Recent advances in inorganic solid electrolytes for lithium batteries

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**INTRODUCTION**

Lithium batteries are being scrutinized as the most promising electrical energy storage for electric vehicles (EVs), which hold great promise in resolving the jeopardy on future transportation. On the other hand, they have not yet been able to meet automobiles’ stringent requirement on high energy density, long cycle life, excellent safety, and wide operating temperature range (Goodenough and Kim, 2009; Kotobuki, 2012).

In order to get lithium batteries ready for their large-scale implementation in EVs, researchers extensively look at all aspects in a cell that would leapfrog the cell performance (e.g., novel electrolytes, high energy-density, and stable electrode materials, high-performance conductive additives/binders/current collectors, and efficient packaging). Among these approaches, the electrolyte holds the key to the success of EV batteries. The state-of-the-art electrolytes mainly consist of lithium salts and organic solvents. Therefore, they cause irreversible capacity losses resulted from the formation of stable solid electrolyte interphase (SEI), hinder the increase in cycle life, limit the temperature window, and, not to mention, pose severe safety concerns on lithium batteries.

In this respect, the replacement of currently used organic liquid electrolytes with inorganic solid electrolytes (SEs) is very appealing. For one thing, inorganic SEs are solid materials. Thus, they can address the above-mentioned concerns on capacity losses, cycle life, operation temperatures, safety and reliability (Hayashi et al., 2012; Sahu et al., 2014). In addition, they present advantages such as the simplicity of design, absence of leakage and pollution, better resistance to shocks and vibrations compared to organic liquid electrolytes (Thangadurai and Weppner, 2006b; Knauth, 2009; Fergus, 2010). For another thing, most of inorganic SEs are single ion conductors. Lithium single ion conductors can have a lithium transference number of unity. As a result, there is no concentration gradient inside the cell while it is operating. This is very beneficial to the lowering of cell overpotential (Quartarone and Mustarelli, 2011).

Also stemming from these two prominent features, great challenges remain for achieving high-performance SEs. One of them is how to create favorable solid–solid interface between electrode and electrolyte (Ohta et al., 2006, 2007; Sakuda et al., 2011). Another one is how to obtain high ionic conductivity at room temperature, e.g., $10^{-3}$ S cm$^{-1}$.

In this review, the advantages, as well as efficient ways to addressing the aforementioned grant challenges, are discussed. The first part is about crystalline electrolytes, including LISICON and thio-LISICON-type, Garnet-type, Perovskite-type, and NASICON-type lithium ion conductors. The second part is about glass-based electrolytes, including glassy and glass-ceramic systems made of oxides and sulfides. Table 1 lists important materials and their conductivities and Figure 1 shows Arrhenius plots for ionic conductivities of some selected SEs.
Table 1 | Conductivity of inorganic SEs for all-solid-state lithium batteries.

| Type | Example | Conductivity (S cm\(^{-1}\)) | Reference |
|------|---------|------------------------------|-----------|
| Crystal (LISICON) | Li\(_{1+x}\)ZnGe\(_4\)O\(_{16}\) | 1.0 \times 10^{-7} | Hong (1978) |
| Crystal (thio-LISICON) | Li\(_{10}\)GeP\(_2\)S\(_{12}\) | 1.2 \times 10^{-2} | Kamaya et al. (2011) |
| Crystal (thio-LISICON) | Li\(_{10}\)SnP\(_2\)S\(_{12}\) | 4 \times 10^{-3} | Bron et al. (2013) |
| Crystal (garnet) | Li\(_{6.5}\)La\(_3\)Ni\(_{1.25}\)Y\(_{0.75}\)O\(_{12}\) | 2.7 \times 10^{-4} | Narayanan et al. (2012) |
| Crystal (garnet) | Li\(_7\)La\(_2\)Zr\(_2\)O\(_{12}\) | 2.1 \times 10^{-4} | Dumon et al. (2013) |
| Crystal (garnet) | Li\(_{6.75}\)La\(_3\)Zr\(_1\)Ti\(_{0.25}\)O\(_{12}\) | 8.7 \times 10^{-4} | Allen et al. (2012) |
| Crystal (perovskite) | Li\(_{3+x}\)La\(_{2-x}\)TiO\(_3\) (x = 0.11) | 1.0 \times 10^{-3} | Stramare et al. (2003) |
| Crystal (NASICON) | Li\(_{1.1+x}\)Al\(_{1-x}\)TiO\(_{4}\) (x = 0.3) | 7 \times 10^{-4} | Aono et al. (1990) |
| Glass | 50Li\(_2\)O-50(0.5SeO\(_2\) – 0.5B\(_2\)O\(_3\)) | 8 \times 10^{-7} | Lee et al. (2002) |
| Glass | 50Li\(_2\)S-17PbS\(_8\) – 33LiBH\(_4\) | 1.6 \times 10^{-3} | Yamauchi et al. (2013) |
| Glass–ceramic | Li\(_{1.6}\)Al\(_{0.3}\)Ge\(_{1.4}\)O\(_{13}\) | 4.0 \times 10^{-4} | Fu (1997a) |
| Glass–ceramic | 70Li\(_2\)O-30PbS\(_8\) | 1.7 \times 10^{-2} | Seino et al. (2014) |

