Recent Advancements in Li-Ion Conductors for All-Solid-State Li-Ion Batteries

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ABSTRACT: Inorganic solid lithium ion conductors are potential candidates as replacement for conventional organic electrolytes for safety concerns. However, achieving a Li-ion conductivity comparable to that in existing liquid electrolytes (>1 mS cm\(^{-1}\)) remains a challenge in solid-state electrolytes. One of the approaches for achieving a desirable conductivity is doping of various elements into the lattice framework. Our discussion on the structure and conductivity of crystalline Li-ion conductors includes description of NAtrium Super Ionic CONductor (NASICON)-type conductors, garnet-type conductors, perovskite-type conductors, and Lithium Super Ionic CONductor (LISICON)-type conductors. Moreover, we discuss various strategies currently used to enhance ionic conductivity, including theoretical approaches, ultimately optimizing the electrolyte/electrode interface and improving cell performance.

The continuous depletion of fossil fuels, increasing oil prices, and the need to mitigate CO\(_2\) emissions have stimulated intensive research on alternative energy technologies based on renewable and clean sources. Among the renewable energy sources, solar and wind energies are the prominent energy options; however, the intensity of sunlight and wind constantly changes with locations. Thus, alternative resources must be stored. Rechargeable Li-ion batteries (LIBs) are one of the promising candidates for storage of alternative energy resources. Moreover, the LIBs have received tremendous attention because of their significant role in today’s consumer electronics market, such as mobile electronic devices, laptops, digital cameras, and electric vehicles.\(^1\) Within the battery class, LIBs have outperformed Pb-acid, Ni–Cd, and Ni–metal hydride batteries in terms of specific energy and power as represented in the Ragone plot (Figure 1).\(^2\) However, commercial LIBs contain toxic and flammable organic liquid as electrolyte, resulting in serious safety issues. Moreover, growth of Li dendrites within the electrode materials due to such organic electrolytes leads to short-circuit and finally death of LIBs. Additionally, the limited electrochemical window of organic liquid electrolytes limits the choice of electrodes in LIBs.\(^3–5\) To address these problems, replacement of organic liquid with inorganic solid electrolytes (SEs) will improve safety and will ensure powering a wide range of electronic devices, from portable devices to heavy locomotives. Also, use of SEs in place of organic electrolytes will suppress formation and growth of Li dendrites during battery cycles.\(^6\) The desirable criterion for SEs for their implementation in real application is the ionic conductivity, which should exceed 10\(^{-3}\) S cm\(^{-1}\) at room temperature. Thermal, chemical, and mechanical stability will ensure the compatibility of the SEs with electrode materials, and this will improve the SE–electrode interface stability and hence minimize the interfacial resistance. Besides, for the optimal ionic conductivity of SEs, the size of the mobile ion should fit in to the size of the migration channel (bottleneck), and the bottleneck should be smooth without very wide or narrow sections.\(^7\) The structural parameters can be finely tuned by dopants and substitutions with ions with different ionic radii into the lattice structure for the suitable sizing of the bottleneck...
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Figure 1. Ragone plot for various rechargeable batteries showing superiority of the Li-based battery systems as the desired energy-storing devices.

in the Li-ion conduction pathway (Figure 2a). The dopant ions with larger size would cause lattice expansion, thus increasing the bottleneck size, reducing the activation energy, and improving the conductivity.

Among the most studied fast ion conductors, NASICON (NAtrium Super Ionic CONductor)-type, garnet-type, perovskite-type, and LISICON (Lithium Super Ionic CONductor)-type inorganic ceramic SEs have displayed ionic conductivities in the order of 10⁻³ S cm⁻¹ at room temperature (Figure 2a). Furthermore, these conductors exhibit outstanding stability within the electrochemical window of 0–9 V vs Li/Li⁺ as revealed by cyclic voltammetry measurements. Figure 2b shows the Arrhenius plots of the ionic conductivities of the selected inorganic SEs. Knauth published a review on the structures and conductivities for each class of SE. Bachman et al. published a review on the ion-transport mechanisms and fundamental properties of solid-state electrolytes.

NASICON-Type Li-Ion Conductors. The general molecular formula of NASICON-type conductors is A

The NASICON NaA2B (PO4)3 (A = Ge, Ti, Sn, Hf, Zr) was first reported in 1968. The term NASICON was coined by Hong and Goodenough for the framework Na1₅₋ₓZrₓP₃₋ₓSiO₁₂ (0 ≤ x ≤ 3) in 1971. These Na superionic conductors display thermal and chemical stability and high ion diffusion properties. NASICON materials form three-dimensional network structures, with [B₆P₃O₁₀]⁻³⁻ covalent skeletons built via corner sharing of BO₆ octahedra and PO₄ tetrahedra along the c-axis direction. NASICONs generally crystallize in thermally stable rhombohedral structures with R3c space group, although triclinic phases have been reported in compositions NaA₂(PO₄)³ with A = Sn, Zr, Hf. In rhombohedral phases, mobile A cations in the skeletons are distributed in two types of interstitial sites (M’ and M”) for charge compensation. M’ sites are surrounded by six oxygen atoms (octahedral symmetry) and situated between two adjacent [B₆P₃O₁₀]⁻³⁻ units along the c-axis, whereas the M” sites are surrounded by 10 oxygen atoms and symmetrically distributed around the 3-fold axis of the structure. The M” sites are located between two columns of [B₆P₃O₁₀]⁻³⁻ units along the c-axis. The mobile A cations migrate through bottlenecks from one site to another, and the size of the bottlenecks depends on the nature of the skeleton ions and concentration of mobile ions at interstitial sites.

Consequently, the ionic conductivity of NASICON materials depends on the concentration of Li ions and composition of the NASICON framework. Among the members of the NASICON family, LiM₂(PO₄)₃ (M = Zr, Hf, Sn, Ti and Ge), LiZr₂(PO₄)₃ (LZP), LiTi₂(PO₄)₃ (LTP), and LiGe₂(PO₄)₃ (LGP) are the most promising materials being investigated in recent years. LiZr₂(PO₄)₃ displays a complex polymorphism, and the phase of the LZP system depends on the synthetic parameters. LiZr₂(PO₄)₃ synthesized at high temperature (>1100 °C) adopts a rhombohedral α phase (R3c) at room temperature and undergoes a phase transition to triclinic α’ phase at low temperature (<55 °C). The triclinic α’ phase displayed a very low ionic conductivity of <10⁻⁹ S cm⁻¹ at 30 °C, whereas the rhombohedral α phase showed a conductivity of ~10⁻² S cm⁻¹ at the same temperature. The conductivities of Ti and Ge-based materials are greatly enhanced by substituting smaller Ti⁺⁺ and Ge⁺⁺ with Zr⁺⁺. The NASICON-type Li₁ₓM₆Ti₁₋ₓ₂(PO₄)₃ (M = Al, Sc, Y, La) Li⁺ conducting SEs were reported by Aono et al. in 1989. The polycrystalline pure LTP sample, namely, Li₁₋ₓMₓTi₂₋ₓ(PO₄)₃ (x = 0), showed a very poor conductivity of ~10⁻⁷ S cm⁻¹ at room temperature, and this was attributed to the high porosity in the Li-ion conduction pathway (Figure 2a). The dopant ions with larger size would cause lattice expansion, thus increasing the bottleneck size, reducing the activation energy, and improving the conductivity.

The crystallographic structure of the NASICON NaA₂B is a combination of three-dimensional networks of B₆O₆ and PO₄ tetrahedra. The A cations are located in interstitial sites (M’ and M”) and are responsible for the ionic conductivity.

Figure 2. (a) Total ionic conductivities of selected solid-state lithium-ion conductors at room temperature. (b) Ionic conductivities of selected solid-state lithium-ion conductors with variation of temperature.

