



# Recent Developments and Challenges in Hybrid Solid Electrolytes for Lithium-Ion Batteries

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Lithium-ion batteries (LIBs) have attracted worldwide research interest due to their high energy density and long cycle life. Solid-state LIBs improve the safety of conventional liquid-based LIBs by replacing the flammable organic electrolytes with a solid electrolyte. Among the various types of solid electrolytes, hybrid solid electrolytes (HSEs) demonstrate great promise to achieve high ionic conductivity, reduced interfacial resistance between the electrolyte and electrodes, mechanical robustness, and excellent processability due to the combined advantages of both polymer and inorganic electrolyte. This article summarizes recent developments in HSEs for LIBs. Approaches for the preparation of hybrid electrolytes and current understanding of ion-transport mechanisms are discussed. The main challenges including unsatisfactory ionic conductivity and perspectives of HSEs for LIBs are highlighted for future development. The present review provides insights into HSE development to allow a more efficient and target-oriented future endeavor on achieving high-performance solid-state LIBs.

**Keywords:** lithium-ion batteries (LIBs), hybrid solid electrolytes (HSEs), solid electrolytes, polymer electrolytes, inorganic electrolytes, ionic conductivity, ion-transport mechanisms

## INTRODUCTION

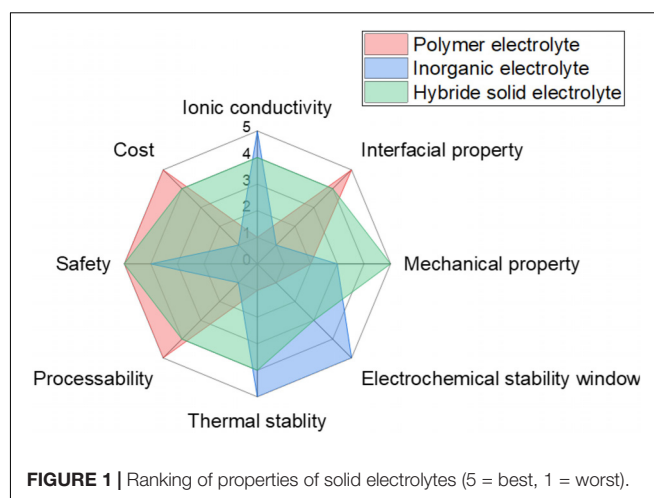
Lithium-ion batteries (LIBs) have revolutionized battery technologies, serving as the key component in personal portable electronics, electric vehicles, and stationary energy storage (Ge et al., 2014; Yanilmaz et al., 2016; Zhu et al., 2016b,d; Luo et al., 2017; Famprakis et al., 2019; Lagadec et al., 2019; Lee et al., 2019; Liu et al., 2019; Zhao et al., 2020). Driven by the growing number of applications and ever increasing use of consumer electronics, significant research effort has been focused on developing improved battery systems and reducing production costs (Fu et al., 2014; Luo et al., 2016; Zhu et al., 2018b,c). Conventional LIBs suffer from potential fire hazards caused by short-circuiting of the battery that may cause thermal runaway (Varzi et al., 2016; Manthiram et al., 2017; Wang X. et al., 2020; Zhang C. et al., 2019). In addition, the high reactivity of liquid electrolytes with the electrodes leads to side reactions and capacity fade over time (Xiao et al., 2020). Solid-state electrolytes, on the other hand, are non-flammable, offering

higher thermal stability, providing improved safety compared to liquid electrolytes batteries. Furthermore, their potential for enabling the use of a high capacity Li metal anode may greatly enhance the energy and power density and cycle life of current batteries (Pomerantseva et al., 2019). Therefore, the replacement of liquid electrolytes with high-performance solid electrolytes is imperative to overcome the related safety issues of conventional batteries, as well as to improve their energy density by enabling the use of high energy density electrodes (Janek and Zeier, 2016).

An ideal solid electrolyte should possess the characteristics of (1) high ionic conductivity, (2) high electronic resistance, (3) high cation-transference number, (4) wide electrochemical stability window, (5) outstanding thermal stability, (6) excellent mechanical strength, (7) reduced interfacial resistance, and (8) low cost and ease of synthesis (Manthiram et al., 2017). Since an alumina-based solid electrolyte was used in a high-temperature sodium-sulfur battery in the 1960s (Kummer and Neill, 1968; Hsueh and Bennion, 1971), tremendous effort has been made to develop advanced solid electrolytes with the above characteristics. Inorganic electrolytes exhibit high ionic conductivity and mechanical strength, while polymer electrolytes provide flexibility, processability and good contact with the electrodes, reducing the electrode/solid electrolyte interface.

Despite significant improvement in solid electrolytes, there are several remaining challenges (Wang et al., 2014; Lopez et al., 2019; Zhao et al., 2020). For inorganic electrolytes, issues with grain boundary resistance, chemical and electrochemical stability with the electrodes, high cost and lack of processability need to be addressed. Plus, inorganic electrolytes are typically brittle. As a result, they do not compensate for volume change of electrodes during charge and discharge. For polymer electrolytes, its practical application remains hindered by low ionic conductivity at ambient temperature (Agapov and Sokolov, 2011; Wang et al., 2014; Manthiram et al., 2017; Liu et al., 2019; Zhao et al., 2020). Their low ionic conductivity renders them incapable of achieving the charging and discharging rates required in practical utilization. Therefore, developing solid electrolytes that meet all the requirements for the realization of high-performance all-solid-state battery technologies is the key to revolutionize modern electrochemical energy storage devices (Liu et al., 2019).

