Progress and perspective of interface design in garnet electrolyte-based all-solid-state batteries

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Abstract

Inorganic solid-state electrolytes (SSEs) are nonflammable alternatives to the commercial liquid-phase electrolytes. This enables the use of lithium (Li) metal as an anode, providing high-energy density and improved stability by avoiding unwanted liquid-phase chemical reactions. Among the different types of SSEs, the garnet-type electrolytes witness a rapid development and are considered as one of the top candidates to pair with Li metal due to their high ionic conductivity, thermal, and electrochemical stability. However, the large resistances at the interface between garnet-type electrolytes and cathode/anode are the major bottlenecks for delivering desirable electrochemical performances of all-solid-state batteries (SSBs). The electrolyte/anode interface also suffers from metallic dendrite formation, leading to rapid performance degradation. This is a fundamental material challenge due to the poor contact and wettability between garnet-type electrolytes with electrode materials. Here, we summarize and analyze the recent contributions in mitigating such materials challenges at the interface. Strategies used to address these challenges are divided into different categories with regard to their working principles. On one hand, progress has been made in the anode/garnet interface, such as the successful application of Li-alloy anode and different artificial interlayers, significantly improving interfacial performance. On the other hand, the desired cathode/garnet interface is still hard to reach due to the complex chemical and physical structure at the cathode. The common methods used are nanostructured cathode host and sintering additives for increasing the contact area. On the basis of this information, we present our views on the remaining challenges and future research of electrode/garnet interface. This review not only motivates the need for further understanding of the fundamentals, stability, and modifications of the garnet/electrode interfaces but also provides guidelines for the future design of the interface for SSB.

KEYWORDS

all-solid-state batteries, garnet electrolytes, garnet/electrode interface, solid-solid interface

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INTRODUCTION

The change from fossil fuels to renewable energy storage systems requires efficient and reliable energy storage systems. Rechargeable Li-ion batteries (LIBs) are one of the greatest inventions that have been widely used in portable electronics and electric vehicles. Safety becomes a major concern as high-energy devices pose the risk of failure and explosion. For LIBs, the major risk stems from the ignition of liquid electrolytes in the case of short-circuit, causing explosion accidents such as the Samsung Galaxy Note 7 scandal. To overcome the safety issue of liquid electrolytes, solid-state electrolytes (SSEs) are considered as the next-generation LIB technology. SSEs are nonflammable and have good mechanical strength, enabling the direct pairing of Li metal as anode. Compared to liquid electrolytes, their mechanical strength, enabling the direct pairing of Li metal as anode. Compared to liquid electrolytes, their better thermal and electrochemical stability also enable the application of a higher working voltage. Therefore, all-solid-state Li-ion batteries (ASSLIBs) are expected to significantly exceed the durability, energy density, and reliability of current LIB technology.

Initially, a large number of efforts have been devoted to improving the ionic conductivity of the SSEs and it reaches $10^{-2} \text{--} 10^{-3} \text{ S cm}^{-1}$ which is comparable with the commercial level. The next challenge is the interfacial issues between electrolyte and electrodes, including resistance, contact and wettability, and interface stability. Those issues arise from the solid--solid interface, which is completely different from the liquid--solid interface in the commercial LIBs. This is an area that new chemistry and materials properties are discovered, leading to a vivid field tackling solid--solid interface for and beyond energy storage systems. The wetting nature of liquid electrolyte enables itself to access all active electrode particles, allowing the rapid transfer of Li-ions at the electrode-liquid electrolyte interface. SSEs have much lower contact surface, due to their rigidity and roughness, thereby limiting the Li-ion diffusion. Therefore, electrode/SSE interfaces are important contributors to charge transfer resistance in ASSLIBs. Interface interactions are also problematic. On the anode side, the poor contact potentially results in the uneven electrochemical deposition of metallic Li, such as the Li dendrites formation that causes short circuit. On the cathode side, not all cathode particles have the access to Li+, leading to limited storage capacity. Interfacial chemical/electrochemical reactions between SSE and electrodes pose another problem. They usually decompose the SSE into a passivating layer that may block the Li+ diffusion, degrade rate capability and reduce capacity.

Meanwhile, the fundamental study of the cathode/SSE interface has been restricted due to the complicated chemical environment at the interface and the limited measurement methods.

Various solid electrolytes, such as garnet, poly(ethylene oxide) (PEO) based, NASICON, Li phosphorous oxynitride (LiPON), and sulfide SSEs, have been developed in recent years. Sulfide based Li10GeP2S12 (LGPS) shows a relatively high ionic conductivity of $10^{-2} \text{ S cm}^{-1}$, which is comparable with liquid organic electrolyte. However, it is highly sensitive to moisture and is easily reduced by Li metal to form insulating products (Li3P, Li2S, Li15Ge4). LiPON typed electrolyte take advantage of higher stability than LGPS by forming a protecting layer. Nevertheless, they suffer from relatively limited Li-ion conductivity ($10^{-6} \text{ S cm}^{-1}$). In comparison, the garnet-typed electrolyte of Li7La3Zr2O12 (LLZO) has a good ionic conductivity of $10^{-3} \text{ S cm}^{-1}$. Both La3+ and Zr4+ are relatively stable cations, enabling a wide working voltage window.

Until now, significant efforts have been spent on solving the interface issues at garnet typed electrolyte-based ASSLIBs. The focuses are as follows: (1) surface modification of garnet electrolyte; (2) application of artificial interlayer; and (3) addition of multifunctional additives in the electrode material. These methods improved the cycling stability of garnet electrolyte-based cells in some degrees. In this review, we begin with the development of garnet electrolytes and their intrinsic chemical and electrochemical properties (section 2). The different interfacial challenges at both anode/ and cathode/garnet interfaces are introduced and summarized in section 3. In particular, the fundamental studies of electrochemical and chemical stability of garnet electrolyte in contact with Li metal and cathode materials are analyzed. The corresponding strategies to the interfacial problems are introduced with regarding their working principles (section 4). On the basis of these analyses, a comprehensive understanding of interfacial properties in garnet electrolyte-based ASSLIBs is concluded in section 5, leading to the discussion of the remaining challenges and future perspectives of garnet electrolyte-based ASSLIBs (section 6).

2 | THE INTRODUCTION OF GARNET-TYPED ELECTROLYTE

2.1 | The development of garnet electrolyte

The first garnet Li-ion conductor was synthesized and reported by Thangadurai et al. in 2003, with the composition
of $\text{Li}_5\text{La}_3\text{M}_2\text{O}_{12}$ ($\text{M} = \text{Nb}, \text{Ta}$) and the conductivity of $\sim 10^{-6} \text{S cm}^{-1}$. The Li$^+$ content can be varied, leading to \text{Li}_5, \text{Li}_5, \text{Li}_5, \text{Li}_5, and \text{Li}_5-phases, in which the conductivity of garnet electrolyte delivers a positive relationship with the Li contents. In 2007, Murugan et al. synthesized highly conductive cubic garnet-type $\text{Li}_5\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) by substitution of Zr for M in $\text{Li}_5\text{La}_3\text{M}_2\text{O}_{12}$, showing a total conductivity of $3 \times 10^{-4} \text{S cm}^{-1}$ at 25°C. LLZO has two stable crystal phase, a cubic phase with a disordered Li-ion distribution and a tetragonal phase formed with an ordered distribution. The cubic phase shows much higher ionic conductivity than the tetragonal one. Such cubic structure of LLZO belongs to the $Ia\overline{3}$d space group (Figure 1A), in which octahedral ZrO$_6$ and dodecahedral LaO$_8$ are connected with shared corners and edges. In the Li-saturated structure, all Li-ions are located at tetrahedral 24d sites (marked by yellow color in Figure 1A) and distorted octahedral 96h sites (marked by pink color in Figure 1A), respectively. During the Li-ions migration, the ions will transport from 24d sites to 96h sites and vice versa, suggesting an overall transport pathway of 24d-96h-24d-96h-24d (Figure 1B). The calculated barrier of Li-ions transportation is 0.3 eV, which is the smallest one among all garnet materials. The crystallization of the cubic phase is favored by the substitution of Li$^+$ and Zr$^{4+}$ with other metal cations. This can also improve Li-ion conductivity. For example, the substitutions of Li by Al, Fe, Ge, and Ga, and the substitution of Zr by Nb, Ti, Ta, and Sb, were reported. The garnet typed electrolyte, $\text{Li}_{6.55}\text{Ga}_{0.15}\text{La}_3\text{Zr}_2\text{O}_{12}$, has achieved an ionic conductivity of $2.06 \times 10^{-3} \text{S cm}^{-1}$, which is comparable to conventional liquid organic electrolyte.

The garnet electrolyte offers the advantages in relatively highest stability with Li metal, wide electrochemical stability window, and high Li-ion conductivity. The interface problems are the current limitation in the garnet type solid-state battery (SSB) performances. Recent years witness a rapid increase of publications in studying the interfacial chemistry of garnet electrolyte (Figure 1C). It is clear that research
about garnet electrolyte interface is gradually becoming a mainstream area.

2.2 | Chemical and electrochemical stabilities of garnet electrolyte

The chemical and electrochemical stabilities of the garnet electrolyte are the main descriptors for determining the interface performances during charge and discharge processes.

2.2.1 | Electrochemical voltage window

On the basis of the first principle calculation prediction, the voltage profile of LLZO upon lithiation/de-lithiation and detailed phase equilibria are shown in Figure 1E.25 The results show LLZO has a stable electrochemical window between 2.91 and 0.05 V versus Li+/Li, which avoids oxidative or reductive decomposition at high or low potentials, respectively.

The electrochemical window of the solid-state LIB system is shown in Figure 1D, where the color bars are electrochemical window versus Li+/Li, and the y axis is the Li chemical potential profile.21 In equilibrium with an opening Li reservoir, the Li chemical potential $\mu_{Li}$ is described as the function of electrostatic potential $\phi$:

$$\mu(\phi) = \mu_{Li}^0 - e\phi,$$

where $\mu_{Li}^0$ is the chemical potential of Li metal and $e$ is the elementary charge.21

With the increase of voltage, the Li-ions transfer from Li metal anode to cathode, in the form of different Li-compounds. These compounds, such as Li metal, interphase (e.g., Li$_2$O), LLZO, interfacial coating, and cathodes, follow the decrease of $\mu_{Li}$.