RT\(^*\), room temperature; HT\(^*\), high-temperature.

**CRYSTALLINE INORGANIC ELECTROLYTES**

**LISICON AND THIO-LISICON-TYPE ELECTROLYTES**

LISICON-type SEs possess relatively low conductivity at room temperature (\(~10^{-7}\) S cm\(^{-1}\)) and Li\(_{14}\)ZnGe\(_4\)O\(_{16}\) is its typical representative, which was first described by Hong (1978). Its one member of Li\(_{14+2x}\)Zn\(_{1-x}\)Ge\(_4\)O\(_{16}\) system and can be viewed as a Li\(_4\)GeO\(_2\)–Zn\(_2\)GeO\(_4\) solid solution. Figure 2 shows the projection of the LISICON structure on the a-b plane, whose framework is related to the γ-GePO\(_4\) crystal structure. Li\(_{11}\)ZnGe\(_4\)O\(_{14}\) forms a three-dimensional (3D) skeleton structure and lithium ions in the skeleton distribute in two sites: 4c and 8d sites. These sites are occupied by four and seven Li\(^{+}\) ions, respectively. The three remaining Li\(^{+}\) ions are located in 4c and 4a interstitial sites and their temperature coefficients are abnormally high, indicating that they can be mobile. Each 4a site is connected to two 4c sites and vice versa. The bottlenecks to Li\(^{+}\) transport between these sites are parallelograms, which have a tilt angle with the a-b plane. On the basis of calculation, the average size of the bottlenecks (4.38 Å) is bigger than the minimum size required for Li\(^{+}\) transport (2r\(_{Li}^+\) + 2r\(_{O}\) = 4.0 Å), which promotes Li\(^{+}\) movement (Zheng et al., 2003).

Although the ionic conductivity of Li\(_{14}\)ZnGe\(_4\)O\(_{16}\) is as high as 0.125 S cm\(^{-1}\) at 300°C, it is only 10\(^{-7}\) S cm\(^{-1}\) at room temperature. This is explained by trapping of the mobile Li\(^{+}\) ions by the immobile sublattice at lower temperatures via the formation of defect complexes (Robertson et al., 1997). Furthermore, Li\(_{14}\)ZnGe\(_4\)O\(_{16}\) is highly reactive with Li-metal and atmospheric CO\(_2\) and the conductivity decreases with time (Thangadurai and Weppner, 2006b).
Recent efforts to improve the ionic conductivity of LISICON-type SEs focus on the replacement of oxide by sulfur in the framework (Figure 3). These sulfide SEs are referred to as thio-LISICON, which was introduced by Kanno et al. (2000).

Material design of inorganic SEs are based on certain structural criteria: (i) mobile ions should have conduction pathways large enough in the lattice, (ii) there should be a disordered mobile ion sublattice, and (iii) highly polarizable mobile ions and anion sublattices are preferable (Kanno and Murayama, 2001). The ionic conduction properties are strongly dominated by the size and polarizability of constituent ions, or interstitial vacancy character caused by the substitutions.

