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Broader context

New horizons for inorganic solid state ion conductors

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Among the contenders in the new generation energy storage arena, all-solid-state batteries (ASSBs) have emerged as particularly promising, owing to their potential to exhibit high safety, high energy density and long cycle life. The relatively low conductivity of most solid electrolytes and the often sluggish charge transfer kinetics at the interface between solid electrolyte and electrode layers are considered to be amongst the major challenges facing ASSBs. This review presents an overview of the state of the art in solid lithium and sodium ion conductors, with an emphasis on inorganic materials. The correlations between the composition, structure and conductivity of these solid electrolytes are illustrated and strategies to boost ion conductivity are proposed. In particular, the high grain boundary resistance of solid oxide electrolytes is identified as a challenge. Critical issues of solid electrolytes beyond ion conductivity are also discussed with respect to their potential problems for practical applications. The chemical and electrochemical stabilities of solid electrolytes are discussed, as are chemo-mechanical effects which have been overlooked to some extent. Furthermore, strategies to improve the practical performance of ASSBs, including optimizing the interface between solid electrolytes and electrode materials to improve stability and lower charge transfer resistance are also suggested.

Driven by the necessity to reduce greenhouse effects caused by the emission of CO₂, the development of new electrochemical energy conversion and storage devices is of prime significance. Lithium ion batteries have revolutionized the portable electronics industry but may not be able to satisfy future customers' demands in the field of large-scale energy storage systems such as electrical vehicles and power grids. In particular, safety concerns have been a long-standing issue hindering the development of commercial liquid batteries with liquid organic electrolytes. In this context, all solid-state batteries (ASSBs) based on solid electrolytes (SEs) can not only address safety concerns, but may also enable the use of high voltage cathode materials and Li/Na metal anodes to enable long life and high energy density batteries. As the most important component in ASSBs, the SE determines the power density, long cycle stability and the safety of batteries. In this review a state of art and comprehensive description of the recent developments in SEs will be given, and general descriptors to guide the design of SEs are proposed. Critical issues of SEs with respect to their potential problems for practical applications (*e.g.*, the chemical and electrochemical stability of SE, chemomechanical effects, large charge transfer resistance at the interface) are discussed, and strategies to overcome these obstacles are also proposed.

1. Introduction

The development of electrochemical energy conversion and storage devices is one of the most important challenges to alleviate the greenhouse effects caused by emission of CO_2 .^{1,2} Owing to their high specific energy, large-scale rechargeable batteries have recently become highly sought after for applications in power grids and electric vehicles.^{2,3} However, the flammable,

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reactive organic electrolytes used in conventional batteries incur severe safety issues.⁴ In addition, although Li metal has an extremely high theoretical specific capacity (3860 mA h g⁻¹), low mass and the lowest negative electrochemical potential (-3.04 V *vs.* SHE), rechargeable batteries using Li metal have not been commercialized because of lithium metal's low cycling efficiency and tendency to form dendrites during repeated charge/discharge.^{5,6} The only exceptions are the Blue SolutionsTM batteries for EVs and buses that use a polymer electrolyte that operates at about 70 °C instead of a liquid electrolyte.

In this context, all solid-state batteries (ASSBs) based on solid electrolytes (SEs) can not only address safety concerns, but may also enable the use of high voltage cathode materials and Li/Na metal anodes to allow for long-term stable and high energy density batteries. An increase of more than 20% in energy density (depending on additional cathode capacity at high voltage) can be achieved by increasing the cell voltage from 4.2 V to 5 V.⁷ Oxide-based inorganic solid electrolytes can endure such high voltages whereas liquid electrolytes are not stable at such very oxidizing potentials.⁷ ASSBs exhibit additional advantages including low self-discharge, versatile geometries, high thermal stability, and thus wide operating temperature,² and as well as resistance to shocks and vibrations.⁸ Moreover, the solidification of the electrolyte allows for the design of highvoltage bipolar stacked batteries and effectively decreases the dead space between single cells with thinner current collectors.

The SE is the most vital component in solid-state batteries – together with the electrode materials – as it determines the power density, long-term stability and the safety of the batteries. To realize ASSBs that can operate at ambient and moderate



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research spans a wide range from fundamental transport studies in mixed conductors and at interfaces to in situ studies in electrochemical cells. Current key interests include new solid electrolytes and solid electrolyte interfaces.



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temperatures, SEs with high ion conductivity (>10⁻⁴ S cm⁻¹, better >10⁻³ S cm⁻¹ in case of thick composite electrodes),⁹ negligible electronic conductivity (<10⁻¹² S cm⁻¹),⁹ and a wide electrochemical window^{10,11} are necessary. The greatest obstacles to the integration of SEs into batteries are the inherently poor ion conductivity of most SEs and the large resistance at the interface between the SE and active material, but also chemomechanical issues related to volume changes of active materials. Favorable interfacial contact and chemical stability between the SE and the electrode materials are both critical to achieve good electrochemical performance. The electrode-electrolyte interface particularly becomes an issue if nanostructured electrodes are to be considered and/or if large volume variations arise during cycling.¹²⁻¹⁴ The chemical stability of SEs is



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(since 1991) of the Max Planck Institute for Solid State Research he co-authored more than 800 papers on chemical and electrochemical phenomena. His major interest are solid state ionics, electrochemistry and nanoionics. not necessarily better than that of liquid electrolytes and, in the majority of cases, relies on kinetic, not thermodynamic factors (as in liquid systems).

Inorganic conductors and organic polymers are the most commonly used solid electrolyte materials in ASSBs. The former are characterized by high ion conductivity (> 10^{-4} S cm⁻¹) in many cases and high thermal stability. Furthermore, typical inorganic SEs are single ion conductors that preclude concentration polarization effects. However, ASSBs using inorganic ceramics often exhibit lower-than-expected electrochemical performance due to their poor interfacial contact with the electrode material.4,15 Inorganic ceramics and organic polymers differ greatly in their mechanical properties and are thus suitable for different battery designs. The high elastic moduli of ceramics lead to poor processability because of their brittleness and hardness. Nevertheless, they are appropriate for rigid battery designs, such as thin-film batteries. In contrast, polymer electrolytes are well suited for flexible battery designs owing to their low elastic moduli. However, they suffer from other drawbacks, such as low ion conductivity ($< 10^{-5}$ S cm⁻¹ at ambient temperature), low cation transference number ($t_+ \approx 0.2$ –0.5) unless the anion itself is tethered to a polymer and poor oxidation resistance.¹⁶ Ceramic/polymer composite electrolytes may combine the high conductivity of ceramics and excellent flexibility of polymers and hence have recently attracted much attention.¹⁷

Full reviews of inorganic Li-ion conductors were published by Knauth in 2009,¹⁸ Shao-Horn's group in 2015,¹⁹ and Chen *et al.* in 2016,²⁰ in addition to many other shorter articles which focus on specific classes of SEs, including perovskites²¹ and garnets.²² Brief accounts of the pros and cons of solid electrolytes in battery systems have been recently provided.^{7,23} Following the fast progress in the search for new and optimized SEs, our current review gives an up-to-date, yet comprehensive description of the



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(1978), followed by new families of highly conductive salts (perfluorosulfonimides and Hückel-stabilized anions) for liquid, polymer electrolytes and as base for ionic liquids. The carbon "nanopainting" process has made $LiFePO_4@C$ the safest cathode. Innovations in redox-active organics include polyquinones and aromatic dicarboxylates.



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recent exciting developments in inorganic solid electrolytes, including Na-ion conductors and covering both oxide and sulfide-based materials. Based on a survey of the previous studies, the major factors that influence the ion conductivity are summarized and general descriptors that govern conductivity are also proposed. Even though low-conductivity phases (*e.g.* LiF) may act as relevant electrolytes for very thin film systems, we concentrate here on bulk phases with high conductivities above 10^{-4} S cm⁻¹. Finally, the chemical and electrochemical stabilities of SEs against Li/Na metal and electrode materials are evaluated, a topic that has been somewhat overlooked except in a few recent reports.^{14,23-25} Moreover, strategies to enhance the stability of SEs and to modify the interface between the SEs and electrode layers are proposed.

2. Lithium ion conductors

Crystalline ion conductors exhibit better thermal stability than polymeric materials. However, several difficulties arise for crystalline electrolytes that are associated with their grain boundaries and their fabrication into thin sheets or layers. Grain boundaries in polycrystalline conductors can lead to a locally perturbed structure – often in conjunction with high defect concentrations⁹ – which may cause a large resistive barrier and hinder ion migration across the interface in materials with otherwise high bulk conductivity. The transport of mobile ions across grain boundaries thus becomes the rate-determining step. The opposite effect can also occur: in solid electrolytes with low bulk conductivity, a high fraction of grain boundaries (*i.e.*, in nanostructured materials) may improve the total conductivity by providing better transport paths. The beneficial effect of interfaces on ion transport is highlighted in Section 4.2.

Compared to crystalline ceramic materials, glasses are superior in terms of isotropic conductivity and lack of grain boundaries. From the technological point of view, glasses are often easy to process into thin films. The use of thin film separators can significantly reduce the internal resistance of batteries. For practical applications, the minimum conductivity required depends on the thickness of the separator layer. A total Li ion conductivity greater than 10^{-6} S cm⁻¹ is required in order to avoid having to use a separator thickness well below one micron to minimize the IR drop across the film. Lithium phosphorous oxide nitride (LiPON) is one of the successful examples that has been employed in thin-film solid-state batteries. LiPON is an amorphous phase deposited by magnetron sputtering of Li₃PO₄ in a N₂ atmosphere.²⁶ The conductivity is a function of the N/O ratio and deposition conditions, with the maximum reported conductivity being *ca.* 2×10^{-6} S cm⁻¹ to 3.3×10^{-6} S cm⁻¹.²⁷⁻³¹ Aside from their moderate ion conductivity, LiPON films exhibit very low electronic conductivities $(8 \times 10^{-14} \text{ S cm}^{-1})$, making them appropriate for practical applications.^{32,33} LiPON can also be used as a protective layer in conventional lithium ion batteries. Thin-film solid-state batteries containing LiPON film as the electrolyte, Li or V₂O₅ as the anode, and LiMn₂O₄ or LiCoO₂ as the cathode display

excellent cycling performance.^{32,33} Another important family of glasses is based on mixtures of Li₂S and P₂S₅, where conductivity on the order of 10^{-3} S cm⁻¹ has been reported with the addition of lithium halides.³⁴⁻³⁶ Interest in glasses has reignited recently due to observations of dendrite growth through grain boundaries in polycrystalline ion conductors such as LLZO.³⁷⁻³⁹ A particularly important advance was reported by Hayashi in 2014, where an extremely high conductivity of 1.7 imes 10⁻² S cm⁻¹ was reported for a Li₂S-P₂S₅ glass-ceramic phase.⁴⁰ By employing glasses, unavoidable local mechanical pressure during cycling in ASSBs may be better compensated, while protective interphases are necessary in order to stabilize anode and/or cathode contacts. Although this review focusses on crystalline oxide and sulfide conductors owing to several major breakthroughs in crystalline conductors, some discussion on glasses and glassceramics is also covered here.

2.1 Crystalline conductors

A wide variety of lithium metal oxides, sulfides, phosphates, nitrides, and halides have been shown to exhibit high ion conductivities, as summarized in Fig. 1.^{41–52} LiI,⁵³ Li₃N,⁵⁴ Li– β'' -Al₂O₃,^{55,56} and LiSICON⁵¹ were the first studied. Although single crystals of Li₃N possess a high ion conductivity (10^{-3} S cm⁻¹ at room temperature),⁵⁷ the low decomposition voltage of Li₃N⁵⁷ (0.44 V based on thermodynamic considerations) and its extreme sensitivity toward moisture have limited its practical use. Nonetheless, thin films of Li₃N formed *in situ* by reaction of Li with N₂ gas can be used to protect other SEs from direct contact with Li.⁵⁸ Sputtering of Cu₃N followed by evaporation of Li metal results in a Cu⁰/Li₃N composite that has been used to



Fig. 1 Ion conductivity of several well-known solid lithium ion conductors, including glass and crystalline conductors. The data are taken from ref. 41–52. Reproduced with permission from ref. 41, 44, 51. Copyright (1978, 1993, 2017), Elsevier. Reproduced with permission from ref. 42. Copyright (2001), The Electro-chemical Society. Reproduced with permission from ref. 43, 48. Copyright (2005, 2011), Wiley. Reproduced with permission from ref. 45, 46. Copyright (2011, 2016), Springer Nature. Reproduced with permission from ref. 47, 49, 50, 52. Copyright (2002, 2012, 2016), American Chemical Society.



Fig. 2 (a) A schematic of the crystal structures of LLTOs: a tetragonal structure (left) and orthorhombic structure (right). FESEM micrographs of LLTOs sintered at different temperatures; (b) low-*T* LLTO (1200 °C) and (c) high-*T* LLTO (1400 °C). HRTEM images combined with SAEDs of (d) low-*T* LLTO and (e) high-*T* LLTO (magnified images are given in the inset): (f) a comparison of Li⁺ conductivities along with schematics of the domain microstructures of the LLTO electrolytes: low-*T* LLTO, high-*T* LLTO and Li-excess LLTO. (g) Arrhenius plots of the boundary conductivities for low-*T* LLTO, high-*T* LLTO and Li-excess LLTO. The activation energy (*E*_a) values calculated are indicated.⁹⁰ Reproduced with permission from ref. 90. Copyright (2017), the Royal Society of Chemistry.

protect another solid electrolyte.⁵⁹ Single crystals of $\text{Li}-\beta''-\text{Al}_2O_3$ also show excellent conductivity (3 × 10⁻³ S cm⁻¹) at room temperature.^{55,56} However, this phase is unlikely to be used in practical applications, since it is extremely hygroscopic and difficult to prepare dry.^{55,56} Following this early work on Li solid electrolytes, several classes of materials were developed. In the following we will discuss the most important inorganic crystalline Li ion conductors. These can be classified as $\text{Li}_{3x}\text{La}_{2/3-x}\Box_{1/3-2x}\text{TiO}_3$ (LLTO, perovskite),⁵⁰ Li₃OCl (anti-perovskite),⁶⁰ Li₁₄ZnGe₄O₁₆ (LiSICON),⁵¹ Li_{1.3}Ti_{1.7}Al_{0.3}(PO₄)₃ (NaSICON type),⁵² Li₇La₃Zr₂O₁₂ (garnet),²² Thio-LiSICON,⁶¹ Li₆PS₅X (X = Cl, Br, I), argyrodites,⁶² and Li₁₀MP₂S₁₂, (M = Ge, Sn).^{45,63}

2.1.1 Oxide based lithium ion conductors

2.1.1.1 Perovskite type conductors. $Li_{3x}La_{2/3-x}\Box_{1/3-2x}TiO_3$ (LLTO, 0.04 < x < 0.17) and its variants have attracted much interest because of their high bulk ion conductivities $(\sim 10^{-3} \text{ S cm}^{-1})$,⁵⁰ negligible electronic conductivities under normal conditions,⁶⁴ and wide electrochemical windows (reported to be greater than 8 V). LLTO has a perovskite (ABO₃) structure, with the A-sites partially occupied by Li or La. The A-site cations are not randomly distributed, but are ordered to form alternately stacked La-rich (La1) and La-poor (La2) layers along the c axis. $^{\rm 65-70}$ Previous studies have shown that the Li-ion conducting behavior in the grain interior is highly dependent on the crystal structure, composition (e.g., A-site vacancy concentration, the degree of A site cation ordering, and dopants) and structural distortions.^{65–70} Li-ion jump events occur only when adjacent vacant A-site cavities are available.²¹ The Li-poor $(0.03 \le x < 0.1)$ compositions are reported to show orthorhombic symmetry (Fig. 2a), with high La occupancy in the La-rich layer (Fig. 2d) and anti-phase tilted TiO₆ octahedra along the *b* axis;^{65–70} while in Li-rich ($0.1 \le x < 0.167$) compositions, the symmetry becomes tetragonal⁷⁰ (Fig. 2a) and the degree of La ordering decreases as the Li⁺ content increases (Fig. 2e). The dimension of the Li⁺ trajectory is determined by the Li⁺ ion concentration and the A-site vacancy. In the Li-poor LLTO, the La-rich layer acts as a barrier to Li⁺ diffusion in the [001] direction because of the high La occupancy (~0.95) and low vacancy concentration (~0.05). The 2D Li ion pathways are thus predominantly confined within the La-poor layer.⁶⁷ On the other hand, Li-rich LLTO has relatively low La occupation (0.65)⁷¹ and a higher concentration of vacancies and Li ions in the La-rich layer. In the latter, the Li migration between alternating La1 and La2 layers becomes possible, resulting in 3D conduction, at least within certain regions.

