Advances in solid lithium ion electrolyte based on the composites of polymer and LLTO/LLZO of rare earth oxides

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Abstract
Composite solid electrolyte is a promising solution for the development of new generation of safe and high-performance all-solid-state lithium batteries (ASSLBs). It combines both the advantages of inorganic electrolyte and organic polymer electrolyte, having high ionic conductivity, mechanical strength, good contact with the electrodes and high processability. In the recent decades, rare earth oxides have attracted wide attentions from researchers because of their high ionic conductivity. China is abundant in rare earth resources, so has a good chance to provide the world with high quality rare earth containing functional materials. This review paper focuses on the recent progress in the studies of composite solid electrolyte of polymer and rare earth containing lanthanum zirconium and lithium lanthanum titanium oxides, and gains insights into the challenges in the field, and hopefully helps in the rational design of high performance electrolyte for the development of ASSLBs.

KEYWORDS
all-solid-state lithium batteries | composite solid electrolyte | functional materials | rare earth oxides

Kun Liu and Yajing Wen contributed equally to this study.
1 | INTRODUCTION

Lithium-ion batteries with high energy density, outstanding output power, low self-discharge, and flexible design have been vastly used in automobiles, portable electronic products, and multifarious energy storage devices. However, organic liquid solvents frequently used as electrolytes in commercial conventional lithium-ion batteries are flammable, volatile, and easy-to-leak, which imposes adverse influence on the performance of the cells. Besides, lithium dendrites developed in the process of charge–discharge cycle could pierce the diaphragm and lead to short circuit when lithium metal is used as anode. Unfortunately, the use of lithium anode might be an inevitable way to achieve extremely high theoretical capacity. Therefore, scientists have recently proposed all-solid-state lithium batteries (ASSLBs) with solid electrolytes to replace traditional organic liquid batteries, which presented satisfactory safetiness. As one of the most critical components of ASSLBs there are several essential criteria for high-performance solid-state electrolytes: high ionic conductivity, good chemical, thermal and interface stability, low electronic conductivity, wide electrochemical window, economical, and eco-friendly.

Rare earth isthe general name of 17 elements in the chemical periodic table, including lanthanide, scandium, and yttrium. Because of the specialized atomic electronic configurations, rare earth elements have special optical, electrical, and magnetic properties, and have been very important natural resources widely used in military, metallurgical, electrical, biological, and other fields. Lithium lanthanum titanium oxide (LLTO) and lithium lanthanum zirconium oxide (LLZO) ceramic containing rare earth oxides are currently the most studied solid lithium ion conducting materials in research. LLTO solid electrolyte has a typical perovskite structure. As shown in Figure 1A, it is mainly composed of Ti-O octahedrons. Li$^+$ migrates in a quadrilateral channels composed of La$^{3+}$ and adjacent four oxygen atoms. In 1993, Chen et al. determined the ionic conductivity of LLTO to be $10^{-5}$ S/cm by alternating current (AC) impedance method, and the bulk ionic conductivity can reach $10^{-3}$ S/cm. However, Ti$^{4+}$ in LLTO is easily reduced to Ti$^{3+}$ when contacted with lithium, Li$^+$ can infiltrate into LLTO, resulting in electronic conductance and poor electrochemical stability. To solve the problem, efforts have been made to introduce Si$^{24}$ or Zr$^{25}$ into LLTO to improve its ionic conductivity and stability. In contrast to LLTO, Weppner et al. reported the excellent performance of LLZO with garnet structure for lithium-ion conductivity, and thermal and chemical stabilities in 2007. Since then, LLZO has become one of the hottest research topics in the field of inorganic solid electrolyte. The structures of LLZO are shown in Figure 1B. It consists of La–O
dodecahedron and Zr–O octahedron. Li\(^+\) transports along the network path formed in the direction of [111]. Moreover, the ionic conductivity of LLZO can be further increased by doping Al, Ta, or Sr.\(^{27,28}\) Another reason for doping is to stabilize the cubic phase of LLZO. LLZO can show two crystal structures, tetragonal phase and cubic phase. The ionic conductivity of cubic phase is relatively high, which is usually 2–3 orders of magnitude higher than that of tetragonal phase.\(^{29,30}\) Nevertheless, the cubic phase of LLZO is unstable and tend to transform into tetragonal phase at high sintering temperature.\(^{31}\) Doping of other elements such as Fe,\(^{32}\) Ga,\(^{33}\) Al,\(^{34}\) Ta,\(^{35}\) Nb,\(^{36}\) and so forth, can help to stabilize the cubic lattice in LLZO and improve the ionic conductivity.

Though the material often shows good ionic conductivity in bulk, the interface can be a big problem. Goodenough et al.\(^{37}\) found that the surface of LLZO solid electrolyte is prone to generating trace amount of Li\(_2\)CO\(_3\), which is the culprit for lowered electrochemical performance, then they successfully achieved a very low interface impedance by carbon reduction in Ar atmosphere. Chen et al.\(^{38}\) also found a very convenient way using pencil graphite to scratch on the surface of the ceramic pellet to considerably improve the performance of solid electrolyte. Although LLTO and LLZO have high lithium-ion conductivity, they also have problems of brittleness, poor processibility and sensitivity to air and moisture (for LLTO), which limit their applications in lithium ion battery industry.

Compared with LLTO, LLZO and other inorganic solid electrolytes, polymeric lithium electrolytes have very good processability, which makes them highly suitable for various forms of battery fabrication, but their low lithium ion conductivity is the major bottleneck to limit the application. The history of polymer electrolytes can be traced back to 1973. At that time, Wright et al.\(^{39,40}\) Armand et al.\(^{41,42}\) published their research on ionic conductivity of complexes containing polyethylene oxide (PEO) and alkali metal salts, attracting much interest in polymer solid-state batteries. PEO has become the most studied solid polymer electrolyte (SPE) therefrom. Since then, polymers of various structures have been developed (Figure 2), such as polycarbonate,\(^{43–47}\) polysiloxane\(^{48–50}\) and other types of polymers.\(^{51–57}\)

Ideas can be sparked taking advantage of the high lithium ion conductivity of inorganic oxide, and combine it with the good processibility of polymeric materials.\(^{63}\) In this way, the problems of brittleness and poor electrochemical stability can be solved using shape-formable polymer materials. In recent years, the composite solid electrolytes have raised booming attentions. Among them, the most studies were on PEO/LLZO composite systems, other system using different polymers and LLTO or LLZO also started to stimulate the nerves of researchers. The sections that follow briefly review the very recent advances on the polymer/LLTO or polymer/LLZO composite solid electrolyte. It is worth mentioning that a few review articles\(^{64–66}\) have been published recently focusing on the composite solid electrolyte, which can be very good signal to foresee the potentials in this field. The current contribution was actually designed as a specialized review to exploit the potential related to rare earth elements in this field, inorganic oxide fillers, polymer matrix, mechanism and study techniques, and so forth. Here, we make efforts to find out to what extent of performances the composite containing rare earth element can achieve, and examine the problems that could be specific and shared in the system.