An efficient way to address the performance issues of solid electrolytes is to hybridize two or more component for combined advantages of each component. Hybrid solid-state electrolytes (HSEs) may combine the advantages of inorganic and polymer electrolytes while overcoming the disadvantages of each component when used separately, as shown in **Figure 1**. The main strategy of HSEs is to disperse high-surface-area inorganic fillers into a polymer matrix, which is the focus of this review. Other morphologies include using ceramic as the matrix, fiber mat and so on. Compared to inorganic and polymer electrolytes, hybrid electrolytes exhibit a combined advantage of each component including high ionic conductivity, good mechanical properties from inorganic component as well as reduced interfacial resistance from polymer component. The up-to-date performance metrics of ionic conductivity, transference number, and electrochemical stability of recently developed



**FIGURE 1** | Ranking of properties of solid electrolytes (5 = best, 1 = worst).

HSEs are summarized in **Table 1**. To date, a number of inorganic fillers have been utilized, such as inert fillers ( $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{LiNbO}_3$ , and  $\text{BaTiO}_3$ ) and active fillers consisting of metal oxides or sulfides (Appetecchi and Passerini, 2000; Adebahr et al., 2003; Kumar, 2004; Zhao et al., 2016a). It is essential to summarize the state-of-the-art progress of HSEs based on the most recently available publications. A brief overview of solid-state electrolytes is provided, and are divided into three categories: inorganic electrolytes, polymer electrolytes, and hybrid electrolytes. Furthermore, the performance of various HSE systems is discussed in detail, along with ion transport mechanisms and fabrication methods. Despite many studies, current HSEs still have relatively low ambient ionic conductivity ( $<10^{-3}$  S/cm), poor interfacial stability, and high interfacial resistance, which greatly restrict the performance of the LIBs. In the end of this review, the current challenge and perspective of HSEs are discussed.

## HYBRID SOLID ELECTROLYTES

### Polymer Matrix

Polymers are widely used as solid electrolytes. Polymer electrolytes are attracting increasing interest because of their flexibility, processability, high safety, and scalability. Polymer electrolytes have been studied for use in a variety of high energy and power density batteries, including lithium-ion, lithium-sulfur, and lithium-air rechargeable batteries (Kim J. G. et al., 2015; Sun et al., 2017). With the incorporation of lithium salts, the ionic conductivity of solid-state polymer electrolytes can reach  $10^{-6}$  to  $10^{-5}$  S/cm at room temperature (Wang et al., 2016; Meabe et al., 2019). With the covalent attachment of anions to the polymer backbone, single lithium ion conducting polymer electrolytes show a lower ionic conductivity of  $10^{-7}$  to  $10^{-6}$  S/cm at room temperature (Cao et al., 2017, 2020; Zhang H. et al., 2017). Recent study demonstrated the remarkably high  $\text{Li}^+$  conductivity of  $5.84 \times 10^{-4}$  S/cm at  $25^\circ\text{C}$  (Ahmed et al., 2019). Due to its flexible nature and good adhesive properties,

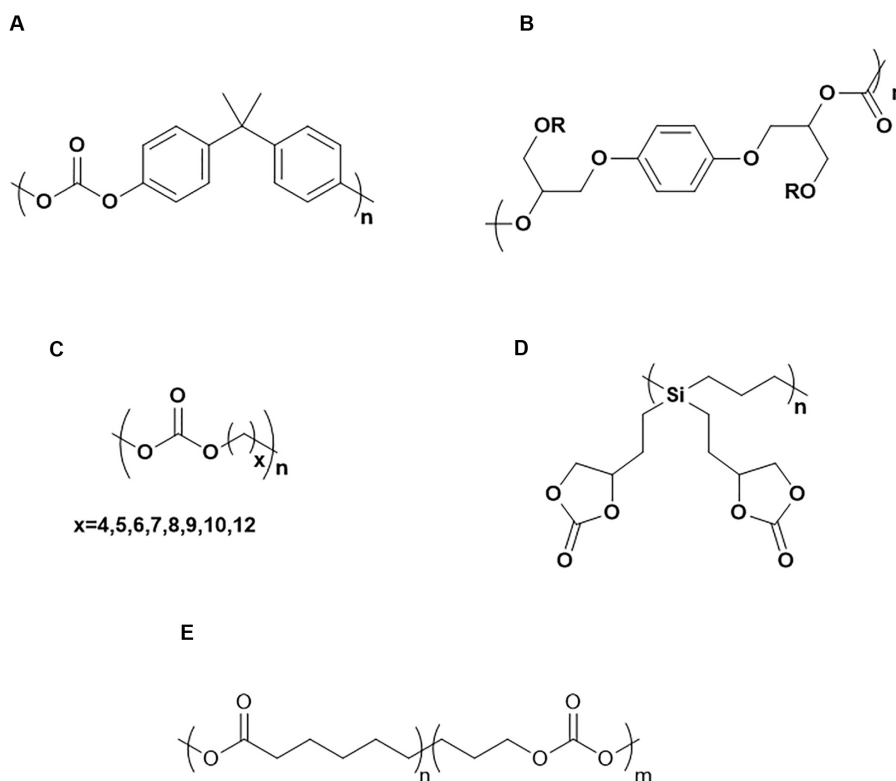
**TABLE 1** | Summary of recent HSE performance.