To further improve the conductivity, efforts have been made to substitute the A-site La³⁺ (ref. 72 and 73) and/or B-site Ti⁴⁺.^{74–77} However, only the substitution of Sr^{2+} ,⁷² Ba²⁺,⁷⁸ and Nd³⁺ (ref. 79) for La³⁺ and the partial substitution of Al³⁺ (ref. 74–76) or Ge⁴⁺ (ref. 77) for Ti⁴⁺ offer improvement in the bulk conductivity, which is nonetheless marginal.

Earlier studies also found the total conductivity of LLTOs is governed by ion transfer across the grain boundary (GB). The latter conductivities are reported to be in the order of 10^{-4} – 10^{-5} S cm⁻¹, which is about 1–2 orders of magnitudes lower than that of the bulk. Scrutiny through high-resolution transmission electron microscopy (HRTEM) reveals LLTOs have complex microstructures: domains with different crystal orientations and periodicities are observed. The relationship between conductivity and microstructures (*e.g.*, density, domain size, atomistic structure, and composition of the domain boundaries)^{70,80–89} were recently examined. The heat-treatment temperature affects the domain size, with a higher sintering temperature leading to a larger domain size and higher domain boundary conductivity (see Fig. 2b–f).⁹⁰ Scanning transmission electron microscopy (STEM) verified the existence of a large fraction of 90° domain boundaries, which was proven by DFT calculations to be detrimental to ion transfer.⁸⁹ Their elimination is predicted to increase the conductivity by about three orders of magnitude.⁸⁹ As shown in Fig. 2f and g, higher conductivity is also achieved when the Li concentration at the boundaries increases.

The origin of the poor grain boundary conductivity in LLTO was explored by Nan's group.⁸⁸ STEM/EELS analysis (Fig. 3a-g) revealed that dramatic structural deviations and chemical variations from the bulk framework can be observed at most grain boundaries. The grain boundary resembled more of a Ti-O binary phase, devoid of La³⁺ and more importantly, of the charge carrier Li⁺; Fig. 3h schematically depicts the atomic configuration of the grain boundary and the Li site distribution. This mechanism explains previous observations that the introduction of Li ion conducting intergranular phases (Li₂O, LiF, Li₃BO₃, Li₄SiO₄, LLZO) may increase the grain boundary conductivity, if the new interface between the perovskite grains and the second phase does not act as a new barrier for Li migration.^{84,91} Adding inert oxides, e.g. SiO₂ and Al₂O₃ as flux agents can also improve the conductivity of LLTO.92-94 In the LLTO/SiO₂ composite, SiO₂ accommodates Li from LLTO grains to form an amorphous lithium silicate which greatly enhances the grain boundary conductivity.⁹² Similarly, the addition of Al₂O₃ formed LiAl₅O₈ leads to a boost in both the bulk and grain boundary conductivity.93

2.1.1.2 Anti-perovskite type conductors. Inspired by high temperature ion-conducting perovskites such as (Na, K)MgF₃,^{95,96} KZnF₃,^{95,96} and CsPbF₃,⁹⁷ a new and promising family of "structurally-inverted" anti-perovskites, Li₃OX (X = Cl⁻, Br⁻, I⁻, or a mixture of halides), was reported.^{47,60,98} The anti-perovskite

compounds have the same space group and similar structure as conventional perovskites (cubic, $Pm\bar{3}m$) but with inverted cation and anion sublattices and, hence, charges. In one representation of the Li₃OX anti-perovskites, X⁻ ions occupy the corner sites of the cube, O²⁻ ions occupy the body-centered site, and Li-ions form octahedra around the oxygen (Fig. 4a).⁶⁰ As noted by Ceder's group, this arrangement of Li ions in a bcc sublattice is optimal for fast ion conduction.⁹⁹ A conductivity of 8.5×10^{-5} S cm⁻¹ (ref. 47) is exhibited by Li₃OCl at room temperature.

The anti-perovskites can be structurally tailored through chemical substitution, either by replacing Cl⁻ with larger Br⁻ or I⁻ anions or by substituting divalent cations for Li, to give rise to an ion conductivity above 10^{-3} S cm⁻¹.^{60,98,100} For example, the mixed halide compound Li₃OCl_{0.5}Br_{0.5} presents an improved conductivity of 1.94×10^{-3} S cm⁻¹, (Fig. 4b).⁴⁷ Cation-substituted $Li_{3-2x}M_xOX$ glassy electrolytes (M = Ca, Mg, or Ba) were prepared by Braga *et al.*,⁶⁰ and an unusually high ion conductivity of 2.5 \times 10⁻² S cm⁻¹ at 25 °C was reported for $Li_{3-2x}Ba_{x}ClO$ (x = 0.005). We note, however, that these results have not yet been reproduced to our knowledge, due to incomplete information on the synthesis. It has also been reported that these materials exhibit low electronic conductivity $(10^{-9}-10^{-7} \text{ S cm}^{-1})$,⁶⁰ an apparently wide electrochemical window (>5 V, 60,98,100 *i.e.*, beyond the oxidation of Cl⁻), good thermal stabilities up to ca. 550 K,^{47,60} and more importantly, stability against Li metal,⁶⁰ but they are highly sensitive to moisture.

The Li⁺ ion transport mechanism in the anti-perovskites is also under intensive debate. Based on DFT calculations, Zhang *et al.*⁹⁸ and Emly *et al.*¹⁰⁰ found that anti-perovskites such as Li₃OCl, Li₃OBr, and their mixed compounds are thermodynamically metastable. A transition at ~150 °C was predicted,



Fig. 3 (a) HAADF-STEM image of a GB exhibiting both dark- and normal-contrast regions, labelled as Type I and Type II, respectively. Within the grains, a row of atomic columns for a La-poor layer and one for a La-rich layer were indicated by green and red arrows on the left-hand side of the image, respectively. The (001) planes of the alternating La-rich/La-poor layers (arbitrarily designated as (001) planes in image) of different regions in the grain were marked to highlight the existence of nanodomains; (b) further magnified Type I GB feature; (c) further magnified Type II GB feature; (d) schematic of the atomic configuration of the Type I GB based on the HAADF-STEM images and EELS analysis, along with an illustration of the Li site distribution across the Type I GB. EELS data of (e) La-M_{4,5}, (f) Li-K, (g) Ti-L_{2,3}, and (h) O-K edges for the Type I GB and the bulk. The spectra were normalized to the integrated intensity of the Ti-L_{2,3} edge. The normalized O-K edge of the bulk was shifted vertically for clarification.⁸⁸ Reproduced with permission from ref. 88. Copyright (2014), the Royal Society of Chemistry.



Fig. 4 (a) Low-barrier migration pathway for a neutral Li split interstitial in Li_3OCl . The barriers range from 145 to 175 meV depending on the charge state of the interstitial (neutral or +1) and host material (Li_3OBr or Li_3OCl).⁴⁷ (b) Arrhenius plots of $log(\sigma T)$ versus 1/T for Li_3OCl and $Li_3OCl_{0.5}Br_{0.5}$ antiperovskites, including E_{ai} .⁴⁷ Reproduced with permission from ref. 47. Copyright (2012) American Chemical Society. (c) Li⁺ diffusion and corresponding lattice dynamics, showing how the lattice adjusts during diffusion from $1 \rightarrow 4$; (d) alternative representation of the crystal structure of Li_3OCl highlighting the formation of a vacancy and three different paths for Li⁺ diffusion upon Ca²⁺-doping; (e) activation energies for different paths in (d), dopants and temperatures calculated by DFT-GGA and the Nudged Elastic Band (NEB) method compared with the experimental values obtained in the solid-like (Arrhenius) regime for $Li_{3-2x0.005}M_{0.005}OCl$ (M = Ca, Mg, Ba).⁶⁰ Reproduced with permission from ref. 60. Copyright (2014), The Royal Society of Chemistry.

which was later deduced to be the glass transition. MD simulations⁹⁸ showed that anti-perovskites with perfect crystal structures are poor Li-ion conductors whereas Li vacancies and structural disorder promote Li-ion diffusion by reducing activation energy barriers. Emly et al.¹⁰⁰ proposed a collective hopmigration mechanism involving Li interstitial dumbbells with a barrier of only 0.17 eV (Fig. 4a), which was approximately 50% lower than that of vacancy driven migration. However, the high ion conductivity of lithium anti-perovskites could not be explained by this mechanism, because of the high formation energy of Li interstitial defects.¹⁰⁰ Later, Mouta et al.¹⁰¹ employed classical atomistic simulation computations to calculate the concentration of Li vacancies and interstitials in Li₃OCl. Vacancies created by Schottky defects were predicted to be the charge carriers in Li₃OCl, since the concentration of interstitials (i.e., Frenkel defects) was 6 orders of magnitude lower due to the very high energy required for their formation. Although the vacancy migration energy (0.30 eV, above room temperature) is larger than that driven by interstitial migration (0.133 eV), the former mechanism likely dominates ion

conduction because of the significantly higher concentration of vacancies. However, in LiCl-deficient materials, the opposite was proposed to be likely true due to charge compensating mechanisms. DFT calculations were also performed to understand the role of aliovalent cation doping. Four snapshots of the Ca-doped structure during Li hopping suggest that the lattice dynamics cause further disorder (Fig. 4c). Doping with higher valent cations, *i.e.*, Ca²⁺, Mg²⁺, Ba²⁺, creates Li vacancies in the cation sublattice and lowers the activation energy for Li ion conduction (Fig. 4d and e).⁶⁰ The deleterious role of resistive grain boundaries on the ion conductivity of polycrystalline Li₃OCl is suggested in a recent theoretical study (namely, the grain boundaries exhibit about one order of magnitude lower conductivity than the bulk).¹⁰²

Recently, Li *et al.*¹⁰³ suggested that the as-prepared "Li₃OX" might be Li₂OHX rather Li₃OX. They reported that replacing some of the OH⁻ by F⁻ was possible. The obtained Li₂(OH)_{0.9}F_{0.1}Cl was claimed to be stable on contact with Li metal with an apparent electrochemical window extending to 9 V *versus* Li⁺/Li.¹⁰³ In addition, Braga *et al.*^{104,105} reported that the existence

of H^+ was beneficial for the formation of an amorphous glassy phase, and a very high ion conductivity of more than 10^{-2} S cm⁻¹ was reported – again the synthesis was not well described, and reproduction of the results is required.

2.1.1.3 NaSICON-type conductors. NaSICON (Na Super Ion CONductors) type electrolytes with the general formula $Na_{1+x}Zr_2Si_{2-x}P_xO_{12}$ ($0 \le x \le 3$) were first reported in 1976 by Goodenough and Hong.^{106,107} They are derived from NaZr₂(PO₄)₃ by partial substitution of Si for P with excess Na to balance the negative charge. Their Li analogues, LiM₂(PO₄)₃ (M = Zr, Ti, Hf, Ge, or Sn),^{108–117} are effectively isostructural.

