, but the introduction of different single-component solid electrolytes is beneficial for the understand of composite electrolytes. In general, single-component solid electrolytes have their own unique properties. We must understand the different types of solid electrolytes clearly before using and designing composite solid electrolytes.

2.1 Oxide-based Solid Electrolytes

Garnet-type, NASICON-type, and perovskite-type solid electrolytes are the most typical oxide-based solid electrolytes, which exhibit high ionic conductivity and excellent mechanical strength. These advantages make them attracted much attention in the competition of solid electrolytes. We will introduce the structural composition, electrochemical performance, and challenges of oxide-based solid electrolytes in following.

The general formula of the garnet-type solid electrolytes can be expressed as $Li_{3+x}A_3B_2O_{12}$, where A is an eight-coordinate cation and B is a six-coordinate cation[Fig.1(A)]. AO_8 and BO_6 are cross-connected in a coplanar manner to form a 3D skeleton, and the skeleton clearance is filled with octahedral vacancy and tetrahedral vacancy formed by O. Li^+ transfers from the tetrahedral vacancy with strong binding force to the octahedral vacancy with relatively weak binding force with the increase of x, which makes the tetrahedral vacancy defective, so that the ionic conductivity increased[29]. $Li_7La_3Zr_2O_{12}$(LLZO) is a typical garnet structure solid electrolyte with a high ionic conductivity and a wide voltage window[30]. According to the different synthesis conditions, LLZO shows two structures: cubic phase and tetragonal phase. The cubic phase is a high-temperature stable phase with a high ionic conductivity(10^{-4}—10^{-3} S/cm)[31]. It is obvious that LLZO in the cubic phase is more suitable for practical application as a solid electrolyte, but it requires harsh preparation conditions, such as high sintering temperatures. The research on garnet-type solid electrolytes mainly focuses on different element-doped LLZO and its derivatives at present[32,33]. LLZO solid

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electrolytes not only have a high ionic conductivity and a wide electrochemical window, but also exhibit good chemical stability to lithium metal anode[34]. Meanwhile, the ceramic body obtains an excellent mechanical strength during high temperature sintering[35], and the Young's modulus of LLZO can reach 150 GPa[36]. Therefore, LLZO is considered to be the most promising oxide solid electrolyte, and the research on its electrochemical performance and interface engineering has also received extensive attention[37]. However, the air stability of LLZO is poor. It can easily produce Li_2CO_3 and LiOH by reacting with H_2O and CO_2. In addition, the interface side reactions are existing between LLZO solid electrolyte and some cathode materials. For example, Co, Zr, and La elements will interdiffusion at the interface of LLZO/$LiCoO_2$[Fig.1(E)]. These side reactions can cause low ionic conductivity at the interface, which affects the capacity performance and cycle life of the battery[38]. Moreover, the actual situation shows that LLZO with a high mechanical strength cannot block lithium dendrites effectively, because lithium dendrites can grow through the grain boundaries in LLZO crystals[Fig.1(F)][39,40]. The high mechanical strength also brings more serious problems, such as interface mismatch phenomenon [Fig.1(G)][41].

The NASICON structure $Na_3Zr_2Si_2PO_{12}$ sodium ion solid electrolytes were first reported by Goodenough *et al*.[42] in 1976. The electrolytes can not only conduct sodium ions, but conduct lithium-ions quickly, when replacing sodium ions with lithium-ions with the same structure. The general structural formula of fast lithium-ion conductor is $LiT_2(PO_4)_3$, where T can be Ti, Ge, Zr or other elements[Fig.1(B)]. Using trivalent ions(Al^{3+}, Cr^{3+}, Ga^{3+}, etc.) substitute and dope can obtain $Li_{1+x}M_xTi_{2-x}(PO_4)_3$, $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$(LATP) and $Li_{1+x}Al_xGe_{2-x}(PO_4)_3$(LAGP) electrolytes, which exhibit a high conductivity(10^{-3}—10^{-2} S/cm)[43]. The crystal structure of LATP[44] belongs to the $R3c$ space point group, which is formed by TiO_6 octahedron and PO_4 tetrahedron. Every TiO_6 octahedron is connected with six PO_4 tetrahedrons, and every PO_4 tetrahedron is connected with four TiO_6 octahedrons. The polyhedrons are connected with the vertex oxygen atoms that are in contact with each other, forming a three-dimensional interconnection skeleton structure and an ion transport channel parallel to the c axis. The special crystal structure brings excellent ionic conductivity to these electrolytes. However, these electrolytes exhibit some disadvantages. The stability of the interface between LATP and lithium metal is poor, because the Ti^{4+} in the electrolyte crystal is easily reduced to Ti^{3+} by lithium metal[Fig.1(D)][45]. In contrast, the LAGP electrolytes prepared by the molten salt quenching have both the advantages of ceramics and glass. It is relatively stable in contact with lithium metal because of the high ionic conductivity[46].

The perovskite-type $Li_{3x}La_{2/3-x}TiO_3$(LLTO) electrolytes can be regarded as a solid solution structure[Fig.1(C)], which is composed of high-temperature cubic phase and low-temperature tetragonal phase, and exhibits the advantages of stable structure, simple preparation process and a wide range of composition adjustment[47—49]. Different preparation conditions can control the crystal to present four different crystal structures: cubic phase, tetragonal phase, orthogonal phase, and hexagonal phase[50,51]. The ionic conductivity of the ceramic electrolytes is determined by the particle conductivity and the grain boundary conductivity. Although the LLTO particle conductivity can reach 10^{-3} S/cm, the high grain boundary resistance results in the low total ionic conductivity of LLTO($<10^{-5}$ S/cm)[52]. The conventional doping method shows no obvious effect on improving the ion conductivity of LLTO, but it is an effective way to improve the ion conductivity by introducing amorphous substances to modify the grain boundary[53]. Mei *et al*.[54] introduced amorphous SiO_2 into the LLTO matrix, then the anisotropy of LLTO grain interface was limited after the modification of the amorphous layer, which greatly reduced the interface impedance and improved the total ion conductivity to 10^{-4} S/cm. However, the poor interface compatibility of LLTO with lithium metal is similar to the LATP solid electrolytes. The Ti^{4+} inside the electrolyte crystal can be reduced to Ti^{3+} by metal lithium, that will introduce undesirable electronic conductance[55], which limits the practicality application of LLTO solid electrolytes.

Although oxide-type solid electrolytes have a high ionic conductivity[56] and an excellent mechanical strength, they also have some common shortcomings, such as interface side reactions and interface mismatch phenomenon[57]. In addition, the complicated preparation process and poor air stability of oxide-type solid electrolytes increase the application cost. Most of the researchers solve these interface side reaction problems by building a stable coating layer between electrode and electrolyte. Liu *et al*.[45] coated the surface of LATP with a thin layer of Al_2O_3 to prevent Ti^{4+} in LATP from being reduced[Fig.2(A) and (B)]. Kobayashi *et al*.[58] coated solid polymer electrolyte on the surface of LLTO to avoid direct contact between LLTO and lithium metal, and the assembled all-solid-state battery showed an excellent cycle performance. In order to decrease the interface impedance between these electrolytes and lithium metal anode, most researchers solidify the molten metal lithium on the solid electrolyte to make the two parts closely bound together[59], because the molten lithium metal exhibits fluidity and can be filled into the gaps of the rough electrolyte surface. However, garnet-type solid electrolytes show apoor wettability to molten lithium metal. In order to bond the electrolyte and lithium metal tightly, researchers introduced some mesosphere(such as Al_2O_3, ZnO, Ge, etc.) with good wettability to lithium metal to solve this

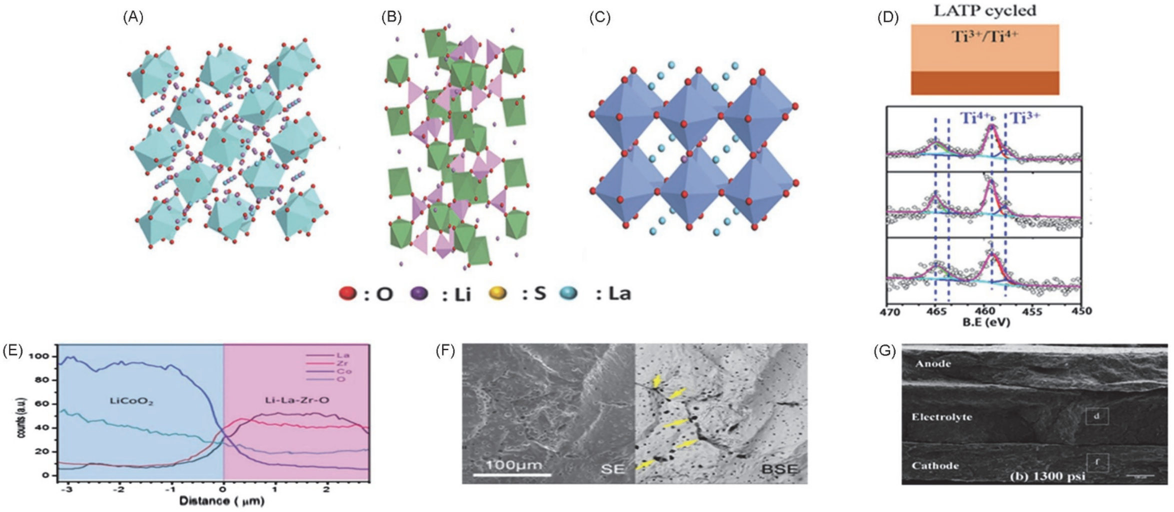

Fig.1 Crystalline structures of garnet(A), NASICON(B), and perovskite solid electrolytes(C)(reprinted with permission from ref.[56], Copyright 2018, Wiley), X-ray photoelectron spectroscopy(XPS) study on the reduction of Ti^{4+} in LATP by lithium metalanode(D, reprinted with permission from ref.[45], Copyright 2018, ACS), EDX line scan profile of LLZO/$LiCoO_2$ interface(E, reprinted with permission from ref.[57], Copyright 2017, ECS), SEM and back scattered electron(BSE) images of short-circuited $Li_{6.75}La_3Zr_{1.75}Ta_{0.25}O_{12}$ pellet after ethanol leaching(F, reprinted with permission from ref.[39], Copyright 2015, Elsevier) and scanning electron microscopy(SEM) image showing the poor contact between NASICON solid electrolyte and Li_2MnO_4(G, reprinted with permission from ref.[41], Copyright 2012, Elsevier)

problem[Fig.2(C) and (D)]. For example, Han *et al.*[60] coated a thin layer of Al_2O_3 on the garnet-type solid electrolyte by atomic deposition, and this modified electrolyte showed an excellent lithium deposition/ exfoliation performance within 90 h at a current density of 0.2 mA/cm². However, this strategy is not suitable for the interface build between these solid electrolytes and cathode, because both cathode active materials and solid electrolytes have high-melting point, and the nano-sized morphology of cathode active materials is not suitable for two-phase fusion. A feasible method can reduce the sintering temperature by introducing sintering additives in oxide-type solid electrolyte and cathode material for mixture[Fig.2(E) and (F)]. Ohta *et al.*[61] combined $LiCoO_2$ and LLZO at 700 °C by selecting $LiBO_3$ as a sintering additive. Wang *et al.*[62] chose $Li_{2.3}C_{0.7}B_{0.3}O_3$ as a sintering additive, which obtained an all-solid electrolyte with an excellent cycle performance. In addition, it is also a feasible strategy to make composite cathode by combining cathode and solid electrolyte together, which can create a porous structure to combine the two parts tightly and expand the contact area between the different materials, so that reducing the interface impedance[63]. However, the volume change of the electrode material during charge and discharge is likely to cause the loose bonded interface[64,65]. Although these methods can alleviate the problem to some extent, the modification of interface, the introduction of intermediate layer, and alloying will complicate the prepared process and increase the cost. In addition, there is no effective solution strategy to solve the air stability of oxide solid electrolytes, and the preparation process of these solid electrolytes requires high equipment requirements. Thus, it is difficult for these single oxide solid electrolytes to meet the performance requirements of solid lithium batteries.