To make the content more organized, abundant literatures have been browsed. It was found that the reports in the field can be classified into different classes, the most widely studied composite was by using of PEO polymer, so PEO-based composites using different oxides, that is LLZO and LLTO were reviewed in the first section that will follow. Then, other different polymers were discussed in fabricating the composite. At almost the end of the review, the conducting mechanism is examined in view of some important points, such as interface issue and chain mobility. As a small subsection, specialized techniques used in the study of mechanism were demonstrated.
FIGURE 2 Examples of the chemical structure for some typical solid polymer electrolytes (SPEs). (A) Poly(ethylene oxide)\(^{58}\); (B) poly(propylene carbonate)\(^{59}\); (C) poly(ethylene oxide-co-ethylene carbonate)\(^{45}\); (D) poly(trimethylene carbonate)\(^{46}\); (E) poly(ethylene carbonate)\(^{97}\); (F) polyether modified polysiloxane\(^{48}\); (G) polysiloxane polar homopolymers\(^{50}\); (H) cyanoethyl polyvinyl alcohol\(^{52}\); (I) polyacrylonitrile\(^{60}\); (J) comb-like cationic polyurethanes\(^{64}\); (K) polyphosphonate\(^{55}\); (L) poly(vinylidene fluoride)\(^{36}\); (M) poly(vinylidene fluoride-co-hexafluoropropylene)\(^{37}\); (N) polyethylene glycol 200 diacrylate\(^{61}\); (O) poly (ethylene glycol) methyl ether acrylate\(^{62}\)

2 | PEO-BASED COMPOSITE SOLID ELECTROLYTE

2.1 | Mixture with LLZO

Hitherto, PEO and its derivatives have been mostly studied in SPEs currently, though the ionic conductivity at room temperature remains quite limited, and the electrochemical stability and inhibition of lithium dendrite growth are not satisfactory. As generally accepted, suppression of crystallinity of PEO chain is an effective way to improve the ionic conductivity, some efforts have been made using inorganic fillers such as SiO\(_2\), Al\(_2\)O\(_3\), and TiO\(_2\) to decrease the crystallization of PEO and thus improve its ionic conduction. Using rare earth oxide inorganic solid electrolyte fillers
such as LLZO can not only reduce the crystallinity, but also increase room temperature (RT) electrochemical stability and ionic conductivity of the composite electrolyte. Besides, good processability can also be obtained.

Robert et al.\textsuperscript{75} synthesized the LLZO of cubic phase and mix it with PEO (10\textsuperscript{5} g/mol) and LiClO\textsubscript{4}. The results of differential scanning calorimetry demonstrated that the crystallinity of PEO matrix presented a significant decrease from 37.9\% to 1.9\% with the addition of LLZO to the composite. Temperature can regulate the lithium ion conductivity of the composite electrolyte, that is, above the melting point of PEO the lithium ion conductivity is determined by LLZO; while under the melting point of PEO, PEO dominates the lithium ion transport in the composite (Figure 3). For example, for a 40 vol\% LLZO composite with PEO, the conductivity is 5 \times 10\textsuperscript{-5} S/cm at 80\degree C, which is close to the pure LLZO electrolyte, and the conductivity rapidly decreases to 8 \times 10\textsuperscript{-9} S/cm at 20\degree C well below the melting point of PEO/LiClO\textsubscript{4} at 58\degree C. The composite containing LLZO possesses much higher mechanical strength than that without, especially above PEO’s melting temperature. In another similar report, Chen et al.\textsuperscript{76} used PEO with a little higher molecular weight (MW) by 6 \times 10\textsuperscript{5} g/mol, and change the lithium salt from LiClO\textsubscript{4} to LiTFSI, a much higher lithium ion conductivity 5.5 \times 10\textsuperscript{-4} S/cm can be achieved at 30\degree C at lower LLZO content by 7.5 wt\% (Figure 4). The researchers also assembled a Li|PEO-LiTFSI-7.5\%
LLZO|LiFePO₄ half-cell with a discharge capacity of 150.1 mAh/g at 0.1 C, meanwhile, showed good cycle and rate performance. So, the better dissociation of LiTFSI can be a very important factor to impact on the performance.

Compared to the study by Robert et al., Murugan et al. used Al doped LLZO (Li₆.2₈A1₀.2₄Lₐ₃Z₉₂O₁₂, abbr. LLZAO), the molecular weight was 10 times higher (5 × 10⁶ g/mol). The optimal mixing ratio was LiClO₄/EO = 1/8, and LLZAO at 20 wt%. At 30°C, the lithium ion conductivity of the electrolyte can achieve 4.40 × 10⁻⁴ S/cm, and the electrochemical window was 4.5 V. The author also assembled Li|composite solid electrolyte|Lithium cobaltate (LCO) battery that showed an initial discharge specific capacity of 142 mAh/g. After 30 charge/discharge cycles, the specific capacity remained 120 mAh/g, and the coulombic efficiency was 96%. Cui et al. synthesized Al³⁺/Nb⁵⁺ co-doped cubic LLZO nanoparticles and combined them with PEO (6 × 10⁵ g/mol) and LiClO₄ to obtain the composite solid electrolyte. The composite showed improved conductivity compared to the sample without the filler. The ionic conductivity of the composite electrolyte containing 15 wt% of LLZO was increased to 9.5 × 10⁻⁶ S/cm and 1.1 × 10⁻⁴ S/cm at 20 and 40°C, respectively.

Generally, the use of element-doped LLZO helps to increase the electrochemical stability, however the increase of lithium ion conductivity may be limited. It can be found that the reported values of lithium ion conductivity is mainly ranged from 10⁻⁶ to 10⁻⁴ at RT even with similar lithium salt and molecular weight of PEO used, the variation might lie in the preparation and measurement process.

Actually, the addition of LLZO doesn’t guarantee the increase of ionic conductivity. Stefano et al. used a solvent-free method to mix PEO with LLZO by grinding to obtain PEO (4 × 10⁶ g/mol)/LiTFSI/LLZO composite solid electrolyte. It showed that addition of LLZO to a pure polymer electrolyte did not result in significant improvement of ion transport properties. The preferred channel for Li⁺ is inside polymer matrix, rather than ceramics-polymer pathway, as shown in Figure 5. Therefore, ion transportation at the LLZO-polymer boundary is a big problem to solve in the composite electrolyte materials. The composite electrolyte exhibits better compatibility with lithium than PEO/LiTFSI or LLZO separately as indicated by lower interfacial resistance. From this paper, it can be found that addition of LLZO into polymer matrix to fabricate composite solid electrolyte may not be a master key, the puzzle remained to be solved is in the interface between polymer matrix and oxide filler. Attention on interfaces started to be paid in examination of the composite electrolyte. One of the effects from the surface of oxides may be from anion-immobilization mechanism, Zhang et al. dispersed the garnet-type Al-doped Lithium lanthanum zirconium tantalum oxide (LLZTO) ceramic particles in the polymer-lithium salt matrix. The LLZTO ceramic filler plays the role of a rigid barrier, blocking the dendrites. Polymer can maintain close contact interface and adequate ion transport by acting flexibly to adapt to the electrode surface. The results show an ultimate conductivity as high as 1.12 × 10⁻⁵ S/cm at 25°C and a electrochemical window as wide as 5.5 V. They also proposed a flexible anion-immobilization mechanism, providing an extra explanation of the lithium conducting property. The acidic surface of LLZO was also used in explaining the improved property by Chen et al. in PEO/LiTFSI/LLZO/SN composite, where SN refers to succinonitrile.