Despite the theoretical window between 0.05 and 2.91 V versus Li$^+$/Li, a slight wider working voltage window of LLZO (~5 V vs. Li$^+$/Li) is normally observed experimentally in many cyclic voltammetry studies, which can be partially attributed to the sluggish kinetics during the decomposition reactions. The driving force for the interphase's formation is the difference of $\mu_{Li}$ between garnet and electrodes. The decomposition reaction energy $E_D$ with an applied voltage $\phi$ can be described as:

$$E_D(\phi) = E(\text{phasequlibria, } \phi) - E(\text{solidelectrolyte}) - \Delta n_{Li}\mu_{Li}(\phi),$$

where $E(\text{phasequlibria, } \phi)$ is the energy of the phase equilibria at the potential $\phi$, $E(\text{solidelectrolyte})$ is the energy of the solid electrolyte and $\Delta n_{Li}$ is the change of Li$^+$ transference number from electrolyte to the phase equilibria during the electrochemical cycling.21 The reduction of LLZO at 0.05 V versus Li$^+$/Li releases the energy of $-0.021$ eV, which is the lowest among most of the SSBs.21

2.2.2 | Surface instability in atmosphere

The surface of garnet electrolyte is sensitive to atmosphere, especially to moisture.53 The surface reaction with H$_2$O leads to an intermediate layer containing LiOH, Li$_2$CO$_3$, and Li oxides.53 Sharafi et al.54 reported the mechanism of the intermediate layer formation based on the density functional theory calculations and photoelectron spectroscopy (XPS) measurements. Li$^+/H^+$ exchanges occur between garnet electrolyte and moisture and form LiOH on the surface of LLZO. Afterward, the LiOH is gradually carbonatized into Li$_2$CO$_3$, which is further confirmed by Xia et al.55 The existence of Li oxides is observed by Sharafi's research group.54

The proton exchange process enables the substitution of surface-active Li sites by H$^+$, changing the surface crystal structure and thus blocking the Li-ions conducting pathway. Furthermore, by-products such as LiOH and Li$_2$CO$_3$ have low Li-ion conductivity and reduce the interfacial contact area between LLZO and electrodes, leading to high interfacial resistance.

A recent study investigates the relations between Li-ion conductivity and the thickness of the LiOH layer.56 A H$_2$O bath for the proton-free Li$_6.55$Ga$_{0.15}$La$_3$Zr$_2$O$_{12}$ (Ga$_{0.15}$-LLZO) is performed for 5, 15, and 30 min, forming the LiOH layer with thickness of 0.85, 1.63, and 1.65 µm, respectively, as determined by focused ion beam secondary ion mass spectrometry (FIB-SIMS). The calculated bulk resistivity from electrochemical impedance analysis shows the calculated bulk resistivity of Ga$_{0.15}$-LLZO is approximately $1 \times 10^5$ Ω cm in samples treated via 100°C H$_2$O for both 15 and 30 min, which is over 100 times of that of pristine Ga$_{0.15}$-LLZO (8.6 $\times 10^5$ Ω cm). When coupling with metallic Li electrodes, the interfacial resistance was dramatically increased from 9.4 to $2.4 \times 10^5$ Ω cm$^2$ in the sample immersed in H$_2$O for 15 min. These results reveal the importance of inhibiting the proton exchange on the garnet surface. Similarly, the formation of Li$_2$CO$_3$ layer on garnet surface also leads to insufficient interfacial contact with Li metal.53 Furthermore, the formation of LiOH and Li$_2$CO$_3$ generates inhomogeneous current distribution during Li plating/stripping process, favouring the growth of harmful Li dendrites.57 Therefore, the removal of the by-product layer formed on LLZO before cell assembly is an efficient way to improve the electrochemical performance of garnet electrolyte based on ASSLIBs.
3 GARNET/ELECTRODE INTERFACE PROPERTIES

3.1 Origins of the Li\(^+\) transfer resistance at cathode/garnet and garnet/Li metal interfaces

In traditional LIBs, the liquid electrolyte can fully wet the electrode surface, allowing uniform and even Li\(^+\) transfer at the solid–liquid interface. In comparison, solid–solid interface suffers from contact loss and wettability which can induce formation of high interfacial resistance and space charge layer (SCL) (Figure 2). SCL is formed because of a chemical potential difference between two contacting species, forming a charge-enriched region and a charge-depleted region that are separated from each other.\(^{58}\) In general, there are three interfaces in the ASSLIBs. They are Li anode/SSE, cathode/SSE, and individual particle interface within the cathode. Those particles include electric conductive additive, binders, ionic conductive additive, and cathode active materials, where the Li transportation between different particles is poor. Different types of cathode will result in different interface properties. For example, Li transition metal oxides cathode will easily form interphases, whereas sulfur cathode has insulating problems at the particle interface. All three interfaces have point contact and suffer from contact loss, which will get even worse during charging and discharging cycles. At the Li anode/SSE interface, the stripping/plating can deposit metallic Li unevenly due to current constriction, forming Li dendrites. Moreover, the formation of interphases with different Li-ion conductivity can change the interfacial resistance. Side reaction occurs, consumes Li-ions, and changes the surface crystal structure of LLZO, affecting the Li-ions conducting pathway. SCL is another factor that can slow the Li\(^+\) transfer.\(^{57}\) Such SCL is formed via significant displacement polarization in the SSB, especially at the interface between electrode and electrolyte.\(^{60–62}\)

For the anode/garnet interface, the main challenges are the solid-state contact resistance and the short circuit caused by metallic Li dendrite growth. The cathode/garnet and particle interfaces have complicated chemical environment. The study related to this side is rare and mostly focuses on improving the interfacial performance.

3.2 Garnet/Li interface

The garnet/Li interface has poor physical contact (Figure 3A), wettability between Li/garnet electrolyte interface (Figure 3B), and interfacial chemical (Figure 3C) and electrochemical stability (Figure 3D).

LLZO is lithiophobic and cannot be wetted by molten Li (Figure 4A).\(^{67}\) This is also visualized locally via scanning electron microscopy (SEM) (Figure 4B), showing the poor physical contact between garnet electrolyte and the solid Li layer at \(\mu\)m scale. The surface compositions and structures of LLZO are also found to be responsible. Formation of Li\(_2\)CO\(_3\) increases the contact angle from 95° for pure LLZO to 146° (Figure 4C).\(^{68}\) First principle calculation shows that Li–Li\(_2\)CO\(_3\) only has 0.1 J m\(^{-2}\) of interfacial work of adhesion, \(W_{ad}\), whereas that for Li–LLZO is 0.67 J m\(^{-2}\). Interestingly, the reported contact angle of Li–LLZO varies from 90° to 122°,\(^{64,67,69–71}\) possibly due to the difference and cleanliness of the surface. Therefore, a standardized measurement procedure, including the precise surface cleaning procedure is required to enable comparison in literature.

The chemical stability problem of the LLZO against Li anode and oxide cathode is realized recently.\(^{72}\) Ma et al.\(^{65}\) applied the in-situ electron microscopy to investigate interface chemical change during the direct

![Figure 2](image-url)
FIGURE 3  The main challenges at garnet/Li interface: (A) poor physical contact. Reproduced with permission: Copyright 2017, Springer Nature.63  (B) Poor wettability. Reproduced with permission: Copyright 2019, Wiley.64  (C) The chemical and electrochemical instability between Li and garnet electrolyte. Reproduced with permission: Copyright 2016, American Chemical Society.65  (D) Inhomogeneous Li nucleation on the Li/garnet electrolyte interface. Reproduced with permission: Copyright 2019, Elsevier.66  LLZO, Li7La3Zr2O12

FIGURE 4  (A) The wettability between Li and garnet electrolyte; (B) the scanning electron microscope (SEM) image of the interface of symmetrical Li-battery LLZO (Li7La3Zr2O12). Reproduced with permission: Copyright 2019, American Chemical Society.67  (C) The contact angle between Li and LLZO, with (top) and without Li2CO3 (bottom); (D) calculated work of adhesion (Wad), contact angle (θ), and atomic structure for the (a) Li–Li2CO3 and (b) Li–LLZO interfaces. Reproduced with permission: Copyright 2017, American Chemical Society66.
contact between Li metal and LLZO electrolyte (Figure 5A). Combined with electron energy loss spectroscopy (EELS), it demonstrates that the direct contact between Li metal and LLZO can induce phase transition of cubic LLZO (c-LLZO) to tetragonal LLZO (t-LLZO), which shares the same chemical composition but different atomic structure and lower ionic conductivity (Figure 5B–D). Fingerle et al.20 applied CO2-laser chemical vapor deposition to synthesize thin garnet film Li5La3Ta2O12 (LLTaO). Then Li metal is stepwise evaporated onto LLTaO. The as-formed interphase was then monitored by XPS and ultraviolet photoelectron spectroscopy.20 As shown in the XPS O 1s (Figure 5G) and Li 1s (Figure 5H) spectra, Li2CO3 on LLTaO surface is removed before the Li deposition. Formation of Li2O is observed along with the Li deposition (Figure 5E), suggesting a passivating Li2O layer that prevents the further reduction and decomposition of LLTaO (Figure 5F). There is no formation of Li peroxide.

Apart from the chemical reaction between Li and solid electrolyte, electrochemical cycling can also form low conducting interphases.10,32 For example, a thick interphase layer enriched with Li is formed between Li metal and electrolyte, which covers the surface of the Li anode. This is visualized via time-of-flight secondary-ion mass spectrometry (TOF-SIMS) (Figure 6A,B).73 However, it is not clear what is the chemical structure/composition of this interphase and how it is formed from the original SSE lattice. The electrochemical interface properties were further studied by Krauskopf et al.74 in the Li6.25Al0.25La3Zr2O12 system. The galvanostatic potential profile of Li/LLZO/Li symmetry cell during stripping/plating under a current of 100 μA cm−2 (Figure 6E) shows an increasing overpotential. During the stripping process (Figure 6C), the vacancy accumulated to contact spots and form pores near the interfaces. The behavior results in a contact loss, leading to an increasing of interfacial resistance and thus restricting the rate

**FIGURE 5**  (A) The configuration of in situ STEM; (B) EELS O K-edges for cubic LLZO (c-LLZO), tetragonal LLZO (t-LLZO), and the Li/LLZO interfacial layer; (C) EELS Li K-edges for the Li/LLZO interfacial layer and t-LLZO; (D) O K-edges of c-LLZO after contacted with Li for different periods of time. Reproduced with permission: Copyright 2016, American Chemical Society.65 Evolution of the Li 1s peak components during Li deposition given as percentage of the total (E) Li 1s signal and (F) schematic model of the proposed interface growth; XPS (G) O 1s and (H) Li 1s region for the stepwise adsorption of Li on an LLTaO thin film. Reproduced with permission: Copyright 2017, Elsevier.20 EELS, energy loss spectroscopy; LLZO, Li7La3Zr2O12; XPS, X-ray photoelectron spectroscopy
capability of Li metal anode. It is also demonstrated that the interface can remain stable only when the anodic load is smaller than that of a critical value around \(100 \mu\text{A cm}^{-2}\), which is not high enough for the practical application.