The NaSICON framework is constituted by a rigid $M_2(PO_4)^{3-}$ skeleton, which is linked by MO_6 octahedra and PO_4 tetrahedra sharing O atoms (Fig. 5a).¹¹⁸ For the $LiM_2(PO_4)_3$ (M = Ti, Ge) series, rhombohedral symmetry ($R\bar{3}c$) was confirmed using X-ray and neutron diffraction,^{112,113} while for compositions

with larger tetravalent cations such as $LiM_2(PO_4)_3$ (M = Zr, Hf, or Sn), a triclinic phase ($C\overline{1}$) of lower symmetry – induced by the displacement of Li ions – was also reported at low temperature.^{114–116} In the rhombohedral phase, two crystallographic sites are possible for Li ions: M_1 (6b) sites, surrounded by six oxygens, and M_2 (18e) sites, which are located between two M_1 positions with 10-fold oxygen coordination. In triclinic phases, the structural distortion drives Li cations to the more stable intermediate M_{12} sites, which are located midway between M_1 and M_2 sites in 4-fold-oxygen coordination.^{115,116}

Among the widely studied LiM₂(PO₄)₃ (M = Zr, Ge, Ti, or Hf) materials, LiTi₂(PO₄)₃ offers the most suitable lattice size for Li ion conduction.¹¹⁹ However, LiTi₂(PO₄)₃ pellets obtained by a conventional sintering process showed very high porosity (34%).¹²⁰ Even the relative densities of hot-pressed ceramics were only ~95%, resulting in a low room temperature conductivity of 2×10^{-7} S cm⁻¹.¹²¹ The partial substitution of Ti⁴⁺



Fig. 5 (a) Unit cell (space group $R\overline{3}c$) of LiTi₂(PO₄)₃. Yellow elongated octahedra (M₁/6b) are occupied by Li⁺; blue octahedra (12c) are occupied by Ti⁴⁺; and green tetrahedra are occupied by P⁵⁺ (18e); O²⁻ is located at the corners of the polyhedra (small red circles, two Wyckoff positions 36f).¹¹⁸ (b) Ion conductivity of NaSICON structured Li ion solid electrolytes.¹³⁴ (c) MEM-reconstructed negative nuclear density maps.⁵² (d) Sections of bond-valence mismatch and negative nuclear densities Li_{1.3}Al_{0.3}Ti_{1.7}(PO₄)₃.⁵² Reproduced with permission from ref. 52, 118, 134. Copyright (2016, 2017) American Chemical Society.

by trivalent cations, such as Al^{3+} , Sc^{3+} , Ga^{3+} , Fe^{3+} , In^{3+} , and Cr^{3+} in $Li_{1+x}R_xTi_{2-x}(PO_4)_3$ materials, improves ion conductivity.¹²²⁻¹³¹ In particular, a high lithium conductivity at room temperature, 7×10^{-4} S cm⁻¹ was reported in the case of $Li_{1.3}R_{0.3}Ti_{1.7}(PO_4)_3$ (R = Al³⁺), abbreviated as LATP.¹²³ Similar effects caused by trivalent cation doping at M sites are also observed in the $LiGe_2(PO_4)_3$ phase and an ion conductivity of 2.4×10^{-4} S cm⁻¹ can be achieved in well-known $Li_{1+x}Al_xGe_{2-x}(PO_4)_3$, abbreviated as $LAGP.^{132}$ The incorporation of trivalent cations influences the conductivity by increasing the concentration of mobile ions in the framework, as well as by invoking additional interstitial migration with lower activation energy.¹³³

Besides the bulk conductivity, the grain boundary conductivity was also augmented by the greater densification of the pellet allowed by R^{3+} substitution. The conductivities of these compositions are shown in Fig. 5b.¹³⁴

In LiTi₂(PO₄)₃, Li ions tend to preferentially occupy the M₁ sites (0, 0, 0) in the space group $R\bar{3}c$,^{113,114} as recently confirmed by single crystal X-ray diffraction analysis.¹¹⁸ A combination of NPD and synchrotron-based high-resolution powder diffraction revealed that the partial replacement of Ti⁴⁺ by Al³⁺ in LATP causes Li ions to occupy an additional interstitial position, a Li₃ site (36f), that is located between two adjacent Li1 sites. Li diffusion preferentially occurs between two adjacent Li positions through this Li₃ site, forming a Li1–Li3–Li1–Li1 zigzag chains in three dimensions (Fig. 5c and d).⁵²

Another effective strategy to improve the conductivity of $LiM_2(PO_4)_3$ is by addition of a second lithium compound such as $Li_2O_1^{119,135}$ $LiNO_3^{136}$ $Li_3PO_4^{,137}$ $Li_4P_2O_7^{,135}$ $Li_3BO_3^{137}$ or LiF_1^{138} which acts as a flux at grain boundaries, generating higher density ceramics with improved conductivities. For example, when 20% Li_2O is incorporated in $LiTi_2(PO_4)_3$, the conductivity can be improved to 5×10^{-4} S cm⁻¹.^{119,135}

Superionic conducting glass-ceramics (lithium–aluminum– titanium–phosphate (LATP) and lithium–aluminum–germanium– phosphate (LAGP)) were first reported by the Ohara company^{139,140} and subsequently by other researchers.^{141–146} An extremely high conductivity of 5.08×10^{-3} S cm⁻¹ at 27 °C, much higher than that of the crystalline analogue, can be obtained by optimizing the heat-treatment conditions.¹⁴⁴ The presence of dielectric phases (Li₂O and AlPO₄) – unavoidable by-products that form during the sintering process of these glass-ceramics which mainly segregate at the grain boundary – have been detected and identified.^{141–144,146} AlPO₄ could either block or increase the conductivity, depending on its concentration and crystallite size.¹⁴⁵

2.1.1.4 Garnet type conductors. Ideal garnets have the general formula $A_3B_2M_3O_{12}$ (A = Ca²⁺, Mg²⁺, or Fe²⁺; B = Al³⁺, Cr³⁺, Fe³⁺, or Ga³⁺; M = Si⁴⁺ or Ge⁴⁺) and crystallize in the space group *Ia*3*d*, in which A, B, and M are filled with eight-, six-, and four-coordinated cation sites in a 3:2:3 ratio, respectively. Li garnets of the general formula Li₃Ln₃Te₂O₁₂ (Ln = Y³⁺, Pr³⁺, Nd³⁺, or Sm³⁺-Lu³⁺) follow this stoichiometry, with Ln and Te occupying the eight- and six-coordinated sites, respectively, and Li fully occupying tetrahedral sites (24d). Li-ion conducting

garnets attracted significant interest after the first report of $\text{Li}_5\text{La}_3\text{M}_2\text{O}_{12}$ (M = Nb or Ta) by Thangadurai *et al.*,¹⁴⁷ in which an ion conductivity of ~ 10⁻⁶ S cm⁻¹ was achieved at 25 °C. The Ta members were reported to be surprisingly chemically stable to reaction with molten Li or moisture, and a wide electrochemical window was reported.¹⁴⁷ Subsequently, the conductivity of $\text{Li}_5\text{La}_3\text{Nb}_2\text{O}_{12}$ was optimized by partial substitution of La^{3+} by K⁺ (ref. 148) and partial substitution of Nb⁵⁺ with either In³⁺ (ref. 148) or Y³⁺.¹⁴⁹ As the tetrahedral M site can not accommodate all five Li cations, excess Li cations occupy the six-coordinate sites (the octahedral or trigonal prismatic sites), which are empty in the original garnet structure. Garnets containing five to seven Li atoms per formula unit are referred to as Li-stuffed, or Li-rich garnets.

Thangadurai *et al.* demonstrated that partial substitution at the La site by divalent alkaline earth ions generates a new class of garnet-like structures, $Li_6ALa_2M_2O_{12}$ (A = Ca²⁺, Sr²⁺, or Ba²⁺; M = Nb⁵⁺ or Ta⁵⁺),^{150,151} among which $Li_6BaLa_2Ta_2O_{12}$ exhibited the highest conductivity of 4×10^{-5} S cm⁻¹ at 22 °C and the lowest activation energy of 0.4 eV.¹⁵¹ Aside from the niobate/ tantalate garnets mentioned above, antimony-containing garnets $Li_5Ln_3Sb_2O_{12}$ (Ln = La, Pr, Nd, or Sm). were also investigated.^{152,153} Moreover, M can be replaced by tetravalent cations to generate Li-rich garnets such as $Li_7La_3M_2O_{12}$ (M = Zr, Sn, or Hf).¹⁵⁴⁻¹⁵⁷

Within the garnet family, cubic Li₇La₃Zr₂O₁₂ (LLZO), first reported by Murugan et al.,¹⁵⁴ is considered the most attractive candidate for solid electrolytes owing to its high room temperature conductivity ($>10^{-4}$ S cm⁻¹), high chemical stability against Li, and a wide electrochemical potential window. It is moisture-sensitive, however. In cubic LLZO (space group: $Ia\bar{3}d$), Li ions are disordered over the tetrahedral 24d Li(1), octahedral 48g and 96h Li(2) sites (Fig. 6a).¹⁵⁸ LLZO also exists in a more thermodynamically stable tetragonal phase $(I4_1/acd)$. It exhibits a conductivity that is one to two orders of magnitude lower than that of the cubic phase because of the fully ordered arrangement of Li ions at the tetrahedral 8a sites and octahedral 16f and 32g sites.¹⁵⁹ Therefore, major efforts have been focused on using substitution strategies to stabilize the highly conductive cubic phase through a reduction in Li content and/or an increase in the Li vacancy concentration. The substituent Al³⁺ either intentionally added or unintentionally introduced from alumina crucibles - was first found to be effective. 49,160-163 Stabilization originates from the increased Li sublattice disorder owing to Li vacancies created via aliovalent substitution of Li⁺ by Al³⁺.¹⁶⁴ However, the site preference (the 24d tetrahedral or 48g/96h octahedral Li sites) for Al3+ ions in the framework remains ambiguous.^{49,160-163,165,166} Düvel et al.⁴⁹ found that with an increase in Al content (above 0.2-0.24 moles per LLZO formula unit), Al³⁺ ions occupy non-Li cation sites. The addition of Al³⁺ or Si⁴⁺ aids the sintering process, leading to a densification of the obtained ceramics and an improvement in the Li ion conductivity (6.8 \times 10⁻⁴ S cm⁻¹).^{167,168} This was attributed to an effective reduction of grain boundary resistance through the formation of nano-crystalline LiAlSiO₄ in the grain boundaries.168



Fig. 6 (a) Crystal structure of cubic-type LLZO ($la\bar{3}d$), and Li environment. The center of the tetrahedral Li₁ sites are the 24d sites, and the center of the octahedral Li₂ sites are the 48g sites. Meanwhile, positions slightly displaced from the 48g sites and near the face (but still inside the Li₂ octahedron) are the 96h sites.¹⁵⁸ (b) Conductivities of doped LLZO.^{147–151,154,156,157,168,169,171,175–178,181,183–186} (c) Snapshots of Li ions' mobility from the MD simulation and enlarged view of the selected Li atoms showing the tetrahedral edge pass according to the trajectory cloud.¹⁵⁸ (d) Anisotropic harmonic lithium vibrations in c-⁷Li₇La₃Zr₂O₁₂ shown as green thermal ellipsoids obtained from Rietveld analysis of room-temperature neutron diffraction data.¹⁹⁷ (e) Nuclear distribution of lithium calculated by MEM from neutron powder diffraction data obtained at 600 °C; three-dimensional ⁷Li nuclear-density data shown as blue contours (equivalue 0.15 fm Å⁻³ of the negative portion of the coherent nuclear scattering density distribution). The green octahedra represent ZrO₆ and the purple dodecahedra represent LaO₈ units.¹⁹⁷ Reproduced with permission from ref. 197. Copyright (2012), The Royal Society of Chemistry. (f) The distribution of lithium calculated by MEM from neutron powder diffraction data obtained at 400 and 600 °C, respectively, and three-dimensional Li nuclear-density data shown as blue contours (equivalue 0.15 fm Å⁻³ of the negative portion of the negative portion of the coherent nuclear scattering density distribution).¹⁹⁷ (g) ⁶Li–⁶Li exchange spectra of Li_{7-2x-3y}Al_yLa₃Zr_{2-x}W_xO₁₂ (x = 0.5) sintered at 1150 °C for 12 h.¹⁷⁹ Reproduced with permission from ref. 158, 179. Copyright (2013, 2015) American Chemical Society.

The aliovalent substitution of Li^+ by Ga^{3+} (ref. 169–172) has the same stabilizing effect. By sintering the ceramic in a dry O₂ atmosphere, an optimum conductivity of 1.3×10^{-3} S cm⁻¹ (ref. 171) at 24 $^{\circ}$ C was achieved, although the Ga³⁺ distribution in the LLZO lattice was difficult to determine.^{171,173,174} Other supervalent dopants for Zr⁴⁺ sites (Sb⁵⁺, Nb⁵⁺, Ta⁵⁺, Te⁶⁺, and W⁶⁺ (ref. 175-179)) have also been employed, resulting in some remarkable improvements in conductivity. The highest conductivities of ca. 1.0 \times 10 $^{-3}$ S cm $^{-1}$ at room temperature were achieved for Ta-doping,¹⁷⁷ and Te-doping.¹⁷⁸ Lower conductivity was reported for simultaneous substitution of Al at Li⁺ site, Y³⁺, Ba²⁺ at La³⁺ site, and/or Ta⁵⁺, Sb⁵⁺, Te⁶⁺ at Zr⁴⁺ sites, however.^{180–182} The conductivities of these compounds and other garnet oxides are listed in Table 1 and Fig. 6b. 147-151,154,156,157,168,169,171,175-178,181,183-186 While it was believed that "accidental" $\mathrm{Al}^{\mathrm{3+}}$ substitution on the $\mathrm{Li^{+}}$ site from crucible contamination was actually responsible for stabilizing the cubic phase in many cases, 163,187 recently it was confirmed that Ta-substituted cubic LLZO exhibits high ion conductivity in the absence of any Al³⁺.^{188,189} Approximately 0.4–0.5 Li vacancies per formula unit are required to stabilize the cubic polymorph of LLZO.188,189

Many X-ray and neutron diffraction studies have been geared towards determining the crystal structure and the Li environment in garnet type electrolytes. However, the phase stability and the ion transport mechanism are still controversial,^{190–192} due to

the limitations of these techniques in determining the exact Li occupancy on the tetrahedral and octahedral sites. Using neutron diffraction, Cussen *et al.*¹⁹³ confirmed that Li₅La₃M₂O₁₂ (M = Nb or Ta) crystallized in the $Ia\bar{3}d$ space group with Li distributed over the tetrahedral and distorted octahedral sites. They also investigated the relationship between ion conductivity and Li site occupation in Li₃Ln₃Te₂O₁₂ (Ln = Y, Pr, Nd, or Sm-Lu).¹⁸⁶ Li ions were found to exclusively occupy the tetrahedral (24d) sites. Given that Li₃Nd₃Te₂O₁₂ exhibits a extremely low conductivity ($\sim 10^{-5}$ S cm⁻¹ at 600 °C) and very high activation energy (1.22 eV), it was deduced that the Li ions at the tetrahedral sites play no direct role in facile ion mobility. Later, the exact location and dynamics of Li ions in Li₅La₃Nb₂O₁₂ were investigated using solid-state nuclear magnetic resonance (NMR).¹⁹⁴ Indeed, the octahedrally coordinated Li cations were revealed to be the only mobile species. Neutron diffraction studies were also performed on $Li_{5+x}Ba_xLa_{3-x}Ta_2O_{12}$ (0 < x < 1.6) by Cussen et al.¹⁹⁵ They found that as the Li content increases, the tetrahedral site occupancy is reduced whereas the fraction of Li in octahedral site increases. This results in a shift in the Li environment from primarily tetrahedral (at x = 0) to octahedral (at x = 1.6). Since the tetrahedra and octahedra are connected by a shared face, simultaneous occupation of adjacent polyhedral sites inevitably leads to reduced Li-Li distances and displacement of Li away from the shared faces. The electrostatic