Because interface has raised great interest in the study of composite solid electrolyte, its direct modification started to be reported. Wang et al. modified the surface of LLZTO with polydopamine (PDA), a highly effective and well used method in surface modification, to increase the surface wettability of LLZTO with PEO allowing a large amount of LLZTO to be mixed more evenly with PEO/LiTFSI electrolyte. The thickness of PDA layer was measured to be 4–5 nm on LLZTO nanoparticles. The LLZTO@PDA/PEO composite solid electrolyte was prepared by solution casting. It was found that the interfacial contact, and so the good compatibility and adhesion of the electrolyte to both electrodes are good owing to the superior wetting ability of PDA so as to lower the interfacial resistance. Another effect of PDA coating could be the
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improved LLZTO nanoparticle dispersion in polymer matrix, and so to facilitate effective percolation pathways for Li$^+$ migration. With PDA surface modification, the conductivity of the composite electrolyte increased significantly from $6.3 \times 10^{-5}$ to $1.1 \times 10^{-4}$ S/cm at 30$^\circ$C. The composite electrolyte also demonstrated improved thermal stability from 463 to 523$^\circ$C compared to that without PDA coating in thermogravimetric-differential thermal analysis (TGA-DTA).

Since silane is a well-known surface treating reagent in material science, Li et al.\textsuperscript{84} grafted brush-like side-chains to the surface of LLZTO nanoparticle (MB-LLZTO) using imidazolium silane. The mixture with PEO showed much increased ionic conductivity in the polymer matrix by the Li$^+$ domain-diffusion effect. The highest ionic conductivity was found at 15 wt% MB-LLZTO at 45$^\circ$C, that is, $3.11 \times 10^{-4}$ S/cm versus $9.16 \times 10^{-5}$ S/cm as presented by the original solid electrolyte.

Usually, in the study of composite electrolyte, composite films were fabricated first, and then taken to electrochemical testing. In contrast to this process, in situ film fabrication method was proposed and evaluated. Marisa et al.\textsuperscript{85} proposed an in situ polymerization method to prepare composite solid electrolytes. The LLZO ceramic particles were first mixed with PEO ($2 \times 10^5$ g/mol), LiTFSI, tetra(ethylene glycol dimethyl ether) (G4) and a hydrogen abstraction photoinitiator, then the mixture was hot pressed and crosslinked under UV light to obtain a nonflammable and non-tacky solid film, as shown in Figure 6. Its mechanical properties are satisfactory and stable at ambient/sub-ambient and even at relatively high temperatures. The ionic conductivity of the composite solid electrolyte can reach $10^{-4}$ S/cm and even up to $10^{-3}$ S/cm at 20 and 80$^\circ$C, respectively.

The conventional method to prepare composite solid electrolyte film is by solution-casting. However, the application of organic solvent may bring extra side effect on the property of composite electrolyte, Huang et al.\textsuperscript{86} compared the two methods either by dry-mixing using Haake Rheomixer (Figure 7) or by conventional solution casting. The targeting composite solid electrolytes consist of 50 wt% LLZTO and 50 wt% PEO ($6 \times 10^5$ g/mol). The internal-mix process using mixer is free of any solvent, thus no agglomeration or solvent remained in the polymer matrix, and the composite solid electrolytes prepared in this way had less undesired Li$_2$CO$_3$, exhibiting better thermal and electrochemical stability. All-solid-state battery assembled showed improved cycling performance than that prepared using composite solid electrolytes via solution casting method. Other benefits can be environmentally friendly process, and cost-saving especially in large-scale manufacture.

As a ceramic oxide filler, LLZO is generally added in the form of zero-dimensional nanoparticles in so many studies on composite solid electrolytes. However, lithium ion transportation seems to be preferably through the pathway of polymer

**Figure 6** A crosslinked composite polymer electrolyte obtained by mixing PEO, LiTFSI, G4, LLZO and BP by hot pressing, and crosslinking the PEO and G4 by using ultraviolet light.\textsuperscript{85} Copyright 2019 American Chemical Society
matrix in many cases (see preceding part of the contribution), a possible cause is that the nanoparticles tend to accumulate, leading to decreased ionic conductivity. To solve this problem, interconnected long-range ion migration pathway inside solid electrolyte was proposed and constructed. Hu et al.\textsuperscript{87} prepared a 3D garnet LLZO nano-network by electrospinning and high-temperature annealing, and combined it with PEO (6 × 10\textsuperscript{5} g/mol) to prepare composite solid electrolyte. In this way, a 3D polymer/LLZO composite solid electrolytes film was obtained, as shown in Figure 8. The 3D network structure not only provided a continuous long-range lithium-ion transport pathway in PEO, but also can enhance the mechanical properties of the electrolyte film. The ionic conductivity of the electrolyte at RT can reach 2.5 × 10\textsuperscript{−4} S/cm, and the dendrite can be effectively blocked in the battery. Another interesting example was also reported by Hu et al.\textsuperscript{88} on a simple method for the preparation of LLZO network structure on large scale. They used bacterial cellulose as the template to absorb the LLZO precursor solution, then porous cubic garnet LLZO nanofibers network was synthesized by calcination. Finally, PEO (6 × 10\textsuperscript{5} g/mol)/LiTFSI solution was infiltrated into LLZO nanofibers network to improve the film flexibility in the composite solid electrolyte, as shown in Figure 9. The high lithium conductivity by 1.12 × 10\textsuperscript{−4} S/cm at RT was achieved due to the long range lithium-ion transportation pathway. Similarly, Fu et al.\textsuperscript{89} prepared a 3D porous Al doped LLZO (LLZAO) membrane using a dust-free chamber wiper of low cost with strong adsorption ability, which was composed of 45 wt% polyester fiber and 55 wt% cellulose. In this work, a flexible composite solid electrolyte for all-solid-state metal lithium battery was successfully prepared by filling PEO/LiClO\textsubscript{4} in three-dimensional porous LLZAO network. The LLZAO network promotes the formation of continuous and rapid migration channels of lithium ions, prevents the growth of lithium dendrites. At 30°C, the ionic conductivity of the PEO/LiClO\textsubscript{4} composite solid electrolyte is as high as 2.25 × 10\textsuperscript{−5} S/cm. Meanwhile, the PEO (9 × 10\textsuperscript{5} g/mol) matrix provides excellent elasticity for the composite solid electrolyte and reduces the interface impedance between the electrodes.
In all the above reviewed studies, lithium salt is an inevitable component in the preparation of composite solid electrolyte film, however they may not be a must in the composite electrolyte of polymer and LLZO. Guo et al.\textsuperscript{90} compounded LLZTO and PEO (10\textsuperscript{6} g/mol), and obtained a flexible composite solid electrolyte film with the thickness about 40 μm. Without lithium salt, the composite solid electrolytes consisting of LLZTO by 5.2 ~ 21.1 vol% exhibited a high lithium ion conductivity by 2.4 × 10\textsuperscript{-4} S/cm at 30°C, which is due to the percolation between the high lithium-ion conductive LLZTO and PEO. In addition, the spatial ionic current which is dominated by LLZTO can be distributed by PEO, and this is beneficial to the improvement of electrochemical stability and the suppression of lithium dendrites growth. In the study, they also found that the smaller the size of the LLZTO nanoparticle, the higher the ionic conductivity of the composite solid electrolytes. However, small size nanoparticles were prone to agglomeration, which can adversely reduce the ionic conductivity. Therefore, Guo et al.\textsuperscript{91} tried to wet the interface between PEO and LLZTO using ionic liquid [BMIM]TF\textsubscript{2}N without adding any extra lithium salt (Figure 10). It was found that the ionic conductivity using wetted LLZTO nanoparticles of 200 nm can be comparable to that of LLZTO with much smaller size of 40 nm without wetting.