2.2 Sulfide-based Solid Electrolytes

Sulfide solid electrolytes can be divided into crystalline solid electrolytes, glass solid electrolytes and glass ceramic solid electrolytes according to their different crystalline forms. In 1999, Kanno *et al.*[66] found that substituting oxygen in LISICON with sulfur can obtain a new crystalline solid electrolyte with a thio-LISICON structure[Fig.3(B)]. Kamaya *et al.*[67] reported a sulfide crystalline electrolyte $Li_{10}GeP_2S_{12}$ (LGPS) with 3D lithium-ion diffusion channels, which exhibited a high ionic conductivity of 1.2×10^{-2} S/cm[Fig.3(C)]. In the crystal structure of LGPS, the one-dimensional lithium-ion transmission channel occupied the 8*f* and 16*h* positions of the LiS_4 tetrahedron[Fig.3(D)]. The one-dimensional transmission channel is along the direction of *c* axis. Kato *et al.*[68] developed a new type of sulfide crystalline electrolyte $Li_{9.54}Si_{1.74}P_{1.44}S_{11.7}Cl_{0.3}$, and the ion conductivity reached 2.5×10^{-2} S/cm, which is twice than that of LGPS at 27 °C. Li_2S-SiS_2[69] and Li_2S-P_2S_5[70] are two typical representatives of sulfide glass solid electrolytes with an ionic conductivity of 10^{-8}—10^{-6} S/cm. The glass ceramic solid electrolytes is obtained from the glass solid electrolytes through high temperature crystallization treatment, and the two-phase structure makes the electrolyte show a significantly improvement of ionic conductivity of

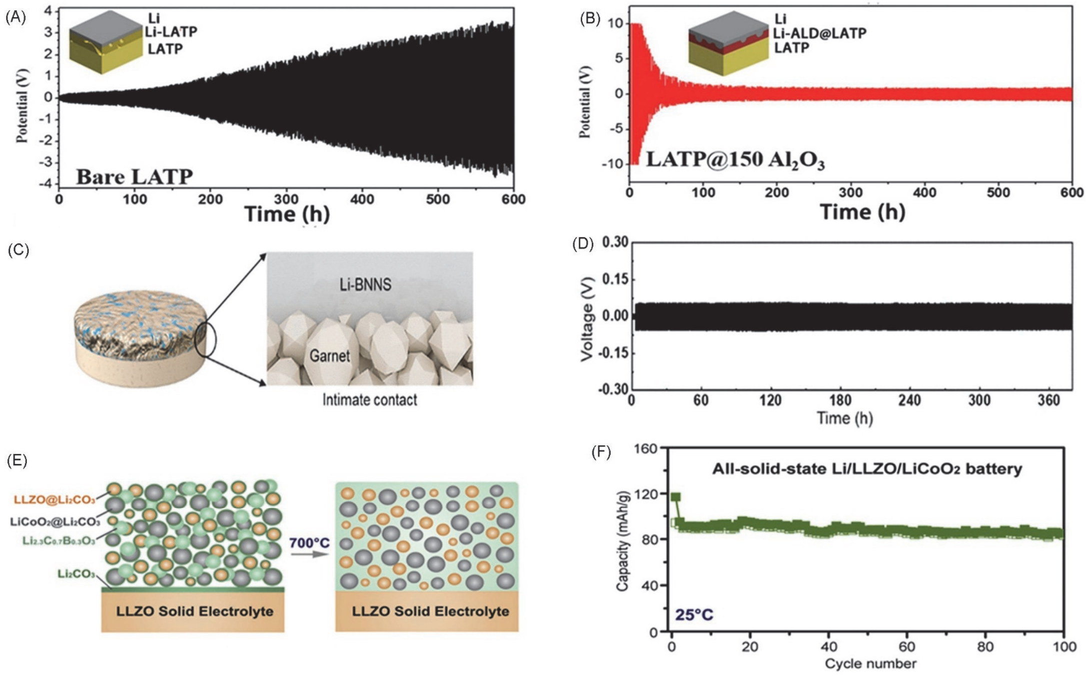

Fig.2 Cycling performance of bare LATP/lithium(A) and ALD Al_2O_3 coating LATP/lithium(B) symmetric cells at a current density of 0.01 mA/cm^2(reprinted with permission from ref.[45], Copyright 2018, ACS), the transition from point contact to complete adhesion between Li metal and ceramic solid electrolyte by adding only a few two-dimensional boron nitride nanosheets(5%, mass fraction) into Li metal(C), the high critical current density of 1.5 mA/cm^2 and stable electrochemical plating/striping over 380 h of the solid electrolyte from (C)(D)(reprinted with permission from ref.[59], Copyright 2019, ACS), the process of co-sintering to make composite cathode with an oxide-based solid electrolyte(E), and cycling performance at room temperature of the composite cathode obtained from (E)(F)(reprinted with permission from ref.[62], Copyright 2018, Elsevier)

10^{-4}—10^{-2} S/cm. Hayashi *et al*.[71] found that the conductivity of glass ceramics electrolytes formed by pyrolytic crystallization of Li_2S-P_2S_5 was improved significantly. The ionic conductivity of $80Li_2S$-$20P_2S_5$ increased from 1.7×10^{-4} S/cm to 7.2×10^{-4} S/cm after mechanical ball-milling and high temperature crystallization treatment. Furthermore, the ionic conductivity of $70Li_2S$-$30P_2S_5$ electrolyte with a lower lithium content increased nearly two orders of magnitude(3.2×10^{-3} S/cm)[72]. In addition, the ionic conductivity of this type electrolyte can further improve by doping. For example, the ionic conductivity of $70Li_2S$-$30P_2S_5$ glass electrolyte can be increased to 10^{-3} S/cm, when halides(such as LiI, LiBr, etc.) are added[73,74].

Sulfide solid electrolytes have high ionic conductivity compared with oxide solid electrolytes[Fig.3(A)], because of the large ion radius and strong polarization ability of sulfur, which constructs a larger lithium-ion transport channel. Sulfur is less electronegative than oxygen, which weakens the bond cooperation between lithium ions and adjacent skeleton structures to increase the concentration of free lithium ions[75]. At the same time, the sulfide solid electrolytes are soft in texture, and the interface impedance between electrolyte and electrode is low. Moreover, most of the sulfide solid electrolytes only through simple cold pressing molding can reach a tight contact, and the preparation process of such sulfide solid electrolytes is much simpler as compared with the high-temperature sintering of oxide solid electrolytes. However, their stability is extremely poor, and it is easy to react with humid air environment and form H_2S. Although the production of H_2S gas can be inhibited by doping other additives into the sulfide solid electrolyte system[76], the sulfide solid electrolytes are still relatively harsh for the preparation conditions, and it is difficult to put into large-scale production. More importantly, the solid electrolytes of sulfide are unstable to both lithium metal anode and conventional oxide cathode materials, which seriously hinders its practical application in solid lithium batteries. The electrochemical window of sulfide solid electrolytes is narrow, which cannot match the high voltage cathode materials[Fig.3(E)][34,77]. For example, an adverse reaction will happen and produce Li_2S, CoS_3, and $Co(PO_3)_2$ at the interface, resulting in the increase of interface impedance, when the sulfide solid electrolytes match the $LiCoO_2$ cathode[78]. Moreover, space charge layer(SCL) is likely to be generated at the interface due to the potential difference between the sulfide electrolyte and $LiCoO_2$, and the high resistance of SCL will significantly reduce the capacity performance of the battery[79]. There are some ways to inhibit the formation of SCL and the occurrence of side reactions through modification of the interface by adding Al_2O_3,

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$Li_4Ti_5O_{12}$, or $LiNbO_3$ coatings at the interface between cathode and electrolyte[80]. The interface problem between sulfide solid electrolyte and lithium metal anode is also very serious. Studies have shown that sulfide can react with lithium metal to generate low ionic conductivity products, such as Li_3P, Li_2S, etc., resulting in the increase of interface impedance[81]. To solve this problem, the first solution is to replace the lithium metal with the indium metal or lithium indium alloy[82] as the anode, while the energy density of the battery decreased. The second method is to build a protective layer on the interface to improve the interface stability[83,84]. For example, Wang *et al.*[85] modified the interface through the molecular layer deposition(MLD) technology. These interface engineering can alleviate these problems encountered by sulfide electrolytes, but the poor flexibility of sulfide is difficult to buffer the volume change of the electrode material during battery charging and discharging. The interface of the battery will gradually be destroyed with the increase of battery working time, leading to the decline of battery performance eventually[86,87].

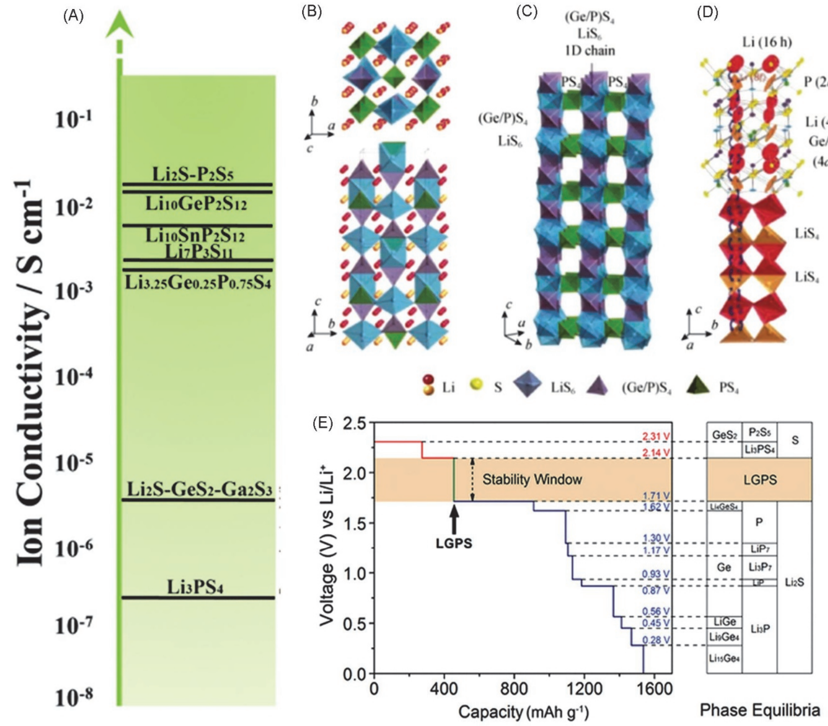

Fig.3 Ion conductivity of sulfide solid-state electrolytes(A, reprinted with permission from ref.[87], Copyright 2016, RSC), crystal structure of LGPS sulfide-based solid electrolytes(B), one dimensional view of LGPS framework(C), Li⁺ ion conduction pathways in LGPS(D)(reprinted with permission from ref.[67], Copyright 2011, Springer Nature), and the first-principle calculation showing the stable window of LGPS of 1.71—2.14 V(E, reprinted with permission from ref.[77], Copyright 2016, Wiley)

2.3 Solid Polymer Electrolytes

In 1973, Wright *et al.*[88] first discovered that the polyethylene oxide(PEO) and alkali metal salt complex exhibited ionic conduction function, that opened up a new direction for the study of solid electrolytes. Take PEO as an example to introduce the conductive mechanism of polymer electrolytes. Li^+ migrates with the movement of the PEO chain segment by complex-decomplex with the ether oxygen group on the PEO chain continuously[Fig.4(A)][89,90]. Therefore, the amount of free Li^+ and the mobility of the PEO segment are the key factors that determine the ionic conductivity of the polymer electrolytes. The key to obtaining polymer electrolytes with high ionic conductivity is to select a suitable polymer and lithium salt. The polymer with a high dielectric constant and a polar functional group is an ideal choice, because it can promote the decomposition of lithium salt and the lithium-ion transportation. At the same time, lithium salt with low lattice energy can be selected, which is easily ionized to increase the amount of free Li^+ in the polymer matrix. The polymer solid electrolyte based on the PEO system has been extensively studied[91] because of its excellent lithium salt solubility and better interface compatibility with the electrode. However, the high crystallinity of PEO limits its ionic conductivity and lithium-ion transference number. The conductivity of PEO based solid electrolytes is only 10^{-7} S/cm at room temperature, which is far below the requirements of normal operation of lithium batteries[Fig.4(B)][92]. Methods, such as introducing plasticizers into the polymer matrix[93] and increasing the content of lithium salts can reduce the crystallinity of the PEO matrix[94], which can speed up the segment movement and promote the dissociation of lithium salt. Although these methods can improve the ionic conductivity, the mechanical strength and stability of the electrolyte will be reduced[95,96]. Apart from PEO-based polymer systems, polyvinylidene fluoride(PVDF)[22] and its derivatives polyvinylidene fluoride-hexa-fluoropropylene(PVDF-HFP)[97], polyacrylonitrile(PAN)[98], polymethyl methacrylate(PMMA)[99] are also employed as polymer matrix. The strong polar group $—CH_2—CF_2—$ and the strong electronegative F atom contained in the PVDF segment promote the dissociation of lithium salt[100]. The PAN-based solid electrolytes can match high-voltage cathode materials, because of its high oxidation resistance. In addition, the lithium-ion transference number of the PAN is higher[101], because the nitrogen atoms in PAN molecules are less electronegative than oxygen atoms, that can provide lone pair electrons and complexing with lithium ions. However, the poor interface compatibility between the strong polar group —CN of PAN segment and lithium anode limits their application in lithium meatal batteries[102]. The polymer solid electrolytes matrix can be modified by blending[103], copolymerization[104] and cross-linking[105], but these effects are not obvious, and increase the process difficulty and cost.