Uncontrollable Li dendrite growth is another major issue related to the electrochemical performance. Although garnet SSEs, such as \(\text{Li}_6.24\text{La}_3\text{Zr}_2\text{Al}_{0.24}\text{O}_{11.98}\), show a high-shear modulus of 60 GPa,\(^7\) the Li dendrites cannot be avoided in the system. Recently, Kazyak et al.\(^7\) studied the Li propagation and dendrite growth in LLZO SSE by \textit{operando} optical microscopy. During the charging at 0.2 V with 0.5 mA cm\(^{-2}\) current density, small Li dendrites start to form on the Li/LLZO interface, as shown in (e) of Figure 6I. Those Li dendrites grow gradually during discharging (e to f). When Li dendrites are large enough to penetrate the whole electrolyte layer, a short circuit occurs (g). On one side, a range of imaging techniques, including optical microscopy, X-ray computed tomography (CT), and electron microscopy can visualize the Li dendrite formation. On the other hand, the study of Li dendrite growth in garnet SSEs has not reached a general agreement. It is widely believed that contact area loss,\(^7\) grain boundaries,\(^6\) defects,\(^1\) and the electronic conductivity of SSEs\(^9\) contribute to the growth of Li dendrites. For example, the contact area loss between garnet electrolyte and metallic Li will contribute to an inhomogeneous deposition of Li\(^+\) ions on the interface, promoting the growth of Li dendrites. Therefore, a universal growth model is yet established. It is then even more difficult to prevent the formation of Li dendrites without an understanding of its chemistry and structure.\(^7\)\textit{Li} NMR (nuclear magnetic resonance) was used to detect the microstructural growth of Li dendrites at the early stage. However, it only confirmed the formation of Li dendrites before the short circuit.\(^1\)

3.3 \textit{Garnet/cathode interface}

A cathode/electrolyte interface, as well as an electrolyte/interparticle interface, can be formed on the cathode side.
In traditional liquid electrolyte-based LIBs, cathode active materials are mixed with electric conductive materials and fully wetted by liquid electrolyte to achieve good ionic transport at solid–liquid interface. In contrast, solid electrolyte cannot provide such wettability, so the electrolyte/cathode interface is a big challenge (Figure 7A,B). The complicated chemical composition of the cathode also leads to the formation of interphase layers (Figure 7C). To address the challenges, several methods have been designed [e.g., nanostructured garnet host (Figure 7D), low melting-point alloy additives (Figure 7E), and artificial interlayer (Figure 7F)], but the most publications related to cathode/garnet electrolyte interface are focused on improving performance instead of understanding the chemistry and mechanism at the interface.

Garnet SSEs are normally stable with most of the common cathode materials at room temperature. However, to achieve a better wettability and interfacial Li-ion conductivity, high-temperature or co-sintering treatment is widely used. The treatment could introduce chemical reactions on the cathode/garnet SSE interfaces.

![Figure 7](https://example.com/f7.png) The main challenges at garnet/Li interface: (A) Poor physical contact; (B) poor contact at cathode particles; (C) the interphases formed by side-reactions. And their related methods: (D) nanostructured garnet host for cathode materials. Reproduced with permission: Copyright 2017, Royal Society of Chemistry. (E) Low melting point alloy additives. Reproduced with permission: Copyright 2018, Royal Society of Chemistry. (F) Artificial interlayer. Reproduced with permission: Copyright 2018, Elsevier.

The chemical compatibilities between garnet electrolyte and metal oxides cathode materials under high temperature were reported by Ren et al. On the basis of the X-ray diffraction pattern of different types of cathode materials mixed with LLZTO at elevated temperature, the LiCoO₂ (LCO) delivered the best stability up to around 700°C, whereas LiMn₂O₄ and LiFePO₄ (LFP) started to react with LLZTO at approximately 500°C. However, other scientists found the LCO could be reactive to garnet type electrolyte even at 500°C, resulting in cross-diffusion and decomposition. The cross-section TEM image of LLZO/LCO interface (Figure 8A, top) and the energy-dispersive spectrometer (EDS) line profile (Figure 8A, bottom) show an intermediate layer. It is a reaction phase by mutual diffusion of elements between LLZO and LCO. The cross-section TEM image of LLZO/LCO interface (Figure 8A, top) and the energy-dispersive spectrometer (EDS) line profile (Figure 8A, bottom) show an intermediate layer. It is a reaction phase by mutual diffusion of elements between LLZO and LCO. This shows the decomposition of the LLZO at the interface. TOF-SIMS is also a powerful tool to study the cathode/garnet electrolyte...
interface chemical compositions. According to Figure 8C, a cross diffusion at the interface between LCO/LLZO (Al contained) is formed, where Co diffuses into LLZO and Zr/La diffuses into LCO. The change of LLZO itself is also observed with air exposure (Figure 8D). Al element is commonly used to occupy the Li sites and stabilize the cubic phase of LLZO. It becomes inhomogeneously distributed after one year, indicating the transition of LLZO from cubic phase to tetrahedral phase, which will lower the ionic conductivity.

Garnet typed electrolyte is also widely used in Li/S battery. Solid electrolyte can block the “shutter effect” in Li/S battery by blocking the transfer of intermediate polysulfides to the Li anode. As the insulating nature of sulfur, current publications focused on using nanostructured garnet to adopt sulfur to increase the contact area, which will be discussed in section 4. However, the chemical or electrochemical stability between garnet and sulfur in such a system is seldom discussed.

4 METHODS TO SOLVE INTERFACIAL PROBLEMS

4.1 Modification of garnet electrolyte

Most of the garnet-typed electrolytes are unstable in moisture, forming Li-ion insulating hydroxides and

FIGURE 8  (A) Cross-sectional TEM image of an LLZ/LCO thin-film interface and the EDS line profile obtained from the region indicated by the red arrow in the direction A to B. Reproduced with permission: Copyright 2010, Elsevier. (B) O K-edge XAS data (partial fluorescence yield mode) for LLZO, LCO, and 60 nm-thick LCO film on LLZO in the as-deposited state after annealing at 300°C and 500°C. Reproduced with permission: Copyright 2018, American Chemical Society. (C) TOF-SIMS-enabled 3D elemental maps of the LCO/LLZO interface that is displayed in the inset SEM image. Color scales next to the maps show ionic concentrations of each ion: Upper side represents a higher concentration; inset below SEM image is EDS mapping of LCO/LLZO interface where LCO film on an LLZO pellet; (D) TOF-SIMS element maps of fresh and 1-year-aged LLZO pellet samples. Reproduced with permission: Copyright 2016, American Chemical Society. 3D, three-dimensional; EDS, energy-dispersive spectrometer; LCO, LiCoO2; LLZO, Li7La3Zr2O12; SEM, scanning electron microscopy; TEM, transmission electron microscopy; TOF-SIMS, time-of-flight secondary-ion mass spectrometry; XAS, X-ray absorption spectroscopy
carbonates (such as Li$_2$CO$_3$) on their surfaces, thereby increasing the interfacial resistance. Therefore, Li$_2$CO$_3$ prevention and removal is the key point to improve the interface properties between garnet-typed SSEs with electrodes. By controlling the grain size of LLZO particles, the surface sensitivity towards moisture and CO$_2$ can be optimized. Two LLZO samples with ~150- and ~20-µm grain sizes were exposed in air for 24 h. Soft X-ray absorption spectroscopy shows the lower content of Li$_2$CO$_3$ on the LLZO with ~20-µm grain sizes than that of the LLZO with ~150-µm grain sizes, indicating less coverage of the Li$_2$CO$_3$ on the surface. The results are also consistent with impedance spectroscopy (Figure 9B).

The mechanical polish and thermal treatment are considered effective ways to remove the by-product formed on garnet SSEs. Li et al. reported that heating Li$_6.5$La$_3$Zr$_1.5$Ta$_0.5$ (LLZT) together with carbon at 700°C could reduce the Li$_2$CO$_3$ layer and other impurities formed on the LLZT surface. Raman mapping (Figure 9C) was applied to detect surface carbonates. The thermal aged LLZT still has very high carbonate contents, whereas the addition of carbon significantly reduced carbonate signals (LLZT-C in Figure 9C). The LLZO-C shows smaller interfacial resistance and better charge and discharge stability compared to the aged LLZT (Figure 9D).

Recently, Huo et al. demonstrated a rapid acid treatment to remove the by-product layer formed on Li$_6.4$La$_3$Zr$_1.4$Ta$_0.6$O$_{12}$ (LLZTO) surface. The LLZTO pellets were immersed into the HCl solutions (1 M) for 30 s and then rapidly washed by ethanol. After the HCl treatment, the surface of LLZTO becomes lithiophilic and an extremely low LLZTO/Li interfacial resistance of 26 Ω cm$^2$ is

**Figure 9** (A) Left: Normalized O K-edge XAS spectra of different type of LLZO and Li$_2$CO$_3$ reference collected in TEY and TFY modes. Right: expanded region of the O K-edge spectra of different type of LLZO samples with fitted LLZO and Li$_2$CO$_3$ peaks, where P_LLZO_L is pristine LLZO with a grain size of ~150 µm, P_LLZO_S is pristine LLZO with a grain size of ~20 µm, E_LLZO_S24h is 24-h air-exposed LLZO with a grain size of ~20 µm, E_LLZO_L24h is 24-h air-exposed LLZO with a grain size of ~150 µm. (B) Nyquist plots of impedance data of Li/LLZO/Li cells containing different materials: Left is P_LLZO_L and E_LLZO_L24h and mid is P_LLZO_S and E_LLZO_S24h. Right: area-specific interfacial resistances (ASRs) of pristine LLZO samples and those exposed to air for 24 h. Reproduced with permission: Copyright 2015, American Chemical Society. (C) Raman mapping of LLZT and LLZT-C and the color represents the integral area calculated from the Li$_2$CO$_3$ peak; (D) EIS and charge and discharge voltage profiles (current density: 100 µA cm$^{-2}$) performance of LLZT-C based symmetric Li cell at 65°C. Reproduced with permission: Copyright 2018, American Chemical Society. (E) Schematic illustration of LLZTO/Li interface before and after the rapid acid treatment; (F) left: comparison of the EIS profiles of Li symmetric cells with LLZTO-air and LLZTO-RAT at 30°C (inset shows the enlarged impedance curve of the cell with LLZTO-RAT. Right: the interfacial resistances of the Li/LLZTO/Li symmetric cells with LLZTO-air and LLZTO-RAT. Reproduced with permission: Copyright 2019, Elsevier. (G) Schematic of the formation process and roles of the Li$_3$PO$_4$ modification layer between the garnet SSE and Li metal. Reproduced with permission: Copyright 2019, Royal Society of Chemistry.
recorded (Figure 9F). Moreover, the Li symmetric cells also deliver a stable Li plating/striping for over 700 h under 0.2 mA cm\(^{-2}\) at 30°C. Ruan et al.\(^93\) used H\(_3\)PO\(_4\) to remove the Li\(_2\)CO\(_3\) and LiOH, and then, a uniform intermediate layer (Li\(_3\)PO\(_4\)) was formed along with the H\(_2\)PO\(_4\) etching reactions. The Li\(_3\)PO\(_4\) intermediate fills the gap between electrolyte and Li metal, improving the contact between LLZO with metallic Li significantly, as shown in Figure 9G.