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in the pellet. Solid-state conductors with higher porosity show lower conductivities because of the longer distances traversed by lithium ions during migration between grains.\textsuperscript{24} Kwatek and Nowiński\textsuperscript{25} reported that a maximum conductivity of $7.3 \times 10^{-6}$ S cm$^{-1}$ at room temperature for LiTi$_2$(PO$_4$)$_3$ was achieved by adding 8 wt % lithium iodide (LiI). LiI produces small crystallites around the intergrain region of the LTP-LiI composite and facilitates Li-ion transport between the grains. Li et al. studied the phase relationships and electrical conductivities of the systems Li$_{1-x}$M$_x$Ge$_2-x$(PO$_4$)$_3$ (M = Al, Cr). The host compound LiGe$_2$(PO$_4$)$_3$ showed very low conductivity of $1.5 \times 10^{-5}$ S cm$^{-1}$ at 300 °C.\textsuperscript{26} However, ionic conductivity was greatly enhanced upon partial substitution of Ti$^{4+}$/Ge$^{4+}$ ions by trivalent and divalent cations, such as Al, Ga, Sc, In, Y, La, Fe, Cr, Zn, and Ca in LTP/LGP systems.\textsuperscript{23,26}

The increased conductivity resulted from increased mobile Li-ion concentration in the framework and increased density of the sintered pellets. Aono et al.\textsuperscript{25} reported that conductivity is significantly enhanced by partially substituting Ti with Al by solid-state reaction, and a maximum conductivity of $7 \times 10^{-5}$ S cm$^{-1}$ at 25 °C was achieved for Li$_{1.5}$Al$_{0.5}$Ge$_1$(PO$_4$)$_3$. Moreover, they reported that addition of polycrystalline Li$_3$PO$_4$ or Li$_3$BO$_3$ lithium compounds as binders increases the density of the pellets and improves overall Li$^+$ conductivities of the NASICON-based materials. These binders form intermediate glassy phases during sintering and act as fluxes for the growth of LTP grains.\textsuperscript{27} The conductivity of Li$_{1-x}$Ge$_x$Al$_{3-x}$P$_{12}$ rapidly increases from $1.5 \times 10^{-3}$ S cm$^{-1}$ to $1.4 \times 10^{-2}$ S cm$^{-1}$ at 300 °C by partially substituting Ge$^{4+}$ with Al$^{3+}$ in LiGe$_2$P$_{12}$ systems.\textsuperscript{26} Depending on the synthetic conditions, sintering parameters, and value of x in Li$_{1-x}$Ti$_x$Ge$_{2-x}$Al$_x$(PO$_4$)$_3$, the total ionic conductivity varies between $10^{-4}$ and $10^{-3}$ S cm$^{-1}$ at room temperature. By using the solid-state reaction, Arbi et al.\textsuperscript{28} prepared Li$_{1-x}$Al$_x$Ti$_{2-x}$(PO$_4$)$_3$ (LATP) and Li$_{1-x}$Al$_x$ Ge$_{2-x}$(PO$_4$)$_3$ (LAGP) (x = 0, 0.2, 0.4, which showed high bulk conductivities of $3.4 \times 10^{-3}$ S cm$^{-1}$ (Li$_{1.2}$Ti$_{1.8}$Al$_{0.2}$(PO$_4$)$_3$) and $\sim 10^{-4}$ S cm$^{-1}$ (Li$_{1.6}$Ge$_{0.4}$Al$_{0.2}$(PO$_4$)$_3$) at room temperature, respectively. It was observed that the amount of Al incorporated in NASICON framework was less than the expected value, and impurity phase AlPO$_4$ was observed for samples with x $\geq$ 0.2 in both LATP and LAGP systems. The segregation of Al at the surface in the LAGP samples was higher than that in the LATP samples, and the low conductivities of the LAGP samples were due to the depletion of Al in the LAGP samples, which could be explained by the core-shell model.\textsuperscript{28} According to this model, some heterogeneous distribution of Al at the surface and inside LATP and LAGP particles has been detected in samples with low Al content (LATP-02 and LAGP-02 have different core and shell contributions) (Figure 3, top). This heterogeneity may cause the formation of less conducting phase (AIPO$_4$), which has a strong influence on the total (bulk + grain-boundary) and grain-boundary resistances. For the sample LAGP (x = 0.2), a thicker poor Al/Li shell contribution (yellow) formed suggests that the low-frequency “bulk” contribution (the intrinsic conductivity of the material at low frequency) displays a lower conductivity than the high-frequency “bulk” contribution (core contribution). In the case of LATP (x = 0.2), the thicker rich Al/Li core particle contribution (blue) formed suggests the high-frequency “bulk” contribution displaying high conductivity dominates, but this is reversed in LAGP samples (Figure 3).\textsuperscript{25} The results suggest that Al incorporation to the LAGP (x = 0.2) samples is more difficult than that to the LATP (x = 0.2) samples. With increase of the Al concentration, the segregation of AIPO$_4$ phase is favored in both LAGP and LATP series, which produces the partial elimination of the core-shell structure, leading to a homogeneous composition and a high Li$^+$ conductivity.\textsuperscript{28} Shang et al.\textsuperscript{30} reported a water-stable Li$^+$ conducting SE system of Li$_{1.2-x}$Al$_x$Nb$_{2-x}$Ti$_{2-x}$(PO$_4$)$_3$ in which Ti ions are partially substituted by Nb ions. Li$_{1.6}$Al$_{0.4}$Nb$_{2.2}$Ti$_{1.3}$(PO$_4$)$_3$ showed a high total conductivity of $7.5 \times 10^{-4}$ S cm$^{-1}$ at 25 °C, and this value is higher than that of Li$_{1.4}$Al$_{0.6}$Ti$_{1.6}$(PO$_4$)$_3$. The Nb-substituted LATP was stable in a saturated LiOH aqueous solution with saturated LiCl.\textsuperscript{30,31} Kothari and Kanchan\textsuperscript{32} investigated the gallium-doped LATP system Li$_{1.3}$Al$_{0.7}$Ga$_{0.3}$(PO$_4$)$_3$ (x = 0.01, 0.03, 0.05, and 0.07) by replacing Al$^{3+}$ with Ga$^{3+}$; this system showed a maximum Li$^+$ conductivity of $\sim 4 \times 10^{-3}$ S cm$^{-1}$ at 140 °C. Leo et al.\textsuperscript{33} synthesized a series of NASICON-based LGP and LAGP materials through simultaneous addition of MgO and Li$_2$O additives as binders. They demonstrated that these additives act as binders rather than being incorporated into the parent system. The connectivity between the grains was improved by the additives, resulting in drastic reduction in porosity. Moreover, the conductivities of LAGP and LAGP series were enhanced by the addition of binders and reached $\sim 10^{-7}$ S cm$^{-1}$, $1.2 \times 10^{-4}$ S cm$^{-1}$, and $1.03 \times 10^{-3}$ S cm$^{-1}$ at 100 °C for LGP0 (LiGe$_2$(PO$_4$)$_3$), LGP5 (LiGe$_2$(PO$_4$)$_3$ + 0.5 MgO + 0.5 Li$_2$O), and LAGP2 (Li$_{1.4}$Al$_{0.6}$Ge$_{0.4}$(PO$_4$)$_3$ + 0.2 MgO + 0.2 Li$_2$O), respectively.\textsuperscript{33} Chung and Kang\textsuperscript{34} prepared Li$_{1.6}$Al$_{0.4}$Ge$_{1.6}$(PO$_4$)$_3$ (LAGP) by adding an excess amount of lithium (10–20% Li) through a solid-state reaction method. The grain boundary and specific grain boundary conductivities (the specific grain boundary conductivity was calculated using the fitted grain capacitance ($C_g$) and grain boundary capacitance ($C_{gb}$) values) increased linearly with the addition of an excess amount of lithium. They explained that the additional lithium can segregate into the surface of the grain or into the grain boundary, resulting in increase of amount of Li$^+$ charge carriers at the grain boundary region (Figure 4). However, the Li segregation in the grain boundary can affect both the morphologies of the particles and contacts between