The ionic conductivity(10^{-8}—10^{-4} S/cm) of most solid polymer electrolytes is low, which cannot meet the requirements of normal operation of lithium batteries. The way of increasing the test temperature can improve the ionic conductivity of the polymer, but the mechanical properties of the polymer will decline, which will lead to the problem of lithium dendrite growth[Fig.4(D)—(I)][106]. It is obvious that it is difficult for polymer solid electrolytes to obtain both high ionic conductivity and high mechanical strength simul-taneously. In addition, although polymer electrolytes are flexible and can be designed as thin films, most polymer solid electrolytes have a narrow electrochemical window, which means that they have poor compatibility with high-voltage cathode materials. For example, the electrochemical window of the PEO-based solid electrolyte system is less than 4 V[Fig.4(C)][107], which

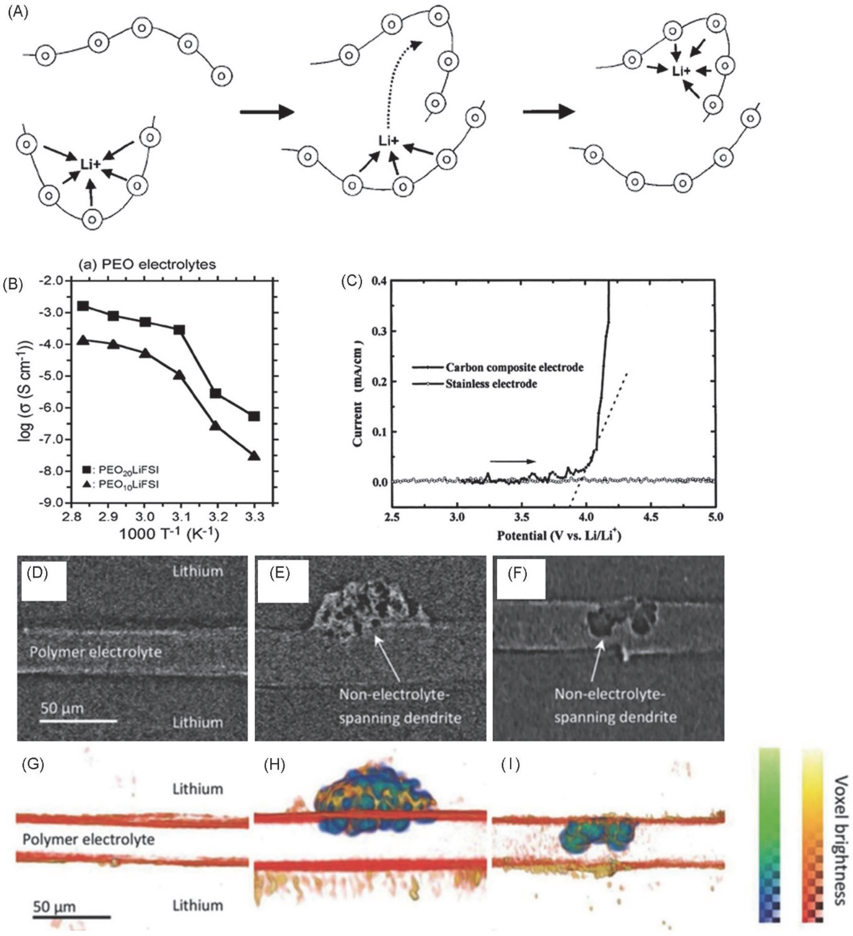

Fig.4 Schematic of the segmental motion assisted diffusion of Li$^+$ in the PEO matrix(A, reprinted with permission from ref.[90], Copyright 1998, Wiley), temperature-dependentionic conductivity of PEO-based solid polymer electrolyte(B, reprinted with permission from ref.[92], Copyright 2014, RSC), the electrochemical stable window of a PEO-based solid polymer electrolyte being only 3.8 V(C, reprinted with permission from ref.[107], Copyright 2001, Elsevier) and X-ray tomography slices showing the evolution of Li dendrite formation in solid polymer electrolyte and their 3D reconstructions diagrams(D—I, reprinted with permission from ref.[106], Copyright 2014, ECS)

cannot match with the high voltage $LiCoO_2$ cathode. Although modifying the interface of these cathode materials by coating Al_2O_3, Li_3PO_4 or others can improve the interface stability and the cycling performance of the battery[108], it is not a simple and long-term effective strategy. In short, serious problems of polymer solid electrolytes, such as low ionic conductivity, poor mechanical strength, narrow electrochemical window, and poor interfacial stability limit their application in the field of high energy density lithium batteries.

3 Composite Solid Electrolytes

Oxide-type solid electrolytes exhibit good ionic conductivity and mechanical properties, while their interface problems are more severe[Fig.5(A)][109]. Although sulfide solid electrolytes have high ionic conductivity close to that of liquid electrolytes, their electrochemical stability and air stability are poor [Fig.5(B)]. Polymer solid electrolytes are easy to prepare and have good interface compatibility, but their low conductivity and Li-ion transference number make it difficult for practical applications at room temperature[Fig.5(C)]. It is obvious that none of these solid electrolytes can meet all the performance requirements for the application of solid-state lithium batteries. The composite solid electrolytes have been prepared by combining the merits of different kinds of solid electrolytes, such as the high ionic conductivity of inorganic solid electrolytes and the flexibility of polymer electrolytes, which become an effective solution to break the limit of solid lithium metal batteries[Fig.5(D)]. Composite electrolytes can not only solve the interface problems of oxide solid electrolytes, but effectively improve the ionic conductivity of polymer electrolytes, which demonstrate great application prospects in the field of solid-state batteries. In the following section, recent processes including preparation methods, lithium-ion conduction, and interface problems of composite electrolytes will be summarized.

The composite electrolytes were formed by adding inorganic fillers to organic polymer electrolytes. The obtained composite electrolytes show an enhanced mechanical strength and good interface compatibility, which can effectively inhibit the growth of lithium dendrites and improve the battery cycle stability. According to the previous researches[110], the decrease of the crystallinity can improve the ion conductivity of the polymer. The addition of inorganic fillers with a relatively high surface area can effectively decrease the glass-transition temperature(T_g) of polymer matrix. In addition, according to the Lewis base centers[111], the acidic surface of the filler can absorb the anions and promote the dissociation of the lithium salt, which can increase the number of freely movable lithium ions. Meanwhile, the surface of the fillers acts as a cross-linking site between the polymer chain segment and the lithium salt anion, which can form a fast lithium-ion transport channel. These are the key reasons for improving the ion conductivity of the composite solid electrolytes. Furthermore, the addition of active fillers, such as inorganic solid electrolytes can further improve the ionic conductivity of these composite solid electrolytes[112]. Moreover, the mechanical properties of the composite electrolytes can also be strengthened when

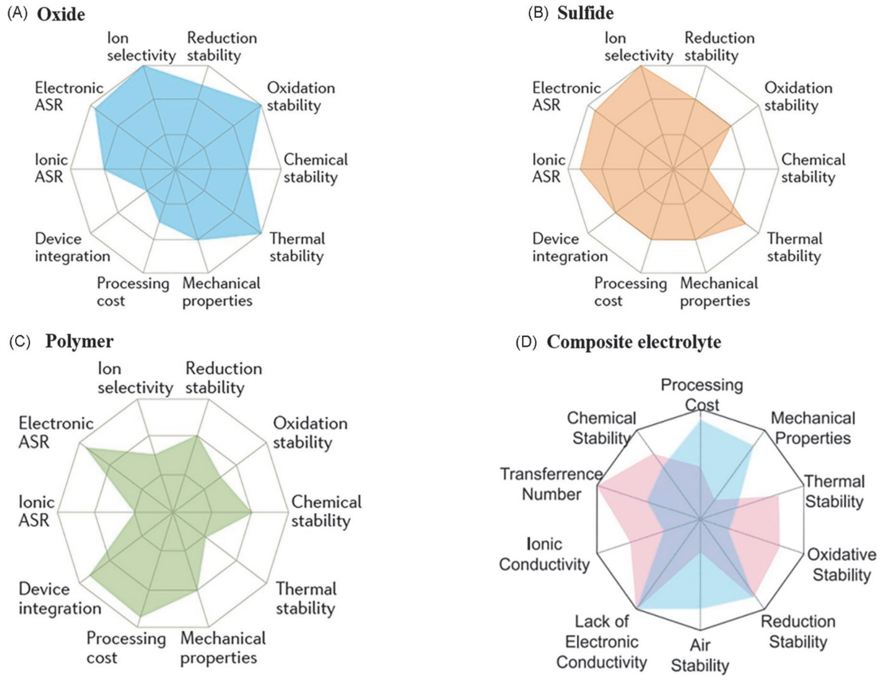

Fig.5 Performance comparisons of oxide(A), sulfide(B), polymer(C), and composite electrolytes(D)

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the inorganic filler forms a supporting framework structure in the polymer matrix. For example, Fu *et al.*[113] introduced a 3D structured $Li_{6.4}La_3Zr_2Al_{0.2}O_{12}$(LLZO) nanofiber into PEO matrix[Fig.6(A)]. The addition of LLZO nanofiber not only increased the continuous transmission path of Li^+, but strengthened the mechanical strength of the polymer electrolyte[Fig.6(B) and (C)]. The ionic conductivity of the composite electrolyte membrane was improved significantly, which reached 2.5×10^{-5} S/cm at room temperature[Fig.6(D)]. In addition, the inorganic fillers can absorb trace amounts of water and other trace impurities in the polymer, making the composite electrolytes more stable in the electrochemical environment and broadening the electrochemical window[114]. Moreover, the design of the composite solid electrolytes with special properties should select different components with special properties and control the structural purpose fully. Cui *et al.*[115] designed a kind of ultra-thin composite polymer solid electrolyte with excellent flame-retardant properties[Fig.6(E)]. The fire-retardant composite solid electrolyte was composed of a high strength porous polyimide film(PI film) and the flame retardant decabromodiphenyl ethane(DBDPE) as supporting skeleton, and the PEO/LiTFSI solid electrolyte with high ionic conductivity being filled to form the pores[Fig.6(F)]. The $LiFePO_4$/Li batteries assembled with this composite polymer solid electrolyte demonstrated excellent cycling performance at 60 °C[Fig.6(G)], and the soft-pack battery can still work under extreme conditions of combustion.