### 2.2 | Mixture with LLTO

Similar to LLZO, LLTO is another well studied lithium conductive material that contains rare earth lanthanum. There are a few studies reported on the composite solid electrolytes of LLTO and PEO. He et al.\textsuperscript{92} designed an ASSLB with high...
discharge voltage and excellent cycling stability, in which poly(2-chloro-3,5,6-trisulfide-1,4-benzoquinone) (PCTB) was used as the cathode, and the PEO-based composite electrolyte containing LLTO nanoparticles was used as the electrolyte. At 70°C, the ionic conductivity of PEO (4 × 10^5 g/mol)-LiClO_4/10 wt% LLTO can reach 7.99 × 10^{-4} S/cm. Moreover, the maximum discharge capacity of PCTB|Composite electrolyte|Li battery can be up to 104 mAh/g and retained 90% of the maximum capacity after 300 cycles.

In the composite solid electrolyte, LLTO nanoparticles have to overcome the energy barrier between particles. Similar to LLZO in the previous section, some studies have been reported using nanofibers or by constructing 3D nano-networks. Zhanget al. prepared ceramic LLTO nano-fiber by electrospinning with assistance of polyvinylpyrrolidone and subsequent calcination, and further dispersed it in PEO (6 × 10^5 g/mol)/LiTFSI to prepare PEO/LiTFSI/15 wt% LLTO composite solid electrolyte. At room temperature, it exhibited a high ionic conductivity by 2.4 × 10^{-4} S/cm and achieved high electrochemical stability up to 5 V versus Li/Li^+.

Introducing ceramic LLTO nano-fibers into the PEO matrix has many advantages. On one hand, it can help to reduce the crystallinity of PEO. On the other hand, LLTO nanofibers with large specific surface area can increase the effective conductive interface between fillers and PEO polymers. Finally, LLTO can also improve the electrochemical stability of PEO polymer electrolytes.

Compared to the two dimensional LLTO networks, three dimensional nanostructure was also studied for LLTO. Yu et al. designed a three-dimensional nanostructured LLTO framework from gel precursor to fabricate composite solid electrolytes PEO/LiTFSI/LLTO. The electrolyte with high ceramic content (44 wt%) showed an increased lithium ionic conductivity to 8.8 × 10^{-5} S/cm at RT. At the same time, its thermal stability and electrochemical stability are also improved. The systematic studies of percolation behavior showed that higher conductivity is attributed to the 3D nanostructured LLTO framework. The 3D nanostructured LLTO framework prevents the agglomeration of the filler, and the formation of continuous lithium-ion pathways also facilitated the conduction of lithium ions. Similar to the study on polymer/LLZO composite solid electrolyte, interfacial issues such as high interface resistance and incompatibility are still to be solved. Liu et al. prepare a flexible composite solid electrolytes with a layer of PEO (6 × 10^5 g/mol) on either side. The introduction of LLTO nanofiber skeleton greatly improved the mechanical strength, ionic conductivity and electrochemical stability of the electrolyte. Meanwhile, LLTO 3D nanofiber networks enhanced the mechanical strength and high ionic conductivity by 1.6 × 10^{-4} S/cm at 24°C. Moreover, the special sandwich structure, afforded good interfacial contact. The results show that the Li symmetrical battery with composite solid electrolyte can stabilize the plating/stripping cycles for
more than 400 h and Li|composite solid electrolyte|LiFePO₄ battery operated for more than 300 cycles at 2 C rate with the capacity retention by about 79% at 60°C.

Generally speaking, the use of LLZO and LLTO in composite solid electrolyte when mixed with PEO is the most popular and has been widely studied. LLTO has long thought not to be as electrochemical stable as LLZO. However, from the reviewed studies above, it can be found that the electrochemical stability window are both good even higher than 5 V.93,94 As for ionic conductivity, both can achieve 10⁻⁴ S/cm at high temperatures. It is hard to see a big difference between the composites made from either LLZO or LLTO.

3 | COMPOSITE MADE WITH OTHER POLYMERS

In addition to PEO, there are many other polymers that can be combined with rare earth containing lithium ion conducting ceramic oxides to form composite electrolyte. Compared with PEO that usually has low lithium-ion migration number (∼0.2), polycarbonate-based polymer electrolytes such as polypropylene carbonate, polyethylene carbonate (PEC), and polytrimethylene carbonate exhibit higher tₐ⁺, which is a great advantage in reducing polarization in batteries. For example, Fan et al.98 synthesized nanocubic Al doped LLZO (Li₆.2₅Al₀.2₅La₃Zr₂O₁₂), by solution combustion method, and then mixed with polyethylene carbonate (PEC [∼2.38 × 10⁵ g/mol] in Figure 2E), LiTFSI, nano Al-LLZO and a small amount of poly(vinylidene fluoride-co-hexafluoropropylene) P(VDF-HFP) (∼4 × 10⁵ g/mol) (Figure 2M) to prepare flexible composite solid electrolyte. PEC, as a fast ion-conducting polymer, possesses high tᵢ⁺, and the addition of Al-LLZO nanoparticles further improves tᵢ⁺ (0.82) and ionic conductivity (5.24 × 10⁻⁵ S/cm). Cui et al.59 mixed polypropylene carbonate (PPC [5 × 10⁴ g/mol] in Figure 2B) with LLZTO to obtain a flexible solid electrolyte which shows good ionic conductivity (5.2 × 10⁻⁴ S/cm), electrochemical window (4.6 V), tᵢ⁺ (0.75) and mechanical strength (6.8 MPa). As shown in Figure 12, the battery assembled by the electrolyte membrane can work between 0 and 160°C, and exhibited excellent rate capability and superior cycling stability.