| Composite                 |                                                                                                                             | Ionic conductivity (S/cm)                                                              | Transference number                                           | Electrochemical stability Vs. Li <sup>+</sup> /Li               | References            |
|---------------------------|-----------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------|---------------------------------------------------------------|-----------------------------------------------------------------|-----------------------|
| Polymer                   | Filler                                                                                                                      |                                                                                        |                                                               |                                                                 |                       |
| PEO                       | Li <sub>1.5</sub> Al <sub>0.5</sub> Ge <sub>1.5</sub> (PO <sub>4</sub> ) <sub>3</sub>                                       | 1 × 10 <sup>-5</sup> (R.T.)                                                            | 0.56                                                          | Up to 4.75 V                                                    | Jung et al., 2015     |
|                           | vertically aligned Li <sub>1.5</sub> Al <sub>0.5</sub> Ge <sub>1.5</sub> (PO <sub>4</sub> ) <sub>3</sub>                    | 1.67 × 10 <sup>-4</sup> (R.T.);                                                        |                                                               | 1–4.5 V                                                         | Wang et al., 2019     |
|                           | Li <sub>1.3</sub> Al <sub>0.3</sub> Ti <sub>1.7</sub> (PO <sub>4</sub> ) <sub>3</sub>                                       | 1.11 × 10 <sup>-3</sup> (60°C)                                                         |                                                               |                                                                 |                       |
|                           | vertically aligned Li <sub>1.3</sub> Al <sub>0.3</sub> Ti <sub>1.7</sub> (PO <sub>4</sub> ) <sub>3</sub>                    | 1.9 × 10 <sup>-4</sup> (40°C)                                                          |                                                               |                                                                 | Nairn et al., 1996    |
|                           | Li <sub>10</sub> GeP <sub>2</sub> S <sub>12</sub>                                                                           | 5.2 × 10 <sup>-5</sup> (R.T.)                                                          | 0.91 (90% Li <sub>10</sub> GeP <sub>2</sub> S <sub>12</sub> ) | –0.5 to 5V                                                      | Zhai et al., 2017     |
|                           | Li <sub>10</sub> GeP <sub>2</sub> S <sub>12</sub>                                                                           | 2.2 × 10 <sup>-4</sup> (R.T.) (70% Li <sub>10</sub> GeP <sub>2</sub> S <sub>12</sub> ) |                                                               |                                                                 | Zheng et al., 2019    |
|                           | Li <sub>10</sub> GeP <sub>2</sub> S <sub>12</sub>                                                                           | 2.2 × 10 <sup>-4</sup> (R.T.) (1% Li <sub>10</sub> GeP <sub>2</sub> S <sub>12</sub> )  |                                                               | 0–5.7 V (1% Li <sub>10</sub> GeP <sub>2</sub> S <sub>12</sub> ) | Zhao et al., 2016b    |
|                           | Li <sub>6</sub> PS <sub>5</sub> Cl                                                                                          | 10 <sup>-3</sup> (R.T.)                                                                |                                                               |                                                                 | Zhang J. et al., 2019 |
|                           | nanofiber Li <sub>0.33</sub> La <sub>0.557</sub> TiO <sub>3</sub>                                                           | 2.4 × 10 <sup>-4</sup> (R.T.)                                                          | 0.33                                                          | Up to 5.0 V                                                     | Zhu et al., 2018a     |
|                           | 3D Li <sub>0.33</sub> La <sub>0.557</sub> TiO <sub>3</sub> network                                                          | 1.8 × 10 <sup>-4</sup> (R.T.)                                                          |                                                               | Up to 4.5 V                                                     | Wang et al., 2018     |
|                           | Li <sub>7</sub> La <sub>3</sub> Zr <sub>2</sub> O <sub>12</sub> nanowires                                                   | 2.4 × 10 <sup>-4</sup> (R.T.)                                                          |                                                               | Up to 5.5 V                                                     | Zhu et al., 2018a     |
|                           | tetragonal Li <sub>7</sub> La <sub>3</sub> Zr <sub>2</sub> O <sub>12</sub>                                                  | 4.45 × 10 <sup>-4</sup> (55°C)                                                         |                                                               | 0–5 V                                                           | Choi et al., 2015     |
|                           | Li <sub>6.4</sub> La <sub>3</sub> Zr <sub>1.4</sub> Ta <sub>0.6</sub> O <sub>12</sub> with solid plasticizer succinonitrile | 1.22 × 10 <sup>-4</sup> (30°C)                                                         | 0.41                                                          | Up to 5.5 V                                                     | Zha et al., 2018      |
|                           | 3D network of Li <sub>1.4</sub> Al <sub>0.4</sub> Ti <sub>1.6</sub> (PO <sub>4</sub> ) <sub>3</sub> /PAN enhanced PEO       | 6.5 × 10 <sup>-4</sup> (60°C)                                                          | 0.32                                                          | 0.5–5 V                                                         | Li D. et al., 2018    |
| PAN                       | Li <sub>0.33</sub> La <sub>0.557</sub> TiO <sub>3</sub>                                                                     | 2.4 × 10 <sup>-4</sup> (R.T.)                                                          |                                                               | Up to 4.7 V                                                     | Liu et al., 2015      |
| PVDF-HPF                  | Li <sub>7</sub> La <sub>3</sub> Zr <sub>2</sub> O <sub>12</sub>                                                             | 7.63 × 10 <sup>-4</sup> (30°C)                                                         | 0.61                                                          | Up to 5.3 V                                                     | Zhang et al., 2018    |
| Poly(propylene carbonate) | Li <sub>6.75</sub> La <sub>3</sub> Zr <sub>1.75</sub> Ta <sub>0.25</sub> O <sub>12</sub>                                    | 5.2 × 10 <sup>-4</sup> (20°C)                                                          | 0.75                                                          | Up to 4.6 V                                                     | Zhang J. et al., 2017 |
| Poly(vinyl carbonate)     | Li <sub>10</sub> SnP <sub>2</sub> S <sub>12</sub>                                                                           | 2.0 × 10 <sup>-4</sup> (R.T.)                                                          | 0.6                                                           | Up to 4.5 V                                                     | Ju et al., 2018       |

polymer electrolytes components can form good contact with the electrodes. These unique electrochemical properties highlight the promise of polymer electrolytes for solid-state battery applications. The polymers commonly used as electrolytes include poly(ethylene oxide) (PEO), poly(carbonate) (PC), poly(siloxane), poly(acrylonitrile) (PAN), and poly(vinylidene fluoride) (PVDF). For many polymer electrolytes, ion mobility is strongly coupled to the segmental motion of the polymer chains, limiting the achievable ambient conductivity (Wang et al., 2014; Porcarelli et al., 2016). In addition, the crystalline phase of polymers (e.g., PEO) generally hinders ion transport below the melting point ( $T_m \sim 65^\circ\text{C}$  for PEO) (Xue et al., 2015). To reduce the degree of crystallinity and the glass-transition temperature ( $T_g$ ) of polymers, a variety of methods have been explored, including polymer blends, copolymerization and crosslinking (Soo, 1999; Wen et al., 2000; Fullerton-Shirey and Maranas, 2009; Lopez et al., 2019; Cao et al., 2020).