Since the radius of $S^{2-}$ is higher than $O^{2-}$, this substitution can significantly enlarge the size of $Li^+$ transport bottlenecks. Besides, $S^{2-}$ has better polarization capability than $O^{2-}$, thus weakens the interaction between skeleton and $Li^+$ ions. Therefore, compared with LISICON systems, thio-LISICON materials can achieve really high ionic conductivity (over $10^{-4}$ S cm$^{-1}$ at room temperature). Thio-LISICON SEs also have advantages, such as easy reduction of grain-boundary resistance by conventional cold-press of electrolyte powders and preferable application to all-solid-state batteries due to its mechanical property (Tatsumisago et al., 2013).

A series of thio-LISICON were firstly synthesized and $Li_{3.25}Ge_{0.25}P_{0.75}S_4$ showed a high conductivity of $2.2 \times 10^{-3}$ S cm$^{-1}$ at room temperature, negligible electronic conductivity, high electrochemical stability, and no phase transition up to 500$^\circ$C (Kanno and Murayama, 2001). Most recently, a very high conductivity of 12 m S cm$^{-1}$ (27$^\circ$C) was achieved by $Li_{10}GeP_2S_{12}$. Its crystal structure was different from typical thio-LISICON structures. As shown in Figure 4A, it had a 3D framework structure consisting of ($Ge_0.5P_0.5$)S$_4$ tetrahedra, PS$_4$ tetrahedra, LiS$_4$ tetrahedra, and LiS$_6$ octahedra. The high ionic conductivity benefited from the 3D diffusion pathways both along c axis and in a-b plane (Kamaya et al., 2011).

Furthermore, Bron et al. (2013) reported the synthesis of $Li_{10}SnP_2S_{12}$ by replacing Ge with Sn, whose total conductivity reached 4 m S cm$^{-1}$ at room temperature. All-solid-state battery with $Li_{10}GeP_2S_{12}$ (cathode: LiCoO$_2$; anode: in metal) exhibited a discharge capacity of over 120 mA g$^{-1}$ and an excellent coulombic efficiency of about 100% after the second cycle as well as a high decomposition potential of over 5 V (Figure 4B).

**GARNET-TYPE ELECTROLYTES**

Garnet-type lithium single ion conductors have a general formula of $Li_5La_3M_2O_{12}$ ($M$ = Ta, Nb). They were firstly reported by Thangadurai and Weppner (2005a) and recently have been intensively studied as SEs for all-solid-state lithium batteries. They have high ionic conductivity and excellent chemical stability in contact with lithium metal.

Figure 5 shows the crystal structure of $Li_5La_3M_2O_{12}$. La and M occupy eight- and six-coordinated sites, respectively,
and Li occupies octahedral sites. The MO₆ octahedra are surrounded by six lithium ions and two Li⁺ vacancies in the parent Li₅La₃M₂O₁₂ structure. Therefore, the structure facilitates lithium ion conduction (Thangadurai and Weppner, 2005b).

Among the materials investigated, Li₂BaLa₂Ta₂O₁₂ exhibited a high ionic conductivity of 4 × 10⁻³ S cm⁻¹ at 22°C with an activation energy of 38.5 kJ mol⁻¹. It had low grain-boundary resistance, which meant that the total and bulk conductivities were nearly identical (Thangadurai and Weppner, 2005b).

Conductivity can be further improved through partially substitution of Y or In at the M site in Li₂La₃M₂O₁₂. For example, Li₅La₃Nb₁.₇₅In₀.₂₅O₁₂ showed an enhanced conductivity (1.8 × 10⁻⁴ S cm⁻¹ at 50°C) with low activation energy of 49.1 kJ mol⁻¹ (Thangadurai and Weppner, 2006a). High conductivity of 2.7 × 10⁻⁴ S cm⁻¹ at 25°C was obtained for Li₅+xZr₁.₇₅O₁₂ with x = 0.75 (Narayanan et al., 2012). The high Li⁺ conductivity resulted from short Li⁺–Li⁺ distances in the edge-sharing LiO₆ octahedra and a high concentration of Li on the octahedral sites.

Recently, garnet-type Li₅La₃Zr₂O₁₂ (LLZO) has attracted much attention since firstly reported (Murugan et al., 2007). In the structure, La is located at the center of a dodecahedron with eight coordinated oxygen atoms while Zr is at the center of an octahedron with six-coordinated oxygen atoms (Figure 6). The lithium ions could migrate within the garnet lattice framework with a 3D conduction mechanism (Dumon et al., 2013).