In summary, strategies based on a garnet electrolyte are mainly focusing on the removal of the contamination layer, to decrease the interfacial resistance and poor wettability resulted from the Li\(_2\)CO\(_3\).

### 4.2 Toward garnet/Li interface aspects

To address the interfacial problem arisen at the garnet/Li interface, molten Li has been widely used to solve the contact problem to some degree.\(^{11}\) However, this does not solve the intrinsic lithiophobic nature of the LLZO. Introduction of an artificial interlayer at the Li/garnet interface is an effective way to improve the wettability between them.\(^{12}\) The most representative example is atomic layer deposition (ALD) of Al\(_2\)O\(_3\) on LLZO electrolyte.\(^{64}\) The ALD method maximizes the contact between Al\(_2\)O\(_3\) and LLZO. Al\(_2\)O\(_3\) is lithiophilic, showing a much smaller contact angle with molten Li (Figure 10B). Therefore, the Al\(_2\)O\(_3\) layer not only physically occupies the voids formed at the garnet/Li interface (Figure 10A), but also improves the wettability between LLZO with metallic Li. The coating of Al\(_2\)O\(_3\) on garnet electrolyte was proved by TEM cross-section image at the interface of ALD-Al\(_2\)O\(_3\)-coated garnet with Ti protection layer, where Al is found between Ti and Li (Figure 10E, a–g). EELS spectroscopy (Figure 10E, h) shows that there is no peak at around 285 eV for C 1s, suggesting the absence of Li\(_2\)CO\(_3\) in the system. Upon heating, Al\(_2\)O\(_3\)-LLZO/Li shows an extremely low interface resistance to 1 \(\Omega\) cm\(^{-2}\) (Figure 10C) and a much better cycling performance than that of LLZO/Li (Figure 10D). In addition to the Al\(_2\)O\(_3\) deposited via ALD, various metal and lithiated materials such as Li\(_3\)N\(^{94}\) and Li\(_x\)Sn\(^{95}\) layer can also improve the wettability between LLZO and metallic Li.

To minimize the interfacial contact resistance between metallic Li and garnet SSEs, an additional organic interlayer has also been used in recent years.\(^{11}\) The soft interlayer is normally consisting of polymer membrane and Li salts. It is deformable, which not only enables the intimate contact between Li metal and SSEs but also serves as a protective shield against Li dendrites, therefore, bridging the Li-ion transport between garnet and metallic Li (Figure 11A). The common organic polymer film is PEO, which has been considered as suitable frame support and it also has provided a good flexibility to meet the interface stress-strain behavior.\(^{96}\) Another representative sample is polyvinylidenefluoride-co-hexafluoropropylene (PVDF-HFP) membrane soaked with 1 M LiPF\(_6\) solution consisted of ethylene carbonate and diethyl carbonate with volume ratio 1:1.\(^{97}\) With PVDF-HFP, the interfacial resistance between Li metal and Li\(_2\)La\(_{2.75}\)Ca\(_{0.25}\)Zr\(_{1.75}\)Nb\(_{0.25}\)O\(_{12}\) (LLCZNO) was decreased from 1.4 \(\times\) 10\(^{4}\) to 214 \(\Omega\) cm\(^{2}\) and a high capacity of 140 mAh g\(^{-1}\) is recorded when corporated with LFP cathode (Figure 11B,C). Similarly, PEO-ceramic particles-Li-salts composites electrolyte is another effective system to deal with the interfacial resistance. In this composite system, LLZO particles were added to influence the recrystallization kinetics of the PEO polymer chains to promote local amorphous regions, thereby increasing the Li salt/polymer system's ionic conductivity.\(^{4}\) This composite system demonstrates a promising strategy to apply LLZO particles to reinforce PEO-based electrolytes in the aspect of mechanical property and ionic conductivity. The mechanical property and ionic conductivity were determined by the loading of LLZO filler in PEO polymer.\(^{98}\) The highest ion conductivity (1.17 \(\times\) 10\(^{-4}\) S cm\(^{-1}\)) can be achieved with 10 wt% LLZO fillers in the PEO electrolytes.\(^{98}\) However, the brittle nature of LLZO particles will crack the membrane when the LLZO loading content is above 80 wt%. A comprehensive understanding of the Li-ion transport mechanism and the corresponding control parameters in this composite electrolyte are very important for achieving good performance. NMR is used to probe the Li-ion mobility and Li-ion transport pathways.\(^{73}\) The sample preparation is shown in Figure 11E–H. By tracking the replacement of \(^7\)Li in electrolyte by \(^6\)Li in Li metal anode after cycling, the Li pathway was identified. As shown in Figures 11K and 11L, \(^6\)Li ions replace \(^7\)Li ions in the LLZO part of composite electrolyte (strong peaks at middle part) instead of LiClO\(_4\) (polymer part, small peaks at right side) and LLZO/polymer interface; therefore, majority of the Li\(^+\) transfer via LLZO particles. This leads to the discussion on how important it is for the LLZO/polymer interface. Theoretical calculations show a space charge layer forms at PEO/LLZO interface, rendering a high resistance.\(^{96}\) Its role in the Li\(^+\) conductive pathway is unclear.

Li-based alloy anode also can be used to address the garnet/Li interface problem. This method modifies the surface tension and viscosity of molten metallic Li. Recently, Duan et al.\(^{100}\) reported a Li-graphite (Li-C) anode for ASSLIBs. The Li-C anode was synthesized by mixing the commercially available graphite powder with molten metallic Li with
FIGURE 10  (A) Schematic of the wetting behavior of garnet surface with molten Li; (B) SEM images of the garnet SSE/Li metal interface. Without ALD-Al$_2$O$_3$ coating, garnet has a poor interfacial contact with Li metal even on heating. With the help of ALD-Al$_2$O$_3$ coating on garnet, Li metal can uniformly bond with garnet at the interface on heating. Insets are photos of melted Li metal on top of the garnet surface clearly demonstrating classical wetting behavior for the ALD-treated garnet surface; (C) comparison of EIS profiles of the symmetric Li non-blocking garnet cells. Inset shows the enlarged impedance curve of the ALD-treated garnet cell; (D) comparison of cycling for symmetric cells of Li/bare garnet/Li (black curve) and Li/ALD-treated garnet/Li (red curve) at a current density of 0.1 mA cm$^{-2}$. The inset is the magnified curve of the ALD-treated cell; (E) (a) typical TEM cross-section image at the interface of ALD-Al$_2$O$_3$-coated garnet with Ti protection layer. (b-g) Typical TEM/HAADF image (b) and corresponding EELS maps (c-g) (Al, Li, O, overlap of Al and Li, and Ti, respectively) for the interfacial cross-section. (h) EELS with energy 250–1000 eV showing peaks of Zr M-edge, O K-edge, and La M$_4,5$-edge. (i) EELS with energy 50–120 eV showing peaks of Li K-edge and Al L-edge. (j) Selected area diffraction of the interlayer between garnet and ALD-Al$_2$O$_3$. Reproduced with permission: Copyright 2017, Springer Nature.

ALD, atomic layer deposition; EELS, energy loss spectroscopy; EIS, electrochemical impedance spectra; SEM, scanning electron microscopy; SSE, solid-state electrolyte; TEM, transmission electron microscopy.
continuous stirring under 250°C. The improvement of the viscosity of the Li-C compound can be directly observed in Figure 12C, where Li-C was easily wetted on the LLZO surface. The interface morphologies between anode and electrolyte were further characterized by SEM. And it shows the intimately contacted Li-C/garnet interface. The Li-C/LLZO/Li symmetric cell delivered a stable plating/striping curve at a high current density of 0.8 mA cm\(^{-2}\) for over 30 h, whereas pure Li-based symmetric cell failed to work in few hours at a current density of only 0.3 mA cm\(^{-2}\). Later, the same group also reported using the graphitic carbon nitride as an additive for Li anode, which not only provides improved viscosity and decreased surface tension but also suppresses the growth of Li dendrites. The work shows a high critical current density of 1.5 mA cm\(^{-2}\), which is around 30 times of that of pure Li metal anode.\(^6\)\(^5\) Similarly, Li-Sn,\(^1\) Li-Al,\(^10\) and Li-Mg\(^10\)\(^3\)-based anodes were reported. However, the composition change of anode can possibly result in the change of redox potential and the volume during cycling,\(^11\) which is seldom discussed in current studies.

In summary, several strategies have been reviewed and proven to effectively reduce the interface resistance between garnet SSEs with metallic Li. Currently, the main barrier across the development of Li-metal-based SSBs is the growth of Li dendrites. Although a lot of studies and methods have been applied to inhibit the Li dendrites growth, fundamentally preventing Li dendrites is still hard to achieve.

4.3 Toward cathode/garnet electrolyte interface

Researches on the cathode/garnet SSEs interfaces are much less than that of the anode side. The solid-solid contact, stability, side reaction, and space-charge layer are major challenges. As discussed in section 3, the common cathode materials require to be mixed with electronic conductive material (conductive carbon) and ionic conductive materials (SSE particles). However, the mixture brings a series of
cathode particle/garnet electrolyte interface, rendering a complicated interfacial chemical process.

A range of deposition methods are used to obtain intimate contact between the LCO cathode and LLZO. They are usually based on coating technology. For example, Asaoka et al. use pulsed-laser deposition (PLD) to coat LCO on the Li₆.7La₃Zr₁.75Nb₀.25O₁₂ interface. The cathode-solid electrolyte composite was fabricated with Li and delivered good cycling stability for 100 cycles with a reversible capacity over 120 mAh g⁻¹. Various buffer layers,
such as LiNbO$_3$, Li$_3$PO$_4$, LiAlO$_2$, and polymer-based membrane were used to block their direct contact, which can enhance the stability of oxide SSEs against cathodes. Kotobuki et al. reported another effective way by using a sol-gel method to prepare LCO on the LLZO surface. Followed by high-temperature treatment, the fabricated Li/LLZO/LCO cell cycled three times under a current density of 10 µA cm$^{-2}$ but a relatively low capacity of 8.4 mAh cm$^{-2}$ was achieved.