![Figure 3. Core-shell model used to explain observed electrical heterogeneity in NASICON samples. Yellow regions indicate poor-Al/Li phases, and blue regions indicate rich-Al/Li phases. Green regions stand for homogeneous materials. Reproduced with permission from ref 28. Copyright 2015 Elsevier.](image-url)
through fast cooling of liquid melt and then were crystallized the melt sintered polycrystalline ceramics in terms of Li1.4Al0.4Ge1.6(PO4)3 glass energies of 0.32 and 0.31 eV for Li1.3Al0.3Ti1.7(PO4)3 and Li2O ceramics, which showed high ionic conductivities of 6.53 × 10−4 S cm−1 at room temperature.38 Mohaghegh et al.39 reported a maximum bulk conductivity of 1.38 × 10−3 S cm−1 at 25 °C for the Fe2O3-added glass—ceramic Li1.4−xFe2OxTi2−xP2O7 (x = 5, GCx). Addition of Fe2O3 into glasses is speculated to loosen the framework structure and promote crystallinity of glasses to enhance ionic conductivity. Kumar et al.40 investigated the ionic properties of LATP glass—ceramics by adding Al2O3 and Ba0.6Sr0.4TiO3 (0.6BST). Unfortunately, the additives reduced the conductivities of the LATP glass—ceramics. They found that space charge and blocking effects coexist in the system and compete with each other. The space charge effect enhances conductivity, whereas the blocking effect diminishes ionic mobility.40 Xu et al.41 studied the influence of Li2O on NASICON-based glass—ceramics of Li7Al5Ge15(PO4)13−xLi2O, which were synthesized using the melt—quench method. The additive Li2O acts as a nucleating agent and enhances the crystallization of the as-prepared glasses during heat treatment. The density of the ceramic plate was improved and the ionic conductivity was enhanced with excess Li2O addition. The Li1.5Al0.5Ge1.5(PO4)3 glass—ceramic displayed a bulk conductivity of 1.18 × 10−3 S cm−1 and a total conductivity of 7.25 × 10−4 S cm−1 at room temperature. The electrochemical measurements revealed that the glass—ceramic LAGP Li1.5Al0.5Ge1.5(PO4)3−0.05Li2O glass—ceramic displayed a bulk conductivity of 1.18 × 10−3 S cm−1 and a total conductivity of 7.25 × 10−4 S cm−1 at room temperature.39 Jadhav et al.42 investigated the conductivities of 0.05 wt % B2O3-added LAGP glass—ceramics. Given its low melting temperature, B2O3 liquefies and segregates along the grain boundary region and facilitates the reorganization of grains during crystallization process. The grains showed better connection between themselves, and the densities of the samples were improved through B2O3 addition (Figure 5). The Li1.5Al0.5Ge1.5(PO4)3−0.05B2O3 glass—ceramic sample crystallized at 825 °C for 5 h displayed a maximum ionic conductivity of 6.7 × 10−4 S cm−1 at room temperature. The B2O3-added LAGP glass—ceramics placed in tetraethylene glycol dimethyl ether containing 1 M lithium bis(trifluoromethane) sulfonimide (LiTFSI-TEGDME) showed good chemical stability, and morphology of the latter was not significantly influenced. The ionic conductivity of Li1.5Al0.5Ge1.5(PO4)3−0.05B2O3 slightly decreased from 6.7 × 10−4 to 2.4 × 10−4 S cm−1 at room temperature after the specimen was immersed for 3 weeks in LiTFSI-TEGDME solvent. The Li—O2 cell containing Li1.5Al0.5Ge1.5(PO4)3−0.05B2O3 glass—ceramic achieved higher discharge voltage

![Figure 4. Schematic of the characteristics of grain boundaries in the LAGP sample and LAGP20%L (LAGP with 20%Li) sample.](image)

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![Figure 5. Formation of LAGP glass—ceramic with B2O3 addition.](image)

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compared to that with the pristine Li$_{1.5}$Al$_{0.5}$Ge$_{1.5}$(PO$_4$)$_3$, indicating a decreased polarization in the cell due to the increased ionic conductivity by the addition of 0.05 wt % B$_2$O$_3$. Zhu et al. synthesized the LAGP Li$_{1.4}$Al$_{0.4}$Ge$_{1.6}$(PO$_4$)$_3$ glass–ceramic by using the melt–quench method, and they studied the effects of crystallization temperature and sintering time. They crystallized the preannealed glass sheets at 750, 775, 800, 825, and 850 °C for 8 h and found that as the crystallization temperature increases, the grain size of the specimen increased rapidly. The glass–ceramic specimen crystallized at 825 °C for 8 h showed the highest conductivity of 2.25 × 10$^{-3}$ S cm$^{-1}$ at room temperature with an activation energy of 0.29 eV. Thokchom and Kumar studied the effects of crystallization parameters on the glass–ceramic LAGP Li$_{1.4}$Al$_{0.4}$Ge$_{2-x}$(PO$_4$)$_3$ (x = 0.5) synthesized via the melt–quench method. The glass–ceramic material crystallized at 825 °C for 8 h displayed the highest total conductivity of 4.22 × 10$^{-3}$ S cm$^{-1}$ at room temperature. The superionic conductivity of the LAGP specimen was illustrated using the ion transport mechanism. The presence of AlPO$_4$ impurity in the specimen forms the space charge complex AlPO$_4$.Li$^+$ through adsorption of an electroactive species (Li$^+$) onto a dielectric (AlPO$_4$) surface in the grain boundary region. The formed space charge complex, AlPO$_4$.Li$^+$, affects the path of lithium-ion conduction. However, with the increase in crystallization temperature and sintering time, a greater amount of the AlPO$_4$ impurity is formed, resulting in a blocking effect. Santagnelli et al. prepared a tin-doped LAGP, Li$_{1.4}$Al$_{0.4}$Sn$_{0.25}$Ge$_{1.5}$(PO$_4$)$_3$ through isovalent substitution of Ge with its larger homologue Sn using the melt–quench method. The tin-doped LAGP displayed a grain ionic conductivity that was slightly higher than that of the tin-free LAGP because of lattice expansion associated with the substitution of Ge by its larger homologue Sn. The glass–ceramic LASGP Li$_{1.25}$Al$_{0.25}$Sn$_{0.25}$Ge$_{1.5}$(PO$_4$)$_3$ showed a high conductivity of 1.73 × 10$^{-3}$ S cm$^{-1}$ at room temperature and a low activation energy of 0.356 eV.

One of the major problems in the melt–quench method is that it requires an extremely high temperature for heat treatment, leading to lithium loss and secondary phase formation in final products. Moreover, formation of a glass sheet is restricted to a few oxides (B$_2$O$_3$, SiO$_2$, P$_2$O$_5$, and GeO$_2$), and they must be present in a molar ratio of approximately 50% to get a glass formation. The use of solution-based preparation methods generally can overcome some of these problems because of low-temperature synthetic processes. Xu et al. reported a high conductivity of 1.12 × 10$^{-3}$ S cm$^{-1}$ at 25 °C for Li$_{1.4}$Al$_{0.4}$Ti$_{1.8}$(PO$_4$)$_3$ glass–ceramic prepared using the citric acid-assisted sol–gel method. The high conductivity of the LATP pellet is attributed to the reduced particle size and the extremely high density (100% of the theoretical density) of the sample, which was obtained using the spark plasma sintering technique. Zhang et al. prepared water-stable Fe$^{3+}$ and Cr$^{3+}$ doped Li$^+$ conducting SEs Li$_{1.5}$Al$_{0.5}$Fe$_x$Ti$_{1-x}$(PO$_4$)$_3$ and Li$_{1.5}$Al$_{0.5}$Cr$_x$Ti$_{1-x}$(PO$_4$)$_3$ (x = 0 to 0.4), respectively, using a sol–gel method. Partial substitution of Al$^{3+}$ by Fe$^{3+}$/Cr$^{3+}$ increased the ionic conductivity of LATP, and the highest total conductivities of 1.1 × 10$^{-3}$ and 1.06 × 10$^{-3}$ S cm$^{-1}$ at room temperature were achieved for Li$_{1.5}$Fe$_{0.25}$Al$_{0.5}$Ti$_{1.8}$(PO$_4$)$_3$ and Li$_{1.5}$Al$_{0.5}$Cr$_{0.4}$Ti$_{1.6}$(PO$_4$)$_3$, respectively. The chromium-doped LATP sample was stable in the saturated LiCl aqueous solution but unstable in distilled water.
increased Li concentration in the system but also from the newly created conduction paths, which substantially reduce the activation energy (Figure 6).\textsuperscript{54}

Along with poor conductivity, issues like compatibility of inorganic solid-state electrolytes with lithium metal were overcome by approaches. Introduction of an additional interfacial layer between the electrode and electrolyte can facilitate easier passage of Li-ion reversibly. Though LATP-based materials reached the conductivity of $10^{-3}$ S cm\textsuperscript{-1} at room temperature, which is the target for the SEs, their applicability as Li\textsuperscript{+} conductors is limited because of the chemical instability toward Li metal due to the reduction of Ti\textsuperscript{4+}. For their application in solid-state batteries, there must have a protective layer placed in the interface between the Li\textsubscript{1.5}Al\textsubscript{0.5}Ge\textsubscript{1.5}(PO\textsubscript{4})\textsubscript{3} (LATP) glass-ceramic plate Li\textsubscript{1.2}Al\textsubscript{0.2}Ti\textsubscript{1.8}(PO\textsubscript{4})\textsubscript{3} (LATP) by partially substituting Ti\textsuperscript{4+} with Al\textsuperscript{3+}, leading to structural changes and influencing the Li\textsuperscript{+} mobility.