LLZO undergoes a phase change from tetragonal to cubic structure as the sintering temperature increases, which belong to the space group Iad and I₄₁/a (I41/amd), respectively. Conductivity of the cubic phase (10⁻⁴ S cm⁻¹, room temperature) is about two orders of magnitude higher than that of the tetragonal phase (Kokal et al., 2011; Tietz et al., 2013).

Therefore, the challenge has been to stabilize the cubic phase, which can be achieved by doping. Geiger et al. (2011) firstly suggested the important role Al could play to stabilize the cubic phase relative to the tetragonal phase. Then Düvel et al. (2012) described in depth the effects of Al incorporation on both structural and dynamic properties of LLZO. It was suggested that at low Al concentrations Al³⁺ ions acted as an aliovalent dopant by replacing three Li⁺ ions. However, with increasing Al content, La³⁺ and Zr⁴⁺ ions were progressively replaced by Al ions. The substitution of La³⁺ and Zr⁴⁺ with Al³⁺ ions stabilized the cubic phase and greatly affected the corresponding Li ion dynamics. Similar stabilization of the cubic phase was observed with Ga and Ta substitution. Allen et al. (2012) recently reported Li₆.₇₅La₃Zr₁.₇₅Ta₀.₂₅O₁₂ cubic garnet with relatively high total Li⁺ conductivity (8.7 × 10⁻⁴ S cm⁻¹ at 25°C).

Owing to its high ionic conductivity, excellent stability with Li and wide electrochemical voltage window (Ishiguro et al., 2013; Jin and McGinn, 2013b), LLZO has been successfully used to fabricate all-solid-state lithium batteries. Jin and McGinn (2013a) reported a Cu₀.₁V₂O₅/LLZO/Li all-solid-state battery, which exhibited an initial discharging capacity of 93 mA h g⁻¹ at 10 μA cm⁻² (at 50°C). A full cell consisting of a LiCoO₂ cathode, a Li₆.₇₅La₃Zr₁.₇₅Nb₀.₂₅O₁₂ electrolyte and Li-metal anode exhibited stable cycle performance (Figure 7). Its discharge capacities were 129 mA h g⁻¹ at the 1st cycle and 127 mA h g⁻¹ at the 100th cycle, respectively (Ohta et al., 2012).

### PEROVSKITE-TYPE ELECTROLYTES

The lithium–lanthanum–titanates, Li₁ₓLaₓ(2/3)−x□(1/3)−xTa₂O₅ (LLTO, 0 < x < 0.16), with the perovskite structure (ABO₃), are characteristic of high bulk conductivity, of the order of 10⁻³ S cm⁻¹ at room temperature (Bohnke, 2008).

LLTO consists of a mixture of phases, i.e., a high-temperature phase with cubic Pm₃m symmetry (α-LLTO) and a lower temperature β-LLTO phase having tetragonal P4/mmm symmetry. Figure 8 shows the crystal structure of LLTO. The A site cations, which were Li⁺ and La³⁺ in the cubic α-LLTO phase, were randomly distributed, while the A sites of the ordered β-LLTO had...
a doubled perovskite structure, with an alternating arrangement of La-rich and Li-vacancy-rich layers along the c axis (Gao et al., 2013; Teranishi et al., 2013). It is believed that the conductivity of LLTO electrolytes is mainly governed by two factors: bottleneck size and site percolation. The crystal structure of tetragonal LLTO explains the high Li\(^+\) conductivity by the large concentration of A site vacancies, allowing motion of lithium ions by a vacancy mechanism and through square planar bottleneck between A sites, formed by four O\(^2\) ions between two neighboring A sites (Alonso et al., 2000).

LLTO-based SEs have many advantages, such as lithium single ion conductors, negligible electronic conductivity, high electrochemical stability (>8 V), stability in dry and hydrated atmospheres, and stability over a wide temperature range from 4 K to 1600 K (Bohnke, 2008). However, there are two major challenges for LLTO electrolytes, i.e., relatively low grain-boundary conductivity (<10\(^{-5}\) S cm\(^{-1}\)) and the instability against Li metal anode (Ban and Choi, 2001).