Co-sintering additives is another effective way to improve contact between the cathode and garnet electrolyte. The additives normally have a low melting point
and good ionic conductivity. For instance, Li$_{2.3}$C$_{0.7}$B$_{0.3}$O$_3$ (LCBO) was used via thermal soldering between LLZO and LCO (Figure 13A). After sintering, the LLZO and LCO particles are embedded together by the chemical reaction between LCBO matrix and Li$_2$CO$_3$, which is formed on the LLZO and LCO particle surface (Figure 13D–I). The reaction contributes to a dense and compact cathode (Figures 13C and 13G). The interfacial contact between LLZO and LCO particles shows an improved wettability on both the cathode/garnet interface (Figure 13C) and particle interface (Figure 13D). The all-ceramic Li/LLZO/LCO cell has good initial capacity with different current rates and a high cycling stability at room temperature (Figure 13J,K). Similarly, other additives, such as Li$_3$BO$_3$, are used in recent years. Although the method is a good way to make an intimate contact between electrolyte and cathode materials, the resulted structure will have no much space to accommodate the volume change of electrode materials. Therefore, the design of the interface needs to consider electronic and ionic contact, as well as the volume change, during battery cycling.

In addition to the additives, nanostructured garnet electrolyte is widely used as a cathode active materials host to improve the contact between SSE with cathode. The high surface area provided by nanostructures can adopt the volume change of cathode materials during the cycling and increase the cathode/LLZO particle contact area. This is particularly important for Li-sulfur batteries. Fu et al. prepared a bilayer structure with a dense layer and the porous layer, as shown in Figure 14A (scaffold structure in Figure 14A–C). The structure was revealed by SEM (Figure 14E) and contributed to a high sulfur loading over 7 mg cm$^{-2}$. A good initial capacity of over 600 mAh g$^{-1}$ was achieved with a current density of 0.2 mA cm$^{-2}$. From the long-term cycling performance (Figure 14K), the high value of Coulombic efficiency (>99%) and gently decreased curve indicate no polysulfides lost and shuttle effect occurred during the cycling.

Apart from the 3D bilayer, another nanostructured LLZO was synthesized via template methods, 3D-printer, and freeze-casting. The scaffold structure also shows promising potential for a corporation with metal oxides. On the basis of screen printing, an LCO/garnet composite cathode delivered a high utilization of active material (81%) at 0.1 C. However, in most of these designs, an ionic liquid electrolyte was added to wet the cathode side.
interface. How to avoid the utilization of liquid electrolyte is required to be investigated in the future.

5 | DISCUSSION

5.1 | SSE/anode interface

A summary of typical methods towards SSE and interface optimization is shown in Table 1. At the anode/SSE interface, the removal of Li$_2$CO$_3$ significantly reduces the interfacial resistance to 7–28 $\Omega$ cm$^2$. However, Li dendrite formation is yet solved, as shown in the limited critical current density (CCD). CCD is defined as the current density at and above which Li metal propagates through an SSE. The best-reported values are in the range of 1.1–2.3 mA cm$^{-2}$, suggesting the very limited safety current window. Such CCD is lower than the commercial level (>3 mA cm$^{-2}$). Direct contact between anode and electrolyte (e.g., Li$_2$CO$_3$ removal, application of some Li-alloy anode) normally contributes to a low CCD. Some Li-alloy anodes show a high CCD, which attributes to their stable alloy products with Li metal (e.g., Li-Al). Similarly, artificial interlayers also show high CCD when stable interphases are generated. Nanostructured garnet electrolyte improves the working current density. However, most publications are focusing on the synthesis and characterization of nanoparticles instead of full cell testing. Hybrid electrolyte systems also show promising potential because they normally have stable cycling performance, but their Li-ion conductivity at room temperature is the bottleneck.

5.2 | Cathode and full cell test

Liquid electrolyte is usually used to improve the wettability between cathode particle/garnet interface. In other words, it is hard to realize all-solid-state batteries at the current state. Polymer membranes are applied with Li salts between the cathode and garnet electrolyte. This is still not liquid-free as a solvent is used to dissolve those Li salts. They will be squeezed to wet the whole cathode during the cell fabrication, which is then not different from the common LIB with liquid electrolyte. The presence of liquid electrolyte and Li salts leverages the overall full cell performance. Thus, the true performance from the garnet electrolyte and any improvement via structure/interface modification are difficult to define. The only successful example is the application of Li$_{2.3}$C$_{0.7}$B$_{0.3}$O$_3$ as a sinter additive. As discussed in section 4.3, the method enables an in-situ connection with LCO and LLZO particles via chemical reaction, which is very meaningful for the future development.

5.3 | Understanding of the interface

With the help of several in-situ characterization methods (e.g., XPS, TOF-SIMS, EELS), some progress has been made in the interfacial understanding in garnet electrolyte-based ASSLIBs (shown in section 3). They are focused on the investigation of chemical interphases formed during the contact between electrolyte and electrode materials. However, most systems cannot avoid the possibility of contamination (e.g., Li$_2$CO$_3$, LiOH, atmosphere). On the basis of the current study, it seems the interphase is consisting of various chemicals and could be varied by not only the composition of the material but also the assembly, external environment, and operation condition (e.g., working current, voltage window) of the batteries.

6 | SUMMARY AND PROSPECTIVE

Garnet typed SSEs were considered as promising candidates in ASSLIBs, attributing to their high ionic conductivity, wide working voltage window, good chemical and electro-chemical stability. Despite the recent progress highlighted in this review, the fundamental understanding and effective control of solid-state interfaces between garnet-typed SSEs with electrodes are still challenging. The poor solid-solid contact and metallic Li dendrite growth are the major bottlenecks. The formation of interphases such as Li$_2$O, via (electro)chemical reactions, can also lead to the poor change transfer behavior across electrode/electrolyte interface. Additionally, mechanical instabilities at garnet-typed SSE/cathode interfaces can also arise because of the deformation or breaking of rigid SSE particles to accommodate the electrochemically induced volume expansion of cathode particles during electrochemical cycling. To address the interface issues, surface treatments of the garnet-typed SSEs, the introduction of the artificial interlayer, and Li-alloy/composite anodes have been used to control chemical and electrochemical processes at garnet-typed SSE/electrodes interfaces. Moreover, imaging and spectroscopic study are used to probe the change of the interface reaction before and after cycling. Few in-situ and operando studies are reported, mainly on the formation of the Li dendrites. X-ray based techniques, including X-ray CT, interface XPS experiments, and X-ray absorption spectroscopy are useful tools to probe the physical and chemical states of the elements in the interface.
| Electrolyte chosen | Categories | Method | Optimized interfacial resistance (Ω cm²) | Symmetric cells’ cycling current and time (mA cm⁻²) | Critical current density (mA cm⁻²) | Full cell test: cathode, cycling performance | Liquid electrolyte |
|-------------------|------------|--------|----------------------------------------|-----------------------------------------------|---------------------------------|----------------------------------------|------------------|
| LLZTO³³ | Li₂CO₃ remove | H₃PO₄ treatment | 7 | 0.5 for 450 h | 0.8 | LFP, −150 (0.09 mA cm⁻²) after 100 cycles | Yes |
| LLZTO³¹ | Li₂CO₃ remove | Carbon treated at 700°C | 28 | 0.1 for 450 h | / | LFP, 110 (0.1 mA cm⁻²) after 40 cycles | No |
| LLZTO³⁶ | Li₂CO₃ remove | HCl treatment | 26 | 0.2 for 700 h | / | LCO, −120 (0.1 C) after 150 cycles | Yes |
| LLZO¹⁰⁰ | Alloy anode | Li-graphite (Li–C alloy) | 11 | 0.3 for 250 h | 1.5 | LFP, −140 (0.5 C) after 100 cycles | Yes |
| LLZTO¹⁰² | Alloy anode | Li–Al | 1 | 0.2 for 3000 h | 2.3 | LFP, −160 (0.5 C) after 100 cycles | Yes |
| LLZTO¹¹⁵ | Alloy anode | Li–Na | 19 | 0.1 for 3500 h | 2.1 | LFP, −105 (0.1 mA cm⁻²) after 150 cycles | No |
| LLZO⁶⁵ | Alloy anode | Li–Graphitic C₃N₄ | 11 | 0.3 for 300 h | 1.5 | LFP, −140 (0.5 C) after 100 cycles | Yes |
| LLZTO⁶⁰ | Alloy anode | Li-boron nitride nanosheets | 9 | 0.3 for 380 | 1.5 | LFP, −135 (0.5 C) after 100 cycles | Yes |
| LLZTO¹¹⁶ | Artificial interlayer | LiF-LiCl layer | 11.6 | 0.5 for 1000 h | 1.8 | NCM 622, −120 (0.2 mA cm⁻²) after 100 cycles | Yes |
| LLZTO⁹⁴ | Artificial interlayer | Li₃N interlayer | 180 | 0.1 for 210 h | / | LFP, −80 (0.1 mA cm⁻²) after 300 cycles | No |
| LLCZN¹¹⁷ | Artificial interlayer | Li–Ag alloy layer | 66 | 0.2 for 100 h | / | LMO, −90 (0.2 C) after 100 cycles | Yes |
| LLZTO¹¹⁸ | Artificial interlayer | Li–Ag alloy layer (via AgNO₃) | 4.5 | 0.2 for 3500 h | 0.75 | LFP, −120 (0.15 mA cm⁻²) after 320 cycles | No |
| LLAWO¹⁹ | Artificial interlayer | Li–C layer (via drawing Graphite) | 105 | 0.3 for 1000 h | / | NCM 523, −130 (0.5 C) after 500 cycles | Yes |
| LLZTO¹²⁰ | Artificial interlayer | Indium tin oxide layer | 32 | 0.2 for 800 h | 1.05 | LFP, −150 (0.2 C) after 100 cycles | Yes | (Continues) |
| Electrolyte chosen | Categories            | Method                                     | Optimized interfacial resistance (Ω cm²) | Symmetric cells’ cycling current and time (mA cm⁻²) | Critical current density (mA cm⁻²) | Full cell test: cathode, cycling performance | Liquid electrolyte |
|-------------------|-----------------------|--------------------------------------------|----------------------------------------|--------------------------------------------------|---------------------------------|----------------------------------------------|-------------------|
| LLZTO₁²¹         | Artificial interlayer | MoS₂ layer                                 | 14                                     | 0.2 for 40 h                                     | 2.2                             | no                                           | /                 |
| LLZTO₁²²         | Artificial interlayer | Li₃PO₄                                     | 1                                      | 1.0 for 180 h                                    | 2.2                             | LFP, ~120 (1.5 C) after 400 h                | Yes               |
| LLZTO₁²³         | Artificial interlayer | Poly-dopamine and PEO@LITFSI               | 171                                    | 0.15 for 500 h                                   | 1.1                             | LFP, ~133.3 (0.1 C) after 100 cycles         | No                |
| LLZO₁²⁴         | Hybrid electrolyte     | PEO@LiTFSI@LLZO nanowires                  | 54.4                                   | 1.0 for 1000 h                                   | /                               | LFP, ~160 (0.1 C) after 80 cycles            | No                |
| LLZTO₁²⁵         | Hybrid electrolyte     | PVDF@PEO@succinonitrile@LiTFSI@garnet      | /                                      | 0.5 for 4800 h                                   | /                               | LCO, ~100 (1 C) after 1000 cycles            | No                |
| Al-doped LLZO₁²⁶| Hybrid electrolyte     | Soft lithiated Nafin                       | /                                      | 1.0 for 200 h                                    | /                               | LFP, ~120 (1 C) after 150 cycles             | No                |
| LLCZN₁²⁷         | 3D-garnet             | 3D structured garnet                       | /                                      | 0.5 for 300 h                                    | >2                              | /                                            | /                 |
| LLZO₁⁰⁷          | Sinter additives       | Li₂ₓC₀.₇BₓO₇                                 | /                                      | /                                                | /                               | LCO, ~94 (0.05 C) after 100 cycles           | No                |