Table 1 Conductivity and activation energy of damet-type electrolytes	Table 1	Conductivity and activation energy	erav of garr	net-type electrolytes ¹⁴	4/-151,154,156,15/,	168,169,1/1,1/5	-1/8,181,183	-186
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Composition	Conductivity (S cm ⁻¹)	Temperature (°C)	$E_{\rm a}$ (eV)	Ref.
$Li_3Nd_3Te_2O_{12}$ (850 °C)	$1 imes 10^{-5}$	600	1.22	186
$Li_5La_3Nb_2O_{12}$ (950 °C)	$1 imes 10^{-5}$	22	0.43	147
$Li_5La_3Ta_2O_{12}$ (950 °C)	$1.2 imes 10^{-6}$	25	0.56	147
Li _{5.5} La _{2.75} K _{0.25} Nb ₂ O ₁₂ (950 °C)	$6.0 imes10^{-5}$	50	0.49	148
Li _{5.5} La ₃ Nb _{1.75} In _{0.25} O ₁₂ (950 °C)	$1.8 imes 10^{-4}$	50	0.51	148
Li _{6.5} La ₃ Nb _{1.25} Y _{0.75} O ₁₂ (1000 °C)	10^{-4}	24	—	149
$Li_6La_3Nb_{1.5}Y_{0.5}O_{12}$ (1000 °C)	10^{-4}	24	—	149
$Li_6CaLa_2Nb_2O_{12}$ (900 °C)	$1.6 imes 10^{-6}$	22	0.55	150
$Li_6SrLa_2Nb_2O_{12}$ (900 °C)	4.2×10^{-6}	22	0.5	150
$Li_6BaLa_2Nb_2O_{12}$ (900 °C)	$6.0 imes10^{-6}$	22	0.44	150
$Li_6SrLa_2Ta_2O_{12}$ (900 °C)	7.0×10^{-6}	22	0.5	151
$Li_6BaLa_2Ta_2O_{12}$ (900 °C)	$4 imes 10^{-5}$	22	0.40	151
$Li_7La_3Zr_2O_{12}$ (1230 °C, cubic)	$3.0 imes10^{-4}$	25	0.31	154
Li ₇ La ₃ Zr ₂ O ₁₂ (980 °C, tetragonal)	1.63×10^{-6}	27	0.54	159
Li ₇ La ₃ Sn ₂ O ₁₂ (900 °C, tetragonal)	$2.6 imes 10^{-8}$	85	0.79	156
Li ₇ La ₃ Hf ₂ O ₁₂ (1000 °C, tetragonal)	$3.17 imes10^{-7}$	27	0.53	157
Li ₇ La ₃ Zr ₂ O ₁₂ (1.7 wt% Al, 0.1 wt% Si, 1125 °C)	$6.8 imes10^{-4}$	25	—	168
$Li_7La_3Zr_{1.89}Al_{0.15}O_{12}$ (1150 °C)	$3.4 imes 10^{-4}$	25	0.33	183
Li _{7.06} La ₃ Y _{0.06} Zr _{1.94} O ₁₂ (1200 °C)	$8.1 imes 10^{-4}$	25	0.26	184
$Li_{6.25}La_3Zr_2Ga_{0.25}O_{12}$	$3.5 imes10^{-4}$	RT	—	169
$Li_{6.55}La_3Zr_2Ga_{0.15}O_{12}$ (1085 °C, O_2)	$1.3 imes 10^{-3}$	24	0.30	171
$Li_{6.4}La_3Zr_2Ga_{0.2}O_{12}$ (1085 °C)	$9.0 imes10^{-4}$	24	—	171
$Li_{6.8}La_3Zr_{1.8}Sb_{0.2}O_{12}$ (1100 °C)	5.9×10^{-5}	30	0.39	175
$Li_{6.6}La_3Zr_{1.6}Sb_{0.4}O_{12}$ (1100 °C)	$7.7 imes10^{-4}$	30	0.34	175
$Li_{6.4}La_3Zr_{1.4}Sb_{0.6}O_{12}$ (1100 °C)	$6.6 imes10^{-4}$	30	0.36	175
$Li_{6.2}La_3Zr_{1.2}Sb_{0.8}O_{12}$ (1100 °C)	$4.5 imes10^{-4}$	30	0.37	175
$Li_6La_3ZrSbO_{12}$ (1100 °C)	$2.6 imes10^{-4}$	30	0.38	175
$Li_{6.75}La_3Zr_{1.75}Nb_{0.25}O_{12}$ (1200 °C)	$8.0 imes10^{-4}$	25	0.31	176
$Li_{6.8}La_3Zr_{1.8}Ta_{0.2}O_{12}$ (1230 °C)	$2.8 imes 10^{-4}$	25	—	177
$Li_{6.6}La_3Zr_{1.6}Ta_{0.4}O_{12}$ (1230 °C)	$7.3 imes10^{-4}$	25	—	177
$Li_{6.5}La_3Zr_{1.5}Ta_{0.5}O_{12}$ (1230 °C)	$9.2 imes 10^{-4}$	25	—	177
$Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$ (1230 °C)	1.0×10^{-3}	25	0.35	177
$Li_{6.2}La_3Zr_{1.2}Ta_{0.8}O_{12}$ (1230 °C)	$3.2 imes 10^{-4}$	25	—	177
$Li_6La_3ZrTaO_{12}$ (1230 °C)	1.6×10^{-4}	25	—	177
$Li_{6.7}La_3Zr_{1.7}Ta_{0.3}O_{12}$ (900 °C)	$6.9 imes10^{-4}$	25	0.36	177
$Li_{6.75}La_3Zr_{1.75}Ta_{0.25}O_{12}$ (1000 °C)	8.7×10^{-4}	25	0.22	185
Li _{6.5} La ₃ Zr _{1.75} Te _{0.25} O ₁₂ (1100 °C)	$1.02 imes10^{-3}$	30	0.39	178
$Li_{6.15}La_3Zr_{1.75}Ta_{0.25}Al_{0.2}O_{12}$ (1000 °C)	$3.7 imes 10^{-4}$	25	0.30	185
$Li_{6.15}La_3Zr_{1.75}Ta_{0.25}Ga_{0.2}O_{12}$ (1000 °C)	$4.1 imes 10^{-4}$	25	0.27	185
$Li_{6.6}La_{2.875}Y_{0.125}Zr_{1.6}Ta_{0.4}O_{12}$ (1200 °C)	$3.17 imes10^{-4}$	27	0.35	181
$Li_{6.6}La_{2.75}Y_{0.25}Zr_{1.6}Ta_{0.4}O_{12}$ (1200 °C)	$4.36 imes10^{-4}$	27	0.34	181
$Li_{6.6}La_{2.5}Y_{0.5}Zr_{1.6}Ta_{0.4}O_{12}$ (1200 °C)	2.26×10^{-4}	27	0.39	181

repulsion associated with this arrangement leads to the high mobility of Li⁺ in these materials.

Several simulations combined with experiments have been performed to explore the Li ion diffusion mechanism. Using the nudged elastic band (NEB) method, Xu et al. found that in the Li-stuffed garnet, $\mathrm{Li}^{\scriptscriptstyle +}$ ions can migrate between tetrahedral and octahedral sites,¹⁹⁶ although only limited insights can be gained from NEB since it reflects the local migration behavior. On the other hand, MD simulations evaluate the Li ion hopping events, and quantitatively assess the collective migration behavior. As shown in Fig. 6b, MD simulations indicate a concerted migration mechanism in cubic LLZO, indicative of a complex cooperative mechanism.¹⁵⁸ The Li diffusion pathways in LLZO and the evolution of Li motion with temperature were also investigated by high-temperature neutron diffraction techniques combined with the maximum-entropy method (MEM).¹⁹⁷ Temperature-driven dynamic Li-ion displacements exhibited a 3D diffusion pathway constituted by an interlocking network of 24d-96h-48g-96h-24d site segments (Fig. 6d-f), indicating that Li ions diffuse through the tetrahedral 24d sites, consistent with

the results of Xu *et al.*¹⁹⁶ NMR results¹⁷⁹ also show evidence of ion exchange between the 24d and 96h sites (Fig. 6g) and the bulk conductivity is found to be limited by the Li mobility at the 24d sites.

2.1.2 Sulfide based lithium ion conductors

2.1.2.1 Thio-LiSICONs. Thio-LiSICONs were first developed by Kanno *et al.*^{42,61} by replacing oxide ions in LiSICON with larger and more polarizable S^{2-} anions. The high polarizability of S^{2-} weakens interactions of Li⁺ with the anionic sub-lattice, leading to higher Li-ion conductivity in sulfides than in their oxide analogues. Sulfide electrolytes are also highly ductile and exhibit a lower grain boundary resistance than oxides. As a consequence, excellent contact with electrode materials can be realized by simple cold-pressing, making the fabrication of bulk solid-state batteries more convenient.^{198,199}

The thio-LiSICON family contains a very wide range of solid solutions with the general formula $\text{Li}_x M_{1-y} M'_y S_4$ (M = Si or Ge; M' = P, Al, Zn, Ga, or Sb), that exhibit ion conductivities ranging from 10^{-7} – 10^{-3} S cm⁻¹,^{61,200,201} amongst which $\text{Li}_{4-x} \text{Ge}_{1-x} P_x S_4$ exhibits the highest conductivity (2.2 × 10^{-3} S cm⁻¹).⁴²

Composition	Conductivity (S cm ⁻¹)	Temperature (°C)	Ref.
Li ₄ GeS ₄	$2.0 imes10^{-7}$	25	61
Li _{3.9} Zn _{0.05} GeS ₄	$3.0 imes10^{-7}$	25	61
Li _{4.275} Ge _{0.61} Ga _{0.25} S ₄	6.5×10^{-5}	25	61
Li _{3.25} Ge _{0.25} P _{0.75} S ₄	$2.2 imes 10^{-3}$	25	42
$Li_{3.4}Si_{0.4}P_{0.6}S_4$	6.4×10^{-4}	25	200
$Li_{4.8}Si_{0.2}Al_{0.8}S_4$	2.3×10^{-7}	25	200
$Li_{2.2}Zn_{0.1}Zr_{0.9}S_3$	$1.2 imes 10^{-4}$	30	202
γ -Li ₃ PS ₄ (crystal)	3.0×10^{-7}	25	203
β -Li ₃ PS ₄ (nanoporous)	$1.6 imes 10^{-4}$	25	201
Li ₂ SiS ₃	$2.0 imes10^{-6}$	25	204
Li ₄ SiS ₄	$5.0 imes10^{-8}$	25	204
$Li_6P_2S_4$	1.6×10^{-10}	25	207
$Li_7P_3S_{11}$	$3.2 imes 10^{-3}$	25	205
Li ₄ SnS ₄	$7.0 imes10^{-5}$	20	206
$Li_{10}GeP_2S_{12}$	$1.2 imes 10^{-2}$	27	45
$Li_{10}SnP_2S_{12}$	$4.0 imes10^{-3}$	27	63
$Li_{10}SiP_2S_{12}$	$2.3 imes 10^{-3}$	27	208
$Li_{10}Ge_{0.95}Si_{0.05}P_2S_{12}$	$8.6 imes 10^{-3}$	25	209
${\rm Li}_{9.54}{\rm Si}_{1.74}{\rm P}_{1.44}{\rm S}_{11.7}{\rm Cl}_{0.3}$	$2.5 imes10^{-2}$	25	46

The conductivities of thio-LiSICON electrolytes and other typical crystalline sulfides such as Li_3PS_4 , Li_4SiS_4 , Li_4SnS_4 , Li_2SiS_3 , $Li_4P_2S_6$ as well as meta-stable $Li_7P_3S_{11}$ are listed in Table 2.^{46,201-209} The role of the different structural building units ($P_2S_7^{4-}$ or PS_4^{3-}) in the conductivity of glass and crystal-line lithium thiophosphates (LPS) phases has recently been clarified by monitoring *in situ* crystallization and phase evolution in this class of material.^{210,211} Glasses with only *ortho*-thiophosphate units show the highest lithium ion conductivity, the lowest activation energy and favorable thermal resistance towards decomposition, while glasses in which the major PS_4^{3-} building units are linked by P–S–P bonds cleave at elevated temperatures to form sulfur and $Li_4P_2S_6$, thereby losing their contribution to lithium ion conduction.

2.1.2.2 The LGPS family. In 2011, Kanno's group discovered a new sulfide - Li₁₀GeP₂S₁₂ (LGPS) - that exhibits an extremely high conductivity of 1.2×10^{-2} S cm⁻¹,⁴⁵ which is comparable to or higher than that of liquid organic electrolytes currently used in commercially available Li-ion batteries. Unfortunately, Li₁₀GeP₂S₁₂ shows a limited electrochemical window,²¹² and poor interfacial stability against Li metal.²¹³ In addition, the low abundance and high cost of Ge restricts its application in batteries. Substitutions of Ge4+ with Si4+ or Sn4+ (ref. 63, 208, 209, 214 and 215) generate $Li_{10}MP_2S_{12}$ (M = Si⁴⁺, Sn⁴⁺) (either experimentally (Sn⁴⁺) or theoretically (Si)) and $Li_{10+\delta}M_{1+\delta}P_{2-\delta}S_{12}$ $(M = Si^{4+}, Sn^{4+})^{216}$ with high ion conductivity, which varied as a function of M, with the Si and Sn systems showing lower conductivity than Ge. While the substitution with smaller Si⁴⁺ leads to a lower conductivity due to narrower diffusion pathways, the structural reasons behind the reduction in conductivity upon moving from Ge4+ to larger Sn4+ were not well understood. The structure-property relationships governing this behavior was employed by Zeier's group²¹⁷ employing a combination of speed of sound measurements and electrochemical impedance spectroscopy (EIS). It was shown that increasing the Sn⁴⁺ fraction

in Li₁₀Ge_{1-x}Sn_xP₂S₁₂ leads to a more tight structural bottleneck along the diffusion channels in the z-direction, and concurrent increase in the lattice softness, which causes stronger local ionic bonding interactions between Li⁺ and S²⁻, and therefore an increased activation barrier.²¹⁷ A different composition, Li₁₁Si₂PS₁₂, shows a conductivity of 2×10^{-2} S cm⁻¹ at room temperature as inferred from NMR diffusivity data. This represents a very high value for solid Li ion conductors; however the phase can only be accessed under pressure.²¹⁵

The tetragonal structure of LGPS (space group P42/nmc (137)) in Kanno's report⁴⁵ was determined from powder diffraction and Rietveld refinement. The reported framework is composed of GeS_4/PS_4 tetrahedra, LiS_4 tetrahedra and LiS_6 octahedra. The tetrahedrally coordinated Li1 (16h) and Li3 (8f) sites form a 1D tetrahedral chain along the *c*-axis while the octahedrally coordinated Li2 position between these chains was assumed to be inactive for ion conduction.⁴⁵ MD simulation performed by Mo *et al.*¹¹ supported this highly anisotropic diffusivity in the LGPS structure. Careful examination of the isosurface from long MD simulation by Adams et al.²¹⁸ suggested the existence of an additional site at (0, 0, 0.22) (marked as Li4, Fig. 7a and b). Single crystal structure analysis identified a similar Li4 site at (0, 0, 0.251(2)) with an occupancy of 0.81(7) and rather large anisotropic displacement parameters similar to the Li1 and Li3 positions.²¹⁹ The thermal ellipsoid of the Li4 site is aligned perpendicular to the c-axis, and provides an extra diffusion pathway connecting the channels along the c-axis formed by Li1 and Li3.²¹⁹ A recent neutron diffraction study combined with nuclear density maps verified the quasi-isotropic lithium diffusion in LGPS and three most prominent pathways for lithium transport, namely, along the (001) direction (Li3–[Li1–Li1]–Li3) and along (110) (*i.e.*, at z = 0, 1/4, 1/2, 3/4; Li4–[Li1–Li1]–Li4 and Li3-[Li2-Li2]-Li3, Fig. 7c and d) are identified.²²⁰ This reconciles the theoretical findings by Adams et al., namely the hops between the Li3 and Li2 pathways along the $\langle 110\rangle$ direction significantly contribute to the overall conductivity (Fig. 7f), along with the previously identified lithium migration channels along the $\langle 001 \rangle$ direction (Fig. 7e).²¹⁸ Their calculations also suggested increasing occupancy in the Li4 site with increasing temperature (Fig. 7g) and its role in connecting Li4-Li1 thus enabling a 3D network for Li ion migration.²¹⁸