Among polymer electrolytes, PEO-based polymer electrolytes are most extensively studied due to its faster polymer dynamics at ambient temperature and excellent capability to solvate various salts (Lopez et al., 2019). Salt-doped PEO exhibits reasonable ionic conductivity as an HSEs component due to its low glass transition temperature ( $\sim 30^\circ\text{C}$  with salts), (Senthil Kumar et al., 2014) remaining in a rubbery state at room temperature. Additionally, PEO demonstrates an outstanding ability to solvate large concentration of lithium salts (Berthier et al., 1983;

Karan et al., 2008) and it may have favorable interactions with inorganic fillers (Croce et al., 1999; Malathi and Tamilarasan, 2014). The ether oxygen atoms in PEO act as a Lewis base to coordinate with the Li-ion (Meyer, 1998). The coordination of PEO with the Li-ion creates pseudo ionic crosslinks that restrict the movement of Li<sup>+</sup> and slows down the segmental motion of the polymer chains when the concentration of salt becomes high (typically above EO:Li = 12) (Lehmann et al., 2019). The restricted segmental motion of the PEO chains results in an increase in  $T_g$  and a reduction in ionic conductivity. The low Li transference number in PEO also originates from the strong coordination of the Li-ion by the ether oxygens. As a result, large anions like trifluoromethanesulfonyl imide (TFSI<sup>-</sup>) moves faster than the small cation. Another weakness of PEO is its high crystallinity (>60%), originating from its linear structure. Due to these properties, the room temperature ionic conductivity of PEO with Li salts is low (10<sup>-6</sup> S/cm), 3–4 orders of magnitude lower than that of commercial liquid electrolytes (Wright, 1975; Lee et al., 2005). To decrease the crystallinity and improve the mechanical properties of PEO, crosslinking has been adopted. The network structure with short PEO chains between crosslinking helps to decrease the crystallinity of PEO; however, the mobility of the polymer segments is also restricted, such that the ionic conductivity is often reduced (Maccallum et al., 1984). Another commonly used method to decrease the crystallinity of PEO, is to add inorganic or organic plasticizers to the polymer,



**SCHEME 1** | Chemical structure of **(A)** PC made from Bisphenol A, **(B)** PC made from hydroquinone group, **(C)** APC with different length of  $\text{CH}_2$ , **(D)** PolySBDC, **(E)** Poly(carbonate-co-ester).

which was first proposed in Liang (1973). PEO with organic plasticizers typically exhibits worse mechanical properties than neat PEO (Quartarone et al., 1998). On the other hand, PEO with inorganic fillers usually shows improved mechanical and thermal stability (Weston and Steele, 1982). In addition to fillers, polymer blending can improve the mechanical strength of a PEO electrolyte. PEO/P(VDF-HFP)/LLZTO electrolyte shows largely enhanced tensile strength of 3.5 MPa and Young's modulus of 53.5 MPa ( $\sim 10$  times higher than that of PEO/LLZTO SPE) (Wang T. et al., 2020). This approach of polymer-polymer hybrid solid electrolytes provides another avenue to enhance the mechanical property and overall electrolyte properties.

PCs have also drawn attention for use as solid electrolytes. The advantage of PCs includes their high dielectric constant and ability to dissolve lithium salts. Spectroscopic techniques and molecular dynamics simulations indicate that both of the oxygen atoms in PC (carbonyl group oxygen and alkoxy oxygen) can coordinate with  $\text{Li}^+$  (Matsumoto et al., 2013; Ong et al., 2015). As a commercially available polymeric material, PC made from bisphenol A (**Scheme 1A**) exhibits high strength, toughness, and good durability. However, bisphenol A PC without any modifications cannot be utilized as an HSE, due to its low ambient temperature ionic conductivity of  $7 \times 10^{-9}$  S/cm (Spiegel et al., 2000). The  $T_g$  of PCs made from bisphenol A is typically above  $100^\circ\text{C}$  (i.e.,  $T_g$  of Lexan is  $145^\circ\text{C}$ ) (Yang and Yetter, 1994) due to the rigid phenol group in the backbone.

Therefore, the mobility of polymer chains is limited at room temperature, resulting in its low ionic conductivity. Matsumoto et al. (2013) synthesized a PC by utilizing hydroquinone in place of bisphenol A (**Scheme 1B**) and by adding plasticizers. Although the conductivity ( $1.5 \times 10^{-6}$  S/cm at  $30^\circ\text{C}$ ) is still not satisfactory, the transference number was improved. The Li-ion transference number was above 0.5, higher than that of PEO (transference number is only 0.2–0.5) (Evans et al., 1987; Pożyczka et al., 2017). The weaker coordinating interaction of both the carbonyl oxygen and alkoxy oxygen groups in PC with  $\text{Li}^+$  compared with that of the ether oxygen in PEO contributes to the higher Li-ion transference number. With the introduction of aliphatic groups into the PC backbone, a highly flexible PC can be fabricated. Meabe et al. (2017) synthesized a series of PCs with  $(\text{CH}_2)_x$  where  $x = 4, 5, 6, 7, 8, 9, 10$ , and 12 (**Scheme 1C**). The results showed that the solid electrolyte made from PCs with  $(\text{CH}_2)_x$  exhibited an optimal conductivity and lowest  $T_g$  when  $x = 7$ . With the addition of 80 wt% LiTFSI, the conductivity of low molecular weight poly(dodecamethylene carbonate) can reach  $1 \times 10^{-4}$  S/cm at room temperature (Meabe et al., 2017). An alternative method to incorporate a carbonate group into a polymer is via sidechain instead of in the backbone. For example, poly-1,1-di[2-(2,4-dioxo-3-pentanoyl)ethyl]silacyclobutane (polySBDC) (**Scheme 1D**), exhibited a significantly decreased  $T_g$  ( $-25^\circ\text{C}$ ) with the ionic conductivity reaching  $1.2 \times 10^{-4}$  S/cm at  $30^\circ\text{C}$  (Matsumoto et al., 2016). Copolymerization of PC with a polyester (carbonate:

ester = 80: 20) achieved a room temperature ionic conductivity of  $4.1 \times 10^{-5}$  S/cm (**Scheme 1E**) (Mindemark et al., 2015).