Polyacrylonitrile (PAN in Figure 2I) is also used to prepare composite solid electrolyte with LLZO/LLTO for its high thermal stability and low cost. Qiu et al.99 prepared the composite electrolyte consisting of PAN (10⁶ g/mol), LLZTO, LiClO₄, and Mg(ClO₄)₂ and a little amount of liquid electrolyte (LiPF₆ in equal volume mixture of ethylene carbonate [EC] and dimethyl carbonate) by electrospinning. The results show that addition of magnesium salt into the electrolyte can effectively improve the cycling stability of the battery, probably by promoting the decomposition of LiPF₆ in the electrolyte to form fluoride ions. The formation of a stable magnesium fluoride protective layer on the surface of lithium anode can effectively hinder the growth of lithium dendrite, reduce the interface impedance and improve the cycle life of the battery. The ionic conductivity was 3.2 × 10⁻³ S/cm with Mg and 1.6 × 10⁻³ S/cm without. Candace et al.79 mixed LLZO nanowire ceramic filler with PAN/LiClO₄ and successfully increased the ionic conductivity of PAN-based polymer

FIGURE 12 Charge and discharge profiles of LiFePO₄|PPCL-SPE|Li batteries at (A) 0°C and (B) 160°C.59 Copyright 2017 The Royal Society of Chemistry
electrolyte at RT to about $10^{-4}$ S/cm. Selective solid-state Li nuclear magnetic resonance (NMR) and isotope labeling indicated that LLZO nanowires altered the local environment of the PAN polymer matrix, and created a priority conduction path for Li$^+$ through the polymer/LLZO interface. In addition, the study indicated that doping of Al or Ta in LLZO had no significant effect on the ionic conductivity of composite solid electrolyte, as shown in Figure 13. Cui et al.\textsuperscript{60} prepared LLTO nanowires by electrostatic spinning and dispersed them into PAN ($1.5 \times 10^5$ g/mol) and LiClO$_4$ to obtain the solid composite polymer electrolyte. The ionic conductivity of nanowire-based electrolyte was higher than the nanoparticle-based one. Later, Cui et al.\textsuperscript{100} also studied the effects of orientation of LLTO nanowires on the electrochemical property of composite solid electrolytes.

The high self-polarization of poly(vinylidene fluoride) (PVDF) can help to dissociate the lithium salt more efficiently than the PEO-based polymer, which can enhance the ionic conductivity of the electrolyte.\textsuperscript{101} At the same time, PVDF also has better mechanical properties, electrochemical and thermal stability than PEO.\textsuperscript{102} Therefore, PVDF is a good matrix for composite solid electrolytes. Shen et al.\textsuperscript{103} mixed PVDF and LLZTO particle by solution casting. At 10 wt% LLZTO loading content, the electrolyte achieved an ionic conductivity by $5 \times 10^{-4}$ S/cm at 25$^\circ$C, at the same time, with good mechanical properties of tensile strength by 5.92 MPa, with Young's modulus by 30.8 MPa and good thermal stability up to 310$^\circ$C. According to Fourier transform infrared, Raman and $^1$H NMR spectroscopy and first-principles calculations, possible complex structures in PVDF/LLZTO composite electrolyte membrane were proposed, as shown in Figure 14. The La atom in LLZTO can be complexed with a N atom and a C=O group of a typical solvent molecule such as N,N-dimethylformamide (DMF), with the N atom in a state of high-electron density. Analogous to the Lewis base, the complex causes partial dehydrofluorination in the composite electrolyte membranes, thus enhancing the interaction between the LLZTO particles, PVDF and lithium salt. In another report by Fan et al.,\textsuperscript{104} separate porous polyimide (PI) film was used to enhance the mechanical property of LLZTO nanoparticles/PVDF/LiTFSI composite solid electrolyte.
The improved mechanical property with high tensile strength by 11.5 MPa can be attributed to the PI network which also helped in uniform dispersion of LLZTO in PVDF. The film showed effective prevention for lithium dendrite growth and high cycling stability (more than 1000 h of cycling for Li symmetric batteries). The composite solid electrolyte with (50% LLZTO) exhibited the highest ionic conductivity by $1.85 \times 10^{-4}$ S/cm at room temperature. The assembled solid-state Li|composite solid electrolyte|NCM523 pouch cell exhibited excellent cycling stability (152.6 mAh/g with capacity retention of 94.9% at 0.1 C after 80 cycles) at RT with high safety to work in harsh circumstances such as by folding, cutting and nail penetration.

Shen et al.\textsuperscript{105} studied the effects of filler size and doping (Nb/Al) in LLZO on the electrochemical and mechanical properties of composite solid electrolytes when mixed with PVDF. The composite solid electrolyte having 10 wt% of mixed-sized LLZO particles showed the maximum ionic conductivity by $2.6 \times 10^{-4}$ S/cm at RT, which is related to the lowest porosity. The electrolyte also shows a lithium ion migration number up to 0.682, stable low interface resistance and good mechanical properties. At the same time, as an important component of ASSLB, the electrolyte also shows a lithium ion transference number of 0.682, good mechanical properties up to 2.0 GPa and stable low interface resistance of 79 $\Omega$ cm$^{-2}$. PVDF-HFP is another widely studied fluoropolymer used. Ng et al.\textsuperscript{106} mixed PVDF-HFP ($4 \times 10^{5}$ g/mol) with LLZO nanofibers to prepare composite solid electrolyte for lithium-ion battery. LLZO nanofibers were prepared by electrospinning and then dispersed into PVDF-HFP/LiTFSI matrix. The composite solid electrolyte exhibited enhanced ionic conductivity by $9.5 \times 10^{-4}$ S/cm and an electrochemical stability window is as high as 5.2 V. In addition, the composite solid electrolyte also shows excellent mechanical properties, which can effectively inhibit the growth of dendrites and improve the cycle life of the battery. Wu et al.\textsuperscript{107} developed a solid ceramic nanofiber-polymer composite electrolyte by aluminum doped lithium lanthanum titanium oxide (LLATO)/PVDF-HFP (1.3 $ \times 10^{5}$ g/mol) with addition of Li$_3$PO$_4$ by dipping LLATO nanofibers in Li$_3$PO$_4$/H$_3$PO$_4$. The existence of Li$_3$PO$_4$ layer between LLATO nanofiber and polymer can improve the ionic conductivity and cycling stability. Therefore, the ionic conductivity of PVDF-HFP/LiTFSI/LLATO/Li$_3$PO$_4$ reached $5.1 \times 10^{-4}$ S/cm and the stable voltage window to 5.0 V versus Li/Li$^+$. Symmetrical Li|composite solid electrolyte|Li battery also remains stable during repeated lithium plating/stripping process (at RT). In addition, the battery assembled with the electrolyte and lithium metal anode has excellent cycling performance and rate performance. This work indicated that interfacial modification can be the key to boost the performances.

Ethylene oxide containing polymer matrix similar to PEO system are studied widely, for example in Figure 2N,O. Zhang et al.\textsuperscript{61} developed a new type of composite solid electrolyte composed of silane-modified LLAZO (s@LLAZO) nanofibers and poly(ethylene glycol) diacylate (PEGDA [575 g/mol])(Figure 2N). The specific polymerization process and crosslinking structure are shown in Figure 15. By adding silane coupling agent 3-(trimethoxysilyl) propyl methacrylate, high content of LLAZO (up to 70 wt%) nanofibers can be compounded with polymer matrix to form a well-permeable, three-dimensional LLAZO network completely embedded in PEGDA matrix. In the presence of silane coating, the performance of s@LLAZO-30PEGDA composite solid electrolyte was improved. At RT, the highest ionic conductivity of s@LLAZO(6h)-30PEGDA composite solid electrolytes can achieve $4.9 \times 10^{-4}$ S/cm, which also reflects the improvement of lithium ion conducting path in s@LLAZO nanofiber composite. The all-solid-state lithium-metal battery assembled showed stable cycling performance in 250 cycles and had extremely high rate capacity (up to 10 C) at RT.