Very recently, a remarkably high conductivity $(2.5 \times 10^{-2} \text{ S cm}^{-1}$ at 25 °C) was reported again by Kanno's group⁴⁶ for a new sulfide material, Li_{9.54}Si_{1.74}P_{1.44}S_{11.7}Cl_{0.3} (Fig. 8a and b) whose structure is related to LGPS. This is the highest value reported to date for Li ion conductors. The anisotropic thermal displacement and nuclear density distribution of Li suggest a three-dimensional (3D) migration pathway (Fig. 8c), in agreement with previous studies.²²⁰ Another LGPS-related composition, Li_{9.6}P₃S₁₂,⁴⁶ exhibits a lower conductivity ($1.2 \times 10^{-3} \text{ S cm}^{-1}$ at 25 °C), but was claimed to be stable in a window of 0–5 V. Both new compositions were not prepared in a phase-pure state, however, and contain significant fractions of other ion-conductive phases. Nonetheless, all-solid-state batteries using these new materials set a record in demonstrating high specific power and long cycle life.⁴⁶



Fig. 7 (a and b) Unit cell of tetragonal $Li_{10}GeP_2S_{12}$ with thermal ellipsoids (p = 0.8);²¹⁹ Reproduced with permission from ref. 219. Copyright (2013) the Royal Society of Chemistry. (c) MEM reconstructed negative nuclear density maps in $Li_10GeP_2S_{12}$ (surface threshold -0.015 fm Å⁻³, cell grid 256 × 256 × 512) and slices in (c) (011) and (d) (001) planes, respectively; (d) shows the diffusion tunnels within $Li_{10}GeP_2S_{12}$ along the (001) direction, whereas the Li distribution along (110) can be seen in (d);²²⁰ Reproduced with permission from ref. 220. Copyright (2016) American Chemical Society. (e and f) Li distribution from a 10 ns *NVT* MD simulation of a 3 × 3 × 2 supercell at T = 300 K projected into a single unit cell (shown (e) along [100] and (f) along [001]). Regions of highest Li density (darkest isosurface) coincide with the 4 Li sites, the easiest path for transport (lighter isosurface) corresponds to the Li(3)–Li(1) channels along [001]. The lightest isosurface reveals a significant probability for hops Li(3)–Li(2) establishing a 3D network of pathways. With a lower probability, Li(4) sites are attached to this pathway network (not shown);²¹⁸ (g) temperature dependence of Li distribution on the four Li sites identified by MD simulations (filled symbols). The corresponding open symbols refer to the neutron refinements by Kanno's group,⁴⁵ who distributed the 20 Li per unit cell onto Li(1), Li(2) and Li(3) sites only.²¹⁸ Reproduced with permission from ref. 218. Copyright (2012) the Royal Society of Chemistry.

2.1.2.3 Argyrodite type. The addition of halides to thiophosphates can increase the conductivity of quasi-binary or quasi-ternary systems. Outstanding examples are the halogen-substituted argyrodites Li₆PS₅X (X = Cl, Br, I).⁶² The "parent" argyrodite of Li₇PS₆ crystallizes both in a cubic high temperature (HT) phase and an orthorhombic low temperature phase. The partial substitution of sulfur by halogen anions can stabilize the cubic HT phase at room temperature^{221,222} and results in a good conductivity of ~10⁻³ S cm⁻¹.²²³

Fig. 9a shows the unit cell of $\text{Li}_6\text{PS}_5\text{X}$. The framework of the lattice is built-up by $\text{PS}_4^{3^-}$ anions that are centered at the 4b sites, with the remaining sulfur occupying the 4a and 4c sites.²²⁴ Upon substitution of sulfur with halogens, sulfur constituting the PS_4 groups are not replaced but instead, halogens occupy the 4a or 4c sites. The Li⁺ ions are located at the 48h and 24g Wyckoff sites, with the 24g sites acting as the transition state between hops from 48h to 48h. Twelve 48h sites surround each 4c site, and form a cagelike structure depicted in Fig. 9b.²²⁴ Li diffusion occurs through three different jump processes: the 48h–24g–48h, which is termed a doublet jump; and the 48h–48h jumps within the cage, and between cages, which are deemed the intracage and intercage jump, respectively.^{222,224} MD simulations show that the low jump rate of intracage jumps limit the macroscopic diffusion, as shown in the trajectory and jump events in Fig. 9c and d.²²² With the replacement of sulfur by a halogen, Li vacancies are introduced *via* charge compensation. The halogen distribution determines the distribution of Li vacancies and thus the local Li ion diffusivity. I⁻ ions only occupy the 4a site, whereas Cl⁻ (or Br⁻) show disorder over the 4a sites (inside the cage) and 4c sites (outside the cage). The disorder of halogen ions over the 4a and 4c site was confirmed responsible for the high conductivity in Li₆PS₅Cl and Li₆PS₅Br; in contrast the I⁻ derivative lacks disorder and hence the conductivity is orders of magnitude lower.²²² The effect of an increase of Li⁺ concentration and the lattice parameters on the ion conductivity was demonstrated by substitution of P⁵⁺ with Si⁴⁺, showing that the conductivity can be improved to 2×10^{-3} S cm^{-1.225}

2.1.2.4 Other new thiophosphates. A few new Li-ion thiophosphate conductors have been recently reported that are not strictly related to the above. One is the very simple compound $\text{Li}_4\text{PS}_4\text{I}$, discovered utilizing a solvent-based synthesis approach. It exhibits a new structure and a room temperature ion conductivity of about 10^{-4} S cm⁻¹.²²⁶ Previously identified as $\text{Li}_7\text{P}_2\text{S}_8\text{I}$, the structure is distantly related to the argryodites, and comprises Li ions and isolated PS_4^{-3-} tetrahedra arranged in layers perpendicular to the *c*-axis that are held apart by I⁻ ions.



Fig. 8 (a) Arrhenius conductivity plots for the LGPS family, $\text{Li}_{9.6}\text{P}_3\text{S}_{12}$ and $\text{Li}_{9.54}\text{Si}_{1.74}\text{P}_{1.44}\text{S}_{11.7}\text{Cl}_{0.3}$. (b) Crystal structure of $\text{Li}_{9.54}\text{Si}_{1.74}\text{P}_{1.44}\text{S}_{11.7}\text{Cl}_{0.3}$. The thermal ellipsoids are drawn with a 50% probability. The framework structure consists of 1D polyhedral chains (edge-sharing M(4d)X₄ and Li(4d)X₆) connected by P(2b)X₄ tetrahedra. Lithium is located on the 16h, 8f and 4c sites. (c) Nuclear distribution of Li atoms in $\text{Li}_{9.54}\text{Si}_{1.74}\text{P}_{1.44}\text{S}_{11.7}\text{Cl}_{0.3}$ at 25 °C, calculated using the maximum entropy method at the iso-surface level of -0.06 fm Å^{-3.46} Reproduced with permission from ref. 46. Copyright (2016), Springer Nature.

Recent calculations give hope that an even higher conductivity $> 10^{-2}$ S cm⁻¹ may be achieved.²²⁷ The first experimental elucidation of fast lithium ion conductors in the Li_{1+2x}Zn_{1-x}PS₄ (LZPS; x < 0.5) solid solution whose existence (and conductivity) had only been predicted by theory²²⁸ has also been recently reported.²²⁹ The presence of excess interstitial Li ions in the structure - resulting from the partial substitution of Zn in the parent phase, LiZnPS₄ - was identified by combined neutron and synchrotron X-ray powder diffraction studies and correlated with ion conductivity upon increasing the Li/Zn ratio. While the ion conductivity of the parent phase was found to be higher than predicted by theory, conductivities of the solid solution series as high as 1.3×10^{-4} S cm⁻¹, were still two orders of magnitude lower than computation suggested. This was ascribed to the fact that although substoichiometric phases close to those targeted were successfully synthesized, all "defect compositions" were in fact highly metastable. As a result, amorphous and potentially less conductive materials formed as side-products in the grain boundaries may have precluded realization of the true crystalline conductivity.

2.1.2.5 Layered sulfides. A series of fast-conducting sulfide solid electrolytes have recently been identified in the solid solution system $\text{Li}_{3x}[\text{Li}_x\text{Sn}_{1-x}\text{S}_2]$. The Li-rich prototype with x = 0.33, $\text{Li}_2\text{Sn}\text{S}_3$, crystallizes in the layered Na₂IrO₃ structure type (space group C2/c), where Li is distributed both in and between Li/Sn-ordered honeycomb sulfide layers according

to Li[Li_{0.33}Sn_{0.67}S₂].²³⁰ Brant *et al.* reported Li₂SnS₃ to be a fast Li ion conductor with a room temperature conductivity of 1.5×10^{-5} S cm⁻¹ and a conductivity of 1.6×10^{-3} S cm⁻¹ at 100 °C.²³¹ In the Li-depleted version, Li₂Sn₂S₅ – with a Li distribution corresponding to $Li_{0.6}[Li_{0.2}Sn_{0.8}S_2]$ (x = 0.2) – only 60% of the interlayer gallery Li sites are occupied, thus giving rise to more facile Li diffusion in the *ab*-plane as compared to Li₂SnS₃.²³² In addition, the Li diffusion pathway in Li₂Sn₂S₅ involves hops between face-sharing octahedral (O) and tetrahedral (T) Li sites (O-T-O), rather than pure O-O trajectories as in Li₂SnS₃. This pathway is expected to reduce the activation energy for Li diffusion (0.17 eV for Li₂Sn₂S₅ as measured by ⁷Li T₁ relaxation time measurements vs. 0.59 eV for Li₂SnS₃, determined from impedance spectroscopy). Indeed, Li⁺ diffusivities on the order of 10^{-7} cm² s⁻¹ were obtained for Li₂Sn₂S₅ by pulsed field gradient (PFG) NMR, corresponding to a bulk conductivity of $\sigma_{\rm NMR}$ = 9.3 × 10⁻³ S cm⁻¹. Polarization measurements and impedance spectroscopy reveal a grain boundary limited conductivity of 1.2 \times $10^{-4}~S~cm^{-1}$ and a bulk conductivity that was extrapolated to be two orders of magnitude larger (1.5 \times 10⁻² S cm⁻¹), in agreement with the PFG NMR measurements.

3. Sodium ion conductors

Sodium-ion batteries (NIBs) have been extensively studied in recent years as candidates for large-scale energy storage,



Fig. 9 (a) Crystal structures of $\text{Li}_6\text{PS}_5\text{X}$ with X = Cl, Br, I. In the ordered structure, X-anions form a cubic close-packed lattice with PS_4^{3-} tetrahedra in the octahedral sites and the free S²⁻ (Wyckoff 4c) in half of the tetrahedral holes.²²⁴ (b) The free S²⁻ anions and the corner of the PS_4^{3-} tetrahedra form Frank–Kasper polyhedra, which enclose two different Li positions. The Li positions form localized cages in which multiple jump processes are possible. Jumps between the lithium positions (48h–24g–48h, doublet jump), intracage jumps (48h–48h), and intercage jumps can occur.²²⁴ (c) Li-ion density in Li₆PS₅Cl unit cell during MD simulations at 450 K.²²² (d) Jump statistics from the MD simulations of Li₆PS₅Cl at 450 K. The lines represent three types of Li-ion jumps; green for doublet, blue for intracage, and red for intercage;²²² thicker lines represent larger jump rates. The colored spheres indicate S at 4c (black), Cl at site 4c (pink) and Li-ion sites (48h) (yellow).²²² Reproduced with permission from ref. 222, 224. Copyright (2016, 2017) American Chemical Society.

because of the high abundance and low cost of sodium.^{233–235} Similar to LIBs, NIBs also face safety concerns associated with the liquid organic electrolytes contained in the batteries. The pursuit of higher safety, lower cost and longer cycle life batteries renders the development of all-solid-state sodium batteries and sodium ion solid electrolytes highly desirable. In this section, different types of inorganic solid sodium ion conductors are described to give a global view of the solid-state sodium ion conductors available to date.