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were protected by the membranes in Li−O2 batteries. The total conductivity of composite membrane was approximately $1 \times 10^{-4}$ S cm$^{-1}$ at room temperature. The LAGP hybrid membranes showed superior stability compared with the pure polymer membranes in aqueous solutions. Very recently, they demonstrated that LAGP ceramic pellets act as anode-protecting membranes for rechargeable aqueous and hybrid Li−air cells (Figure 9). Rechargeable Li−air batteries were fabricated by sandwiching LAGP ceramic pellets between lithium anodes and catholyte solutions with various pH values; the Li−air batteries displayed very low overpotentials. The Li/LAGP interfacial resistance gradually increased because of the evaporation of catholyte in the cell, limiting the cycle life. Filling the anode chamber with electrolyte restores the contact between Li and LAGP. The hybrid Li−air cell with a current density of 0.03 mA cm$^{-2}$ was cycled for more than 60 h (59 cycles). The charge−discharge overpotential was lower than 0.1 V for the first 59 cycles. Liu et al. fabricated an all-solid-state Li−air battery consisting of Li metal as anode and LAGP SE with single-walled carbon nanotubes (SWCNTs/LAGP nano-particles composite) as air electrode (Figure 10); the battery showed a large capacity of 2800 mAh g$^{-1}$ in the first-cycle discharge.

**Garnet-Type Li-Ion Conductors.** SEs crystallizing in garnet structure with general formula Li$_x$M$_3$(XO$_4$)$_3$, where M = La and X = Zr, Nb, Ta, have increasingly received attention because of their high lithium-ion conductivities and wide electrochemical stability windows. The garnet-based Li-ion conducting electrolytes (Li$_3$La$_3$M$_2$O$_{12}$, M = Ta, Nb) were first synthesized by Hyooma and Hayashi and then optimized by Thangadurai and Weppner. The garnet-type Li-ion conducting oxides Li$_3$La$_3$M$_2$O$_{12}$, where M = Ta, Nb, displayed total Li-ion conductivities of $\sim 10^{-6}$ S cm$^{-1}$ at room temperature. The Ta-contained garnet Li$_3$La$_3$Ta$_2$O$_{12}$ displayed better electrochemical stability against the reaction with molten Li metal with a wider voltage window of >6 V vs Li/Li$^+$ than the Nb-contained garnet Li$_3$La$_3$Nb$_2$O$_{12}$. The Li-ion conductivity can be enhanced significantly by partial substitution of La$^{3+}$ or M$^{5+}$ sites with aliovalent cations. The Ba-substituted garnet Li$_3$Ba$_3$Ta$_2$O$_{12}$ displayed a high ionic conductivity of $4 \times 10^{-5}$ S cm$^{-1}$ at 50 °C. The garnet system shows that the bulk and total conductivities are nearly of the same magnitude, indicating a low grain boundary resistance. The conductivity was further enhanced upon substitution with Y or In. The In-substituted garnet Li$_5$La$_3$Nb$_{1.75}$In$_{0.25}$O$^{12}$ prepared at 950 °C displayed an enhanced bulk ionic conductivity of $2.7 \times 10^{-4}$ S cm$^{-1}$ at 25 °C. The yttrium-doped samples were chemically stable up to 400–600 °C after water treatment and were chemically compatible in the presence of the high-voltage cathode materials Li$_5$CoMn$_2$O$_8$ and Li$_2$FeMn$_2$O$_6$. Li-La$_3$Zr$_2$O$_{12}$ (LLZO) with garnet-related structure has been widely studied in recent years because of its good ion conductivity at room temperature and stability against lithium metal. In 2007, Murugan et al. first reported the synthesis of the garnet-type LLZO through substitution of Zr$^{4+}$ for M$^{5+}$ in Li$_5$La$_3$M$_2$O$_{12}$; this LLZO showed an ionic conductivity of 2.44 $\times 10^{-4}$ S cm$^{-1}$.

**Figure 8.** (a) Photo of hybrid solid electrolyte film LAGP-70 (70% LAGP to PEO-based polymer). (b) Schematic presentation of solid-state Li/LiFePO$_4$ cell assembled with hybrid solid electrolyte and composite positive electrode. Reproduced with permission from ref 57. Copyright 2015 Electrochemical Society Inc.

**Figure 9.** Schematic representation of rechargeable hybrid Li−air cell. Reproduced with permission from ref 59. Copyright 2017 Elsevier.
at room temperature with a relative density of 92%. However, LLZO was found in two crystalline polymorphs: a low-temperature stable tetragonal structure with a space group of $I41/acd$ and a high-temperature stable cubic structure with a space group of $Ia3d$. Figure 11 shows the tetragonal phase of the garnet-type solid conductor LLZO with its connectivity pattern in the lattice structure. The garnet-type tetragonal LLZO framework structure consists of edge-sharing dodecahedral La(1)O$_8$ and La(2)O$_8$ and octahedral ZrO$_6$ units. In the tetragonal framework structure, Li atoms occupy three types of crystallographic sites: Li(1) atoms occupied the tetrahedral-8a sites, while the other tetrahedral-16e was unoccupied; Li(2) and Li(3) atoms fully occupied octahedral-16f and octahedral-32g sites, respectively.

Awaka et al. synthesized a tetragonal Li$_7$La$_3$Zr$_2$O$_{12}$ garnet by using the flux method; this garnet showed a bulk conductivity of $1.63 \times 10^{-6}$ S cm$^{-1}$ and a grain-boundary conductivity of $5.59 \times 10^{-7}$ S cm$^{-1}$ at room temperature. Wolfenstine et al. suggested that the use of a hot-press technique could further enhance the conductivity of tetragonal Li$_7$La$_3$Zr$_2$O$_{12}$. The hot-pressed tetragonal LLZO showed a high relative density of $\sim$98% and exhibited a total ionic conductivity of $\sim 2.3 \times 10^{-3}$ S cm$^{-1}$ at room temperature. Choi et al. synthesized composite membranes composed of organic polymer matrices and inorganic solid electrolytes. The conductivity of as-synthesized tetragonal LLZO pellet-type membrane showed $6.2 \times 10^{-7}$ S cm$^{-1}$ at room temperature. The ionic conductivity was synergistically enhanced by the incorporation of the inorganic SE (LLZO) into the organic polymer matrix ($\text{PEO-LiClO}_4$). The composite membrane containing 52.5% LLZO displayed an ionic conductivity of $4.42 \times 10^{-4}$ S cm$^{-1}$ at 55 °C.

The Li-ion conductivity of the cubic phase is higher than that of the tetragonal phase by 2 orders of magnitude for the garnet-type electrolytes. Therefore, to stabilize the cubic phase of garnet, researchers have developed many methods, and the conductivity was improved to the order of $\sim 10^{-4}$ to $10^{-3}$ S cm$^{-1}$ at room temperature (Figure 12). Awaka et al. studied the detailed crystal structure of cubic Li$_7$La$_3$Zr$_2$O$_{12}$ by single-crystal X-ray structure analysis. In the cubic phase, the Li(1) atoms occupied the tetrahedral-24d sites and the Li(2) atoms occupied the octahedral-32g sites, respectively.

Figure 10. Schematic diagram of an all-solid-state Li–air battery using Li anode, LAGP ceramic electrolyte, and an air electrode composed of SWCNTs and solid electrolyte particles. Reproduced from ref 60. Copyright 2015 American Chemical Society.

Figure 11. Crystal structure of tetragonal Li$_7$La$_3$Zr$_2$O$_{12}$ with connectivity pattern of Td (8a and 16e) and Oh (16f and 32g) cages projected on two dimensions.