The interaction of organic-inorganic components at the interface of composite solid electrolytes can improve the ionic conductivity and other electrochemical properties, which provide the possibility for the practical application of composite solid electrolytes in lithium metal batteries. In addition, the composite solid electrolytes combine the inorganic materials with high strength and the polymer solid electrolytes with light mass. Thus, the composite electrolytes can be designed to be lighter, thinner, and softer, which bring the possibility for the commercialization of flexible lithium battery in electronic devices.

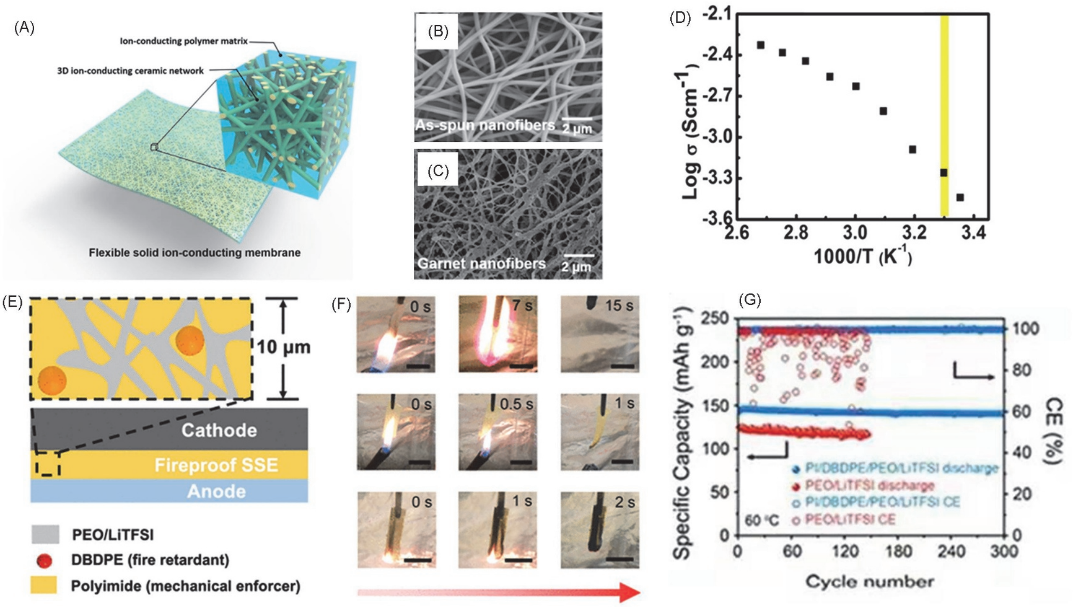

Fig.6 Schematic of acomposite solid-state electrolyte(A), SEM image of the as-spun nanofiber network(B), SEM image of the garnet nanofiber network(C), Arrhenius plot of the electrolyte membrane at elevated temperatures(D)(reprinted with permission from ref.[113], Copyright 2016, National Academy of Sciences, USA), design principles of the fire proof and light mass composite polymer solid-state electrolyte(E), flame tests of PEO/LiTFSI(the first line), PI/DBDPE(the second line), and PI/DBDPE/PEO/LiTFSI(the third line)(F), and cycling performance of Li/PEO/LiTFSI/LFP and Li/PI/DBDPE/PEO/LiTFSI/LFP cells(G)(reprinted with permission from ref.[115], Copyright 2020, ACS)

3.1 Synthesis of Composite Electrolytes

Composite solid electrolytes are usually composed of polymer matrix, inorganic filler, lithium salt, and ionic liquid additives. It is also possible to use inorganic substance as the matrix and polymer as the filler in some new composite solid electrolyte structures. Understanding the preparation of composite solid electrolytes is significative for the design of new type composite solid electrolytes and understanding the ion transportation mechanism in the microscopic structure of the composite electrolytes. Generally, the composite solid electrolytes can be prepared by the following four type methods, such as mechanical physical method, solution casting, infusion method, and tape-casting.

The mechanical physical method generally includes two steps[Fig.7(A)]. Firstly, the different components are uniformly mixed together by grinding, stirring, or ball milling. Then, the mixture is compressed into an electrolyte membrane by hot/cold pressing. The mechanical physics method generally can be applied into the following three situations: the situation that organic solvents cannot be used, such as composite electrolytes based on sulfide and halide electrolytes, which are chemically active and easily cause undesirable reactions with solvents. However, these electrolytes can be combined with some melted polymers without solvent by mechanical physical method. Avoiding the problem of the introduction of solvents, which cause the active components invalid, for example, Liang *et al*.[116] prepared LLZO-β-Li_3PS_4 (LPS) mixed electrolyte by mechanical physical method, and the mixed electrolyte showed reduced grain boundary resistance only through cold-pressing process. The ionic conductivity of the composite solid electrolyte reached about 10^{-4} S/cm at room temperature. The mechanical physical method also can be used as a "solvent-free" method. For example, Fan *et al*.[117] prepared an LLZO based composite electrolyte using the polytetrafluoroethylene(PTFE) as the binder, and the composite electrolyte showed high ionic conductivity of 1.2×10^{-4} S/cm and high ionic transference number of 0.53. The mechanical physical method also can be used to prepare the composite cathode. It is necessary to compress the interface between cathode and electrolyte by mechanical physical method to reduce the interface impedance. The mechanical physical method is easily to operate, but it is not suitable for mass production, because the mechanical strength of the composite electrolytes prepared by the compression molding is ordinary and the thickness of the obtained electrolytes is uneven.

Solution casting is the most widely used preparation method[Fig.7(B)]. The solution casting is easy, which also can prepare a thinner electrolyte film. However, solution casting is strict in the choice of solvent, which should meet the following two conditions: (1) the solvent needs to be chemically inert, which cannot react with the polymer and filler components; (2) the solvent should be volatile to facilitate the subsequent curing process. Acetonitrile is the most commonly used solvent for the preparation of polymer electrolytes. The solvents used for PVDF-based electrolytes are DMF and NMP commonly. However, the two solvents are not easy to volatilize, causing the composite solid electrolytes contained solvent to residue easily. Water can also be an important solvent in some cases[118], but LLZO-based solid electrolytes[119] and sulfide-based electrolytes[120] are unstable to water. In particular, plasticizers can be conveniently added to composite electrolytes by the solution casting method. For example, Zhang *et al*.[121] designed a flexible composite electrolyte membrane by the solution casting method, which consists of the ceramic conducting $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$(LATP) filler, polye-mthylene oxide(PEO) matrix, and 1-butyl-1-methylpyrrolidiniubis(trifluoromethanesulfonyl)imide(BMP-TFSI) ionic liquid. Benefitting from the synergistic effect of organic-inorganic hybrids and ionic liquid, the obtained composite electrolyte membrane exhibits an excellent ionic conductivity of 2.42×10^{-4} S/cm at 30 °C and a wide electrochemical stability window of 5 V(*vs*. Li^+/Li).

The composite solid electrolytes prepared by solution casting generally take the polymer as the main body, while the infusion method is used when the inorganic filler is used as the main body of the composite electrolytes. The operation process of infusion methods is relatively complicated[Fig.7(C)]. Firstly, a support skeleton composed of inorganic components must be prepared. Then polymer electrolyte with fluidity is injected into the porous skeleton. Last, the solvent is evaporated to obtain a composite solid electrolyte. For example, Hu *et al*.[113] injected PEO/LiTFSI solution into the LLZO nanofiber membrane with a 3D structure repeatedly to obtain a PEO-LLZO-LiTFSI mixed electrolyte, and the ion conductivity of this composite electrolyte reached 10^{-4} S/cm. The inorganic materials occupied the main phase in this composite electrolyte, the inorganic LLZO ceramic conductor has an interconnected structure, and this connected lithium-ion conductor skeleton can not only improve the ionic conductivity of the composite electrolytes, but strengthen the mechanical strength of the composite electrolyte simultaneously.

None of the above three preparation methods is suitable for large-scale commercial production, and the tape-casting is the most ideal method for commercial preparation of electrolyte membranes[Fig.7(D)]. Tape-casting is suitable for commercial large-scale and continuous production. Meanwhile, the thickness of the electrolyte prepared by tape-casting is relatively thin, which is suitable for application in high energy density batteries. Wang *et al*.[122] prepared the $Li_{0.34}La_{0.56}TiO_3$(LLTO) electrolyte film with the thickness of only 25 μm by tape-casting. The thickness of the LLTO film was only one tenth of the piece obtained by cold pressing[123]. In addition, the obtained electrolyte film exhibits a high shear modulus of 264 MPa and a high ionic conductivity of 2×10^{-5} S/cm[124,125].

3.2 Lithium-ion Conduction in Composite Electrolytes

As a key component of lithium battery, the electrolyte is used to separate cathode and anode, and conduct lithium-ions. Therefore, the solid electrolyte with an excellent electrochemical performance is significant for the performance of the battery. Ionic conductivity and Li-ion transference number are the two most important indicators for composite solid

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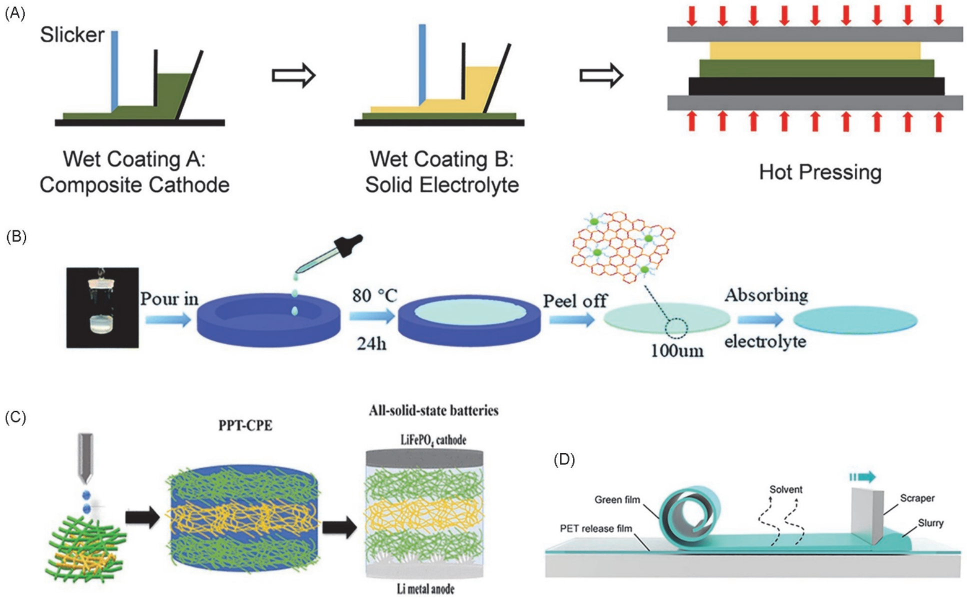

Fig.7 Fabrication methods of composite electrolytes: mechanical physical method(A, reprinted with permission from ref.[123], Copyright 2019, Elsevier), solution casting(B, reprinted with permission from ref.[114], Copyright 2019, RSC), infusion method(C, reprinted with permission from ref.[124], Copyright 2020, ACS) and tape-casting(D, reprinted with permission from ref.[125], Copyright 2020, Wiley)

electrolytes. Thus, the microscopic mechanism, problems, and latest strategies for the improvement of ionic conductivity and Li-ion transference number will be reviewed in the following section.