In another example, Guo et al.\textsuperscript{62} reported the preparation of composite solid electrolyte from Li$_6$Ga$_{0.25}$La$_3$Zr$_2$O$_{12}$ (Ga-LLZO) nanoparticle via in-situ polymerization of an acrylate monomer (poly(ethylene glycol) methyl ether acrylate [480 g/mol])(Figure 2O). It showed an ionic conductivity by $1.8 \times 10^{-4}$ S/cm, high Li-ion transference number by 0.58 at 30°C, and high electrochemical stability up to 6.5 V versus Li/Li$^+$ at RT.

The synthesis of various polymeric material of different chemical structure allows the tremendous imagination in the design and fabrication of composite solid electrolyte combined with LLZO or LLTO. Recently, some new polymers\textsuperscript{108–110} such as polyphosphazene and new fluoro-containing polymers have just been reported in the application of lithium ion conductors, showing very promising applications in all solid state lithium ion battery. It is believed that the exploitation of new polymers in the composite lithium ion conductor will be paid a lot more attentions in the near future.

\section*{4 CONDUCTING MECHANISM OF LITHIUM ION IN THE COMPOSITE}

Composite solid electrolyte can be very promising to be used in all solid state battery, so it is very important to understand the mechanism of ionic migration and so as to facilitate the rational design in material development. In this section, we review some typical studies on the ion conducting mechanism in composite solid electrolyte containing ceramic oxide with rare earth elements in view of some specific aspects including interface, phase change and instrumental methodology.
4.1 Decrease of crystallinity and enhancement of segmental mobility of polymer chain

As the most studied polymer matrix, PEO is known for its semicrystalline structure. However, it is widely accepted that the ion transport is mainly in amorphous phase because the motion of lithium cations depends heavily on the local segmental relaxation of polymer chain. In the composite solid electrolyte of LLZTO/PEO/LiTFSI, LLZTO particles can help in reducing the crystallinity of PEO and immobilizing the TFSI\(^{-}\) anion, resulting into a well-distributed lithium and dendrite-free deposition, as studied by Zhang et al. and is shown in Figure 16. Similarly, Huang et al. studied the effects of adding LLZO and LLZTO on the performance of PEO polymer electrolytes, respectively. The addition of ceramic particles inhibited the crystallization of PEO and increased the amorphous region to promote lithium ion migration, and so improved the electrochemical performances. The melting temperature \((T_m)\) of the composite solid electrolyte was reduced from 68.2°C of PEO to 55.8°C (PEO/10 wt% LLZO) and 56.6°C (PEO/10 wt% LLZTO), after addition of ceramic particles, respectively, and the peak area was correspondingly reduced as well, allowing the composite solid electrolyte more free volume to facilitate the transport of Li\(^{+}\). The ceramic particles also increased the dissociation of the salt, inhibited the movement of TFSI\(^{-}\) and so increased the lithium ion transference numbers to 0.50.

Other semi-crystalline polymers, such as PVDF and PVDF-HFP can also been used to mix with LLZTO or LLTO to make composite solid electrolyte. Recently, Shen et al. studied the LLZTO/PVDF composite solid electrolyte, and found that the addition of 10 wt% LLZTO to PVDF could significantly improve the ionic conductivity up to \(5 \times 10^{-4}\) S/cm at 25°C. The decreased crystallinity of PVDF matrix can be one of the reasons that accelerated ionic migration. Similar effects can also be found in PVDF-HFP matrix, as studied by Wu et al. It is noted that the chemical mechanism of dehydrofluorination should exist in the composite solid electrolyte when using PVDF and PVDF-HFP polymers as seen by the color change of the films cast from DMF solution.
However, it has to be reminded that the crystallinity may not be affected by the addition of inorganic ceramic nanoparticles, and the enhancement of ionic conductivity should be due to more fundamental interfacial effect (see the followed part of the review).\textsuperscript{117}

Lowering the crystallinity of polymer matrix apparently enhances the mobility of chain segments, as a second choice, plasticizer additives such as dimethyl ether (TEGDME),\textsuperscript{118,119} EC,\textsuperscript{99} fluoroethylene carbonate,\textsuperscript{120,121} and succinonitrile (SN)\textsuperscript{82} can help to do the same thing, and contribute to the much increased ionic conductivity by several orders of magnitude. However, more addition of plasticizer would make the composite similar to liquid or gel system, so beyond the scope of this review on composite solid electrolyte. A balance should be carefully considered between the mechanical property and ionic conductivity.

### 4.2 Ionic conducting pathway in the composite solid electrolyte

It is well accepted that three possible pathways exist for lithium ion conduction in composite solid electrolyte, as shown in Figure 5, that is, inorganic ceramic oxide (LLZO in the figure) pathway, polymer pathway, and a mixed pathway. The similar demonstration is shown in Figure 17 by Gupta et al.\textsuperscript{122} However, the results often don’t guarantee a considerable
enhancement of ionic conductivity with the increase of LLZO content. It is very necessary to compare the results and find where the problem is. Gupta et al. found that the dominant ionic transport pathway is in PEO matrix instead of through LLZO particles. Similarly, Stefano et al. (in Figure 5) found that addition of LLZO to the pure polymer PEO didn’t substantially improve the ionic transportation, and the lithium ions preferentially take the way within the tortuous polymer matrix rather than through the LLZO particles. Kato et al. carefully examined the conducting mechanism by electrochemical impedance spectroscopy (EIS) using Li|electrolyte|SS asymmetric and Li|electrolyte|Li symmetric batteries. When comparing the conductivity/temperature dependence profiles, it is clear to see that the addition of LLZO submicron particles didn’t actually considerably enhance the conductivity up to 80°C. The resistance from bulk, grain boundary (between LLZO grains in the polymer matrix as speculated by the author of the current review from the text) and Li+ charge transfer with electrode can be well discriminated on EIS spectra. The study clearly demonstrated the formation of local percolation pathways between LLZO particles in the polymer matrix. Zhao et al. prepared composite solid electrolyte by adding 0–40 wt% submicron LLZTO in PEO using solvent-free method. At 10 wt%, the ionic conductivity at 30°C increased slightly, and with the further increase of LLZTO, the ionic conductivity decreased considerably, even lower than the membrane without LLZTO. Percolation behavior has been used to explain the contradiction (see reference therein), the direct contact of LLZTO of each other leading to a blockage of lithium ion pathway. In another study, Fan et al. fabricated composite solid PEO/LLZTO electrolytes from “ceramic-in-polymer” to “polymer-in-ceramic” by hot-pressing. The ionic conductivity increases slightly with the addition of 10 wt% LLZTO particles for the fact that the LLZTO particles enhanced the free volume for the motion of PEO chain segments. However, further decrease of ionic conductivity with the increase of LLZTO from 20 to 80 wt% was attributed to the high interfacial impedance. The study indicated that the relationship between ionic conductivity and the amount of LLZTO in composite solid electrolyte are highly dependent. At low LLZTO content (below the percolation threshold), the conductivity is determined by the transport of Li+. It is a critical question to answer why lithium ion conductors such as LLZO cannot help to considerably increase the ionic conductivity in composite solid electrolyte. In other words, how to increase the percolation threshold concentration in composite solid electrolyte. The experimental results have indicated that the high interfacial impedance should be lowered to facilitate the transport of lithium ion. Three possible resolutions may be underlined, (1) wetting to enhance good contact; (2) removal of impurities on LLZO surface; and (3) decreasing lithium ion concentration disparity across the interface. It is noted that the impure surface layers have been known, especially for Li2CO3 that has been well studied by Guo et al. and Sun et al. Acidic and thermal surface modifications can be very effective to remove the harmful Li2CO3 layers. To address the factor of lithium ion concentration disparity across the interface between PEO and LLZTO, Gupta et al. constructed a sandwiched Au|PEO-LiTFSI/LLZTO/PEO-LiTFSI|Au symmetric cell, and used EIS to monitor the interface resistance between PEO-LiTFSI matrix and LLZTO pellet. By modulating the lithium salt concentration from [EO]/[Li+] = 3/1 to 27:1, the optimal concentration was found to be 15/1, too high [Li+] in PEO may lead to lithium salt precipitation, and the precipitate acts as inactive filler instead to hinder the lithium ion transport. From the above discussions, it can be seen that to push the lithium ion across the interface between polymer matrix and inorganic lithium ion ceramic conductors, and make it fully engaged in ionic conduction is a critical issue to obtain the synergetic performance of high ionic conductivity from all the components in composite solid electrolyte. And a prerequisite is the chemical stability when they are mixed together.