Figure 12. Parameters in obtaining the cubic phase of the garnet structure.
occupied the distorted octahedral-96h sites. The disordered cubic structure and partial occupation of Li atoms at the Li(2) sites play key roles for fast ion conduction. In the cubic garnet structure, Li ions could conduct from 24d sites to 96h sites through a three-dimensional pathway. The basic unit of the arrangement is drawn as a loop built by the Li(1) and Li(2) sites (Figure 13a,b). Geiger et al.71 found that LLZO synthesized in Pt crucible led to a tetragonal phase, whereas that synthesized in alumina crucible became a mixture of tetragonal and cubic phases. The accidental incorporation of Al from crucible to the garnet should contribute to stabilize the cubic phase. Rangasamy et al.72 examined the effect of doping of Al into the Li-La3Zr2O12 garnet structure by intentionally incorporating Al during synthesis, and the cubic phase was stabilized by optimizing Al amount to 0.24 in molecular formula. The hot-pressed cubic garnet Li6.24La3Zr2Al0.24O11.98 displayed a conductivity of 4.0 × 10−4 S cm−1 at room temperature with a relative density of 98%. Xu et al.73 proposed a multistep sintering process for the synthesis of the LLZO Li7La3Zr2O12 doped with 0.2 mol % Al2O3 by holding the sample at 900 °C for 6 h and at 1100 °C for 6 h and finally at 1200 °C for 12 h. By holding the sample at 900 °C for 6 h, the precursors undergo partial decomposition to yield the mixture of tetragonal and cubic phase; by continuously holding at 1100 °C for 6 h, the formed tetragonal LLZO completely turns into cubic garnet; finally by holding at 1200 °C for 12 h, the relative density of the sample increases without formation of impurities in cubic phase. They reported that multistep sintering enhanced the relative density of garnet and the ionic conductivity. The Al-LLZO pellet sintered via a multistep process exhibited a pure cubic phase with a relative density of 94.25% and displayed an ionic conductivity of 4.5 × 10−4 S cm−1 at room temperature.65 Moreover, 0.25 mol % Al doped Li7La3Zr2O12 samples were synthesized in Pt and alumina crucibles, and ionic conductivity and air stability of the samples were studied.74 The Al-doped LLZO garnet sintered in Pt crucible exhibited higher relative density, conductivity, and air stability than that sintered in alumina crucible. The sample sintered in alumina crucible found with excess Al content coming from alumina crucible may undergo Li loss during high-temperature sintering. The LLZO garnet sintered in Pt crucible displayed an ionic conductivity of 4.48 × 10−4 S cm−1 at room temperature with a relative density of ∼96%.75 El-Shinawi et al.76 developed a hybrid sol–gel solid-state approach to synthesize Al-doped Li7La3Zr2O12 with low Al-incorporation level (~0.12 mol %). Obtaining dense cubic Li7La3Zr2O12-type phases, however, often required the prolonged calcination at elevated temperatures of up to 1230 °C.66 However, using the hybrid sol–gel solid-state approach, dense LLZO ceramic pellets obtained by mixing Al2O3 nanosheets with sol–gel processed LLZO solid precursor and followed by single calcination step at lower temperature, 1100 °C for 3 h (Figure 14). The minor secondary phases of LiAlO2 and Li2ZrO3 formed in situ during the calcination process could help to stabilize the cubic phase and increase the density of the garnet. The Al-doped Li7La3Zr2O12 exhibited total conductivity of ∼3 × 10−4 S cm−1 at room temperature with an activation energy of 0.27 eV.75 Dumon et al.76 synthesized strontium-doped cubic Li7La3Zr2O12 by adding 0.9–8.4 wt % Sr. The additive SrCO3 acts as a sintering aid to stabilize the cubic phase, and it increased the grain size and enhanced the conductivity. The total ionic conductivity of 1.7 wt % Sr-doped LLZO was approximately 5 × 10−4 S cm−1 at room temperature with an activation energy of approximately 0.31 eV.76 Very recently, our group77 demonstrated that the conductivity of Al-doped LLZO solid electrolyte can be enhanced by employing cheap and relatively simple voltammetric treatment in an all-solid-state Li LiLLZO Li cell configuration. The Li deposition–dissolution signal has been observed in the voltammograms, which was
supported by neutron powder diffraction measurements, which showed that lithium content in the lattice increased after voltammetric treatment. Furthermore, a local rearrangement of O atoms was detected by X-ray photoelectron spectroscopy, which indicated reduction of oxygen defects. The enhancement in conductivity of LLZO was attributed to both the reduction of oxygen defects and the increase of lithium content.

The garnet-type Li$_5$La$_3$Zr$_2$O$_{12}$ shows remarkably high ionic conductivities upon doping of the superivalent Ta, Nb, and Y ions at the Zr sites.78 Ohta et al.82 synthesized the Nb-doped LLZO Li$_{6.75}$La$_3$Zr$_{1.75}$Ta$_{0.25}$O$_{12}$ (LLZTO) by doping Ta into the LLZO framework; LLZTO showed the highest conductivity of 1.8 $\times$ 10$^{-4}$ S cm$^{-1}$ at room temperature. The increase in conductivity upon Nb substitution is supported by neutron powder diffraction measurements, which showed that lithium content in the lattice increased after voltammetric treatment. Furthermore, a local rearrangement of O atoms was detected by X-ray photoelectron spectroscopy, which indicated reduction of oxygen defects. The enhancement in conductivity of LLZO was attributed to both the reduction of oxygen defects and the increase of lithium content.

The dual-substituted LLZO, Li$_{6.65}$Ga$_{0.15}$La$_3$Zr$_{1.9}$Sc$_{0.1}$O$_{12}$, exhibited the highest conductivity of 1.8 $\times$ 10$^{-4}$ S cm$^{-1}$ at room temperature with an activation energy of 0.27 eV and was electrochemically stable up to 9 V vs Li/Li+.79 Allen et al.83 investigated the cubic garnet Li$_{6.75}$La$_3$Zr$_{1.75}$Ta$_{0.25}$O$_{12}$ (LLZTO) by doping Ta into the LLZO framework; LLZTO displayed a relatively high total ionic conductivity of 8.7 $\times$ 10$^{-4}$ S cm$^{-1}$ at room temperature with a low activation energy of 0.22 eV. Li et al.80 reported that the ionic conductivity of cubic Li$_{6.75}$La$_3$Zr$_{1.75}$Ta$_{0.25}$O$_{12}$ (LLZTO-Al) SE prepared in an oxygen sintering atmosphere was approximately 7.4 $\times$ 10$^{-4}$ S cm$^{-1}$ at room temperature. Buannic et al.81 enhanced the conductivity of LLZO by doping Ga and Sc at the Li and Zr sites, respectively. The first dopant, Ga$^{3+}$, doped at Li sites, stabilizes the cubic garnet phase, and simultaneous incorporation of the second dopant Sc$^{3+}$ at the Zr$^{4+}$ site increases the amount of mobile Li ions. The dual-substituted LLZO, Li$_{6.65}$Ga$_{0.15}$La$_3$Zr$_{1.9}$Sc$_{0.1}$O$_{12}$, exhibited the highest conductivity of 1.8 $\times$ 10$^{-4}$ S cm$^{-1}$ at room temperature with an activation energy of 0.29 eV.

Gu et al.82 studied the influence of pentavalent and trivalent doping on LLZO garnet by combining experimental results with molecular dynamics simulations. They showed that the conductivity of cubic garnet was enhanced upon pentavalent doping (Ta$^{5+}$ or Nb$^{5+}$) which increased the disorder and vacancy concentrations, whereas the trivalent doping of Al$^{3+}$ or Ga$^{3+}$ on the Li sites was showed to be slightly less effective. The immobile Al$^{3+}$ or Ga$^{3+}$ preferentially occupies 24d sites which blocks conduction pathway of Li ions. The doping of Ga$^{3+}$ on the La sites stabilized the cubic phase and had no effect on the Li$^+$ concentration.82 Parameters in obtaining the cubic phase of the garnet structure are shown in Figure 12, including the sintering temperature and time, additives, sintering atmosphere, element doping, Li content (occupation sites), crucibles, etc.