3.2.1 Ionic Conductivity

The conventional methods for improving the ionic conductivity of composite solid electrolytes are adding inert or active fillers to the polymer matrix. The addition of inorganic fillers can reduce the crystallinity of the polymer and increase the area of the amorphous region. Meanwhile, the acidic surface of the inorganic filler can also absorb the anions dissociated from the lithium salt, that can promote the dissociation of the lithium salt and increase the number of freely movable lithium ions according to the Lewis base centers[111]. These effects brought by inorganic fillers are beneficial to improve the ionic conductivity of the composite electrolytes. The ionic conductivity of the composite electrolytes modified by this method is generally 1—3 orders of magnitude higher than the pure phase polymer electrolytes[27]. Although the effect of ionic conductivity improvement is obvious, these conventional composite solid electrolytes are still difficult to meet the performance requirements of the solid lithium batteries at room temperature. And studies have shown that as the amount of inorganic filler added continues to increase, the ionic conductivity of the electrolyte will decrease because the aggregation of particles hinders the transmission of lithium ions when the filler content is too high[126]. If the uniform dispersion of the inorganic fillers and the appropriate addition amount cannot be ensured, it will cause the agglomeration of the inorganic fillers, the weakening of the interaction between the fillers and the polymer matrix, and the decrease of the proportion of the amorphous polymer. In addition, the size of the fillers also has a great influence on the conductivity of the composite electrolytes. The principle of its effect is the change of the contact area between the inorganic fillers and the polymer. The smaller the filler particle, the larger the specific surface area and the sites interacted with the polymer improve the ionic conductivity of the electrolyte. However, it is not that when the filler particles are smaller, the conductivity of the composite electrolyte will be better. The filler particles with smaller particles are easy to agglomerate, which shows an adversely affection on the ion conduction. For example, Li *et al.*[127] explored the influence of the particle size of $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$(LLZTO) on the ion conductivity of LLZTO/PEO composite electrolyte. The results show that the ionic conductivity of the composite electrolyte formed by LLZTO and PEO with a size of 40 nm is two orders of magnitude higher compared with that with micron-sized LLZTO[Fig.8(A)]. Moreover, the types of inorganic fillers also exhibit great impacts on the performances of the composite electrolytes. Different fillers with different degrees of Lewis acidity and alkalinity show different interaction forces for anions. For example, Chan *et al.*[128] found that LLZO with a Lewis-based surface structure[129] can produce stronger interaction with anions, promote the dissociation of lithium salt and release more lithium ions. Compared with the inert fillers, active fillers can not only reduce the crystallinity of the polymer, but conduct lithium ions[Fig.8(B)]. With the increase of the filler component, the ionic conductivity of the composite electrolytes first increases, then decreases[Fig.8(C) and (D)][18].

The percolation effect has brought us inspiration that the interconnected inorganic phase structure is constructed in the composite solid electrolytes to provide a continuous ion transmission paths, which make the full use of the advantages of inorganic active fillers to improve the ionic conductivity. The ionic conductivity of the composite electrolytes is closely related to the percolation structure formed by the inorganic fillers in the polymer matrix, while the percolation structure mainly depends on the structure of the inorganic filler (nanoparticles, nanofibers, 3D network structure, etc.). Therefore, the design and develop of frame structure with 3D continuous inorganic conductive phase is particularly important for improving the ionic conductivity of the composite electrolytes. For example, Yang *et al*.[130] filled the PEO-based electrolyte into the vertically arranged LATP solid electrolytes prepared by ice template method[Fig.8(E)]. The vertical conduction structure of LATP acts as a fast ion conductor in the composite electrolyte, and the results showed that the ionic conductivity of the composite electrolyte reached 5.2×10^{-5} S/cm at room temperature[Fig.8(F)]. Li *et al*.[131] took inspiration from the structure of the pearl shell, and used LAGP microporous ceramic electrolyte sheets as "bricks", PEO, PEA, and epoxy electrolytes as "slurry" to prepare ceramic/polymer composite electrolyte[NCPEs, Fig.8(H)]. The author coated the ceramic particle suspension on the polyester film substrate and dried it to obtain the film. The stacked film was sintered to obtain multilayer ceramic block. Then it was immersed into the polymer electrolyte under vacuum conditions, and the ceramic/polymer composite electrolytes(NCPEs) were obtained after hot pressing. The volume fractions of LAGP to the prepared LAGP-PEO, LAGP-PEA and LAGP-Epoxy three composite electrolytes were 90.8%, 87.0% and 85.9%, respectively. It can be observed from the SEM image that the LAGP ceramic sheets were stacked closely and regularly, and the polymer electrolyte permeated into the interlayer and internal gaps[Fig.8(I) and (J)]. The ionic conductivity values of the obtained NCPEs reach 1.25×10^{-4} S/cm at 25 °C and 1.3×10^{-3} S/cm at 60 °C, which are higher than that of the polymer phase(1.0×10^{-5} S/cm at 25 °C) and close to that of pure LAGP particles(2.0×10^{-4} S/cm at 25 °C)[Fig.8(G)]. This work not only solved the dilemma between pure ceramic electrolytes and pure polymer electrolytes, but significantly improved the conductivity, providing a new design idea for the future lithium metal batteries.

The ionic conductivity of composite electrolytes can be further improved by adding plasticizers. Plasticizers generally include the small molecular structure organics, organic solvents, and ionic liquids. The reason of the improvement of the ionic conductivity of electrolytes is the reduce of the crystallinity of polymers, which promotes the lithium dissociation and increases the content of free lithium ions. The succinonitrile(SN) is a typical plastic crystal, and its combination with lithium salt exhibits a high ionic conductivity(10^{-4} S/cm) at room temperature[132]. Therefore, the SN is accustomed to be used as a plasticizer in the composite solid electrolyte to improve ionic conductivity. Studies have shown that the ionic conductivity of PEO-LAGP-$LiClO_4$ composite solid electrolyte at room temperature increased from 3.0×10^{-5} S/cm to 1.1×10^{-4} S/cm after the addition of 9%(mass fraction) SN[133]. And the assembled $LiFePO_4$/Li battery using this electrolyte can obtain high discharge specific capacity at 25 °C. Recently, Xiong *et al*.[134] reported an interface research about NASCION-based solid-state batteries, the interface between LAGP and lithium metal was embellished by introducing a mixed quasi-solid intermediate layer of LAGP nanoparticles and ionic liquid(IL), and the Li symmetric cell achieved a high critical current density of 2.0 mA/cm^2[Fig.8(K)]. And NASCION-based solid-state lithium metal battery realized excellent cycle stability. The introduction of ionic liquids may explore a new way for the practical application of LAGP-based solid-state lithium metal batteries. Some researchers also use ordinary electrolytes as plasticizers in some quasi-solid composite electrolytes[135]. It can improve the interface performance and increase the ionic conductivity of the composite electrolytes, because a trace amount of electrolyte can ensure the wettability between electrodes and electrolytes and reduce the interface impedance. Although the addition of the liquid component in the composite electrolytes belongs to gel electrolytes or quasi-solid electrolytes, it can be used as a transition product of all-solid-state lithium batteries before being popularized.

In summary, the guiding ideology for improving the ionic conductivity of composite solid electrolytes is to adjust the composition and design the structure to reduce the crystallinity of the polymer component, increase the number of free lithium ions, and use the percolation effect to build fast lithium ions conduction channel. Moreover, the structure of the inorganic phase components to form a 3D structure inside the composite electrolyte should be designed, when the active fillers dominated the main body in the composite electrolytes, which can improve the ionic conductivity of the composite electrolyte effectively. In addition, the addition of appropriate plasticizers can not only reduce the interface impedance between the inorganic filler and the polymer, but also improve the wettability between the electrolyte and electrodes. As a result, the strategy of adding plasticizers can improve the ionic conductivity and further enhance the interface stability effectively. It is of great significance to promote the industrial

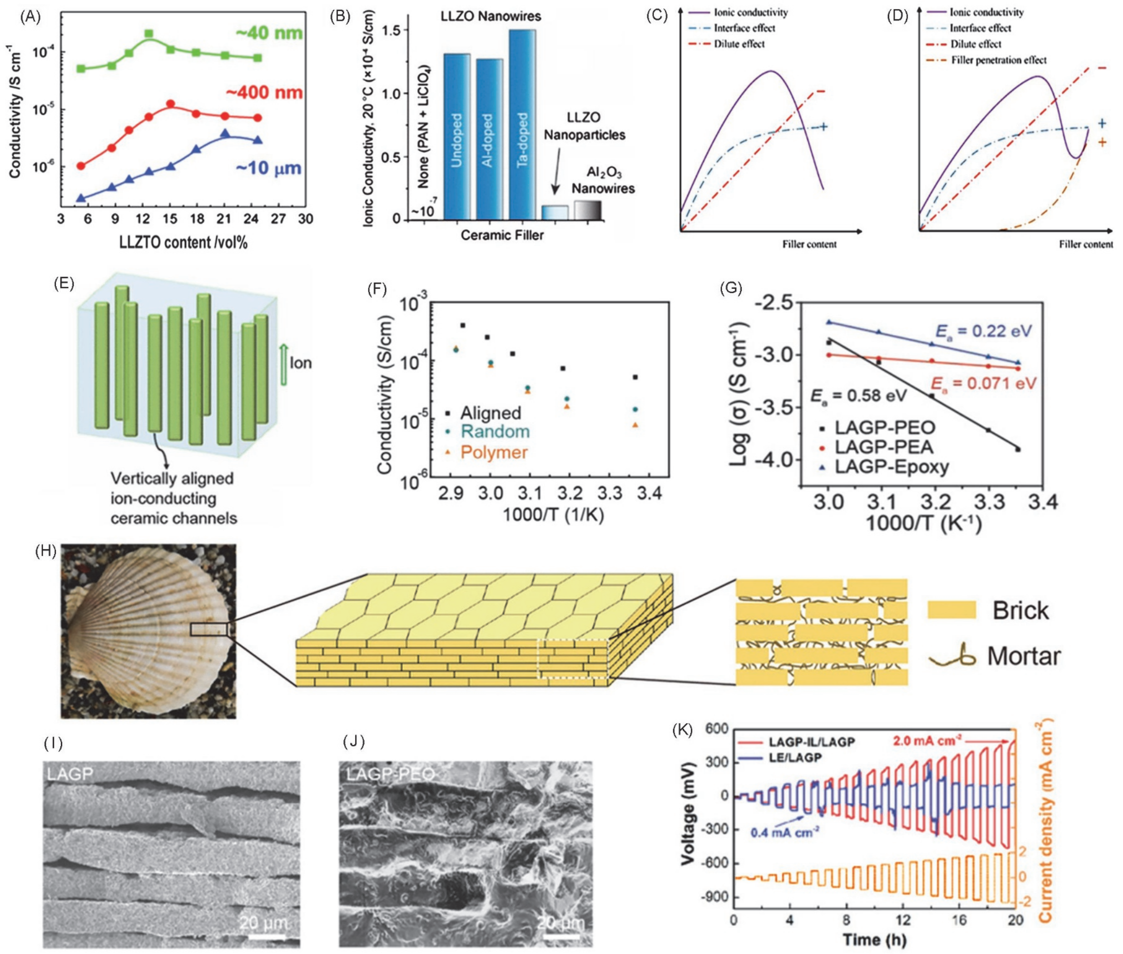

Fig.8 Effect of size and concentration on the ionic conductivity of PEO-LLZO composite electrolyte(A, reprinted with permission from ref.[127], Copyright 2016, Elsevier), the role of filler type on the conductivity of composite solid electrolyte(B, reprinted with permission from ref.[128], Copyright 2017, ACS), changes in filler effects and ionic conductivity with inert filler(C) and active filler(D)(reprinted with permission from ref.[18], Copyright 2021, Elsevier), vertically aligned Li$^+$ ion transporting channels to enhance the ionic conductivity(E), the conductivity *versus* temperature of the special composite electrolyte in (E)(F)(reprinted with permission from ref.[130], Copyright 2017, ACS), the ionic conductivity versus temperature plot of NCPEs(G), schematic of staggered "brick-and-mortar" microstructure in nacre(H), cross-sectional SEM images of layered LAGP tablets before PEO infiltration and hot pressing(I) and an LAGP-PEO NCPE film showing the staggered microstructure after hot pressing(J) (reprinted with permission from ref.[131], Copyright 2020, Wiley) and galvanostatic cycling of Li/LAGP-pellet/Li symmetric cells at increased current densities from 0.05 mA/cm^2 to 2.0 mA/cm^2(K, reprinted with permission from ref.[134], Copyright 2020, Wiley)

application of composite solid electrolytes.