Abbreviations: 3D, three-dimensional; LCO, LiCoO₂; LFP, LiFePO₄; LLAWO, Al, W-doped LLZO; LLCZN, Ca, Nb-doped LLZO; LLZO, LiₓLaₓZr₂O₇; LLZTO, LiₓLaₓZr₂O₇; LCO, LiMn₂O₄; LMO, LiMnO₂; PEO, poly(ethylene oxide); PVDF, polyvinylidene fluoride; LITFSI, Lithium bis (trifluoromethyl)sulfonyl) azanide; NCM, Li (NiₓMn₁₋ₓ)O₂ (x+y+z=1)
On the basis of these understandings, three perspectives are discussed below:

1. How to permanently prevent the formation of Li dendrites inside the garnet electrolyte, especially when the high current density is applied? In addition to the method of artificial interlayer applied to suppress Li dendrites on the Li/garnet interface, introduction of active nanoadditives in the grain boundary and defective sites of garnet electrolyte could be a direction. It can eliminate the defects in SSE so that the formation of Li dendrites in the electrolyte is possibly prohibited. Eventually, the target is to achieve uniform distribution of current density at the interface, preventing the hotspot formation. This also calls for in situ imaging technique to reveal the current density distribution.

2. Cathode side interface requires more attention. As discussed in section 5, most publications use liquid electrolytes to solve the interfacial challenge at this side, which is not “fully solid.” Sintering in the presence of additives is an effective method to deal with the problem, but the number of publications using this method is very limited. In addition, hybrid solid electrolyte system with inorganic SSEs and organic filler also shows its potential when applied in ASSLIBs. However, how the fillers work is still questionable. The particle interface is not well defined and difficult to understand, calling for a combination of theory and experimental studies.

3. Advanced characterization methods for operando observation of electrode/garnet electrolyte interface are required, especially at the full cell level. Growing activity in this area is expected along with the development of four-generation synchrotron X-ray sources worldwide. The major challenges are as follows: (1) extract the interface information out of the bulk information; (2) identify the difference between chemical and engineering problems; (3) probe light element, such as Li and O in the full cell. Operando study can also reveal the relationship between the decay in cycling performance and the evolution of garnet electrolyte. To achieve this, the battery needs to be charged and discharged at relevant conditions in commercial applications. Ideally, the chemical environment of Li can be determined along with the decay of the cell. This can be coupled with theoretical calculations to determine the change of Li chemical potential, and thus map the structure/potential diagram in the battery.

In conclusion, garnet typed electrolytes have shown their potential in the fabrication of realistic ASSLIBs. Although the interfacial problem is still difficult to overcome, garnet electrolyte-based solid batteries have a great future with continuous efforts.

CONFLICT OF INTERESTS
The authors declare that there are no conflict of interests. [Correction added on 28 July 2021, after first online publication: Conflict of Interest section has been added.]

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REFERENCES
1. Thangadurai V, Narayanan S, Pinzaru D. Garnet-type solid-state fast Li ion conductors for Li batteries: critical review. Chem Soc Rev. 2014;43:4714-4727.
2. Teng S, Tan J, Tiwari A. Recent developments in garnet based solid state electrolytes for thin film batteries. Curr Opin Solid State Mater Sci. 2014;18:29-38.
3. Din MMU, Murugan R. Garnet structured solid fast Li+ conductor as polysulfide shuttle inhibitor in Li-S battery. Electrochem Commun. 2018;93:109-113.
4. Song S, Qin X, Ruan Y, et al. Enhanced performance of solid-state lithium-air batteries with continuous 3D garnet network added composite polymer electrolyte. J Power Sources. 2020;461:228146.
5. AbdelHamid AA, Cheong JL, Ying JY. Li7La3Zr2O12 sheet-based framework for high-performance lithium–sulfur hybrid quasi-solid battery. Nano Energy. 2020;71:104633.
6. Paolella A, Zhu W, Bertoni G, et al. Discovering the influence of lithium loss on garnet Li7La3Zr2O12 electrolyte phase stability. ACS Appl Energy Mater. 2020;3:3415-3424.
7. Yun JJ, Jeon JH, Park KB, Zhao X. Benefits and costs of closed innovation strategy: analysis of Samsung's Galaxy Note 7 explosion and withdrawal scandal. J Open Innov Technol Mark Complex. 2018;4:20.
8. Lou S, Zhang F, Pu C, et al. Interface issues and challenges in all-solid-state batteries: lithium, sodium, and beyond. Adv Mater. 2020;2000721:1-29.
9. Li Y, Gao Z, Hu F, et al. Advanced characterization techniques for interface in all-solid-state batteries. Small Methods. 2020;4:2000111.
10. Gao Z, Sun H, Fu L, et al. Promises, challenges, and recent progress of inorganic solid-state electrolytes for all-solid-state lithium batteries. Adv Mater. 2018;30:1705702.
11. Wang C, Fu K, Kammampata SP, et al. Garnet-type solid-state electrolytes: materials, interfaces, and batteries. Chem Rev. 2020;120:4257-4300.
12. Zhang L, Yang J, Jing K, et al. Thickness-dependent beneficial effect of the ZnO layer on tailoring the Li/Li7La3Zr2O12 interface. ACS Appl Mater Interfaces. 2020;12:13836-13841.
13. Xu L, Tang S, Cheng Y, et al. Interfaces in solid-state lithium batteries. Joule. 2018;2:1991-2015.
14. Wang K, Wu Y, Liu K, Wu H. A review on anode side interface stability micromechanisms and engineering for garnet electrolyte-based solid-state batteries. Chem Res Chin Univ. 2020;36:351-359.
15. Banerjee A, Wang X, Fang C, et al. Interfaces and interphases in all-solid-state batteries with inorganic solid electrolytes. Chem Rev. 2020;120:6878-6933.
16. Marbella LE, Zekoll S, Kasemchainan J, Ernge SP, Bruce PG, Grey CP. ‘Li NMR chemical shift imaging to detect micro-
structure growth of lithium in all-solid-state batteries. Chem Mater. 2019;31:2762-2769.
17. Tian HK, Liu Z, Ji Y, Chen LQ, Qi Y. Interfacial electronic properties dictate Li dendrite growth in solid electrolytes. Chem Mater. 2019;31:7351-7359.
18. Kim S, Jung C, Kim H, et al. The role of interlayer chemistry in Li-metal growth through a garnet-type solid electrolyte. Adv Energy Mater. 2020;10:1903993.
19. Han F, Westover AS, Yue J, et al. High electronic conductivity as the origin of lithium dendrite formation within solid electrolytes. Nat Energy. 2019;4:187-196.
20. Fingerle M, Loho C, Ferber T, Hahn H, Hausbrand R. Evidence of the chemical stability of the garnet-type solid electrolyte Li15-
La2Ta2O12 towards lithium by a surface science approach. J Power Sources. 2017;366:72-79.
21. Zhu Y, He X, Mo Y. Origin of outstanding stability in the lithium solid electrolyte materials: insights from thermodynamic analyses based on first-principles calculations. ACS Appl Mater Interfaces. 2015;7:23685-23693.
22. Mindemark J, Lacey MJ, Bowden T, Brandell D. Beyond PEO—alternative host materials for Li+—conducting solid polymer elec-
trolytes. Prog Polym Sci. 2018;81:114-143.
23. Yang J, Gao Z, Ferber T, et al. Guided-formation of a favor-
able interface for stabilizing Na metal solid-state batteries. J Mater Chem A. 2020;8:7828-7835.
24. Yao X, Huang N, Han F, et al. High-performance all-solid-state lithium-sulfur batteries enabled by amorphous sulfur-coated reduced graphene oxide cathodes. Adv Energy Mater. 2017;7:1602923.
25. Han F, Zhu Y, He X, Mo Y, Wang C. Electrochemical stability of Li15GeP3S12 and Li15La3Zr2O12 solid electrolytes. Adv Energy Mater. 2016;6:1501590.
26. Perea SA, Cambaz MA, Thangadurai V, Fichtner M. Interface in solid-state lithium battery: challenges, progress, and outlook. ACS Appl Mater Interfaces. 2019;11:22029-22205.
27. Thangadurai V, Kaack H, Weppner WJF. Novel fast lithium ion conduction in garnet-type Li15La3M2O12 (M = Nb, Ta). J Am Ceram Soc. 2003;86:437-440.
28. O’Callaghan MP, Lynham DR, Cussen EJ, Chen GZ. Structure and ionic transport properties of lithium-containing garnets Li5Ln3Te2O12 (Ln = Y, Pr, Nd, Sm-Lu). Chem Mater. 2006;18:4681-4689.
29. Murugan R, Thangadurai V, Weppner W. Lattice parameter and sintering temperature dependence of bulk and grain-boundary conduction of garnet-like solid Li-electrolytes. J Electrochem Soc. 2008;155:A90.
30. Wang WG, Wang XP, Gao YX, Fang QF. Lithium-ionic diffusion and electrical conduction in the Li15La3Zr2O12 compounds. Solid State Ion. 2009;180:1252-1256.
31. Murugan R, Thangadurai V, Weppner W. Fast lithium ion conduction in garnet-type Li15La3Zr2O12. Angew Chem Int Ed. 2007; 46:7778-7781.
32. Samson AJ, Hofstetter K, Bag S, Thangadurai V. A bird’s-eye view of Li-stuffed garnet-type Li15La3Zr2O12 ceramic electrolytes for advanced all-solid-state Li batteries. Energy Environ Sci. 2019; 12:2957-2975.
33. Awaka J, Takashima A, Katoaka K, Kijima N, Idemoto Y, Akimoto J. Crystal structure of fast lithium-ion-conducting cubic Li15La3Zr2O12. Chem Lett. 2011;40:60-62.
34. Liu Q, Geng Z, Han C, et al. Challenges and perspectives of garnet solid electrolytes for all-solid-state lithium batteries. J Power Sources. 2018;389:120-134.
35. Rangasamy E, Wolfenstein J, Sakamoto J. The role of Al and Li concentration on the formation of cubic garnet solid electrolyte of nominal composition Li15La3Zr2O12. Solid State Ion. 2012;206:28-32.
36. Wagner R, Redhammer GJ, Rettenwander D, et al. Fast Li-ion-conducting garnet-related Li15-3xFexLa3Zr2O12 with un-
common 14-3d structure. Chem Mater. 2016;28:5943-5951.
37. Bruggen RH, Kilner JA, Aguadero A. Germanium as a donor dopant in garnet electrolytes. Solid State Ion. 2019;337:154-160.
38. Li C, Liu Y, He J, Brinkman KS. Ga-substituted Li15La3Zr2O12: an investigation based on grain coarsening in garnet-type lithium ion conductors. J Alloys Compd. 2017;695:3744-3752.
39. Wolfenstein J, Ratchford J, Rangasamy E, Sakamoto J, Allen JL. Synthesis and high Li-ion conductivity of Ga-
stabilized cubic Li15La3Zr2O12. Mater Chem Phys. 2012;134: 571-575.
40. Qin S, Zhu X, Jiang Y, Ling M, Hu Z, Zhu J. Growth of self-
textured Ga+-substituted Li15La4Zr2O12 ceramics by solid-
state reaction and their significant enhancement in ionic conductivity. Appl Phys Lett. 2018;112:113901.
41. Ohta S, Seki J, Yagi Y, Kihira Y, Tani T, Asaoaka T. Co-
sinterable lithium garnet-type oxide electrolyte with cathode for all-solid-state lithium-ion battery. J Power Sources. 2014; 265:40-44.
42. Shao C, Yu Z, Liu H, Zheng Z, Sun N, Diao C. Enhanced ionic conductivity of titanium doped Li15La3Zr2O12 solid electrolyte. Electrochim Acta. 2017;225:345-349.
43. Allen JL, Wolfenstein J, Rangasamy E, Sakamoto J. Effect of substitution (Ta, Al, Ga) on the conductivity of Li15La3Zr2O12. J Power Sources. 2012;206:315-319.
44. Li Y, Han JT, Wang CA, Xie H, Goodenough JB. Optimizing Li+ conductivity in a garnet framework. J Mater Chem. 2012; 22:15357-15361.
45. Ramakumar S, Satyanaarayana L, Manorama SV, Murugan R. Structure and Li+ dynamics of Nb-doped Li15La3Zr2O12 fast lithium-ion conductors. Phys Chem Chem Phys. 2013;15:11327-11338.
46. Liu X, Li Y, Yang T, et al. High lithium ionic conductivity in the garnet-type oxide Li15-2xLa3Zr2-xMo4O12 (x=0-0.3) ceramics by sol-gel method. J Am Ceram Soc. 2017;100:1527-1533.
47. Song S, Yan B, Zheng F, Duong HM, Lu L. Crystal structure, migration mechanism and electrochemical performance of Cr-
stabilized garnet. Solid State Ion. 2014;268:135-139.
48. Murugan R, Ramakumar S, Janani N. High conductive yttrium doped Li15La3Zr2O12 cubic lithium garnet. Electrochim Commun. 2011;13(12):1373-1375.
49. Hitz GT, Wachsmann ED, Thangadurai V. Highly Li-stuffed garnet-type Li15-La3Zr2-Y4O12. J Electrochem Soc. 2013;160: A1248-A1255.
50. Li Y, Wang Z, Cao Y, et al. W-doped Li15La3Zr2O12 ceramic electrolytes for solid state Li-ion batteries. Electrochim Acta. 2015;180:37-42.
51. Deviannapoorani C, Dhiyva L, Ramakumar S, Murugan R. Lithium-ion transport properties of high conductive tellurium substituted Li$_7$La$_3$Zr$_2$O$_{12}$ cubic lithium garnets. J Power Sources. 2013;240:18-25.