Bernstein et al.83 studied the driving force behind the phase transition from low-conducting tetragonal phase to high-conducting cubic phase by using density functional theory and a variable cell shape version of molecular dynamics (MD). DFT calculations showed that the Li sublattice in tetragonal phase was ordered which was either fully occupied or unoccupied with Li ions, whereas that in the cubic phase was disordered, which was partially filled with Li ions. In the cubic structure, the tetrahedral 24d sites (Li$^1$) were fully occupied and surrounded by four pairs of octahedral 96h sites (Li$^2$), which were partially occupied. The Li$_2$—Li$_2$ pair was energetically prohibited to occupy both sites at the same time because of the short distance between the pair, which causes strong Coulomb repulsion between two Li. In the tetragonal structure, cubic Li$^1$ sites converted to fully occupied 8a sites (Li$^1$) and unoccupied 16e sites (Li$^2$). The partially filled cubic Li$^2$ sites adapted into fully occupied 16f (Li$^2$) and 32g (Li$^3$) sites in tetragonal structure (Figure 15). For MD simulations, 0.25 vacancies per formula unit were applied at 600 K.

The vacancies were formed randomly in the ordered, tetragonal unit cell by removing Li ions from Li$^1$ and Li$^3$ sites. The system spontaneously transformed into cubic within 5–10 ps of simulation time. At 15 ps, the system fluctuated between cubic and tetragonal states and finally settled into a cubic phase after 30 ps. When the tetragonal phase transforms into the cubic phase, the ratios of lattice constants, $a/a$, and $a/a$ (the lattice constants along $x$ and $y$ to that along $z$), drop from 1.04 to 0.98 (Figure 16, top panel). When this drop...
occurs, there is a redistribution of Li ions in tetrahedral sites. The occupancies of tetrahedral Li1t (red) sites and tetrahedral Li2ut (blue) sites are initially near 1 and 0, respectively, consistent with experimental tetragonal structure (Figure 16, bottom panel). When the system transforms from tetragonal to cubic, there is a sharp drop in the occupancies of Li1t (red, bottom panel) and Li2t and Li3t sites (red, middle panel), while Li2ut sites (blue, bottom panel) did not experience increase or decrease in their occupancies during phase transition, indicating that Li-ion redistribution took place between occupied Li1t sites and unoccupied Li2ut sites during simulation studies. So the calculated disorder in cubic structure originated not only from the change in the lattice constants but also from filling the empty Li2ut octahedral sites.

Shin et al. studied the enhancement in conductivity and lithium-ion transport phenomena in cubic Li7La3Zr2O12 upon multidoping by combining the experimental and density functional theory calculations. The blocking effect of immobile Al at 24d sites and 96h sites in cubic structure is shown in Figure 17. When Al occupies 24d sites, the relative energy significantly decreased by 11.9 meV per atom, compared with the condition that Al occupies 96h sites, suggesting that Al occupation at 24d sites is more favored (Figure 18). It is widely believed that the immobile Al dopant in the Li sites may reduce the Li-ion diffusion by blocking the conduction paths of Li ions in the garnet.78 The blocking effect of Al at 24d sites is more serious in decreasing the ionic conductivity compared with the blocking effect of Al at 96h sites. By multidoping on LLZO garnet with Al and Ta atoms, the 96h sites were stabilized and the preference of Al occupation at 24d sites was reduced. At higher levels of Ta doping, the 96h sites were further stabilized, indicating that the blocking of Al at 24d junction sites was reduced by multidoping on LLZO. The ionic conductivity of multidoped cubic Li6.2Al0.2La3Zr1.8Ta0.2O12 exhibited about 6.14 × 10−4 S cm−1 at room temperature with activation energy of 0.29 eV.

Kotobuki et al. successfully used the lithium-ion conducting garnet Li1−xAlxLa3Zr2O12 (LLZO) as electrolytes to fabricate all-solid-state rechargeable lithium batteries with Li metal. The cyclic voltammogram of the Li/LLZO/Li cell shows that the dissolution and deposition reactions of lithium occurred reversibly without any reaction with LLZO, indicating stability of the LLZO against Li metal. A full cell with a LiCoO2/LLZO/Li configuration was successfully operated and demonstrated a
discharge capacity of 15 μAh cm⁻². However, an irreversible behavior was observed at the first charge and discharge cycle because of an interfacial issue between LiCoO₂ and LLZO. Kim et al.⁸⁵ reported that the interfacial layer La₃CoO₇ formed between the Li⁺ conducting SE LLZO and LiCoO₂ cathode because of mutual diffusion, suppressing the lithium insertion—extraction at the LLZO/LiCoO₂ interface. Ohta et al.⁸⁶ fabricated an all-solid-state lithium-ion battery consisting of LiCoO₂/La₅₋xLiₓZr₁.₇₅Nb₀.₂₅O₁₄/Li configuration to investigate its electrochemical performance and charge-transfer resistance. The cell showed good cycle performance and displayed a capacity retention of approximately 98% after 100 charge—discharge cycles. The discharge capacity at the first cycle was 129 mAh g⁻¹ and stabilized at 127 mAh g⁻¹ after the 100th cycle (theoretical capacity of LCO is 137 mAh g⁻¹, which corresponds to 0.5 Li per CoO₂). Moreover, they introduced Li₅BO₃ as buffer layer between LiCoO₂ cathode and Nb-doped LLZO SE to increase the interfacial contact between them. The obtained battery showed a good charge—discharge capacity with a low interfacial resistance between electrodes and SE. The charge and discharge capacities at the first cycle were 100 and 85 mAh g⁻¹, respectively (theoretical capacity of LCO is 115 mAh g⁻¹, which corresponds to 0.42 Li per CoO₂).²⁷ Du et al.⁸⁸ studied the stability of Al-doped Li₇La₃Zr₂O₁₂ in air by conductivity measurements on cubic perovskite structure, and the LLTO-based materials attracted considerable attention for application in electrochemical devices, such as high-energy lithium-ion batteries, electrochromic systems, supercapacitors, and pH sensors.⁶ However, the relatively low grain boundary conductivities (<10⁻⁵ S cm⁻¹) of the LLTO systems limit their application in batteries. Inaguma et al.⁹⁴ studied the conductivity measurements on cubic perovskite structure, Li₃Sc₂MnO₁₀ whose cell parameter was 3.8710(2) Å. The total conductivity of the cubic perovskite was 2–4 × 10⁻⁵ S cm⁻¹ at room temperature, but the value reached to 1 × 10⁻² S cm⁻¹ after 3 days, and the color of the sample changed from ivory to blue-black. They found that the enhancements in conductivity and color changes are from electronic conduction due to the reduction of Ti⁴⁺ by Li metal, which causes the increment of electron carriers. Mei et al.⁹⁷ introduced an amorphous silicate layer to improve the grain boundary conductivity of ceramic electrolyte. By the introduction of a silicate layer, the total ionic conductivity exceeded 1 × 10⁻⁴ S cm⁻¹ at room temperature. Morata-Orrantia et al.⁹⁸ achieved a high ionic conductivity of 2.95 × 10⁻³ S cm⁻¹ for La₀.₅₁ₓSrₓLa₁₋ₓ₋₀.₃Y₂O₃ at room temperature by doping Al into the perovskite. Abreu-Sepúlveda et al.⁹⁹ synthesized chromium-substituted Laₓ(La₀.₃⁻ₓ,₆₋ₓ₋₀.₃)Ti₁₋ₓ₋₁₋₀.₃CrₓO₃ perovskites using a conventional solid-state reaction and the Pechini process method. Neutron diffraction refinements were performed on

Though perovskite-type conductors have high bulk conductivities, the total conductivities were lower (~2 × 10⁻⁵ S cm⁻¹ at room temperature) because of higher grain boundary resistances.

The increase in pH of the LLZO powder/water suspension resulted from the H⁺/Li⁺ exchange reaction between water and the LLZO electrolyte.