3.2.2 Lithium-ion Transference Number

The lithium-ion transference number reflects the contribution of lithium-ion mobility in the total ion conductivity, which is an important electrochemical performance indicator for the electrolytes. For most electrolytes, they are called multi-ion conductors due to that their ionic conductivity is contributed by the migration of anions and cations. The migration directions of anions and cations in the electrolytes are opposite under the action of an electric field. As a result, a large lithium-ion concentration gradient is formed between cathode and anode, which will hinder the subsequent transmission of lithium ions, and lead to the uneven lithium deposition, that caused the poor battery power performance and the generation of lithium dendrites. Different from the polymer electrolytes, most inorganic solid electrolytes are single-ion conductors, which exhibit a high Li-ion transference number close to 1. These single-ion conductor electrolytes can effectively reduce the polarization caused by the lithium-ion concentration. The uniform distribution of lithium ions promotes the uniform deposition of lithium, which inhibited the formation of dendrites[136]. However, the serious interface problems of the inorganic solid electrolytes limited the advantage of high lithium-ion transference number used in all-solid-state batteries. The problem of low lithium-ion transference number is also unsolved for the composite solid electrolytes, because most composite electrolytes contain lithium ions and other anions, and both of them can migrate. For example, the lithium-ion transference numbers of the composite electrolytes of PEO and PAN system are only 0.1 to 0.2[137].

There are two ways to increase lithium-ion mobility, increasing lithium-ion mobility or decreasing anion mobility. The addition of inorganic fillers can promote the dissociation of lithium salts and adsorb anions[138], while the fillers can also occupy the sites of interaction between lithium ions and polymer polar groups, which reduce the binding energy of the polymer and lithium ions[139]. Furthermore, the active fillers are single-ion conductors, which also can increase the lithium-ion transference number. All these exhibit positive effects on the increase of lithium-ion migration. For example, Guo *et al*.[140] prepared an LLZO/PEO(LiTFSI) composite electrolyte used polyurethane foam as a template that exhibited a 3D framework structure[Fig.9(A)]. The continuous 3D structure of the LLZO framework not only improves the mechanical strength of the composite electrolyte, but improves the ion conductivity(1.2×10^{-4} S/cm) and the lithium-ion transference number(0.33). Because the network-like inorganic phase LLZO provides fast lithium-ion conduction channels and improves the lithium-ion conduction environment inside the polymer matrix. Liu *et al*.[141] prepared PEO-SiO$_2$ composite solid electrolyte through an *in-situ* reaction, which formed polymer network and inorganic nanoparticles in the composite electrolytes imultaneously. The polymer matrix was formed by irradiating PEO macromers with ultraviolet light, while SiO$_2$ is produced by the *in-situ* sol-gel method. The lithium-ion transference number of the composite electrolyte can reach 0.56[Fig.9(C)]. The reason for the high ion transference number of the electrolyte is mainly attributed to the interaction between the surface of the inorganic particles and the other oxygen atoms on the PEO main chain[Fig.9(B)]. Sun *et al*.[142] constructed a composite solid electrolyte(PMLSE) with a double-layer heterostructure[Fig.9(D)], which showed a high ionic conductivity of 2×10^{-4} S/cm, a high lithium-ion transference number(0.62), and a wide oxidation resistance potential(4.92 V) at room temperature[Fig.9(E)]. The one-dimensional garnet (Li$_{6.75}$La$_3$Zr$_{1.75}$Nb$_{0.25}$O$_{12}$, LLZN) nanowire with a high aspect ratio was prepared by electrostatic spinning technology and reasonable calcining. And the prepared nanofibers were introduced into the PVDF-HFP/LiTFSI system obtained a composite solid electrolyte. The significant increase of the lithium-ion transference number was due to the addition of nanowire-like inorganic filler, which enlarged the interaction site with the polymer matrix and formed a fast two-dimensional lithium-ion transmission channel. In summary, the strategy of increasing the lithium-ion transference number can be realized by adjusting the number and morphology of the inorganic components, which changes the interaction between inorganic and polymers, and improves the conductive environment of lithium-ion.

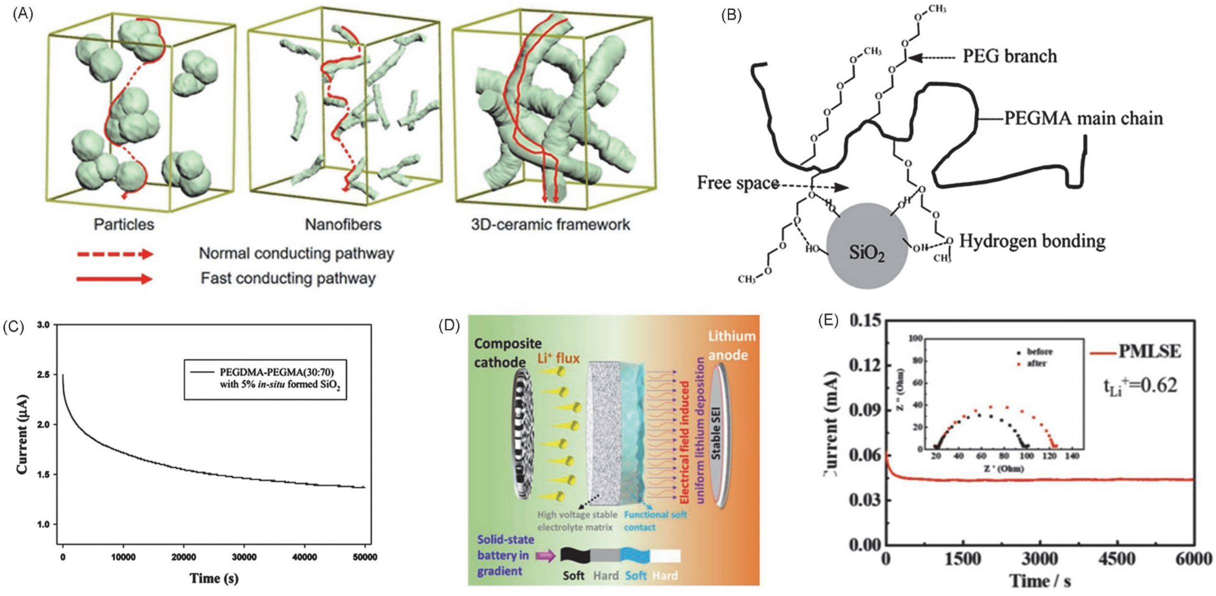

Fig.9 Schematics of conducting pathways for three geometrical structures filled in composite electrolytes(A, reprinted with permission from ref.[140], Copyright 2019, ACS), schematic representation of the interaction between polymer chains and surface groups of SiO$_2$ particles(B) and the current response to the amorphous PEO-SiO$_2$ composite electrolyte assembly under dc voltage(10 mV) as a function of time(C)(reprinted with permission from ref.[141], Copyright 2004, Elsevier), schematic illustration for configuration of the solid-state battery and probable mechanism of Li deposition process about PMLSE(D) and the lithium-ion transference number of PMLSE(E)(reprinted with permission from ref.[142], Copyright 2020, Wiley-VCH)

3.3 Problems of Electrolyte/Electrode Interface

The interface between electrolyte and electrode should also be considered when improving the lithium-ion conduction of solid electrolytes(Fig.10). The electrolyte not only has the function of separating anode and cathode, but connects anode and cathode through lithium-ion conduction. Therefore, excellent interface compatibility between electrolyte and electrode is the guarantee for the normal operation of solid-state lithium batteries. Interface problems mainly include physical compatibility and chemical stability. Compared with the rigid contact between ceramic solid electrolytes and electrodes interface, the composite solid electrolytes have better interface compatibility with electrodes because of the soft polymer components. Thus, there is no serious interface mismatch problem. But, the mechanical properties of the composite electrolytes are greatly weakened compared with the ceramic solid electrolytes, because the presence of polymer components in the composite electrolytes. This short coming is generally manifested at the interface of the anode, because the rigidity of the composite electrolytes is not enough to inhibit the growth of lithium dendrites, and the composite electrolytes may even be pierced by the lithium dendrites to cause battery failure. In addition, most composite solid electrolytes have narrow voltage window, and are difficult to match high-voltage cathode materials. It is negative for improving the energy density of solid-state lithium batteries. Thus, the problems of lithium dendritic growth and electrochemical window in view of the interface of composite solid electrolytes should be concerned.

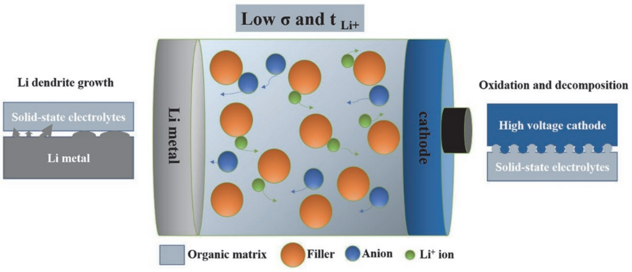

Fig. 10 Main problems of electrolyte/electrode interface

3.3.1 Lithium Dendrite of Anode/Electrolyte Interface

The studies show that the growth of lithium dendrites can be effective inhibited by physical barrier when the shear modulus of the solid electrolyte is twice higher than that of the metallic lithium(3.4 GPa)[9]. However, it is difficult to obtain high mechanical strength of most composite electrolytes due to the presence of polymer. The use of lithium metal anode is the most important means to increase the energy density of batteries. Therefore, the solid electrolytes with an excellent performance must overcome the problem of lithium dendrite. Although the composite electrolytes show an improved ionic conductivity, the poor mechanical properties are difficult to inhibit the growth of lithium dendrites. Therefore, the balance between the mechanical strength and the softness of the composite electrolytes is important for the composite electrolytes to achieve high ionic conductivity and lithium dendrite inhibition.

The introduction of the porous 3D matrix framework with a high mechanical strength can improve the mechanical strength of the composite electrolytes. Fan *et al*.[143] reported a 3D composite solid electrolyte that can be used in high-voltage lithium batteries. The electrolyte used the porous ultra-thin polyimide(PI) membrane as a mechanical support, and the nano ceramic powder LLZTO and the polymer binder PVDF were uniformly filled in the pores of the membrane by the coating method that formed a 3D continuous lithium conducting channel[Fig.11(A)]. The introduction of PI membrane can improve the mechanical properties and electrochemical stability of the solid electrolyte greatly [Fig.11(D)]. The LLZTO/PVDF solid electrolyte also shows good flexibility and mechanical properties after the introduction of PI film. Although the thickness of the electrolyte is reduced, its tensile strength is increased by nearly twice. It shows that the PI membrane matrix can significantly improve the mechanical properties of the composite electrolyte. For single-component polyvinylidene fluoride(PVDF) polymer electrolyte, lithium dendrites were formed rapidly and grown continuously during the charging and discharging process, and caused the battery short circuit eventually. Although the growth of lithium dendrites can be inhibited by introducing the ceramic fillers into the polymer electrolyte, the uneven lithium deposition still degraded the battery performance. The all-solid-state batteries with a PI-LLZTO/PVDF solid electrolyte showed greatly improvement of the cycle stability, because of the promotion of the uniform deposition of lithium, which inhibited the growth of lithium dendrites. In addition, the introduction of PI membrane also improved the ability of LLZTO/PVDF solid electrolyte withstanding large currents. The Li||PI/LLZTO/ PVDF||Li symmetric battery could be cycled stably for 1000 h, while the Li||LLZTO/PVDF||Li symmetric cell was short-circuited after only 426 h of cycling at a current density of 0.1 mA/cm^2 [Fig.11(J)], which indicated the introduction of PI film can improve the inhibition ability of lithium dendrites [Fig.11(E) and (F)]. Not only the PVDF in this structure improved the electrode/electrolyte interface contact and relieved the volume expansion, but the La in LLZTO could be combined with N and C═O of the *N*,*N*-dimethylformamide (DMF) solvent. The interaction caused the defluorination of PVDF, which

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enhanced the interaction of PVDF matrix, lithium salt, and LLZTO particles, and enhanced the structural stability[144]. The mechanical and electrochemical properties of the composite electrolyte were significantly improved, ensuring that the short-circuit does not happen during the long-term charge and discharge cycle of the battery.