3.1 Na- β'' -Al₂O₃

Na- β'' -Al₂O₃ ceramics are well-known fast Na⁺ ion conductors and are widely used as solid electrolytes for Na–S and Na–metal chloride batteries.²³⁶ Owing to its high ion conductivity (0.2–0.4 S cm⁻¹ at 300 °C), Na- β'' -Al₂O₃ is considered as one of the best solid electrolytes for solid-state sodium batteries.²³⁶ However, its extremely high sintering temperature (1200–1500 °C) limits its application. The development, applications as well as the challenges of Na- β'' -Al₂O₃ in high temperature Na batteries have been reviewed by Rojo's group.²³⁶

3.2 NaSICON-type sodium ion conductors

NaSICON-type Li conductors were introduced in Section 2.1.5; in this part, NaSICON-type Na-ion conductors will be reviewed. NaSICONs derive from NaZr₂(PO₄)₃ by partial substitution of Si for P, yielding the general formula Na_{1+x}Zr₂Si_xP_{3-x}O₁₂ ($0 \le x \le 3$). The optimum total ion conductivity is obtained when $x \approx 2$, *i.e.* Na₃Zr₂Si₂PO₁₂ (6.7×10^{-4} S cm⁻¹ at 25 °C and 0.2 S cm⁻¹ at 300 °C).^{107,237} The prominent ion conductivity of this system is due to the high mobility of Na ions throughout the open three-dimensional (3-D) framework, which is created by cornersharing SiO₄/PO₄ tetrahedra and ZrO₆ octahedra *via* common oxygen atoms. Apart from its excellent ion conductivity, NaSICON ceramics are reported to show low thermal expansion, and are thus suitable for use at medium or high temperature. The open framework of NaSICON allows a wide range of chemical substitutions, for example, the Zr^{4+} site can be occupied by a variety of di, tri, tetravalent and pentavalent cations, and the Si/P site can be substituted by Ge^{4+} or As^{4+} .^{238,239}

The efforts at chemical substitution have shown some success in improving the conductivity. For example, Hf-substituted NaSICON - Na_{3.2}Hf₂(SiO₄)_{2.2}(PO₄)_{0.8} - exhibits a much higher ion conductivity than its Zr analogue (2.3×10^{-3} S cm⁻¹ at room temperature).²⁴⁰ Unfortunately, Hf is a rare metal and in limited supply. Takahashi et al. investigated the effects of divalent (Mg²⁺, Zn^{2+}), trivalent (Y³⁺), tetravalent (Ti⁴⁺, Sn⁴⁺), and pentavalent dopants (V⁵⁺, Nb⁵⁺, Ta⁵⁺) on the electrical conductivity and density of NaSICON.²⁴¹ All of these result in well-sintered, dense ceramics and enhanced electrical conductivity at high temperature, but the conductivity at low temperature was not reported. However, these doped systems are mixed conductors and only for Mg-doped and Nb-doped systems can the electronic conductivity be neglected. NaSICON ceramics are often not monophasic but are accompanied by a glassy phase.²⁴² The glassy phase generally comprises sodium, phosphate or silicate and the doping element,²⁴¹⁻²⁴³ as demonstrated in the Mg^{2+} , ²⁴¹ Co²⁺, ²⁴¹ Ce⁴⁺, ²⁴³ Yb³⁺ (ref. 243) and Gd³⁺ doped²⁴³ NaSICON systems. In addition, monoclinic zirconia is easily formed from the liquid phase during the sintering.²⁴³⁻²⁴⁷ Some studies found that the doping and sintering conditions also affect the microstructure and the nature of grain boundaries, and hence influence the conductivity.²⁴⁸

Recently, a high ion conductivity of 4.0×10^{-3} S cm⁻¹ at room temperature was reported for Sc-doped NaSICON, which is the highest value amongst the reported NaSICON-type conductors.²⁴⁹ Based on a range of ion conductivity and structural data of NaSICON-type materials, Guin *et al.*²⁵⁰ concluded that the highest ion conductivity was obtained when the Na content approximates 3.3 mol of Na per formula unit and the mean size of the M cations is close to 0.72 Å. In addition, the monoclinic-to-rhombohedral phase transition temperature was found to be influenced by doping. Jolley *et al.*²⁵¹ found that aliovalent substitution of Zr⁴⁺ stabilized the higher symmetry rhombohedral phase of NaSICON, among which Y³⁺ substitution resulted in the lowest phase transition temperature and the smallest lattice distortion.

Zhang *et al.* proposed a self-forming strategy to develop composite solid electrolytes with high ion conductivity, which was demonstrated by modifying NaSICON with La^{3+, 252} For example, in the case of La³⁺, its very limited solubility in the NaSICON framework ultimately results in separation of Na₃La(PO₄)₂ as a second phase, which mediates both the composition of the bulk and the grain boundary, leading to improved conductivity $(3.4 \times 10^{-3} \text{ S cm}^{-1} \text{ at}$ 25 °C). This strategy can be extended to design other fast ion conductors. Extensive studies of the stability of NaSICON with respect to metallic Na have been conducted.^{253,254} Unfortunately, especially when phosphorus is present, NaSICONs are not stable at 300 °C in contact with molten sodium, but at lower temperatures (100 °C) no reaction is seen.^{253,254}

3.3 Sulfide based sodium ion conductors

As in the case of Li, sodium thiophosphate materials have attracted much attention in recent years because of their relatively high ion conductivity, negligible grain boundary resistance and good ductility.^{45,255} Nonetheless, there are much fewer Na superionic conductors compared to Li sulfides, and their room temperature ion conductivities remain low. Exploration of highly conductive sulfide-based sodium ion conductors is eagerly underway.

An exciting milestone in the development of Na ion conductors was the stabilization of the high-temperature cubic phase of Na₃PS₄ (c-Na₃PS₄, space group: $I\bar{4}3m$) by crystallization from the glassy state, which exhibited high Na⁺-ion conductivity $(2 \times 10^{-4} \text{ S cm}^{-1})$.¹⁹⁸ The conductivity was subsequently improved to 4.6×10^{-4} S cm⁻¹ by using high purity (>99%) Na_2S as a precursor. This achievement for c- Na_3PS_4 ignited a resurgence of interest in sodium thiophosphates, given that the tetragonal phase of Na_3PS_4 (t- Na_3PS_4 , space group: $P\overline{4}2_1c$) exhibits a conductivity one order of magnitude lower.²⁵⁶ The substantial difference in the ion conduction properties was initially assumed to imply that fast ion conduction is causally related to the symmetry of Na₃PS₄. Fig. 10a shows the average cubic and tetragonal Na_3PS_4 crystal structures along the *b*-axis.²⁵⁷ Only small structural differences exist between the two polymorphs of Na₃PS₄, mostly in the Na cation distribution, the orientation of the PS_4^{3-} tetrahedral, and the lattice dimensions.

Nevertheless, despite the experimental discrepancy between the cubic and tetragonal phases, theoretical calculations indicated, in fact, that both pristine c-Na₃PS₄ and t-Na₃PS₄ structures exhibit extremely poor and similar ion conductivity.²⁵⁸ Systematic investigations of the synthesis parameters for Na₃PS₄ under different conditions (e.g., temperature, nature of the reaction vessel, mass of the precursors) revealed that reaction of the precursors with the reaction vessels produced different polymorphs.²⁵⁹ These results suggest that the stabilization of metastable c-Na₃PS₄ can not be explained only by an entropy contribution, but is more likely induced by the precursors reacting with the silica reaction tubes. Elements from the tubes may be incorporated into the structure of Na₃PS₄ or alternatively, off-stoichiometry may be induced in the structure by consumption of some precursors via the reaction with the tubes. The latter is more likely,²⁵⁹ considering that aliovalent doping (e.g., the replacement of P⁵⁺ with Si⁴⁺) appears to be not energetically favorable.²⁵⁸

New efforts have been made to uncover the origin of the enhanced ion conductivity in cubic Na₃PS₄, and to determine if the difference in the transport behaviour between the cubic and tetragonal phases arises from structural differences, microstructural variations, or disparities in the defect concentration. Rietveld and pair distribution function (PDF) analyses were performed to probe the average and local structures of Na3PS4 prepared through two different synthetic routes (ball-milling and high temperature synthesis).257 While Rietveld analysis indeed points to the average structure of Na3PS4 prepared through ballmilling and high temperature routes being cubic and tetragonal, respectively, PDF analyses showed that both Na₃PS₄ compounds exhibit the same tetragonal structural motif on the local scale (Fig. 10b). EIS suggests that the high ionic conductivity of "c"-Na₃PS₄ is not related to the crystal structure, but rather the defects induced by the harsh ball-milling conditions.²⁵⁷



Fig. 10 (a) Crystal structure of cubic and tetragonal Na_3PS_4 projected in the (010) plane. The perfectly cubic phase (*i.e.*, no occupancy of the 12d positions) shows PS_4^{3-} tetrahedra in a body centered lattice. In the tetragonal modification, a minor rotation of the tetrahedra leads to a splitting of the Na positions and an elongation of the *c*-lattice parameter;²⁵⁷ (b) experimentally obtained *G*(*r*) data for (a) HT-t-Na₃PS₄ and BM-"c"-Na₃PS₄ showing that there is no significant difference in the local structure. BM-"c"-Na₃PS₄ was fitted using a tetragonal model, shaded in green and a cubic model shaded in red. Experimental data are shown as black points. The red line denotes the calculated pattern, and the difference profile is shown in blue.²⁵⁷ Reproduced with permission from ref. 257. Copyright (2018) American Chemical Society. (c) Temperature-dependent ionic conductivities of various Na⁺ ion solid electrolytes, including both oxides and sulfides.^{198,252,256,261,262,265-270} Reproduced with permission from ref. 198, 265. Copyright (2012, 2017), Springer Nature. Reproduced with permission from ref. 252, 261, 262. Copyright (2015, 2016), Wiley. Reproduced with permission from ref. 256, 268, 269, 270. Copyright (1980, 1981, 1992, 2012), Elsevier. Reproduced with permission from ref. 266, 267. Copyright (2014, 2018), Royal Society of Chemistry. (d) Schematic diagram of Na ion diffusion in Na₃PS₄ and related phases.²⁶⁵

Although stoichiometric Na₃PX₄ (X = S, Se) compounds were determined to be poor Na ion conductors, theoretical work also suggested that reasonably high conductivity can be realized with the introduction of Na⁺ interstitials or Na vacancies that induce disorder.^{258,260} A computational study on the effect of aliovalent doping of M⁴⁺ (M = Si, Ge, Sn) for P⁵⁺ in c-Na₃PS₄ predicted a conductivity of 1.66 × 10⁻³ S cm⁻¹ for 6.25% Si-doped Na₃PS₄, in very good agreement with the reported experimental value of 7.4 × 10⁻⁴ S cm⁻¹. Remarkably, Sn⁴⁺ doping at the same concentration contributed to a much higher predicted conductivity of 1.07 × 10⁻² S cm⁻¹ even though the dopant formation energy is higher than the Si⁴⁺ dopant.²⁵⁸ These studies prove that the presence of defects are essential to enable fast Na-ion diffusion in Na₃PX₄.

Anion substitution with Se^{2–} – larger than S^{2–} – is another strategy to improve conductivity. Due to its higher polarizability, the replacement of Se^{2–} for S^{2–} expands the lattice and weakens the binding energy between the mobile cations and anion framework. Cubic Na₃PSe₄ with a conductivity of 1.16×10^{-3} S cm⁻¹ and a low activation energy of 0.21 eV was first reported by Zhang *et al.*²⁶¹ They also reported vacancycontaining tetragonal Na₃SbS₄ with a very high conductivity of 3×10^{-3} S cm⁻¹ formed by substituting Sb⁵⁺ for P⁵⁺ in Na₃PS₄.^{262–264} Na₃SbS₄ was reported to be stable in dry air,²⁶² as rationalized by hard and soft acid and base (HSAB) theory. Very surprisingly (and questionably), Na₃SbS₄ is reported to show good compatibility with metallic Na, and to be electrochemically inert up to 5 V based on cyclic voltammetry (CV) measurements. Nonetheless, although CV is a valuable technique, it is not sufficient to assess stability of an SE since it is too fast to detect slow decomposition reactions in ASSBs. Recently, Zhang's group successfully synthesized Sb- and Se-substituted Na₃SbSe₄ with a high conductivity of 3.7×10^{-3} S cm⁻¹ and low activation energy of 0.19 eV.²⁶⁵ The conductivity of these compositions and the schematic illustration of anion and cation size on Na ion transport are shown in Fig. 10c and d, respectively.^{198,252,256,261,262,265-270}

The Na version of LGPS represents another class of sulfide conductors. Na10GeP2S12 (NGPS) was computationally predicted to have a conductivity of 4.7×10^{-3} S cm⁻¹ by Kandagal et al.²⁷¹ Richards et al.²⁷² subsequently predicted an increase in the Na⁺ diffusivity and a decrease in activation energy in the series Sn < Ge < Si for $Na_{10}MP_2S_{12}$ (M = Si, Ge, Sn). They reported the composition Na10SnP2S12 with an experimental conductivity of 4×10^{-4} S cm⁻¹,²⁷² but the structure was not disclosed. MD simulations suggested it is a 1D ion conductor, with chains of NaS₄ tetrahedra linked along the *c*-axis providing facile diffusion. Later, Hayashi's group reported a glass-ceramic with a nominal composition of "Na10GeP2S12" that showed a conductivity of 2.4×10^{-5} S cm⁻¹ and a XRD pattern similar to the simulated "Na₁₀SnP₂S₁₂". However, the structure was again not resolved.²⁷² Very recently, the targeted synthesis of stoichiometric Na₁₁Sn₂PS₁₂ as a polycrystalline powder provided a pure phase material that exhibits a very high conductivity of $1.4 \times 10^{-3} \text{ S} \times \text{cm}^{-1}$ and low activation energy of 0.24 eV.²⁶⁷ The structure of the new phase, Na₁₁Sn₂PS₁₂ was solved from single crystal X-ray diffraction (Fig. 11a and b). In contrast to the LGPS (or NGPS) structure type, the Na⁺ ions occupy only octahedral sites and the Na ion conductivity is completely three dimensional as demonstrated by AIMD simulations (Fig. 11c-e).²⁶⁷ Vital to ion conduction in this 3D percolating network is the disorder of the Na⁺ ions over the almost-fully occupied and

partially occupied sites that alternate in all crystallographic directions. Low energy Na⁺-ion hopping is favored by the equienergetic octahedral sites, and spacious iso-energetic pathways for transport. Experimental measurement of ion conductivity and activation barrier for Na-ion mobility closely matched that from AIMD simulation (0.20 eV), with the E_a being the lowest reported for a sodium thiophosphate in the literature to date. Following this publication, the same phase was also reported elsewhere, with a higher conductivity (3.7 × 10⁻³ S cm⁻¹) but also with an unusually higher activation energy (0.39 eV).²⁷³

4. Ion conduction mechanism and principles to design fast ion conductors

4.1 Mechanism of ion conduction

Understanding the ion transport mechanism is critical to guide the design of fast ion conductors. The conventional knowledge of ion transport in solid materials is based on the classic diffusion model which depicts ion diffusion as the hopping of an individual ion from one lattice site to its adjacent vacant site, which is termed "direct-hopping" (Fig. 12a).

The ion conductivity of solid materials is closely related to crystal structure and is governed by the ion concentration (n), activation energy (E_a), and the mobility of mobile ion carrier (μ):

$$\sigma = nq\mu$$
 and $\mu \propto \exp(-E_{\rm a}/k_{\rm B}T)$

where q is the charge of the mobile ions, $E_{\rm a}$ is the activation energy, and $k_{\rm B}$ is the Boltzmann constant.

A low activation energy and high concentration of mobile ion carrier species (vacancies or interstitials) are necessary to obtain high conductivity. The underlying crystal framework



Fig. 11 Structure of $Na_{11}Sn_2PS_{12}$ from single crystal data. (a) The framework showing ordering of the SnS_4 (dark blue) and PS_4 (light blue) tetrahedra; yellow spheres are S; and rose/red ellipsoids are sodium ions. The Na(1)/Na(2) ions (sites with fractional occupancy) are represented by pink ellipsoids and the Na(3)/Na(4)/Na(5) ions (almost fully occupied sites) are shown as red ellipsoids; (b) the small tetragonal cell ($a' \times a' \times c'$) equivalent to $Li_{10}GeP_2S_{12}$ is related to the actual tetragonal cell ($a \times a \times c$) of $Na_{11}Sn_2PS_{12}$ as follows: $a = a'\sqrt{2}$; c = 2c'; Na-ion probability density isosurface (yellow) obtained from *ab initio* molecular dynamics (AIMD) studies at 1050 K for 40 ps, showing the nature of the 3D Na⁺ ion conduction paths: (c) sodium diffusion along the c axis involves a pathway along -Na(4)-Na(1)-Na(3)-Na(1) chains; the Na-ion probability density obtained from the AIMD Na-ion trajectories in the *ab* plane shows the pathways at (d) z = 0.25.²⁶⁷ Reproduced with permission from ref. 267. Copyright (2018), Royal Society of Chemistry.