From the above discussions, it can be seen that to push the lithium ion across the interface between polymer matrix and inorganic lithium ion ceramic conductors, and make it fully engaged in ionic conduction is a critical issue to obtain the synergetic performance of high ionic conductivity from all the components in composite solid electrolyte. And a prerequisite is the chemical stability when they are mixed together.

To highlight the interfacial issue of ionic conduction in composite solid electrolyte, and to look at it in a little more detailed aspect, we put this part in a separate section that follows.

### 4.3 Interface and space charge effect

In the preceding section, surface modifications to remove impurities such as Li2CO3 is important to achieve a high ionic conductivity. Besides, surface wetting treatment is equally important, such as by PDA or silane coatings. Well surface contact is a fundamental condition for lithium conductivity, as is often concerned for the electrolyte to contact with lithium metal. In a thermodynamic view of point, a direct contact between polymer and LLZO or other
rare earth containing inorganic ceramic nanoparticles would incur a redistribution of lithium ion across the border of interface, similar to a p-n junction in semiconductors, due to the intrinsic difference of chemical potential of lithium ion in each component. So, a very specific space charge region/layer would be induced.\textsuperscript{133–136}

Guo et al.\textsuperscript{117} used a Ga doped LLZO (Li$_{6.25}$Ga$_{0.25}$La$_3$Zr$_2$O$_{12}$, abbr. Ga-LLZO) to fabricate composite solid electrolyte with PEO ($6 \times 10^5$ g/mol), and found that the addition of 16 vol% Ga-LLZO resulted in a conductivity by $7.2 \times 10^{-5}$ S/cm at 30$^\circ$C, about four orders of magnitude than pure PEO. Transmission electron microscopy (TEM) study indicated the thickness of the space charge region by 3 nm (Figure 18). By simulation, Li$^+$ rich areas (space charge regions) were built up at the surface of Ga-LLZO nanoparticles as driven by the decrease of free energy, and new highly conductive surface regions formed. In this way, percolation mechanism starts to take over the overall ionic conductivity in material. The space charge region can well explain the abnormally high conductivity in the composite mixture of LiI-Al$_2$O$_3$ where Al$_2$O$_3$ is actually insulating.\textsuperscript{137} Obviously, one of the key parameters would be the high specific interface area. A typical study was made by Guo et al.,\textsuperscript{90} where it is very interesting to see that the percolation threshold concentration of LLZTO can be highly dependent on the particle size. They used LLZTO with different particle sizes to compound with PEO without lithium salt, and investigated the influence of particle size on the properties of electrolyte. At $D_{50} = 40$ nm and 400 nm for LLZTO, the conductivity of composite solid electrolyte showed a similar result as what has been reviewed above, that is, increased at the maximum to 12–15 vol%, then decreased again with more LLZTO added. As for the case of LLZTO with $D_{50} = 10$ μm, the percolation threshold increased to 21 vol%. And the ionic conductivity was found much lower than those of smaller sizes ($D_{50} = 40$ nm and 400 nm) by approximately two orders of magnitude at the same LLZTO content. In another literature from the same group, LLZTO by 200 nm and 5 μm in particle size were used, and similar evolution tendency can be found. The highest conductivity can be found at 20 vol% LLZTO. With more LLZTO added up to 50 and 80 vol%, the conductivity decreased instead.\textsuperscript{138}

The conducting mechanism through space charge region is important to understand the percolation effect with the concentration of LLZO particles, the surface area is extremely important. However, the major ionic conduction path has been limited, if true, to the interface region. Inside the bulk LLZO particles seems to be less utilized. How to push lithium ions crossing the border, that is, to transport perpendicular to the space charge layer could be an interesting topic. Brogioli et al.\textsuperscript{139} stacked the Al doped LLZO pellet and PEO film, and measured the interfacial resistance between LLZO and PEO, and compared the experimental results with simulations (Figure 19). The efforts were to try to explain the high resistance of the interface between PEO and LLZO. At large positive or negative cell voltages, the interface resistance increased dramatically mainly due to the depletion of lithium ions, this space charge effect is detrimental for the conductivity of the composite solid electrolyte and raises a high activation energy barrier in ionic conduction. A similar experimental setup by Gupta et al. actually implied the same difficulties to push lithium ion across the border between polymer and LLZTO.\textsuperscript{122}

4.4 Techniques in studying the lithium ion conducting mechanism

In order to understand the mechanism of ionic conduction in composite electrolytes and the space charge effect at the interface of solid electrolytes/electrodes, solid state NMR,\textsuperscript{84,107,140} X-ray tomography,\textsuperscript{141} neutron diffraction (ND) (or neutron powder diffraction),\textsuperscript{142–144} phase-shifting electron holography, and spatially resolved electron energy loss spectroscopy (SR-EELS)\textsuperscript{145} have been used and proven very effective to learn the ion and potential distribution in space.
Most of the above-mentioned techniques have been used to help in understanding the interfacial behavior of electrode/solid electrolyte and helpful for the detailed study of solid composite electrolyte. For example, through phase-shifting electron holography and SR-EELS (Figure 20), Nomura et al.\textsuperscript{145} have successfully visualized the ion and potential distribution in the space charge layer formed at the interface between copper electrode and $\text{Li}_{1+x+y}\text{Al}_{x}(\text{Ti,Ge})_{2-y}\text{Si}_{y}\text{P}_{3-y}\text{O}_{12}$ (LASGTP) (LASGTP is less susceptible to air to form contamination layer than LLZO and sulphide-based solid electrolytes). The visualization is helpful to explain the high resistance of solid/solid interface to hinder lithium ion transport.