However, the further research found that even the all-solid-state battery using a solid ceramic electrolyte with a high mechanical strength still cannot avoid the generation of dendrites[145]. Compared to liquid metal lithium batteries, the lithium dendrites emerge at a lower current density in the solid electrolytes. Currently, the explanation for this phenomenon is that lithium ions are induced to deposit into the defects and the cracks of the solid electrolytes, due to the local electric field caused by defects in the electrolytes. Another explanation is that the uneven contact interface between metal lithium and solid electrolyte causes a local over-potential, which induces the uneven lithium-ion deposition. Therefore, the growth of dendrite was always inhibited by introducing a transition interface layer between electrolyte and lithium cathode. Zhang *et al*.[146] designed a composite electrolyte(HSE) with a rigid $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$(LAGP) nucleus and a flexible poly(vinylidene fluoride-hexafluoropropylene)(PVDF-HFP) shell interface[Fig.11(B)]. The ultra-thin flexible shell can provide a soft contact between the LAGP nucleus and the lithium metal and suppress the Ge^{4+} reduction problem near the lithium metal. The nano-sized LAGP nucleus can ensure the close contact between the lithium metal and electrolyte, which benefited for the uniform distribution of Li^+. In order to study the role of the special structure on lithium deposition, the researchers prepared three compared electrolytes: composite solid electrolyte(HSE-I) with a micron-sized LAGP; composite solid electrolyte(HSE-II) with relatively few nanometer LAGP nucleus; and PVDF-HFP-based gel electrolyte(GPE) without an LAGP nucleus. The protective effect of different electrolytes on lithium metal deposition was observed under an *in-situ* optical microscope. The lithium dendrites were nucleated and grown rapidly on the surface of the bare Li with the increase of deposition time, and lithium dendrites were also observed on the surface of lithium, protected by HSE-I, HSE-II, and GPE[Fig.11(G)]. On the contrary, no dendrites were formed throughout the deposition process on the HSE-protected lithium anode. These phenomena indicated that the HSE with a number of nano-nucleus can achieve dendrite-free lithium deposition.

In order to suppress the formation of lithium dendrites, the research mainly focused on the improvement of solid electrolyte and the modification for the electrolyte/lithium metal interface. Recent studies have shown that one of the important reasons for the formation of lithium dendrites is the uneven lithium deposition and exfoliation on the surface of lithium metal. Therefore, promoting the uniform lithium nucleation and growth by controlling the structure of the electrolyte is an effective method for inhibiting the formation of lithium dendrites. Li *et al*.[147] poured the sulfide electrolyte (Li_6PS_5Cl) into the wood's vertical and consistent pore structure(such as the directional pipes of wood formed in nature) using the sulfide liquid phase synthesis method [Fig.11(C)]. The solid electrolyte structure(Li_6PS_5Cl@wood) with adjustable lithium-ion transport was prepared. XRD and SEM proved the structural stability of the Li_6PS_5Cl@wood solid electrolyte. Wood was selected as the template material in this work due to its dense, vertical, and uniform pore structure. Moreover, the ion beam is restricted to transport in a specific pore, while cannot cross to the adjacent pores since the walls of wood's pores are insulated to lithium ions. Therefore, the ion beam transmits uniformly to form a relatively uniform electro-chemical deposition on the surface of the lithium metal. This is extremely critical for controlling the uniform nucleation and the growth of lithium metal. This structure can promote the formation of a uniformly distributed lithium-ion beam in each channel, which causes uniform lithium nucleation and dissolution. In addition, the lithium ions in the electrolyte tend to transport in a vertical direction rather than random direction due to the limitation of the ion insulating wall, which limits the continuous accumulation of lithium deposition and the uncontrolled amplification growth to inhibit the formation of lithium dendrites[Fig.11(H) and (I)]. In addition, some new materials with special structures can also serve as an excellent matrix for composite solid electrolytes. Covalent organic frameworks(COFs) with well-controlled structures and highly aligned channels could offer good conditions for ion migration[148]. Hollow micro-/nanostructures with abundant compositional and geometrical feasibility could also serve as a functional interlayer/separator to improve the performance[149]. The design concept of these structures provides a new idea for the composite solid electrolyte to suppress lithium dendrites.

In summary, the composite solid electrolytes show great advantages in terms of the inhibition of lithium dendrites. The following three strategies can be used to design the composite electrolytes with an excellent lithium dendrite suppression function. Firstly, the introduction of the high-strength inorganic phase supporting network inside the composite electrolyte can improve the overall mechanical strength. Secondly, introducing a protective layer between electrolyte and lithium anode can avoid the interfacial reactions and guide the uniform deposition of lithium ions. Thirdly, to form a specific lithium-ion conductive channel inside the composite electrolyte through the special structural design, which confines lithium ions in a specific channel, regulates and constrains the transmission of the lithium-ion beam, and promotes uniform lithium deposition and stripping.

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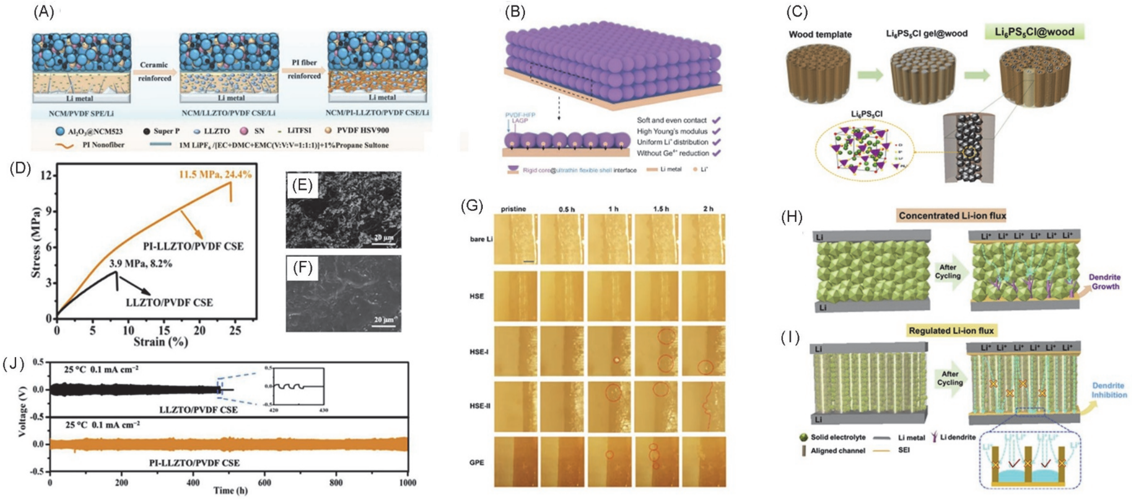

Fig.11 Schematic illustration of lithium plating/stripping processes in different electrolyte systems(A, reprinted with permission from ref.[143], Copyright 2020, Elsevier), schematic representation of dendrite-free lithium deposition enabled by HSE(B, reprinted with permission from ref.[146], Copyright 2020, Oxford Academic), graphical diagrams for the fabrication of Li_6PS_5Cl@wood solid electrolyte(C, reprinted with permission from ref.[147], Copyright 2020, Elsevier), stress-strain curves of LLZTO/PVDF and PI-LLZTO/PVDF composite solid electrolyte(D), SEM images of the Li surface obtained from lithium symmetrical cells assembled with PVDF/LLZTO after 426 h(E) and PI-PVDF/LLZTO after 1000 h cycling at 0.1 mA/cm^2 and 25 °C (F), respectively(reprinted with permission from ref.[143], Copyright 2020, Elsevier), optical microscope pictures of lithium metal protected by different electrolytes during the deposition process(G, reprinted with permission from ref.[146], Copyright 2020, Oxford Academic), Li metal anode with bare solid electrolyte(H) and solid electrolyte structure containing aligned channels(I)(reprinted with permission from ref.[147], Copyright 2020, Elsevier), and the voltage profiles obtained from galvanostatic cycles at a current density of 0.1 mA/cm^2 with 1 h stripping and 1 h plating alternating steps at 25 °C(J, reprinted with permission from ref.[143], Copyright 2020, Elsevier)

3.3.2 Electrochemical Stability of Cathode/Electrolyte Interface

To increase the energy density of solid-state batteries, the combination of lithium metal anode and high-voltage cathode is considered to be an effective way. Therefore, the solid electrolytes that are suitable for the lithium metal anode and high-voltage cathode have become the research focus. The advantages of composite solid electrolytes in the application of lithium anode had been explained in detail above. The performances and coping strategies of the composite electrolytes with high-voltage cathodes will be discussed in the following section. The electrochemical window is an important indicator that determines whether the electrolytes can be used in high-voltage lithium metal batteries, and represents the stable potential range where the electrolytes do not undergo electrochemical reactions. The electrolytes exhibiting a wide electrochemical stability window can guarantee the stable operation of the battery under high voltage. It is in great significance for the realization of high energy density lithium batteries.

However, most composite electrolytes show a relatively narrow electrochemical window, and their voltage window does not exceed 4.2 V at room temperature. The main reason of narrow electrochemical window is that the polymer matrix, anions and other residual impurities are easy to decompose under a high voltage. For example, PEO-based polymer electrolytes only have a voltage window that less than 4 V, because the —OH in the PEO polymer matrix is easy to decompose at a high voltage[150]. However, the voltage window of the composite electrolytes based on the PEO system can be increased to about 5 V when the inorganic fillers were added. Some groups on the surface of the inorganic filler and the highly active groups of PEO can form the new chemical bonds to prevent their oxidation[139]. In addition, the ceramic solid electrolytes are expected to realize the application of high energy density solid lithium metal batteries due to their unique high ionic conductivity and wide electrochemical window. However, the interface problem is always one of the difficulties in the research of high stability solid state batteries. In recent years, the researches on the modification of ceramic electrolytes have made great progress, which mainly focus on the construction of organic-inorganic composite solid electrolytes and the modification of interface wettability. It is difficult to develop the composite solid electrolytes that can match a high-voltage cathode and stabilized a lithium metal anode simultaneously. Therefore, it is a very urgent problem to choose differentially functionalized polymers to match anode and cathode interfaces, while exerting the intrinsic ion regulation properties of ceramics. Guo *et al*.[151] modified the

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high-pressure resistant PAN and the PEO polymer electrolytes to block the reduction reaction on the interface of $Li_{1.4}Al_{0.4}Ti_{1.6}(PO_4)_3$(LATP) ceramic electrode, which can solve the problem about $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$(NCM622) cathode compatibility and lithium anode stability successfully. Researchers used polymer electrolyte PAN and PEO with different functions to stabilize the anode and cathode interfaces, respectively, because LATP ceramic has different interface instabilities for high-voltage cathode and lithium metal anode[Fig.12(A)]. The total thickness of the modified ceramic electrolyte is about 340 μm with elements evenly distributed. This structure is beneficial to promote the reversible lithium deposition and dissolution with a wide electrochemical window(4.5 V)[Fig.12(B)]. A stable and compatible interface between electrode material and solid electrolyte was constructed, because the PAN in filtrates and buffers of the ternary cathode(NCM622) and PEO effectively inhibits the reduction reaction. The protected LATP ceramic exerts its inherent interface ion regulation properties, fixes anions, weakens the concentration gradient, inhibits the space charge layer, reduces polarization, and reduces side reactions, and all these can improve the cycle stability and kinetic performance. The understanding of the dual-interface differential protection strategy provides a simple and effective solution for improving the stability and dynamic performance of the interface in all-solid-state lithium batteries.