Fig. 12 (a) Schematic illustration of the direct hop mechanism and knock-off mechanism; (b) schematic drawing of pore diffusion in the porous organic layer of SEI and knock-off diffusion in the dense inorganic layer of SEI (Li₂CO₃).²⁷⁵ The open circles represent the Li⁺ already in the SEI. In the porous organic layer, the blue solid lines denote channels through which Li⁺ in the electrolyte (green filled circles) transports with anions (yellow filled circles) *via* pore diffusion. The red arrows denote that only Li⁺ can diffuse in the dense inorganic layer *via* the knock-off mechanism;²⁷⁵ Reproduced with permission from ref. 275. Copyright (2012) American Chemical Society. (c) Schematic illustration of single-ion migration *versus* multi-ion concerted migration. For single-ion migration (upper insets), the migration energy barrier is the same as the barrier of the energy landscape. In contrast, the concerted migration of multiple ions (lower insets) has a lower energy barrier as a result of strong ion–ion interactions and unique mobile ion configuration in super-ion conductors.²⁷⁴ Reproduced with permission from ref. 274. Copyright (2017), Springer Nature.

determines the energy landscape of ion migration, while the energy barrier depends on the highest energy of the energy landscape along the decisive migration pathway (saddle-point). For the same crystal framework, similar migration barriers were predicted according to the classic diffusion model, which failed to explain the significantly lower activation energy barriers and abrupt increase in ion conductivity observed at certain doped composition (*e.g.*, doped LLZO and NaSICON).²⁷⁴

Besides the classical "direct hopping" mechanism, another conduction mechanism was also proposed. Using DFT calculations, Shi *et al.*²⁷⁵ predicted that the dominant intrinsic defect in Li₂CO₃, Li_{*i*}⁺, prefers to diffuse through a correlated migration mechanism (Fig. 12b and c), as opposed to the direct hop mechanism. Later, they also found that in β -Li₃PS₄, the correlated migration of Li_{*i*}⁺ along [010] has the lowest migration barrier.²⁷⁶ The correlated mechanism is in fact the same as the later proposed "concerted mechanism" or "collective mechanism". The lower migration barrier of the concerted mechanism compared to the conventional direct hop mechanism was also reported in Li₃OX (X = Cl, Br),¹⁰⁰ doped Li₃PO₄,²⁷⁷ and LLZO.¹⁵⁸ Recently, Mo's group²⁷⁴ surveyed ion diffusion in a series of fast ion conductors, including Li₇P₃S₁₁, β -Li₃PS₄, LiSICON, LLTO, revealing that the mobile ions occupying the high-energy sites can activate concerted migration with a reduced diffusion barrier. Strong ion-ion Coulomb interactions in the unique mobileion configuration with high-energy site occupancy are key for achieving low-barrier concerted migration in these solid ion conductors. During the concerted migration of multiple ions, the ions located at the high energy sites migrate downhill, and cancel out a fraction of the energy barrier caused by the uphill-climbing ions. This explains why the super-ionic conduction in doped LLZO and NaSICON is activated at certain compositions with increased alkali ion concentration, and provides a simple strategy to design fast ion conductors: inserting mobile ions into high energy sites to trigger concerted migration with a lower energy barrier.

4.2 Principles to design fast ion conductors

In general, certain structural prerequisites should be satisfied in order to ensure fast ion conduction in solid materials: (1) as ion transport proceeds locally by thermally activated jumps between adjacent sites (local energy minima), jumps need to be connected in "conduction channels" that allow long range transport. These conduction channels should have a suitable geometry that enables direct passage of the mobile ions but obviates energetically high transition states. While narrow bottlenecks obviously restrict mobility, passages that are too wide also impair motion. For example, the β'' -Al₂O₃ and NaSICON structures are more suitable for Na ions, and exhibit higher conduction for Na than Li ions. This may seem counterintuitive, but results from the interplay between polarizing effect and polarizability. (2) Materials with face-sharing polyhedra, as opposed to edge-sharing, have favorable ion mobility since the bottleneck in the face-shared case is larger. Thus, ion channels with high mobility are easily formed when facesharing polyhedra are connected throughout the structure of the SE.⁹⁹ (3) Different alkali ion sites along the transport path should ideally have similar potential energies with low migration barriers for ion transport between adjacent sites.²⁷⁸ (4) Structural disorder and hence "partial" vacancies or interstitials in the mobile ion sub-lattice are necessary.²⁷⁹ Compounds that exhibit only small concentrations of well defined vacancies or interstitials, formed by either Frenkel or Schottky-type defect formation reactions, are usually poor room temperature electrolytes, as the defect formation enthalpy is then included in the activation energy of ion conductivity. (5) The anion sub-lattice arrangement is also paramount for the diffusion of ions as recently highlighted.⁹⁹ (6) High polarizability of the anion sub-lattice is advantageous for good cation mobility. Numerous sulfide, thiophosphate, and iodide materials show higher conductivity than oxides for this reason. The important role of the polarizability of the anion sublattice has recently been highlighted using lithium superionic argyrodites Li_6PS_5X (X = Cl, Br, I) and sodium superionic $Na_3PS_{4-x}Se_x$ as examples: softer bonds lower the activation barrier but simultaneously decrease the prefactor of the moving ions.^{224,280} In fact, the softer lattice is associated with smaller attempt frequencies, and thus, a smaller pre-factor.²⁷⁹ This explains some old empirical rules connecting prefactors and activation energies, and suggest that design rules for SEs need to consider both the energy landscape (activation barriers) and the phonon spectrum (attempt frequencies).^{224,279,280} (7) General thermodynamic arguments have led to - at least in simple structures - a powerful search strategy that is based on the correlation between charge carrier concentrations and melting points (also Tammann's rule²⁸¹) that has been elucidated by Maier's group.²⁸²

Ceder's group proposed (geometric) design principles for superionic conductors and suggested that a body-centered cubic-like (bcc) anion framework allows the Li⁺ ions to migrate within a network of interconnected tetrahedral sites with a lower activation barrier than other close-packed frameworks and is most desirable for achieving high ionic conductivity.⁹⁹ This feature was verified in recently discovered highly conducting materials such as $\text{Li}_{10}\text{GeP}_2\text{S}_{12}^{220}$ and $\text{Li}_7\text{P}_3\text{S}_{11}$,²¹⁰ whose sulfide sub-lattices match a bcc lattice very closely (note α -AgI is a prototype bcc structure and an excellent SE²⁸³). Poorer conductors such as Li_2S have a fcc sulfide sublattice, while Li_4GeS_4 , Li_3PS_4 and thio-LiSICON have a hcp sulfide sublattice. This can be readily explained by considering that for all the sulfide sublattices, tetrahedral sites are energetically most stable for Li⁺ ions. In the bcc sulfide sublattice, the Li⁺ ion migrates with an extremely low barrier of 0.15 eV along the path connecting two face-sharing tetrahedral sites (Fig. 13a). In the fcc lattice, Li⁺ ions migrating between two tetrahedral sites have to pass through an intermediate octahedral site, which makes the energy barrier much higher (Fig. 13b). The same situation exists in the *a*-*b* plane of the hcp lattice (Fig. 13c). The frameworks of some structures cannot be closely matched to either a bcc, fcc or hcp sublattice, but accommodate a network composed entirely of tetrahedral sites for the mobile cations, in which cation migration through the percolating face-shared tetrahedral sites also shows low activation energy. Such frameworks can be found in argyrodite-type Li₆PS₅Cl²²⁴ and cubic-Na₃PS₄.¹⁹⁸ Li₄PS₄I is another example, where PS₄³⁻ and I⁻ ions together form a bbc anion sublattice.²²⁶

Additionally, it is worth noting that more efforts are needed to reduce the grain boundary resistance for crystalline materials, especially oxides. In heterogeneous systems, the contribution of interfaces determines the overall conducting property. The research on synergistic ion conduction effects in heterogeneous systems originated from the discovery of solid-solid composite electrolytes (typically formed by uniformly admixing fine oxide particles in an ion conducting matrix, e.g., LiI:Al₂O₃ or CaF₂:SiO₂) which show an anomalously high conductivity in comparison with pure phases²⁸⁴ due to increased carrier contributions.²⁸⁵ The space charge concept was introduced to interpret the adsorption effect of one type of ion on an insulating surface along with the significance of boundary layers with regard to ionic conduction. There is the possibility of excess storage in nano-composite materials due to the space charge effects.

This composite concept proved powerful for increasing carrier concentrations but not mobilities. In Section 2.1.1.1 we briefly mentioned LLT composites in which the admixture of SiO₂ or Al₂O₃ decreased the grain boundary resistance by affecting the grain boundary structure directly. The conductivity of glass-ceramic electrolytes is influenced by the interface between them.²⁸⁶ The existence of a fast ion conduction interfacial regime between the glassy and crystalline phases was verified by Schirmeisen *et al.*²⁸⁷ A general explanation for these anomalies relies on space charge models that consider the depletion or accumulation of lithium vacancy point defects as a consequence of the defects at the interface.

Solid–liquid composite systems such as soggy-sand electrolytes^{288,289} or ion-exchange polymers^{290,291} deserve a brief mention in this context as they can offer excellent compromises between electrical properties (high conductivities and high Li-transference numbers) and mechanical properties (malleability, flexibility and good contact to electrode particles) that are difficult to achieve with pure solid phases. Similarly, enhanced conductivity with a percolation behavior has also been observed in these heterogeneous systems.²⁸⁸

Another very interesting synergistic coupling between $Li_{6.75}La_3Zr_{1.75}Ta_{0.25}O_{12}$ (LLZTO) ceramics and poly(vinylidene fluoride) (PVDF) polymer electrolyte was reported by Nan's group.²⁹² A combination of experiments and DFT calculations



Fig. 13 (a–e) Crystal structure of the Li-ion conductors: (a) $Li_2P_3S_{11}$, (b) Li_2S ; (c) γ -Li_3PS₄. The Li ions, partially occupied Li^+ sites, S^{2-} anion, PS₄ tetrahedra and GeS₄ tetrahedra (partially occupied in $Li_{10}GeP_2S_{12}$) are coloured green, green-white, yellow, purple and blue, respectively. In both $Li_{10}GeP_2S_{12}$ and $Li_7P_3S_{11}$, the sulfur anion sublattice can be closely mapped to a bcc framework (red circles connected by red lines). In Li_2S , the anion sublattice is an exact fcc matrix (yellow-red circles). The anion sublattices in γ -Li₃PS₄ and Li_4GeS_4 are closely matched to a hcp framework.⁹⁹ Reproduced with permission from ref. 99. Copyright (2015), Springer Nature.

imply that the La atom of LLZTO could complex with the N atom and C—O group of solvent molecules such as *N*,*N*-dimethylformamide, along with electrons enriched at the N atom, which behaves like a Lewis base and induces the chemical dehydrofluorination of the PVDF skeleton. Partially modified PVDF chains activate the interactions between the PVDF matrix, lithium salt, and LLZTO fillers, hence leading to significantly improved conductivity.²⁹³

5. Evaluation of the electrochemical stability of SEs

Although significant progress has been made in the search for solid electrolytes with high ion conductivity, there are still many fundamental challenges impeding the commercialization of solid-state batteries.^{7,294} Most notably, these include chemical/ electrochemical stability and resistance at the interface between

the solid electrolytes and electrode materials. The properties of the SE/electrode interface – at both the positive and negative sides – are of vital importance to the function of the ASSBs.

Although some fast-ion conducting solid electrolytes (mainly sulfides, thiophosphates and their derivatives, *e.g.*, $Li_{10}GeP_2S_{12}$, $Li_7P_3S_{11}$, Li_6PS_5Cl) show promising conductivity comparable to – or even higher than – liquid electrolytes, the ASSBs assembled with these SEs typically exhibit inferior electrochemical performance than their liquid-cell counterparts. The sluggish charge-transfer across the SE/electrode interface caused by high interfacial resistance is usually the limiting factor for the poor cell kinetics.⁷ The origins of the interfacial resistance are nested in one or more factors: poor physical interfacial contact;²⁹⁵ mechanical failure of the contact with volume variation;²⁹⁶ formation of lithium/sodium-depleted space-charge layers due to the large chemical potential difference between SE and electrode materials;²⁹⁷ and degradation at the interface that is caused by mutual diffusion of elements and/or reactivity that results in



Fig. 14 Types of interfaces between lithium metal and a solid lithium ion conductor. (a) Non-reactive and thermodynamically stable interface. (b) reactive and mixed conducting interphase (MCI). (c) Reactive and metastable solid–electrolyte interphase (SEI).²⁹⁹ Reproduced with permission from ref. 299. Copyright (2015), Elsevier. (d) *In situ* lithiation of solid electrolytes during XPS surface analysis. The argon ion gun is used to sputter from a lithium metal foil placed in the vicinity of the sample of interest. (e) XPS detail spectra of an LATP and LAGP sample before (bottom, black line) and after lithiation (middle, red line). (f) SEM cross-section image of a LATGP sample after approximately 12 h contact with lithium metal. The white arrow indicates the chemical diffusion of lithium into the material.³⁰⁰ Reproduced with permission from ref. 300. Copyright (2013), American Chemical Society.

formation of an interphase.²⁹⁸ Interphase formation may be ascribed²⁹⁹ to several different sources. One is the reduction (at the negative electrode) or oxidation of SEs (at the positive electrode) due to the intrinsic thermodynamic instability of the SEs. SEs are often claimed to exhibit excellent stability based on wide electrochemical windows of 0-5 V or even higher that are typically derived from relatively fast CV measurements on the Li/SE/inert blocking electrode. These experiments do not reflect the practical battery situation as they are too fast to detect slow decomposition reactions at the interfaces. A second source is reactions between the SE and the electrode materials caused by the chemical instability between these two layers. Finally, interphases can be formed in situ by electrochemical reactions of the SE/electrode interface during charge/discharge processes. These three reaction types are different at the positive and negative electrodes, and are explained in more detail below.