Thus, it is of utmost importance to increase the grain-boundary conductivity of LLTO electrolytes. It has been reported that the introduction of silica (Mei et al., 2010) and LLZO (Chen et al., 2012, 2013) could modify the grain-boundary layer of LLTO, and the total ionic conductivity could be over 1 \times 10^{-4} and 1.2 \times 10^{-4} S cm\(^{-1}\) at room temperature, respectively. A high conductivity was also achieved by doping Al (Morata-Orrantia et al., 2000) or Nb (Teranishi et al., 2013), whereas the addition of Ag (Abhilash et al., 2013) led to a decrease in conductivity. The replacement of some oxygen with fluorine did not significantly affect the conductivity (Fergus, 2010). Furthermore, effective sintering to decrease grain boundary is important to improve total conductivity (Vidal et al., 2014).

Another issue that lies with LLTO is its instability against Li metal anode. Lithium can be intercalated into LLTO at a potential below about 1.7–1.8 V vs. Li (Chen and Amine, 2001), which causes the reduction of Ti\(^{4+}\) to Ti\(^{3+}\) and induces high electronic conductivity. Nevertheless, chemical substitutional studies have been undergoing motivated by the discovery of new applications for LLTO compounds in future configurations of lithium ion batteries: as cathode coatings (Qian et al., 2012) or electrolyte separators (Inaguma and Nakashima, 2013). As shown in Figure 9, the stable discharge/charge behaviors of a rechargeable lithium/air cell with LLTO separator were confirmed.

**NASICON-TYPE ELECTROLYTES**

The term NASICON, which stands for Na\(^{+}\) super ionic conductors, was first given to the solid solution phase Na\(_{1+x}\)Zr\(_2\)Si\(_x\)P\(_3-x\)O\(_{12}\), \(x = 2.0\), discovered by Hong (1976). The general formula of NASICON-type SE can be described as Li\(_{A^IV}\)(PO\(_4\)\(_3\))(A\(_{IV}\) = Ti, Zr, Ge, Hf).

In the structure, AO\(_6\) octahedra are linked by PO\(_4\) tetrahedra to form 3D interconnected channels and two types of interstitial positions (M' and M'') where mobile cations are distributed, as shown in Figure 10. The mobile cations move from one site to another through bottlenecks, the size of which depends on the nature of the skeleton ions and on the carrier concentration in both type of sites (M' and M'') (Cretin and Fabry, 1999).

Among the Li\(_{A^IV}\)(PO\(_4\)\(_3\)) NASICONs, the systems with Ti exhibited high Li\(^+\) conductivity (about 10\(^{-3}\) S cm\(^{-1}\) at room temperature) (Takada, 2009). This could be explained by the ionic radius of Li\(^+\) matching well with the size of skeleton framework, which consists of TiO\(_6\) octahedra. Great efforts have
been made for maximizing the ionic conductivity of LiAl\textsubscript{1.3}Ti\textsubscript{1.7}(PO\textsubscript{4})\textsubscript{3} systems, especially LiTi\textsubscript{2}(PO\textsubscript{4})\textsubscript{3}. An increase in conductivity was observed when Ti\textsuperscript{4+} was partially substituted by Al\textsuperscript{3+} in Li\textsubscript{1+x}Al\textsubscript{x}Ti\textsubscript{2−x}(PO\textsubscript{4})\textsubscript{3} (LATP) (Key et al., 2012; Duluard et al., 2013; Morimoto et al., 2013) or when P\textsuperscript{5+} was substituted by Si\textsuperscript{4+} in Li\textsubscript{1+x+y}Al\textsubscript{x}Ti\textsubscript{2−x}Si\textsubscript{y}P\textsubscript{3−y}O\textsubscript{12} (Fu, 1997; Tan et al., 2012). Conductivity was enhanced significantly to 3 × 10\textsuperscript{−3} S cm\textsuperscript{−1} for Li\textsubscript{1.3}Al\textsubscript{0.3}Ti\textsubscript{1.7}(PO\textsubscript{4})\textsubscript{3} at room temperature.

Due to their excellent Li\textsuperscript{+} conductivity and stability in air and water, LiTi\textsubscript{2}(PO\textsubscript{4})\textsubscript{3}-based SEs have been applied to electrochemical energy devices, such as all-solid-state lithium batteries (Yada et al., 2009) and lithium/air secondary batteries (Shimonishi et al., 2011). Besides, NASICON-type SEs can have high electrochemical oxidative voltage. For example, LiGe\textsubscript{2}(PO\textsubscript{4})\textsubscript{3}-based SEs were reported to show high electrochemical oxidative voltage of about 6 V (vs. Li/Li\textsuperscript{+}) (Xu et al., 2007), as shown in Figure 11. However, similar to LLTO, LiTi\textsubscript{2}(PO\textsubscript{4})\textsubscript{3}-based SEs are instable toward Li metal, with the reduction of Ti\textsuperscript{4+} to Ti\textsuperscript{3+} (Hartmann et al., 2013).