PAN is the first polymer to be used as a solid electrolyte that contains the nitrile group. The nitrogen atom in PAN is considered to have the ability to coordinate with  $\text{Li}^+$  due to its strong electronegativity. In fact, nitrile groups can be found in liquid electrolytes and additives. PAN (**Scheme 2A**) is a semi-crystalline polymer at room temperature with a  $T_g$  of  $\sim 80^\circ\text{C}$ . Based on these thermal properties, PAN was not expected to have high ionic conductivity, because the PAN chains are less flexible than that of PEO. PAN exhibited an ionic conductivity of  $6.5 \times 10^{-7}$  S/cm with 20 wt% of  $\text{LiClO}_4$  at room temperature (Yang et al., 1996). The main challenge for PAN is its limited solubility in organic solvents. Dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) are commonly used to dissolve PAN. Since they are high boiling point solvents, it is very challenging to remove them from a solvent-cast polymer electrolyte. As a result, the residual solvent trapped in the polymer matrix significantly affects the  $\text{Li}^+$  transport and electrochemical stability of the solid electrolyte (Gutmann, 1976). Forsyth et al. (2000) utilized a hot-press method to prepare solvent-free PAN films. With 72 wt%  $\text{LiCF}_3\text{SO}_3$ , its conductivity reached  $2 \times 10^{-6}$  S/cm at  $65^\circ\text{C}$  (Forsyth et al., 2000). To make the nitrile-based polymer more soluble, a methyl group can be introduced into the backbone. Poly(methacrylonitrile) (PMAN) (**Scheme 2B**) can be dissolved in acetone. The film contained no residual solvent with the use of the low boiling point casting solvent. The reported conductivity of PMAN is  $\sim 10^{-5}$  S/cm at  $75^\circ\text{C}$ . However, the PMAN film has a high  $T_g$  ( $110^\circ\text{C}$ ), which limits its performance at room temperature (Saunier et al., 2002). Another strategy to improve the solubility of PAN is to incorporate PAN with other polymer segments. Florjańczyk et al. reported a copolymer of PAN with butyl acrylate (**Scheme 2C**). The butyl acrylate group makes it possible to prepare the electrolyte using a solvent casting method with acetonitrile. In addition, the  $T_g$  of the copolymer decreases to  $42\text{--}44^\circ\text{C}$  and shows a high capability of dissolving lithium salts (Florjańczyk et al., 2004, 2005).

## Fillers

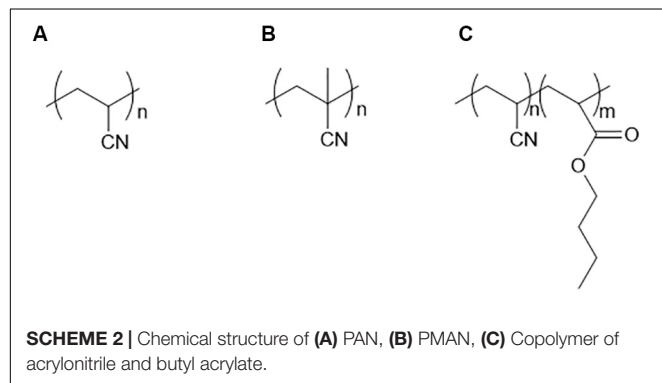
Many types of inorganic materials such as perovskite-type, garnet-type, sodium superionic conductor (NASICON)-type, amorphous oxides, and sulfide materials have been developed as

a LIB electrolyte (Inaguma et al., 1993; Zheng et al., 2018). As reported, perovskite-type [e.g.,  $\text{Li}_{0.34(1)}\text{La}_{0.51(1)}\text{TiO}_{2.94(2)}$  (LLTO)] (Inaguma et al., 1993) and garnet-type [e.g.,  $\text{Li}_5\text{La}_3\text{M}_2\text{O}_{12}$  ( $\text{M} = \text{Nb}$  or  $\text{Tb}$ ) and  $\text{Li}_6\text{Ala}_2\text{M}_2\text{O}_{12}$  ( $\text{A} = \text{Ca}$ ,  $\text{Sr}$  or  $\text{Ba}$ ;  $\text{M} = \text{Nb}$  or  $\text{Ta}$ )] (Geiger et al., 2011; Murugan et al., 2011) solid electrolytes exhibit high ionic conductivity of  $> 10^{-3}$  S/cm at room temperature. NASICON-type materials generally have an  $\text{AM}_2(\text{PO}_4)_3$  formula ( $\text{A} = \text{Li}$ ,  $\text{Na}$ , or  $\text{K}$ ;  $\text{M} = \text{Ge}$ ,  $\text{Zr}$ , or  $\text{Ti}$ ) (Thangadurai and Weppner, 2006). For this type of solid electrolyte, their ionic conductivity can be improved by the substitution of the metal ( $\text{Ge}$ ,  $\text{Zr}$ , or  $\text{Ti}$ ) by  $\text{Hf}$  or  $\text{Sn}$  (Martinez-Juarez et al., 1995). Among all inorganic solid electrolytes, sulfide-type solid electrolytes (i.e.,  $\text{Li}_2\text{S-SiS}_2$ ) are another popular electrolyte and investigated due to exhibiting some of the highest reported ionic conductivities. Kamaya et al. reported that the ionic conductivity of a  $\text{Li}_3\text{PS}_4$  crystal was significantly increased to  $2.2 \times 10^{-3}$  S/cm at room temperature by doping with phosphorus and germanium (Kamaya et al., 2011). In addition, their wide electrochemical stability window could be beneficial for use in high-voltage solid-state batteries (Chen et al., 2018b). However, the major drawback of inorganic materials, whether amorphous or crystalline, is their brittleness, making large scale production quite challenging. Furthermore, maintaining good contact between the electrolyte and electrodes is difficult because of their lack of flexibility and volume changes during charging and discharging (Muramatsu et al., 2011). Therefore, by using polymer as the matrix with inorganic fillers, the interfacial property between the electrolyte and electrode will be significantly improved, thus improving the overall battery performance.