Though perovskite-type conductors have high bulk conductivities, the total conductivities were lower (~2 × 10⁻⁵ S cm⁻¹ at room temperature) because of higher grain boundary resistances. In 1987, Belous et al.⁹⁵ conducted the pioneering study on the conduction behavior and on the stoichiometric range of stable perovskite type LiₓLa₃₋ₓ(1−x)TiO₃. The perovskite structure with a general formula of ABO₃ exists in different stable phases at different temperatures, that is, high-temperature stable phase with cubic Pm₃m symmetry (α-LTLO) and a low-temperature stable phase with tetragonal P4/mmm symmetry (β-LTLO). In the cubic structure (α-LTLO), the A-site La³⁺, Li⁺ and vacancies are evenly distributed; by contrast, the tetragonal structure had a double-perovskite structure with La-rich layers and Li-rich layers along the c-axis. In the cubic structure, conduction of the Li ions happens through the A-sites, which are partially occupied by Li and La ions. Because of high conductivity, good electrochemical stability, negligible electronic conductivity, and good stability in a wide temperature range of 4–1600 K, the LLTO-based materials attracted considerable attention for application in electrochemical devices, such as high-energy lithium-ion batteries, electrochromic systems, supercapacitors, and pH sensors. However, the relatively low grain boundary conductivities (<10⁻⁵ S cm⁻¹) of the LLTO systems limit their application in batteries. Inaguma et al.⁹⁴ studied the conductivity measurements on cubic perovskite structure, Li₃Sc₂MnO₁₀ whose cell parameter was 3.8710(2) Å. The total conductivity of the cubic perovskite was 2–4 × 10⁻⁵ S cm⁻¹ at room temperature, but the value reached to 1 × 10⁻² S cm⁻¹ after 3 days, and the color of the sample changed from ivory to blue-black. They found that the enhancements in conductivity and color changes are from electronic conduction due to the reduction of Ti⁴⁺ by Li metal, which causes the increment of electron carriers. Mei et al.⁹⁷ introduced an amorphous silicate layer to improve the grain boundary conductivity of ceramic electrolyte. By the introduction of a silicate layer, the total ionic conductivity exceeded 1 × 10⁻⁴ S cm⁻¹ at room temperature. Morata-Orrantia et al.⁹⁸ achieved a high ionic conductivity of 2.95 × 10⁻³ S cm⁻¹ for La₀.₅₁ₓSrₓLa₁₋ₓ₋₀.₃Y₂O₃ at room temperature by doping Al into the perovskite. Abreu-Sepúlveda et al.⁹⁹ synthesized chromium-substituted Laₓ(La₀.₃⁻ₓ,₆₋ₓ₋₀.₃)Ti₁₋ₓ₋₁₋₀.₃CrₓO₃ perovskites using a conventional solid-state reaction and the Pechini process method. Neutron diffraction refinements were performed on
four different models of chromium-substituted perovskite to determine the site occupation of Li ions. The rietveld refinement analysis showed that lithium most likely occupies at the B-site (Ti site) with a composition of La$_{1/3}$(Ti$_{2/3}$Cr$_{1/3}$)$_3$O$_3$ with minor cubic phase of Li$_{1-x}$Ti$_x$O$_2$. The chromium-substituted LLTO, La$_{2/3-x}$Li$_x$Ti$_{0.9}$Cr$_{0.1}$O$_3$ showed an enhancement in the conductivity ($1.2 \times 10^{-4}$ Sc m$^{-1}$ at room temperature) as well as good mechanical strength due to the well-connected grains without porosity. Kwon et al.$^{100}$ prepared Li$_{1-x}$La$_{2/3-x}$Ti$_x$O$_3$ solid electrolytes by the Pechini method at various sintering temperatures to investigate the effect of microstructural modifications and change of Li-ion conducting behavior. The crystal structures of tetragonal and orthorhombic LLTO perovskites with a general formula of ABO$_3$ are shown in Figure 19a. The sample sintered at high temperature (high-\textit{T} = 1400 °C) showed larger grain size than that sintered at the low temperature (low-\textit{T} = 1200 °C), indicating that when the sintering temperature is increased, the domain growth of the LLTO can be facilitated (Figure 19b,c). The LLTO sintered at low temperature showed the total conductivity of $4.4 \times 10^{-5}$ S cm$^{-1}$ at room temperature, whereas the conductivity was significantly improved for the LLTO sintered at high temperature ($2.0 \times 10^{-3}$ S cm$^{-1}$). Moreover, the 30 mol % Li-excess LLTO sintered at 1400 °C has fine microstructure with well-developed grain/domain boundaries, exhibiting a total Li$^+$ conductivity of $4.8 \times 10^{-4}$ S cm$^{-1}$ at room temperature (Figure 19d). The activation energy ($E_a$) for Li migration across the domain boundary was reduced in the order of low-\textit{T} LLTO (0.453 eV) > high-\textit{T} LLTO (0.432 eV) > Li-excess LLTO (0.391 eV) (Figure 19e). Chen et al.$^{101}$ reported the improved ionic conductivity of Li$_{0.33}$La$_{0.67}$TiO$_3$ by mixing Li$_{1.9}$Zr$_2$O$_{12}$ (LLZO) sol into its precursor powder. The Zr doped into the LLTO mainly prefers the grain boundary region. The grain boundary conductivity of LLTO was largely increased by the introduction of LLZO. The LLTO-based electrolyte mixed with 5 wt % LLZO exhibited a total conductivity of $1.2 \times 10^{-4}$ S cm$^{-1}$ and a grain boundary conductivity of $1.5 \times 10^{-4}$ S cm$^{-1}$ at room temperature.