In another study, Harry et al.\textsuperscript{141} used X-ray tomography to study the lithium deposition at the electrolyte/anode interface. The electrolyte used is polystyrene-block-poly(ethylene oxide) copolymer/LiTFSI SPE. With the accumulation of electric charge, the nucleation, growth, and finally penetration of the SPE can be clearly visualized.

The major characterization techniques for the study of lithium ion conducting mechanism are solid-state NMR and ND. At present, ND is mainly used in the study of inorganic solid electrolytes, owing to its high sensitivity towards light elements, it can help in the determination of the locus and content of lithium ions, especially through Rietveld refinement analysis. For example, Liu et al.\textsuperscript{144} studied the effect of multi-element-doping on the conductivity of Li$^+$ in LLZO by ND. The calculated occupancy of tetrahedral-$24d_{\text{Li}^+}$ and octahedral-$96h_{\text{Li}^+}$ indicated that its ratio is critical for the conductivity of lithium ion. By multi-doping, the occupancy of lithium in tetrahedral-$24d_{\text{Li}^+}$ site increases from 0.36 (5) to 0.77 (5), while the Li$^+$ occupation rate of octahedral-$96h_{\text{Li}^+}$ site remains almost unchanged, so the authors believe that the multi-ion doping in the garnet framework would lead to the structural change to provide more space at the tetrahedral-$24d_{\text{Li}^+}$ position, thus improving the total ionic conductivity of the garnet structure. Similarly in another report, Rao et al.\textsuperscript{143} used ND to study the formation and phase transformation process of LLZO and the influence further on the ionic conductivity. The results show that in order to maximize the conductivity, the cooling rate needs to be slow enough to keep a balance of Li$^+$ distribution between tetrahedral and octahedral coordination sites.

Solid state NMR is another powerful technique to study the chemical structure and dynamic process in solid, so is widely used to characterize the distribution and diffusion of ions in composite solid electrolyte. Hu et al.\textsuperscript{140} studied the classical PEO-LiClO$_4$/LLZO composite solid electrolyte, and determined the local structural environment of lithium-ions in PEO, LLZO and LLZO/PEO interfaces by high-resolution solid-state Li NMR. They used $^6\text{Li}$ to label the lithium foil electrodes and $^7\text{Li}$ in the electrolyte. During charging and discharging, $^6\text{Li}$ in the electrode enters and deposits into another $^6\text{Li}$ electrode through diffusion, so $^6\text{Li}$ partially replaces $^7\text{Li}$ ion in the electrolyte every time it passes through the electrolyte, leaving evidences of traces of Li$^+$ pathway behind. Finally, experimental evidence shows that Li$^+$ mainly transports through LLZO ceramic phase, instead by PEO/LLZO interface or PEO (Figure 21). In another report, Wu et al.\textsuperscript{107} studied...
FIGURE 20 Electric potential distribution near Cu|LASGTP interface was measured by phase shift electron holography.\textsuperscript{145} Copyright 2019 Wiley VCH Verlag GmbH & Co. KGaA, Weinheim

FIGURE 21 (A) The possible Li\textsuperscript{+} transport path in the composite electrolyte. (B) Cycling at a constant alternate current every 300 s. (C) Comparison of the \textsuperscript{6}Li NMR spectra of the composite solid electrolytes before and after cycling. (D) Quantitative analysis of \textsuperscript{6}Li in different part of the electrolyte before and after cycling.\textsuperscript{140} Copyright 2016 Wiley VCH Verlag GmbH & Co. KGaA, Weinheim
the local environment and migration pathway of Li ion in the PVDF-HFP/LiTFSI/LLATO/Li$_3$PO$_4$ composite solid electrolyte by $^6$Li and $^7$Li solid NMR spectroscopy, and can quantify the contribution to lithium ion conductivity from different component of the composite. When there was a Li$_3$PO$_4$ layer present between LLATO nanofiber and polymer, the $^6$Li signal much increased, so confirmed the transport pathway improved at the interface. Similarly, Wen et al.$^{84}$ used $^6$Li solid NMR to check the local chemical environment of Li$^+$ so as to find out the lithium diffusion pathway in the mixture of molecular brush (MB) modified LLZTO and PEO composite solid electrolyte. From the chemical shift after incorporation of MB, an altered Li$^+$ environment in LLZTO can be concluded. Irregular structure of interface was suggested to provide the fast ion diffusion pathway for lithium ion.

5 | SUMMARY

Exploring new solid electrolyte is crucial for the development of all-solid-state lithium-ion batteries in the future. Although a lot of different kinds of solid inorganic lithium ion conductors have been discovered and reported, these inorganic materials are mainly brittle and costly with poor processibility, limiting their applications. As a promising resolution, composite solid electrolyte prepared from the mixture of organic polymers and the just mentioned inorganic lithium ion conducting materials comes into the sight. China is abundant of rare earth elements, and so this review focuses on the development of composite solid electrolyte containing rare earth elements, especially LLZO, LLTO, and their derivatives. Though these oxide ceramics have been synthesized and well-studied more than 10 years ago. Their surface modifications and solid forms (2D or 3D) are the interesting topics to check with. It is quite necessary to put the studies together, to analyze and to make comparison to find any correlation or clues right inside. At present, PEO/LLZO system is still the most widely studied solid-state composite electrolyte. Other polymers with excellent performances started to be developed. “Interface issue” seems to be the key point that has to be addressed to improve the conductivity of composite solid electrolyte. It requires insights into the interface both experimentally and theoretically, and truly understanding of the conducting mechanism of the transport of lithium ion. More advanced and in situ techniques are required to uncover the theory underneath. Hopefully, this review paper can help in finding some clues. At the end, another important point what may interest people is the mysterious 4f chemistry,$^{146}$ especially for rare earth elements, how it would help in the design of new functional materials? And to the end of our interest, to fabricate high performance lithium ion conducting materials.

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CONFLICT OF INTEREST

Authors have no conflict of interest relevant to this article.

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Data sharing not applicable - no new data generated. Data sharing is not applicable to this article as no new data were created or analyzed in this study.
AUTHOR CONTRIBUTIONS

Qian Zhang: Conceptualization; formal analysis; resources; supervision; writing - original draft; writing-review & editing. Kun Liu: Conceptualization; writing - original draft. Yajing Wen: Conceptualization; investigation; resources; writing - original draft. Yaqi Kong: Investigation; writing - original draft. Yuhao Wen: Investigation; writing - original draft. Qi Zhang: Data curation; writing-review & editing. Nailiang Liu: Formal analysis; resources; supervision. Junpeng Li: Data curation; resources. Chunjie Ma: Data curation; resources. Yaping Du: Conceptualization; formal analysis; resources; supervision; writing - original draft; writing-review & editing.

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