GLASS-BASED INORGANIC ELECTROLYTES

GLASSY ELECTROLYTES

The glassy electrolytes have attracted much attention mainly due to their several advantages over the crystalline materials: isotropic ionic conduction, no grain-boundary resistance, ease to be fabricated into film, a wide range of compositions, etc. (Ravaine, 1980; Minami, 1987). In addition, the ion conductivity of amorphous glasses is generally higher than that of the corresponding crystalline ones because of their so-called open structure (Tatsumisago, 2004), as shown in Figure 12.
Generally, lithium ion conducting glasses can be divided into two categories: oxide and sulfide. For most of the oxide glassy electrolytes, the lithium ion conductivity at room temperature is too low to be practical for high energy batteries, normally on the order of 10\(^{-6}\) – 10\(^{-8}\) S cm\(^{-1}\) (Tatsumisago et al., 1987; Lee et al., 2002). While in sulfide glasses, high lithium ion conductivities of 10\(^{-3}\) – 10\(^{-5}\) S cm\(^{-1}\) at room temperature can be achieved due to high polarizability of sulfur ions, such as Li\(_2\)S–SiS\(_2\) and Li\(_2\)S–P\(_2\)S\(_5\) (Machida and Shigematsu, 2004; Tatsumisago, 2004; Ohtomo et al., 2013c).

However, these sulfide glass electrolytes can react with ambient moisture and generate H\(_2\)S gas (Knauth, 2009). Therefore, handling of sulfide SEs must be done in an inert atmosphere. However, partial substitution of oxygen atoms for sulfur atoms in sulfide electrolytes can be effective in suppressing H\(_2\)S gas generation (Ohtomo et al., 2013b). Very recently, Hayashi et al. (2014) reported a composite electrolyte with 90 mol% of 75Li\(_2\)S-21P\(_2\)S\(_5\)-4P\(_2\)O\(_5\) glass and 10 mol% ZnO via mechanical milling. In the work, partial substitution of P\(_2\)O\(_5\) for P\(_2\)S\(_5\), as well as the addition of ZnO, decreased the rate of H\(_2\)S generation when exposed to air. The conductivity on the other hand decreased with the addition of P\(_2\)O\(_5\).

In order to improve the conductivity of glassy electrolytes, several approaches have been proposed. One effective way is to mix two different anion species, so called “mixed anion effect” or “mixed former effect” (Tatsumisago et al., 1987; Raguenet et al., 2012). For instance, the addition of network former or modifier SeO\(_2\) into binary Li\(_2\)O–B\(_2\)O\(_3\) glassy electrolyte led to the increase in ionic conductivity at room temperature from 1.2 x 10\(^{-8}\) to 8 x 10\(^{-7}\) S cm\(^{-1}\) (Lee et al., 2002). The addition of lithium salts such as lithium halides (Ujiie et al., 2012) and lithium ortho-oxosalts (Aotani et al., 1994) is another effective way to enhance the conductivity of glassy electrolytes, because of the increase in lithium concentration and the decrease in activation energy for conduction. For example, the lithium ion conductivity of 67Li\(_2\)S-33P\(_2\)S\(_5\) glass at room temperature could increase from 10\(^{-4}\) S cm\(^{-1}\) to 10\(^{-3}\) S cm\(^{-1}\) by adding 45 mol% of LiI (Mercier et al., 1981).

However, increasing the amount of network modifiers with lithium ions facilitates the crystallization of glass. Thus the glasses with large amount of lithium ions are often prepared by twin-roller rapid quenching (Tatsumisago et al., 1981; Hayashi et al., 2002). This technique allows a cooling rate as high as 10\(^{6}\) K s\(^{-1}\) (Tatsumisago and Hayashi, 2009) to prevent crystallization.