The perovskite-type Li$_{0.33}$La$_{0.67}$TiO$_3$ (LLTO) with high ionic conductivities of $10^{-3}$–$10^{-4}$ S cm$^{-1}$ at room temperature could be used as the electrolytes for all-solid-state batteries (ASSBs). However, the reduction of Ti$^{4+}$ by Li metal limits their applicability in ASSBs. Kotobuki et al.$^{102}$ fabricated an all-solid-state battery with the composition of LiCoO$_2$/LLTO/Li$_4$Mn$_5$O$_{12}$ using a honeycomb-structured Li$_{0.33}$La$_{0.67}$TiO$_3$ which has microporous holes on both sides of the membrane. The impregnation of active materials LiCoO$_2$ and Li$_4$Mn$_5$O$_{12}$ particles mixed with respective precursor sols into the honeycomb holes forms good active materials/solid electrolyte interfaces, which reduces the internal resistance of the cell and thus improves the discharge capacity. Li et al.$^{103}$ showed the charge–discharge performance of an all-solid-state Li/LiPON/LLTO/LiCoO$_2$ cell using LiPON/LLTO thin film as solid electrolyte. Amorphous lithium lanthanum titanate (LLTO)
solid electrolyte thin films have been fabricated using e-beam evaporation. LiPON thin film was used as coating layer to avoid undesirable reaction between LLTO and lithium metal. The cell exhibited a discharge capacity of about 50 μAh cm⁻², and the capacity degradation was about 0.5% per cycle after 100 charge-discharge cycles at a current of 7 μA cm⁻². Le et al. examined the stability and durability of Al-substituted LLTO ceramic by immersing it in aqueous solution for one month. The Al-substituted lithium lanthanum titanate (A-LLTO) sintered at 1350 °C for 6 h exhibited ionic conductivity of about 3.17 × 10⁻⁴ S cm⁻¹ at room temperature. The Li-LiCoO₂ and Li–O₂ cells with LiPON/A-LLTO as electrolytes exhibited good cyclability, stability, and superior electrochemical performance after the electrolytes were immersed in an alkaline aqueous solution. The charge-discharge capacity of the Li-LiCoO₂ cell maintained 59.3% of the initial capacity with a Li₃.⁷⁵Si₀.⁷⁵P₀.²⁵O₄ and 2Li₄Al₀.₃₃Si₀.₁₇Ge₀.₁₇P₀.₃₃O₄ with cationic substitution of Si in the lithium-ion conductivity (0.125 S cm⁻¹). They have synthesized a series of compounds, including (300 °C performance after the electrolytes were immersed in an alkaline aqueous solution. The charge–discharge capacity of the Li-LiCoO₂ cell maintained 59.3% of the initial capacity with a Coulombic efficiency of 98.3% after 100 cycles at 1C rate. Two comprehensive reviews on the structure and properties of LLTO were published by Bohne and Stramare et al. LISRCON-Type Li-Ion Conductors. A polycrystalline Li⁺ conducting SE LISRCON Li₁₂₋₃Zn₉₋₁Ge₄O₁₆ was first reported by Bruce and West in 1983. The LISRCON framework is similar to the γ-Li₂PO₄ crystal structure. Although Li₁₂₋₃Zn₉₋₁Ge₄O₁₆ stoichiometry (x = 0.75) showed the highest lithium-ion conductivity (0.125 S cm⁻²) at high temperature (300 °C), its conductivity at room temperature is only 1 × 10⁻⁷ S cm⁻¹. For LISRCON compounds, the ionic conductivity tends to decrease with time at low temperature because of the formation of a defective complex, namely, Li₄GeO₄, which traps the mobile lithium ions through the immobile sublattice. Attempts to restore their conductivities to original values by reannealing the samples were unsuccessful in Li₂₋₃Zn₋₁Ge₄O₁₆ compounds because of aging problems. Furthermore, LISRCON, Li₄ZnGe₄O₁₆ is highly reactive with lithium and atmospheric CO₂. In the LISRCON family, various materials displaying the γ-Li₂PO₄ framework have been synthesized. The germanium-doped framework (Li₁₆GeₓV₁ₓO₁₆) displayed the highest conductivity of approximately 4 × 10⁻⁶ S cm⁻¹ at room temperature. Deng et al. reported enhanced conductivities of LISRCON SEs by doping Si in Li₅SiₓO₄ system with P, Al, or Ge. They have synthesized a series of compounds, including Li₁₂₋₃Si₁ₓ₋₃P₀.₂₅Oₓ₄ and Li₁₂₋₃Si₁ₓ₋₃P₀.₂₅Oₓ₄ and Li₄AlₓSi₃₋ₓP₀.₃₀₃O₄ and Li₄AlₓSi₃₋ₓP₀.₃₀₃O₄ with cationic substitution of Si in the parent LISRCON-like Li₄SiO₄ framework. The ionic conductivity of Li₄SiO₄ is very low (σ₄₇₃K = 4 × 10⁻⁶ S cm⁻¹); upon substitution of P or Al at Si sites, the conductivity was increased by 2 orders of magnitude to 1 × 10⁻⁴ S cm⁻¹ for Li₁₂₋₃Si₁ₓ₋₃P₀.₂₅Oₓ₄ and 2 × 10⁻⁴ S cm⁻¹ for Li₁₂₋₃Si₁ₓ₋₃P₀.₂₅Oₓ₄ at 473 K. A further increase in the ionic conductivity was observed for “ternary” composition Li₄AlₓSi₃₋ₓP₀.₃₀₃O₄ with σ₄₇₃K = 1 × 10⁻³ S cm⁻¹. Molecular dynamics simulations were used to explain the enhanced conductivities and Li-ion diffusion mechanisms for substituted compositions. Depending on the temperature, they have proposed three Li-ion diffusion mechanisms: (i) local oscillation at low temperature, (ii) isolated hopping at intermediate temperature, and (iii) superionic motion at high temperature (Figure 20). MD simulations reveal that the Li-ion diffusion mechanism in each composition was temperature-dependent. The Li-ion mobility became higher when the diffusion mechanism transforms from local oscillation to isolated hopping or from isolated hopping to superionic flow. The mixed polyanion substitution lowers the temperature at which the transition to the superionic state with high Li⁺ conductivity occurs. Song et al. reported a facile strategy of substituting Cl for O to adjust bottleneck size and binding energy to enhance the conductivities and electrochemical stability of LISRCON systems. The lattice parameters of Cl-substituted Li₁₀.₅SiₓP₁₁ClₓO₁₂−ₓ solid solutions are lower than those of the pure Li₄PO₄ indicating expansion of bottlenecks and decrease of energy barriers, which enhanced the ionic conductivities. Li₁₀.₄₂SiₓP₁₁ClₓO₁₂−ₓ exhibited ionic conductivities of about 1.03 × 10⁻⁵ and 3.7 × 10⁻⁵ S cm⁻¹ at room temperature, respectively, with electrochemical stability windows of up to 9 V vs Li/Li⁺. All-solid-state batteries were assembled with 0.3Li₄MnO₄, 0.7LiMn₁₋₁₂Ni₀.₃O₄ as cathode and lithium metal as anode. The battery based on the Li₁₀.₄₂SiₓP₁₁ClₓO₁₂−ₓ showed initial charge and discharge capacities of 114.5 and 114.1 mAh g⁻¹, respectively, with Coulombic efficiencies of 100%. The battery based on the Li₁₀.₄₂GeₓP₁₁ClₓO₁₂−ₓ showed initial charge and discharge capacities of 330.1 and 133.2 mAh g⁻¹, respectively. The battery based on Li₁₀.₄₂SiₓP₁₁ClₓO₁₂−ₓ showed better cycle performance than that based on Li₁₀.₄₂GeₓP₁₁ClₓO₁₂−ₓ.

Interfacial Stability. The use of highly conductive solid-state inorganic electrolytes in all-solid-state lithium-ion batteries has been extensively researched in recent years because of the safety and good performance of this state-of-the-art battery technology. However, incorporation of these materials in all-solid-state batteries remains very challenging because of their reactivity with the electrode materials at interfaces. Introduction of a buffer layer between the electrode and electrolyte reduces interfacial resistance. Kato et al. introduced a thin Nb layer (~10 nm) to interface between SE Li₄La₄Zr₂O₁₂ and cathode LiCoO₂ to reduce interfacial resistance. The Nb layer suppresses the growth of mutual diffusion layer at the interface and produces an amorphous Li–Nb–O material through an in situ process, which is reported to be Li⁺ conductive. Introduction of the Nb layer reduces the interfacial resistance and improves the cycle stability and rate capability of charge-discharge reactions of a Li/Li₄La₄Zr₂O₁₂/LiCoO₂ solid-state battery. Zhou et al. constructed an all-solid-state battery using a NASICON Li₄Al₃Tiₓ(PO₄)₃ (LATP) ceramic membrane sandwiched with a cross-linked polymer, poly(ethylene glycol) methyl ether acrylate (CPMEA), on both sides. Insertion of a polymer layer between the SE and anode

![Insertion of a polymer layer between the SE and anode suppresses dendrite formation because of uniform Li⁺ flux across the polymer/lithium interface.](https://example.com/polymer_layer.png)
suppresses dendrite formation because of uniform Li⁺ flux across the polymer/lithium interface. At the same time, the polymer layer showed a better ability of wetting toward lithium metal, and the ceramic layer was protected from contact with lithium metal. The all-solid-state battery, Li/CPMEA/LATP/CPMEA/LiFePO₄ cell, delivered a stable capacity of 130 mAh g⁻¹ after 100 cycles with Coulombic efficiency of 99.7%–100%. Garnet-type LLZO SEs could react with carbon dioxide and moisture in ambient air to form Li-ion-insulating Li₂CO₃ layers on the surfaces, resulting in large interfacial resistances. Moreover, they reported that by addition of 2 wt % LiF to the garnet Li₆.5La₃Zr₁.5Ta₀.5O₁₂, stability of the garnet electrolyte against moist air was effectively increased. Additionally, they fabricated an all-solid-state battery, Li/polymer/LLZT-2LiF/LiFePO₄, which demonstrated high Coulombic efficiency and long cycle life with reduced interfacial resistance.

Because of the low interfacial resistance, the low overpotential further decreased to 0.2 V at 80 μA cm⁻². Summary and Future Outlook: In conclusion, LiBs with liquid electrolytes are still providing a large part of the current energy demand. However, serious safety concerns arise because of the use of liquid electrolytes. Leakage of electrolytes and growth of Li dendrites caused by contact of anodes with liquid electrolytes greatly hinder the performance of LiBs. Devices operated at elevated temperatures also suffer from electrolyte evaporation when liquid electrolytes are used. Hence, inorganic SEs with room-temperature conductivities >10⁻³ S cm⁻¹ and wide electrochemical stability windows (6 V vs Li/Li⁺) have been intensively studied to develop all-solid-state batteries that can be used for applications with a wide temperature range. Stability of SE/electrode interface is a challenge for facile passage of Li ions across the interface. From this perspective, we have discussed recent published research activities in synthetic methods and possible dopants and respective effects on the crystal lattices of NASICON-type, garnet-type, perovskite-type, and LISICON-type SEs. Doping with isovalent or aliovalent elements and addition of additives into the parent structural frameworks enhance the ionic conductivities of SEs because of the framework expansion and increase of mobile Li ions. We have also discussed the interfacial reactions between SEs and electrodes. For example, the solid Li-ion conductor Li₁₀(PO₄)₃-based material, which exhibited high ionic conductivity, was chemically unstable with Li metal because of the reduction of Ti⁴⁺. Introduction of a protective layer (LiPON film) between SE and Li metal improved the stability. Good interfacial contacts between the solid electrolytes and the electrodes can be achieved given the nondeformable nature of the inorganic ceramic SEs. However, further studies are needed to better understand the interfacial processes between solid electrolytes and electrodes.

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