In HSEs, inorganic fillers play an important role in determining the performance of the battery. In the following section, we divide the polymer-inorganic composite electrolyte into two categories based on the function of the filler; inert fillers, with no bulk Li-ion conduction, and active fillers usually with high bulk Li-ion conduction.

### Inert Fillers

Inert fillers do not conduct  $\text{Li}^+$  themselves. Ceramic nanoparticles utilized in HSEs include  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ , and  $\text{SiO}_2$  (Croke et al., 1998). Even though ceramic oxides do not participate in ion conduction directly, it was reported that ionic conductivity increased with the addition of the ceramic filler over a wide temperature range ( $30\text{--}100^\circ\text{C}$ ) (Croke et al., 1998). In hybrid electrolytes, the inorganic fillers not only act as solid plasticizers to inhibit the crystallization kinetics of the polymer segments but also promote ion mobility. Lin et al. (2016) reported that the crystallinity of PEO was highly decreased by  $\text{SiO}_2$  via the *in situ* hydrolysis method compared to the blending method, attributing to their much stronger chemical/mechanical interactions between monodispersed 12 nm diameter  $\text{SiO}_2$  nanospheres and PEO chains, and thus facilitates polymer segmental motion for ionic conduction. This led to good ionic conductivity ( $1.2 \times 10^{-3}$  S/cm at  $60^\circ\text{C}$ ,  $4.4 \times 10^{-5}$  S/cm at  $30^\circ\text{C}$ ). Besides the ionic conductivity, incorporating inert fillers with the polymer electrolyte was also reported to widen the electrochemical stability window up to 5.5 V (Lin et al., 2016).



Weston and Steele (1982) firstly studied the effects of incorporating inert  $\text{Al}_2\text{O}_3$  fillers to a  $\text{LiClO}_4/\text{PEO}$  electrolyte in 1982. From then on, inert fillers with different sizes as well as surface functionalities have been extensively investigated attributing to the important role of the fillers surfaces/interfaces in improving conductivity. The interfacial area is strongly dependent on the size and content of inert fillers.

Ceramic nanoparticles influence not only the electrochemical properties but also the mechanical properties of polymer electrolytes. Ramesh et al. (2007) studied the effect of  $\text{SiO}_2$  on the mechanical properties of a poly(vinyl chloride)-PEO polymer electrolyte. The Young's modulus increased from 500 to 2300 Pa with the addition of 10%  $\text{SiO}_2$  (Ramesh et al., 2007). Wen et al. investigated the effect of  $\text{BaTiO}_3$  on a PEO-poly(propylene oxide) crosslinked amorphous polymer. With 10%  $\text{BaTiO}_3$ , the tensile strength improved from 1.42 to 2.12 MPa at 80°C (Wen et al., 2003).

Another interesting direction of the inert filler is the interaction between the functional group on the inert filler surface and the polymer chains. Liu et al. studied the interaction between the  $-\text{OH}/\text{H}$  functional group on the  $\text{SiO}_2$ ,  $\text{Li}^+$ , and the PEO chains. It was concluded that with  $\text{SiO}_2$ , the ionic conductivity of PEO was not improved. Instead, the transference number was highly increased up to 0.56. The results were ascribed to the hydrogen bond between the  $-\text{OH}/\text{H}$  functional group on the  $\text{SiO}_2$  surface and the PEO chain. The hydrogen bonding provided a free space around the  $\text{SiO}_2$  particle and the free space would favor an absorption-like process. The anion, which contains  $-\text{F}$  elements, was trapped in the free space. Thus, the mobility of the anion was hindered (Liu et al., 2004).

## Active Fillers

Active fillers participate in ionic conductivity. Metal oxides or sulfides are promising lithium-ion conductors. Li-ion transport in an active filler composite system is complex, and the proposed mechanisms are discussed in Section "Hybrid Solid Electrolytes." In this section, we provide an overview of several active fillers and their electrochemical performance.

$\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$  (LATP) and  $\text{Li}_{1+x}\text{Al}_x\text{Ge}_{2-x}(\text{PO}_4)_3$  (LAGP) are superionic conductors with the same structure as NASICON, but in Li-ion conducting form (Xu et al., 2004). When the Ti/Ge elements are partially substituted with Al, the ionic conductivity can be elevated from  $10^{-4}$  S/cm to  $10^{-3}$  S/cm for LATP (Aono, 1990; Xu et al., 2006) and  $10^{-2}$  S/cm for LAGP (Kumar et al., 2009) at room temperature. The use of  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$  as an active filler in a PEO matrix was first reported in Nairn et al. (1996). With a 66% LATP loading in PEO (w/w), the ionic conductivity was increased to  $10^{-4}$  S/cm at 40°C, two orders of magnitude higher than pure PEO. Wang et al. further systemically studied  $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3/\text{PEO}$  composites with varied Li/EO ratios, amount of  $x$  in LATP, and LATP/PEO weight ratios (Wang Y.-J. et al., 2006). At a fixed EO to Li ratio of  $\text{EO}/\text{Li} = 8$ , the ionic conductivity of  $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$  reaches its maximum value when  $x = 0.5$ . For  $\text{PEO}-\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ , ( $x = 0.3$ ) composite, the maximum ionic conductivity ( $10^{-6}$  S/cm at room temperature) occurs when  $\text{EO}/\text{Li} = 16$ . The presence of LATP was found to