The composite solid electrolytes with a layered structure are suitable for high-voltage lithium batteries, which can be constructed through a multilayer electrolyte design according to the interface properties. Xu *et al.*[152] constructed a double-layer LAGP electrolyte with a porous/dense structure to increase the contact between electrolyte and cathode. The cross-linked composite electrolyte with a high oxidation resistance(>5.1 V) and high chemical stability was synthesized [Fig.12(C)]. The results showed that the solid electrolyte with a three-layer structure effectively encapsulated the cathode material and isolated LAGP from Li. The stable cycles(2 mA·h/cm² cycle 50 times) of the solid-state battery with a high NCM811 loading were realized. The traditional flat-plate LAGP was replaced by a three-layer solid electrolyte to form the all-solid-state lithium battery with a 3D interpenetrating structure and a high NCM811 cathode material loading [Fig.12(D)]. It achieved a higher cathode material loading, better interface compatibility, and a lower solid electrolyte mass. On the one hand, the researchers built a three-dimensional solid electrolyte structure to realize the high-load packaging of the cathode materials under the high interface contact condition in the LAGP all-solid-state battery. On the other hand, a new type of cross-linked composite solid electrolyte was synthesized to solve the compatibility of the high nickel cathode and LAGP interface. The results showed that the solid electrolyte with the three-layer structure made the stable operation of the nickel all-solid-state battery. It provided a feasible idea for the research on the interface

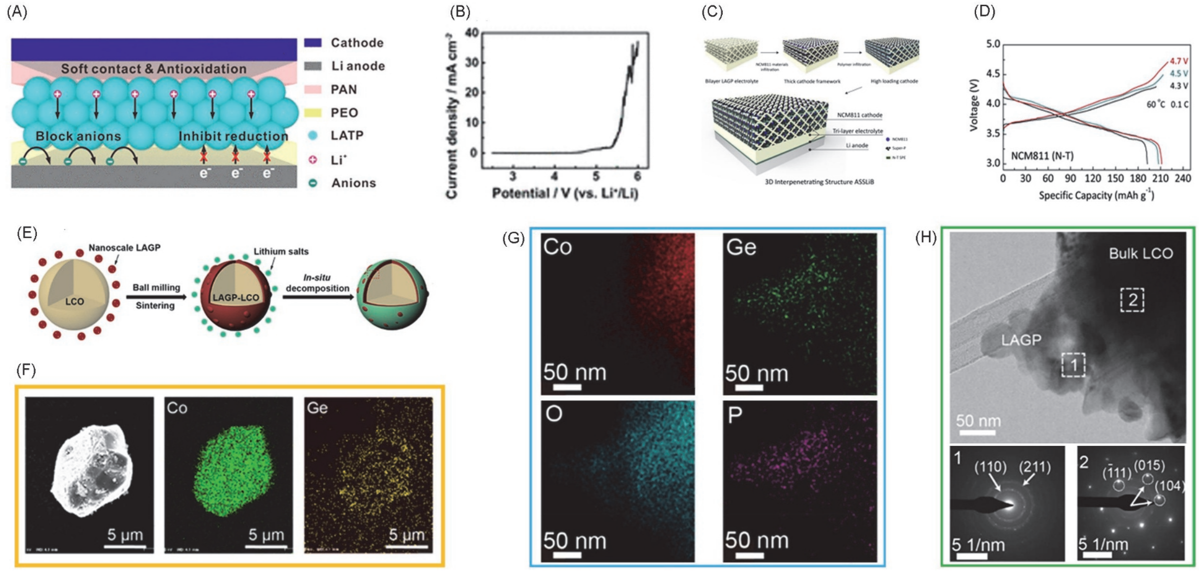

Fig.12 Structure of the bifunctional modified ceramic electrolyte(A), and linear sweep voltammetry(LSV) curves of the ceramic electrode of (A) at 60 °C(B)(reprinted with permission from ref.[151], Copyright 2019, ACS), schematic of the 3D interpenetrating structure with high loading NCM811 cathode(C) and the battery with the cathode loading of 2 mg/cm²(D) (reprinted with permission from ref.[152], Copyright 2020, Elsevier), the schematic illustration for the synthetic process to produce both LAGP nano-coating and salt-based passivation(E), SEM image and corresponding EDS elemental maps of Co and Ge on an LAGP-LCO particle(F), EDS elemental maps of Co, Ge, O, and P on an LAGP-LCO particle(G), and TEM images of LAGP-LCO and diffraction patterns of marked regions 1 and 2 in the above TEM image, respectively(H)(reprinted with permission from ref.[153], Copyright 2020, Elsevier.

between solid electrolyte and material high-load cathode in all-solid-state lithium metal batteries.

The poor interface stability between the cathode and the composite electrolytes is due to two reasons: the narrow electro-chemical window of the electrolytes and the strong chemical activity of the high-voltage cathode. The methods to improve the electrochemical window of the composite electrolytes have been analyzed above. The strategies of solid electrolytes to face the high-voltage cathode directly are introduced next. The high-voltage cathode materials are isolated by chemical coating, which can protect the electrolyte with low electrochemical stability. Generally, the ceramic solid electrolytes with a high electrochemical window are used to coat the cathode materials, while the polymer solid electrolytes with excellent interface compatibility are used to conduct lithium ions. Yang *et al*.[153] developed a method to stabilize the 4 V cathode/PEO interface by using the synergistic effect of ceramic electrolyte coating and lithium salt[Fig.12(E)]. The researchers prepared a nano-LAGP coatings using ball milling and sintering methods. The LCO and LAGP nanoparticles were ball milled in isopropanol with a mass ratio of 96.5:3.5.Then the mixture was dried and sintered at 650 °C to form a better bond between LAGP and LCO. This method allows Li^+ to pass through the interface layer and prevents the oxidation of the PEO electrolyte. The surface of the LAGP-LCO particles becomes rough after modified with LAGP nanoparticles. The energy dispersive X-ray spectrum(EDS) of a single LAGP-LCO particle showed clear signals from Co and Ge[Fig.12(F)]. Transmission electron microscopy(TEM) further showed that LAGP formed a layer of about 20—50 nm, and LAGP nanoparticles were dispersed on the LCO[Fig.12(H)], which indicated that LAGP penetrated and diffused well on the surface of LCO. LAGP nano-coating was further confirmed by EDS pattern, in which Ge, O, and P signals diffuse to the LCO particles[Fig.12(G)]. All these results indicated that LAGP nanoparticles were successfully coated on LCO while did not change the crystal structure of LCO. This method made the Li/LAGP-LCO battery maintain a stable cycle with the charge cut-off voltage of 4.25—4.4 V at 60 °C, and a stable cycle with an NCM523 cathode was also achieved successfully at room temperature, indicating that there were almost no side reactions of PEO oxidation. In this work, the researchers proposed a method to improve the stability between the 4 V cathode and the PEO-based electrolyte by using the synergistic effect of the ceramic electrolyte nano-coating and the lithium salt. These results indicated that the LAGP nano-coating has a significant effect on suppressing side reactions and stabilizing the LCO/electrolyte interface, and opened up a new way for stabilizing the electrode/electrolyte interface and developing high energy density lithium metal batteries.

Through the analysis about increasing the electrochemical window of the composite solid electrolytes above, the following four possible reasons for its internal mechanism have summarized. First, some groups on the surface of the inorganic fillers forming chemical bonds with the polymer matrix and the highly reactive groups of the anion can prevent oxidation. Second, the acidic surface of the inorganic fillers fixes the anions to reduce their accumulation on the electrode[154]. Third, the electrochemical stability window of the inorganic fillers is very wide. For example, the high-voltage stable potential of LLZO and LLTO is above 5 V[155]. Fourth, inorganic fillers can adsorb some impurities in the polymer matrix and prevent the adverse reaction at the interface[156]. In addition, there are some effective ways to improve the stability of composite electrolyte and high-voltage cathode by coating high-voltage materials, adding a protective layer at the electrode interface, and designing a multilayer electrolyte structure.

4 Summary and Outlook

Solid electrolytes are the inevitable requirement for realizing all-solid-state lithium metal batteries with high safety and a high energy density, but there are no solid electrolytes that can be applied to the practical production and application so far. The oxide-type solid electrolytes have high ionic conductivity and excellent mechanical properties while they exhibit poor interface compatibility with electrodes. Although the sulfide-type solid electrolytes have high ionic conductivity, their electrochemical window is low and the air stability is poor, which is not conducive to large-scale production. The polymer electrolytes have good compatibility with the electrode and good flexibility, but their low ionic conductivity and electrochemical window make it almost impossible to apply at room temperature. The performance of the single-component solid electrolytes is not balanced enough, and it is difficult to meet all the performance requirements of solid-state lithium batteries. The composite solid electrolytes can be formed by combining the merits of different electrolyte component. They can achieve high ion conductivity and high lithium-ion transference number, inhibit the growth of lithium dendrites effectively, and maintain interface stability to improve battery cycle stability and Coulomb efficiency.

The types and design methods of composite electrolytes are diverse, but only suitable components and structures can achieve the performance advantages of composite electrolytes. Adjusting the type, quantity, and morphology of inorganic fillers can directly affect the performance of ion conductivity and lithium-ion transference number. The use of the percolation effect to combine the inorganic phase solid electrolytes with the internal skeleton structure of the composite electrolytes can greatly improve the ionic conductivity and the Li-ion transference number. However, the control of the orientation distribution and structure construction of the fillers, and the complex preparation process are the factors restricting the development of composite electrolytes in the actual research process. The inhibition ability to lithium dendrites of composite solid electrolytes and the electrochemical window decrease greatly due to the presence of polymer components. The mechanical strength of composite electrolytes can be improved by constructing appropriate inorganic phase skeleton structure, and its inhibition ability to lithium dendrites can be enhanced simultaneously. However, inhibiting lithium dendrites physically is not the most suitable method. By adding an interface modification layer to guide and regulate the uniform deposition of lithium ions, the formation of lithium dendrites can be inhibited at the root. Moreover, the electrolyte is protected by the interface modification layer, and the high-voltage cathode material is coated with a ceramic solid electrolyte. These methods can increase the electrochemical window of the composite electrolytes and make it possible to match the high-voltage cathode. According to the properties of different interfaces, different electrolytes with special functions are selected purposefully, and they are combined together to prepare a composite electrolyte with a multilayer structure to meet the performance requirements of different interfaces. These methods are of great significance to realize the application of high-voltage solid-state lithium metal batteries.

To improve the overall performance of the composite electrolytes including ionic conductivity, electrochemical window, mechanical properties, interface contact, and interface compatibility to meet the development needs of high-safety and high-energy density solid lithium metal batteries, four basic requirements for high-performance composite electrolytes are summarized: (1) high ionic conductivity and lithium-ion transference number, which are the basic guarantee of solid-state batteries working normally; (2) wide electrochemical window and high electrochemical stability. The excellent electrochemical stability enables the composite electrolyte to match the high voltage anode, which is of great significance to the promotion of lithium battery energy density; (3) mechanical strength and wettability. The appropriate physical properties are good at the inhibition for lithium dendrite, and the excellent wettability of electrolyte/electrode interface is beneficial to reduce the interface impedance; (4) high air stability and low manufacturing cost, which are the advantages of the large-scale commercial application for composite electrolytes.

Compared with other single-component solid electrolytes, composite solid electrolytes with excellent comprehensive performances are considered to be the most industrialized electrolytes. But from the current development trend, there are still many problems limiting the practical application of composite solid electrolytes. When improving the performance of composite electrolytes, the electrolyte problems with other battery components could be considered together, which may bring different inspirations. Combining cathode and electrolyte to form a composite cathode can greatly alleviate the incompatibility of cathode interface. The electrolyte membrane can combine with the lithium foil and the cathode film to make a battery by the winding method, so that the thickness advantage of the electrolyte membrane can be used to offset the disadvantage of its low ion conductivity. The interface between electrolyte membrane and cathode membrane in close contact is not easily damaged, because the battery cell obtained by the winding method with a certain internal pressure. In general, there are still many challenges to realize the industrialization of all-solid-state lithium batteries, and it is urgent to make efforts in materials research and process improvement to improve the ionic conductivity and wettability of the composite solid electrolytes. It is believed that the composite solid electrolytes with many advantages can greatly promote the industrialization of all solid-state lithium batteries.

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Conflicts of Interest

The authors declare no conflicts of interest.

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