52. Zheng J, Tang M, Hu YY. Lithium-ion pathway within Li$_{60}$La$_{20}$Zr$_{10}$O$_{50}$-polyethylene oxide composite electrolytes. Angew Chem Int Ed. 2016;55:12538-12542.

53. Cheng L, Crumlin EL, Chen W, et al. The origin of high electrolyte-electrode interfacial resistances in lithium cells containing garnet type solid electrolytes. Phys Chem Chem Phys. 2014;16:18294-18300.

54. Sharafi A, Yu S, Naguib M, et al. Impact of air exposure and surface chemistry on Li$_7$La$_3$Zr$_2$O$_{12}$ interfacial resistance. J Mater Chem A. 2017;5:13475-13487.

55. Xia W, Xu B, Duan H, et al. Reaction mechanisms of lithium garnet pellets in ambient air: the effect of humidity and CO$_2$. J Am Ceram Soc. 2017;100:2832-2839.

56. Brugge RH, Hekselman AKO, Cavallaro A, et al. Garnet electrolytes for solid state batteries: visualization of moisture-induced chemical degradation and revealing its impact on the Li-ion dynamics. Chem Mater. 2018;30:3704-3713.

57. Huo H, Chen Y, Zhao N, et al. In-situ formed Li$_2$CO$_3$-free solid-garnet/Li interface by rapid acid treatment for dendrite-free solid-state batteries. Nano Energy. 2019;61:119-125.

58. Gittleson FS, El Gabaly F. Non-Faradaic Li$^+$ migration and chemical coordination across solid-state battery interfaces. Nano Lett. 2017;17:6974-6982.

59. Wang TH, Ciucci F. Electro-chemo-mechanical modeling of solid-state batteries. Electrochim Acta. 2020;331:135355.

60. Krauskopf T, Richter FH, Zeier WG, Janek J. Physico-chemical concepts of the lithium metal anode in solid-state batteries. Chem Rev. 2020;120:7745-7794.

61. De Klerk NJJ, Wagemaker M. Space-charge layers in all-solid-state batteries; important or negligible? ACS Appl Energy Mater. 2018;1:5609-5618.

62. Augustyn V, McDowell MT, Vojvodic A. Toward an atomistic understanding of solid-state electrochemical interfaces for energy storage. Joule. 2018;2:2189-2193.

63. Han X, Gong Y, Fu K, et al. Negating interfacial impedance in garnet-based solid-state Li metal batteries. Nat Mater. 2017;16:572-579.

64. Huang Y, Chen B, Duan J, et al. Graphitic carbon nitride (g-C$_3$N$_4$): an interface enabler for solid-state lithium metal batteries. Angew Chem Int Ed. 2020;59:3699-3704.

65. Ma C, Cheng Y, Yin K, et al. Interfacial stability of Li metal-solid electrolyte elucidated via in situ electron microscopy. Nano Lett. 2016;16:7030-7036.

66. Krauskopf T, Dippel R, Hartmann H, et al. Lithium-metal growth kinetics on LLZO garnet-type solid electrolytes. Joule. 2019;3:2030-2049.

67. Wen J, Huang Y, Duan J, et al. Highly adhesive Li-BN nanosheet composite anode with excellent interfacial compatibility for solid-state Li metal batteries. ACS Nano. 2019;13:14549-14556.

68. Sharaﬁ A, Kazya E, Davis AL, et al. Surface chemistry mechanism of ultra-low interfacial resistance in the solid-state electrolyte Li$_{6}$La$_{2}$Zr$_{2}$O$_{12}$. Chem Mater. 2017;29:7961-7968.

69. Duan J, Huang L, Wang T, et al. Shaping the contact between Li metal anode and solid-state electrolytes. Adv Funct Mater. 2020;30:1908701.

70. Fu KK, Gong Y, Liu B, et al. Toward garnet electrolyte-based Li metal batteries: an ultrathin, highly effective, artificial solid-state electrolyte/metallic Li interface. Sci Adv. 2017;3:1-12.

71. Xiang X, Cao S, Chen F, Shen Q, Zhang L. Communication—Li/Li$_{7}$La$_{3}$Zr$_2$O$_{12}$ interfacial modification by constructing a layer of Cu-Li alloy. J Electrochem Soc. 2019;166:A3028-A3030.

72. Gao B, Jalem R, Tatyeyama Y. Surface-dependent stability of the interface between garnet Li$_7$La$_3$Zr$_2$O$_{12}$ and the Li metal in the all-solid-state battery from first-principles calculations. ACS Appl Mater Interfaces. 2020;12:16350-16358.

73. Wang S, Xu H, Li W, Dolocan A, Manthiram A. Interfacial chemistry in solid-state batteries: formation of interphase and its consequences. J Am Chem Soc. 2018;140:250-257.

74. Krauskopf T, Hartmann H, Zeier WG, Janek J. Toward a fundamental understanding of the lithium metal anode in solid-state batteries—an electrochemo-mechanical study on the garnet-type solid electrolyte Li$_{6.25}$Al$_{0.25}$La$_3$Zr$_2$O$_{12}$. ACS Appl Mater Interfaces. 2019;11:14463-14477.

75. Kazya E, Garcia-Mendez R, LePage WS, et al. Li penetration in ceramic solid electrolytes: operando microscopy analysis of morphology, propagation, and reversibility. Matter. 2020;2:1025-1048.

76. Ni JE, Case ED, Sakamoto JS, Rangasamy E, Wolfenstein JB. Room temperature elastic moduli and Vickers hardness of hot-pressed LLZO cubic garnet. J Mater Sci. 2012;47:7978-7985.

77. Tsai CL, Roddatis V, Chandran CV, et al. Li$_7$La$_3$Zr$_2$O$_{12}$ interfacial modification for Li dendrite prevention. ACS Appl Mater Interfaces. 2016;8:10617-10626.

78. Fu K, Gong Y, Hitz GT, et al. Three-dimensional bilayer garnet solid electrolyte based high energy density lithium metal-sulfur batteries. Energy Environ Sci. 2017;10:1568-1575.

79. Liu T, Zhang Y, Zhang X, et al. Enhanced electrochemical performance of bulk type oxide ceramic lithium batteries enabled by interface modification. J Mater Chem A. 2018;6:4649-4657.

80. Chi SS, Liu Y, Zhao N, Guo X, Nan C-W, Fan L-Z. Polymer electrolyte soft interface layer with 3D lithium anode for all-solid-state lithium batteries. Energy Stor Mater. 2019;17:309-316.