At the negative electrode, three different types of interfaces can be distinguished in the Li metal/SE contact, as schematically presented in Fig. 14a: (1) a thermodynamically stable interface; (2) a mixed conducting (growing) interphase (MCI); (3) and a metastable (non-growing) interphase (SEI).²⁹⁹ The properties of these three interfaces influence the charge transfer kinetics differently. In the first case, Li metal and the SE in contact are *a priori* in thermodynamic equilibrium and metal ion transfer and associated relaxation steps will be rate-limiting. In the second and third cases, Li metal and the SE are thermodynamically unstable when in contact, and the reaction products control the transport properties of the interphase. As shown in Fig. 14b, a mixed conducting interphase forms and grows "into" the bulk of the SE material, if the formed products possess sufficient partial electronic and ion conductivity, resulting in the destruction of the electrolyte and eventual self-discharge of the battery. On the other hand, a stable interphase may form if the reaction products are ion-conducting but electronically insulating or if the electronic conductivity is fairly low (Fig. 14c). The decomposition products inhibit continuous decomposition, acting as SEIs. While such interphases are inevitably formed, they are extremely difficult to monitor because of their thickness and the sparse techniques that are available to explore their buried nature. High resolution transmission electron microscopy studies - an obvious first choice - can in fact result in extensive beam damage, occluding the subject of investigation. Both surface science and theory have proven more insightful in predicting and identifying the interphase. In particular, in situ XPS (Fig. 14d), in combination with EIS has been shown to be a powerful tool to investigate the compatibility of SEs with lithium metal.213,299,300

DFT calculations suggest that most Li–SEs are thermodynamically unstable against lithium metal as expected.^{10,301} Sulfides show a significantly narrower thermodynamic stability window than oxide-based SEs.³⁰¹ The reduction products of thiophosphates at the Li interface are predicted to include Li₃P and Li₂S, and for those SE materials containing Ge, Cl, and I, a Li–Ge alloy, LiCl and LiI are formed, respectively. Theory¹¹ and XPS results³⁰² both show that LGPS is reduced at 0–1.7 V

and oxidized at 2-2.5 V. The final decomposition products in equilibrium with Li metal are Li₁₅Ge₄, Li₃P and Li₂S. These data are in contrast to the originally reported 0-5 V electrochemical window from CV measurement.⁴⁵ The electrochemical stability window of SEs is overestimated by CV method because of the slow kinetics of the decomposition reactions due to the limited contact area between the SE and the inert blocking electrode.³⁰³ However, in practical bulk ASSBs, the reduction/ oxidation kinetics of SE in the composite electrode is greatly accelerated, owing to the much larger contact area between the SE and electronic conductive additives that are poised at the electrode potential. Along the same lines, even though LiPON is reduced at 0.69 V according to theory, it was thought to be stable in contact with lithium metal; however, in situ XPS reveals that it actually reacts with lithium metal to form Li₃PO₄, Li₃P, Li₃N and Li₂O.³⁰⁴ Similarly, Ge-containing oxide materials Li1.5Al0.5Ge1.5(PO4)3 (LAGP) and Li3.5Zn0.25GeO4 (LiSICON), are reduced at 2.7 V and 1.4 V, respectively, in agreement with in situ XPS experimental studies18,305,306 (see Fig. 14e and f). In their calculations, Mo et al. found that in Ti containing oxide-based SE materials (*i.e.*, LLTO and LATP), Ti^{4+} is reduced to $Ti^{(3-x)+}$ at low potentials, again consistent with the results of *in situ* XPS (see Fig. 14e and f).^{299,300} We note that a new method using a Li/SE/SE-carbon cell has been proposed to identify the intrinsic electrochemical stability window of SE materials. The viability of this method was confirmed by the examination of the reduction and oxidation of LGPS and LLZO by a combination of in situ XPS and DFT calculations.³⁰³ Among all the oxides investigated, garnet type SEs, in particular, LLZO, exhibit the best resistance to Li reduction.

However, LiPON, as well as sulfides such as Li₃PS₄, and $Li_7P_2S_8I$ (which appears to be better described as Li_4PS_4I),²²⁶ are practically found to be compatible with Li metal. This is due to kinetic factors: the interphase that is formed passivates the SE and mitigates continued reaction. For example, the decomposition products of LiPON, Li₃PS₄, and Li₇P₂S₈I are Li₂O, Li₂S, Li₃P, Li₃N, and LiI, which are all electronically insulating, and thermodynamically stable against Li reduction. The electrochemical potential of Li⁺ is constant across the interface. However, due to the poor electronic conductivity of the interphase, the electrochemical potential of the electronic carrier decreases abruptly from the anode to the SE. Therefore, the Li chemical potential (the sum of $\tilde{\mu}_{Li^+}$ and $\tilde{\mu}_{e^-}$) decreases in the interphase layer from the anode to the SE and is within the electrochemical window of the SE. As a result, the decomposition of the SE has no thermodynamic driving force to continue into the bulk and the SE materials are stabilized by the reduction interphase layer. This is the case illustrated by Fig. 14c, above. In contrast, passivation is not possible when the interphase layer is electronically and ionically conductive. The decomposition interphases of Ge-containing LAGP and LiSICON with Li metal, or Ti-containing LLTO and LATP are mixed electronic and ion conductors (see above), which leads to continuous decomposition of the SEs. Thus, the reduction reaction advances into the bulk of the SE (Fig. 14b and g). In the case of sodium SEs much

less work has been reported, but in principle sodium SEs exhibit the same thermodynamic instability against Na metal. Janek's group has recently proven the stability of Na- β ''-Al₂O₃ against Na metal and the instability of Na₃PS₄ in a combined XPS and impedance study.³⁰⁷

The electrochemical stability of many Li-ion solid electrolytes against oxidation with respect to cathode materials has also been investigated by DFT calculations,^{10,301} showing that many Li-SEs are thermodynamically unstable at high voltages (Fig. 15a).^{10,301} While some oxide-based SEs show a higher reduction potential than sulfides, they also exhibit a much higher oxidation potential, up to 4 V and higher; particularly, NaSICON type materials (i.e., LATP and LAGP) are thermodynamically stable up to 4.2 V. In reality, an even higher nominal oxidation threshold of >5 V is exhibited due to the sluggish kinetics of oxidation and the electronically insulating properties of the decomposition products, which give rise to a significant overpotential. In the case of sulfides, a lower oxidation potential is predicted by calculations, namely, the oxidation of Li₆PS₅Cl and LGPS starts at 2.0 V and 2.15 V, respectively, and Li₃PS₄ exhibits a similar oxidation potential of 2.31 V. Both calculations³⁰⁸ and experiments³⁰⁹ show thermodynamically unstability of the interface between sulfide SEs and LCO. The formation of electronically conductive cobalt sulfides are detrimental to the stability of the interface. With the carbon additive in sulfide-based SSBs, the electrochemical decomposition reactions of sulfide SEs at the cathode/SE interface is facilitated by transferring the low chemical potential of lithium in the charged state deeper into the SE and extending the decomposition region.³¹⁰ The accumulation of highly oxidized sulfur species at the interface causes a large charge transfer resistance and thereby capacity fading (Fig. 15b).³¹⁰ Furthermore, considerable redox activity of sulfide SEs in contact with cathode active materials presents more critical issues at the interface.³¹¹ This sulfide SEs oxidation is verified to occur predominantly in close proximity to the current collector. The thickness of the formed degradation layer is determined by the cut-off voltage and the associated potential drop at the interface between the current collector and the SE.311

Fortunately, the better oxidation stability of oxides has enabled engineering of the interface between fast-ion conducting thiophosphate-based solid electrolytes, and positive electrode materials such as lithium transition metal oxides. The reaction between the SE and cathode is hence ameliorated by surface coatings that protect the SE material. Calculations demonstrate that commonly used coating layer materials, including $\text{Li}_4\text{Ti}_5\text{O}_{12}$,^{312,313} LiTaO₃,³¹⁴ LiNbO₃,^{315,316} Li₂SiO₃,³¹⁷ Li₃PO₄,³¹⁸ are stable between 2 and 4 V and show low electronic conductivity in this voltage domain (Fig. 15c).³⁰⁸ These coating materials for cathode materials can act as artificial SEIs to passivate the their surface and extend the electrochemical window, as illustrated in Fig. 15d. The large interfacial resistance that would otherwise arise from solid–solid contact is thus mitigated, contributing to excellent performance of ASSBs.⁴⁶



Fig. 15 (a) Electrochemical window (solid color bar) of solid electrolyte and other materials. The oxidation potential to fully delithiate the material is marked by the dashed line.³⁰¹ (b) Direct comparison of the first charge curves of carbon-free (blue) and carbon-containing (red) SSBs and a schematic representation of situations that occur on the cathode/SE interface of the SSB during charge processes (insertion). The presence of carbon leads to an additional slope during the first charge. Compared to the case without carbon, a growing overpotential directly results in capacity loss. The presence of carbon facilitates oxidation processes by providing sufficient electronic percolation paths toward the current collector.³¹⁰ (c) Electrochemical window of the proposed and previously demonstrated coating layer materials applied between SEs and cathode materials. The dashed line marks the equilibrium voltage to fully delithiate the materials.³⁰⁸ Reproduced with permission from ref. 308. Copyright (2016), the Royal Society of Chemistry. (d) Schematic diagram illustrating the electrochemical window (color bars) and the Li chemical potential profile (black line) in the solid-state Li-ion battery. The profile of the chemical potential is schematic in this plot and may not be linear. The high μ_{Li} in the anode (silver) and low μ_{Li} in the cathode (blue) are beyond the stability window of the solid electrolyte (green). The observed nominal electrochemical window is extended by the overpotential (dashed line) and by the interphases (orange and yellow), which account for the gap of μ_{Li} between the solid electrolyte and electrodes across the interfaces.³⁰¹ Reproduced with permission from ref. 301, 310. Copyright (2015, 2017), American Chemical Society.

6. Conclusions and future prospects for solid electrolytes and solid state batteries

To realize high performance solid-state batteries, solid electrolytes with high Li/Na ion conductivity, good chemical and electrochemical stability against cathode materials are required. If Li metal anodes need to be employed, SEs need also to be stable against reduction or have to be protected by a suitable protecting film. The total conductivity of oxide-based ceramics is highly dependent on the sintering conditions, the dopants, the density of the samples, and the nature of the grain boundaries. Alkali thiophosphate-based conductors show high conductivities ranging from 10^{-3} to 10^{-2} S cm⁻¹ even for cold-pressed pellets. However, they must be handled under an ultra-dry atmosphere since most of them are prone to hydrolysis because of their hygroscopic nature. Oxides are typically unstable in contact with Li metal and exhibit slightly lower ion conductivities than sulfides, but are more stable in air and easier to handle. A severe disadvantage of oxide crystalline conductors is their large grain boundary resistance, which is often several orders of magnitude higher than bulk values. Further efforts are needed to decrease this contribution. It should be noted that oxide or phosphate conductors should not contain elements that are easily reduced when in contact with a Li metal anode, such as Ti or Ge. Garnet conductors exhibit both excellent conductivities and high chemical stability, and thus they are thought to be one of the most promising oxide crystalline Li ion conductors. Nevertheless, the preparation of thin-films is necessary to reduce the total ohmic

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Fig. 16 Configurations of solid-state batteries and fabrication processes for performance improvement. (a) In a bipolar configuration, the electrode materials are coated on the two sides of the current collector, reducing the weight and volume of the battery package. (b) A typical solid-state battery consists of a cathode, an anode and a solid electrolyte. (c) A zoomed-in image of the contact between the electrolyte (yellow spheres) and the electrode (red spheres), which is limited in a typical solid-state battery. The black spheres represent carbon black and the black arrows indicate the Li⁺ migration pathway. (d) By putting a mixed conducting network coating (green) on the surface of electrode materials, the electrolyte-electrode contact is enhanced. (e) A powder pressing process for fabricating solid-state batteries. (f) A pasting route analogous to that used in solid oxide fuel cell fabrication. (g) A wet coating process for fabricating solid-state batteries. The electrode slurry is fed into a coating machine and spread on a current collector followed by a drying process and another electrolyte coating process. The obtained electrodes are cut and laminated together to make the solid-state batteries. ³¹⁹ Reproduced with permission from ref. 319. Copyright (2016), Springer Nature.

resistance of these oxide electrolytes, and ceramic processing of garnets requires high temperatures.

Although the search for solid electrolytes has experienced a recent upsurge, the development of ASSBs is still in its infancy. Compared with conventional liquid batteries, ASSBs can be stacked within a single package by alternating SE and bipolar electrodes (Fig. 16a),³¹⁹ thus reducing the weight and volume of the package and increasing the energy density. However, some challenges still remain in the development of ASSBs: the instability of most SE in contact with Li/Na metal; the large interfacial resistance between SE and electrode materials mostly because of the limited contact area (Fig. 16b and c); and the incompatibility between SE and electrodes. The challenges and requirements for the large-scale production of all-solid-state lithium ion and lithium metal batteries are evaluated in a recent review.³²⁰

To effectively utilize active materials and achieve good rate performance, appropriate techniques are needed to increase the electrode–electrolyte contact area and reduce the interfacial resistance between the electrodes and electrolyte, and allow for sufficient mechanical flexibility during charge/discharge. The mechanochemical preparation of nanocomposite electrodes and the surface modification of active material particles using electrolyte thin-films are effective strategies for achieving a favorable contact between the electrodes and electrolytes and enhancing the energy density of bulk solid-state batteries.³¹⁹ One other possible strategy is to form a mixed conducting network into the active material, so as to achieve fast electron conduction and create Li^+ ion transport channels. This conducting network could be an amorphous material or a wetting agent such as a non-flammable ionic liquid (indicated in green in Fig. 16d). As demonstrated in a recent paper, improved interface kinetics can be realized by adding a very small amount of ionic liquid (PP₁₃FSI) at the cathode side of the solid-state battery.²⁵² These solid-state batteries exhibit excellent cycling performance (10 000 cycles at room temperature without capacity decay) and rate capability. Another possible solution is to develop hybrid electrolytes that combine inorganic electrolyte and polymer electrolytes to assemble a flexible all-solid-state battery, as demonstrated by Nan's group.^{292,321–323} Obvious solutions that are not fully explored are solid-liquid composites.^{288,289}

Another challenge associated with ASSBs is the thickness of the SE layer and the electrode layer, which is determined by the fabrication technology. Well-known cold pressing methods (Fig. 16e), largely used for sulfide based ASSBs, will limit energy density and are difficult to scale up for practical applications. One strategy to reduce the electrode thickness is to spray cathode and anode materials on both sides of the electrolyte (Fig. 16f) by adding small amount of a wetting agent. Another approach is to employ a wet coating process that is widely used in commercial production of conventional batteries (Fig. 16g). This approach has the advantages of controllability of the layer thickness and the scalability, and has been employed to fabricate solid polymer batteries.³²⁴ Future research should focus on the understanding of interfacial reactions and developing strategies to solve the incompatibility and instability of SE and electrode materials, as well as developing approaches to protect the electrodes and reduce the large resistance of the interface. It is also especially necessary to develop highly scalable methods for SE synthesis.

Conflicts of interest

There are no conflicts to declare.

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