In all-solid-state batteries, the glasses need to be ground into fine powders by mechanical milling techniques (Morimoto et al., 1999) in order to make good contact with the electrodes. Mechanical milling also is a commonly used method to form amorphous materials (Hayashi et al., 2001; Ohtomo et al., 2013a,b). It has two major advantages: the process is very simple and the synthesis can be performed at room temperature.

**GLASS–CERAMIC ELECTROLYTES**

Glass–ceramic electrolyte can be produced by the crystallization of a precursor glass. The crystallization usually would decrease the ionic conductivity, but the precipitation of a superionic conducting crystal from a precursor glass can enhance ionic conductivity. The grain-boundaries around crystal domains in glass–ceramics are filled with amorphous phases. Thus, glass–ceramic electrolytes usually have lower grain-boundary resistance than polycrystalline systems do (Tatsumisago et al., 2013).

Similar to the case of glassy electrolytes, the glass–ceramics also can be categorized into oxides and sulfides. For glass–ceramic oxides, NASICON-type systems have been studied the most, such as LATP (Fu, 1997b; Kotobuki and Koishi, 2013; Patil et al., 2013) and LAGP (Fu, 1997a; Nikolic et al., 2013; He et al., 2014) glass–ceramics. Their ionic conductivities at room temperature can reach 10\(^{-3}\) – 10\(^{-4}\) S cm\(^{-1}\).

Sulfide glass–ceramics can have higher ionic conductivity than that of oxides due to the large ionic radius and high polarizability of sulfur ions than those of oxide ions. For example, the conductivity of Li\(_2\)S–P\(_2\)S\(_5\) glass–ceramics can reach 10\(^{-3}\) S cm\(^{-1}\) at room temperature (Tatsumisago et al., 2002).

A superionic crystal with a structure analogous to that of the tho-LISICON phases can be precipitated by mechanical milling Li\(_2\)S–P\(_2\)S\(_5\) glasses (Hayashi et al., 2003). Very recently, Seino et al.
(2014) reported a Li$_2$S–P$_2$S$_5$ glass-ceramic conductor that had a very high ionic conductivity of 1.7 x 10$^{-2}$ S cm$^{-1}$ at room temperature by optimized heat treatment. The optimized conditions of heat treatment reduced the grain-boundary resistance and thus the total conductivity was five times higher than that previously reported for the Li$_2$S–P$_2$S$_5$ system (Mizuno et al., 2005). As shown in Figure 13, it suggested that the densification process increased overall conductivity, not by enhancing ionic conduction in the bulk, but reducing the grain-boundary resistance.

CONCLUDING REMARKS

Solid electrolytes are being viewed as a necessary component for a safe and high-performance lithium battery in future, thereby drawing extensive attention in the field. Many efforts have been made to advance their performance.

Since the high resistance at the electrode/SE interface is one crucial issue for the development of high power all-solid-state lithium batteries, it is of utmost importance to form a favorable contact between electrodes and the electrolyte. Both the achievement of close contact and the increase in contact area are essential (Tatsumisago et al., 2013). Coating of SE thin films on electrode active materials is being explored as an effective route. For instance, Li$_2$S–GeS$_2$ sulfide electrolyte thin films with the conductivity of 1.8 x 10$^{-4}$ S cm$^{-1}$ on LiCoO$_2$ particles were prepared by a pulsed laser deposition (PLD) technique (Ito et al., 2013). From a cross-sectional SEM image, this obtained thin film was dense and attached firmly to the Si substrate. Besides, other techniques, such as preparation of nanocomposites by a ball milling process (Nagao et al., 2012) or utilization of supercooled liquid of glass such as preparation of nanocomposites by a ball milling process and attached firmly to the Si substrate. Besides, other techniques, a cross-sectional SEM image, this obtained thin film was dense in Figure 13, it suggested that the densification process increased overall conductivity, not by enhancing ionic conduction in the bulk, but reducing the grain-boundary resistance.

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Conflict of Interest Statement: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Received: 16 April 2014; accepted: 11 June 2014; published online: 27 June 2014.

Citation: Cao C, Li Z-B, Wang X-L, Zhao X-B and Han W-Q (2014) Recent advances in inorganic solid electrolytes for lithium batteries. *Front. Energy Res.* 2:5. doi: 10.3389/fengr.2014.00025

This article was submitted to Energy Storage, a section of the journal Frontiers in Energy Research.

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