suppresses the crystallinity of PEO at low loadings (5 wt%) but the degree of PEO crystallinity increases with increasing addition of LATP. In addition, compared to the randomly dispersed LATP, it was found that a vertically aligned structure of LATP in PEO can enhance the ionic conductivity to  $5.2 \times 10^{-5}$  S/cm (Zhai et al., 2017). A similar strategy was applied to LAGP with PEO. The room temperature ionic conductivity increased 6 times for a composite with an aligned ceramic structure ( $1.7 \times 10^{-4}$  S/cm) compared to the randomly dispersed one ( $2.7 \times 10^{-5}$  S/cm). The aligned composite electrolyte in a  $\text{Li}/\text{LiFePO}_4$  cell showed a capacity retention (above 85% after 400 cycles) at 0.6 C (Wang et al., 2019). Li et al. fabricated a 3-dimensional fiber network consisting of LATP and PAN, which they embedded into a PEO matrix. The LATP/PAN/PEO composite electrolyte exhibited an electrochemical stability window of 5 volts and a 10.7 MPa tensile strength (Li D. et al., 2018). LAGP has higher ionic conductivity than LATP because LAGP has a lower resistance at the interface with the polymer (Mariappan et al., 2012). Jung et al. (2015) studied a LAGP-PEO composite electrolyte with different weight ratios. It was found that with 60% (w/w) LAGP, the cells showed the lowest electrode-electrolyte interfacial resistance and best rate capability (Jung et al., 2015).

Perovskites are another family of inorganic ionic conductors, among which  $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$  (LLTO) is the most commonly used.  $\text{Li}_{0.34}\text{La}_{0.51}\text{TiO}_{2.94}$  exhibits an ionic conductivity of  $10^{-5}$  S/cm at room temperature, which was first reported in Inaguma et al. (1993). LLTO nanowire and nanoparticle PAN composite electrolytes were studied by Liu et al. (2015). An LLTO nanowire/PAN composite showed improved ionic conductivity compared to the one with dispersed nanoparticles at the same ceramic loading, due to the continuous conductive networks formed by the nanowires. The same strategy was also applied to PEO-based composite, resulting in an increased ionic conductivity of  $2.4 \times 10^{-4}$  S/cm at room temperature (Zhu et al., 2018a).

Garnet type inorganic ion conductors are also commonly used in composite electrolytes.  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  (LLZO) is a promising material for use in Li-ion batteries. With an LLZO loading of 52.5% (w/w), the ionic conductivity of PEO-based HSE can achieve  $10^{-4}$  S/cm at 55°C (Choi et al., 2015). Further studies have developed integrated all-solid-state batteries based on this composite electrolyte. The batteries exhibited stable performance in a  $\text{Li}/\text{LiFePO}_4$  cell. When LLZO was placed in a PVDF-HFP matrix, the electrochemical stability window was widened (Zhang et al., 2018). A derivative material of LLZO was fabricated by the partial substitution of Zr by Ta (LLZTO) and was also studied as a composite electrolyte. However, there was little improvement in the ionic conductivity of the LLZTO/PEO composite electrolyte ( $1.9 \times 10^{-5}$  S/cm) compared to the LLZO/PEO composite ( $1.0 \times 10^{-5}$  S/cm) at 30°C (Choi et al., 2015; Zha et al., 2018). With the utilization of a poly(propylene carbonate) matrix instead of PEO, the conductivity of an LLZTO/poly(propylene carbonate) composite was improved to  $5.2 \times 10^{-4}$  S/cm at 21°C (Zhang J. et al., 2017).

In addition to the oxides mentioned above, sulfides are another class of inorganic ionic conductors, and the various types are comprehensively reviewed by Chen et al. (2018c).

Compared with oxides,  $S^{2-}$  has a larger ionic radius and lower electronegativity, thus, providing a weaker association with  $Li^+$ . The ionic conductivity of sulfides is generally higher than oxides. One of the highest reported ionic conductivities ( $10^{-2}$  S/cm at room temperature) of a sulfide-based inorganic electrolyte is for  $Li_{10}GeP_2S_{12}$ . The high ionic conductivity is attributed to the formation of anisotropic  $Li^+$  diffusion pathway in the  $Li_{10}GeP_2S_{12}$  crystalline structure. The combination of sulfides with a polymer not only show improved ionic conductivity but also have an extended electrochemical stability window of 5.7 V (Zhao et al., 2016b). A study utilizing high loadings (95 wt%) of a  $78Li_2S-22P_2S_5$  glass type ceramic compared the performance of HSEs with PVDF and PEO polymer matrices (Zhang et al., 2020). While PVDF provided a higher ionic conductivity ( $4.54 \times 10^{-4}$  S/cm) than PEO ( $1.27 \times 10^{-4}$  S/cm) at room temperature, the LiTFSI salt was found to be inhomogeneously distributed in the PVDF composite. The composites achieved a charge/discharge capacity of 566 mA h/g for the PVDF and 725 mA h/g for the PEO in a Li//sulfur-carbon nanotube cell after 100 cycles.

## ION CONDUCTION MECHANISMS IN HYBRID SOLID ELECTROLYTES

Ion conduction mechanisms in inorganic solid electrolytes are quite straightforward and generally occurs by ion hopping. The ions diffuse through the connected available vacant and interstitial sites in the crystal. The ionic conductivity of the solid electrolytes is determined by the concentration and distribution of the defects. In polymer electrolytes, the current understanding of ion conduction is the combination of ion movement with local polymer segmental motion and ion jumping over some potential energy barrier if the segmental motion is slow (Gibbs and DiMarzio, 1958; Cohen and Turnbull, 1959; Fan et al., 2018; Bocharova and Sokolov, 2020). The addition of inorganic fillers to the polymer electrolytes has proven to be an effective way to increase its ionic conductivity (Chen and Vereecken, 2019; Dirican et al., 2019). Recent efforts on explaining how ceramic fillers positively enhance the ionic conductivity is described below.