81. Xu L, Li J, Deng W, et al. Garnet solid electrolyte for advanced all-solid-state Li batteries. Adv Energy Mater. 2021;11:2000648.

82. Park K, Yu BC, Jung JW, et al. Electrochemical nature of the cathode interface for a solid-state lithium-ion battery: interface between LiCoO$_2$ and garnet-Li$_7$La$_3$Zr$_2$O$_{12}$. Chem Mater. 2016;28:8051-8059.

83. Ren Y, Liu T, Shen Y, Lin Y, Nan CW. Chemical compatibility between garnet-like solid state electrolyte Li$_{6.75}$La$_{2}$Zr$_{1}$Ta$_{0.25}$O$_{12}$ and major commercial lithium battery cathode materials. J Mater. 2016;2:256-264.

84. Kim KH, Iriyama Y, Yamamoto K, et al. Characterization of the interface between LiCoO$_2$ and Li Li$_7$La$_3$Zr$_2$O$_{12}$ in an all-solid-state rechargeable lithium battery. J Power Sources. 2011;196:764-767.

85. Vardar G, Bowman WJ, Lu Q, et al. Structure, chemistry, and charge transfer resistance of the interface between
Li$_3$La$_{5}$Zr$_2$O$_{12}$ electrolyte and LiCoO$_2$ cathode. *Chem Mater.* 2018;30:6259-6276.

86. Li Y, Xu B, Xu H, et al. Hybrid polymer/garnet electrolyte with a small interfacial resistance for lithium-ion batteries. *Angew Chem Int Ed.* 2017;56:753-756.

87. Gong Y, Fu K, Xu S, et al. Lithium-ion conductive ceramic textile: a new architecture for flexible solid-state lithium metal batteries. *Mater Today.* 2018;21:594-601.

88. Xu S, McOwen DW, Zhang L, et al. All-in-one lithium-sulfur battery enabled by a porous-dense- porous garnet architecture. *Energy Stor Mater.* 2018;15:458-464.

89. Shao D, Yang L, Luo K, et al. Preparation and performances of the modified gel composite electrolyte for application of quasi-solid-state lithium-sulfur battery. *Chem Eng J.* 2020;389:124300.

90. Fu X, Wang T, Shen W, et al. A high-performance carbonate-free lithium/garnet electrolyte enabled by a trace amount of sodium. *Adv Mater.* 2020;32:2000575.

91. Cheng L, Wu CH, Jarry A, et al. Interrelationships among grain size, surface composition, air stability, and interfacial resistance of al-substituted Li$_3$La$_5$Zr$_2$O$_{12}$ solid electrolytes. *ACS Appl Mater Interfaces.* 2015;7:17649-17655.

92. Li Y, Chen X, Dolocan A, et al. Garnet electrolyte with an ultralow interfacial resistance for Li-metal batteries. *J Am Chem Soc.* 2018;140:6448-6455.

93. Ruan Y, Lu Y, Huang X, et al. Acid induced conversion towards a robust and lithiophilic interface for Li-Li$_3$La$_5$Zr$_2$O$_{12}$ solid-state batteries. *J Mater Chem A.* 2019;7:14565-14574.

94. Xu H, Li Y, Zhou A, et al. Li$_2$N-modified garnet electrolyte for all-solid-state Li-metal batteries operated at 40°C. *Nano Lett.* 2018;18:7414-7418.

95. Shi K, Wan Z, Yang L, et al. In situ construction of an ultrastable conductive composite interface for high-voltage all-solid-state lithium metal batteries. *Angew Chem Int Ed.* 2020;132:11882-11886.

96. Brogioli D, Langer F, Kun R, La Manta F. Space-charge effects at the Li$_3$La$_5$Zr$_2$O$_{12}$/poly(ethylene oxide) interface. *ACS Appl Mater Interfaces.* 2019;11:11999-12007.

97. Liu B, Gong Y, Fu K, et al. Garnet solid electrolyte protected Li-metal batteries. *ACS Appl Mater Interfaces.* 2017;9:18809-18815.

98. Chen L, Li Y, Li SP, Fan LZ, Nan CW, Goodenough JB. PEO/garnet composite electrolytes for solid-state lithium batteries: from “ceramic-in-polymer” to “polymer-in-ceramic”. *Nano Energy.* 2018;46:176-184.

99. Zhou W, Wang S, Li Y, Xin S, Manthiram A, Goodenough JB. Plating a dendrite-free lithium anode with a polymer/ceramic/polymer sandwich electrolyte. *J Am Chem Soc.* 2016;138:9385-9388.

100. Duan J, Wu W, Nolan AM, et al. Lithium–graphite paste: an interface compatible anode for solid-state batteries. *Adv Mater.* 2019;31:1807243.

101. Wang C, Xie H, Zhang L, et al. Universal soldering of lithium and sodium alloys on various substrates for batteries. *Adv Energy Mater.* 2018;8:1701963.

102. Lu Y, Huang X, Ruan Y, et al. An in situ element permeation constructed high endurance Li-LLZO interface at high current densities. *J Mater Chem A.* 2018;6:18853-18858.

103. Yang C, Xie H, Ping W, et al. An electron/ion dual-conductive alloy framework for high-rate and high-capacity solid-state lithium-metal batteries. *Adv Mater.* 2019;31:1804815.

104. Ohta S, Kobayashi T, Seki J, Asaoka T. Electrochemical performance of an all-solid-state lithium ion battery with garnet-type oxide electrolyte. *J Power Sources.* 2012;202:332-335.

105. Okada K, Machida N, Naito M, et al. Preparation and electrochemical properties of LiAlO$_2$-coated Li(Ni$_{0.2}$Mn$_{0.17}$Co$_{0.13}$)O$_2$ for all-solid-state batteries. *Solid State Ion.* 2014;255:120-127.

106. Kotobuki M, Munakata H, Kanamura K, Sato Y, Yoshida T. Compatibility of Li$_3$La$_5$Zr$_2$O$_{12}$ solid electrolyte to all-solid-state battery using Li metal anode. *J Electrochem Soc.* 2010;157:A1076.

107. Han F, Yue J, Chen C, et al. Interphase engineering enabled all-ceramic lithium battery. *Joule.* 2018;2:497-508.

108. McOwen DW, Xu S, Gong Y, et al. 3D-printing electrolytes for solid-state batteries. *Adv Mater.* 2018;30:1707132.

109. Tao X, Liu Y, Liu W, et al. solid-state lithium-sulfur batteries operated at 37°C with composites of nanostructured Li$_3$La$_5$Zr$_2$O$_{12}$/carbon foam and polymer. *Nano Lett.* 2017;17:2967-2972.

110. Van den Broek A, Afyon S, Rupp JLM. Interface-engineered all-solid-state Li-ion batteries based on garnet-type fast Li$^+$ conductors. *Adv Energy Mater.* 2016;6:1600736.

111. Shen H, Yi E, Heywood S, et al. Scalable freeze-tape-casting fabrication and pore structure analysis of 3D LLZO solid-state electrolytes. *ACS Appl Mater Interfaces.* 2020;12:3494-3501.

112. Buannic L, Navirio M, Miller SM, Zagorski J, Faber KT, Llordés A. Dense freeze-cast Li$_3$La$_5$Zr$_2$O$_{12}$ solid electrolytes with oriented open porosity and contiguous ceramic scaffold. *J Am Ceram Soc.* 2019;102:1021-1029.

113. Shen H, Yi E, Amores M, et al. Oriented porous LLZO 3D structures obtained by freeze casting for battery applications. *J Mater Chem A.* 2019;7:20861-20870.

114. Finsterbusch M, Danner T, Tsai CL, Uhlenbruck S, Latz A, Guillou O. High capacity garnet-based all-solid-state lithium batteries: fabrication and 3D-microstructure resolved modeling. *ACS Appl Mater Interfaces.* 2018;10:22329-22339.

115. Zhang Y, Meng J, Chen K, Wu H, Hu J, Li C. Garnet-based solid-state lithium fluoride conversion batteries benefiting from eutectic interlayer of superior wettability. *ACS Energy Lett.* 2020;5:1167-1176.

116. Ruan Y, Lu Y, Li Y, et al. A 3D cross-linking lithiophilic and electronically insulating interfacial engineering for garnet-type solid-state lithium batteries. *Adv Funct Mater.* https://doi.org/10.1002/adfm.202007815.

117. Feng W, Dong X, Li P, Wang Y, Xia Y. Interfacial modification of Li/garnet electrolyte by a lithiophilic and breathing interlayer. *J Power Sources.* 2019;419:91-98.

118. Cai M, Lu Y, Su J, et al. In situ lithiophilic layer from H$^+$ /Li$^+$ exchange on garnet surface for the stable lithium-solid electrolyte interface. *ACS Appl Mater Interfaces.* 2019;11:35030-35038.

119. Shao Y, Wang H, Gong Z, et al. Drawing a soft interface: an effective interfacial modification strategy for garnet-type solid-state Li batteries. *ACS Energy Lett.* 2018;3:1212-1218.
120. Lou J, Wang G, Xia Y, et al. Achieving efficient and stable interface between metallic lithium and garnet-type solid electrolyte through a thin indium tin oxide interlayer. J Power Sources. 2020;448:227440.

121. Fu J, Yu P, Zhang N, et al. In situ formation of a bifunctional interlayer enabled by a conversion reaction to initiatively prevent lithium dendrites in a garnet solid electrolyte. Energy Environ Sci. 2019;12:1404-1412.

122. Deng T, Ji X, Zhao Y, et al. Tuning the anode-electrolyte interface chemistry for garnet-based solid-state Li metal batteries. Adv Mater. 2020;32:2000030.

123. Chen L, Huang Z, Pang W, Jin Z, Li Y, Wang CA. Dual interface layers for solid-state Li metal battery with low interfacial resistance and small polarization based on garnet electrolyte. Electrochim Acta. 2020;330:135352.

124. Wan Z, Lei D, Yang W, et al. Low resistance-integrated all-solid-state battery achieved by Li7La3Zr2O12 nanowire upgrading polyethylene oxide (PEO) composite electrolyte and PEO cathode binder. Adv Funct Mater. 2019;29:1805301.

125. Sun J, He C, Yao X, et al. Hierarchical composite-solid-electrolyte with high electrochemical stability and interfacial regulation for boosting ultra-stable lithium batteries. Adv Funct Mater. 2021;31:2006381.

126. Xu R, Xiao Y, Zhang R, et al. Dual-phase single-ion pathway interfaces for robust lithium metal in working batteries. Adv Mater. 2019;31:1808392.

127. Yang C, Zhang L, Liu B, et al. Continuous plating/stripping behavior of solid-state lithium metal anode in a 3D ion-conductive framework. Proc Natl Acad Sci USA. 2018;115:3770-3775.

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