### Ionic Conduction With Inert Fillers

Current understanding of the effects of the inert fillers, such as micro/nanoparticles,  $Al_2O_3$  (Weston and Steele, 1982; Croce et al., 1998, 1999, 2000; Appetecchi et al., 2000),  $SiO_2$  (Fan et al., 2003; Tominaga et al., 2005; Wang X.-L. et al., 2006; Tominaga and Endo, 2013),  $TiO_2$  (Croce et al., 1999, 2000; Appetecchi et al., 2000; Croce et al., 2000),  $ZrO_2$  (Croce et al., 2006), molecular sieves (Munichandraiah et al., 1995; Xi et al., 2004), and ferroelectric materials, has focused on two mechanisms: (1) the promotion of salt dissociation to create more free  $Li$ -ions by acting as centers of Lewis acid-base interactions; (2) the suppression of polymer crystallization.

The first hypothesis, the Lewis acid-base theory, was first proposed by Wiczeorek in 1995 to explain the interactions between inorganic filler, polymer, and salt (Przytulski et al., 1995;

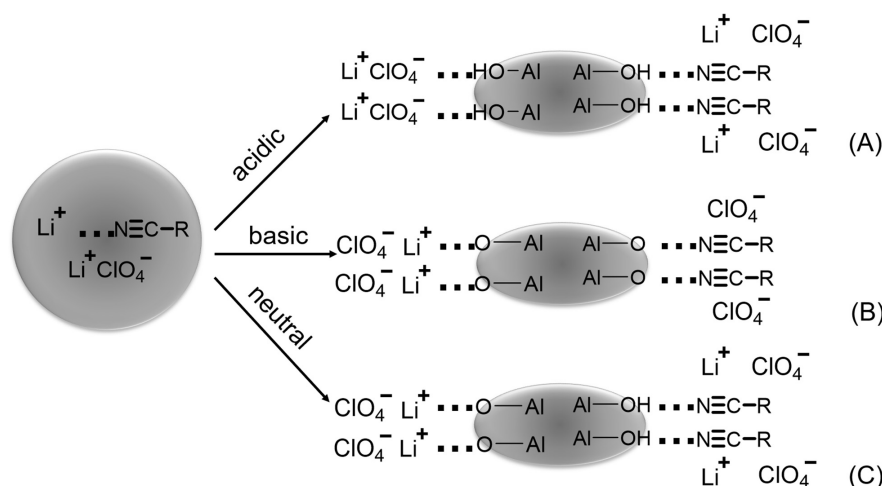
Wiczeorek et al., 1995, 1996). With the Lewis acid-base theory, the explanation is that in HSEs systems, the  $Li$ -ion is considered as a Lewis acid, and the solvating groups of polymers and  $ClO_4^-$  anions act as Lewis bases. The fillers can be considered a Lewis acid or base, depending on their surface chemistry (Figure 2). Hence, several acid-base interactions are occurring in these systems. An acidic surface can attract the polymer solvating groups or  $ClO_4^-$ , leading to free associated  $Li^+$  cations. The addition of a basic surface attracts  $Li$ -ions and polymer functional groups, improving the dissociation of  $Li^+-ClO_4^-$  ion pairs. Croce et al. added superacid  $ZrO_2$  to a PEO/ $LiBF_4$  complex. The  $Li$ -ion transference number was greatly improved as the acidic surface of the ceramic filler demonstrated a higher affinity toward  $ClO_4^-$  than that of  $Li^+$ , promoting the separation  $Li^+-ClO_4^-$  ion pairs (Croce et al., 2001).

In PEO-based electrolyte systems, studies have shown that the crystallization of the polymer is suppressed with the addition of inert fillers, which further increases the ionic conductivity (Bouchet et al., 2013; Hanson et al., 2013; Khurana et al., 2014; Das and Ghosh, 2015; Zhu et al., 2018a). Ion transport in PEO is strongly coupled to segmental dynamics, and freezing of segmental motion in crystalline phase suppresses ionic conductivity. The addition of inert fillers suppresses the crystallinity of PEO, which leads to increased segmental dynamics, resulting in a higher conductivity. Researchers have shown that the addition of  $\gamma$ - $LiAlO_2$  filler into PEO-based electrolyte greatly reduces the crystallization rate, increasing ionic conductivity, and the lithium/electrolyte interfacial stability (Hu et al., 2007; Tan et al., 2016).

However, Lewis interactions and polymer crystallinity are not the full picture of ion conduction mechanisms in HSEs with inert fillers. Marcinek et al. (2000) have shown that the ionic conductivity for a PEG-based electrolyte increases with the addition of neutral, acidic, or basic inert filler  $Al_2O_3$  (Croce et al., 2001). The ionic conductivities of the electrolytes for acidic and basic surfaces are similar, and both are higher than the one with a neutral surface. However, the trend of the fraction of ion pairs measured for the electrolytes in the order of acidic > neutral > basic surface is inconsistent with the trend of the fraction of free ions. Fan et al. added fumed-silica particles into PEG-based electrolytes with lithium salts, leading to a better conductivity of the composite electrolyte. However, no conductivity differences were observed between the non-polar PEG with modified polar PEG electrolytes (Fan, 1997). Hanson et al. (2013) reported theoretical results of atomistic molecular dynamics simulations to study lithium ion diffusivities in PEO/ $TiO_2$  and observed that the lithium ion diffusivities decrease with increased particle loading. Those contradictions may indicate the involvement of other factors or ion conduction mechanisms functioning in parallel, which are not yet fully revealed.

### Ionic Conduction With Active Fillers

The ion conduction mechanisms in HSEs with active fillers are complicated, as not only the active fillers can influence the polymer chain structure, but also it can create additional  $Li^+$  pathways within the composites. The pathways include active



**FIGURE 2 |** Schematic demonstration of the Lewis acid-base dissociation effects of (A) Lewis acidic, (B) Lewis basic, and (C) neutral surface groups on ionic conductivity. Reprinted with permission from reference Wang et al. (2003). Copyright 2003 The Electrochemical Society, Inc.

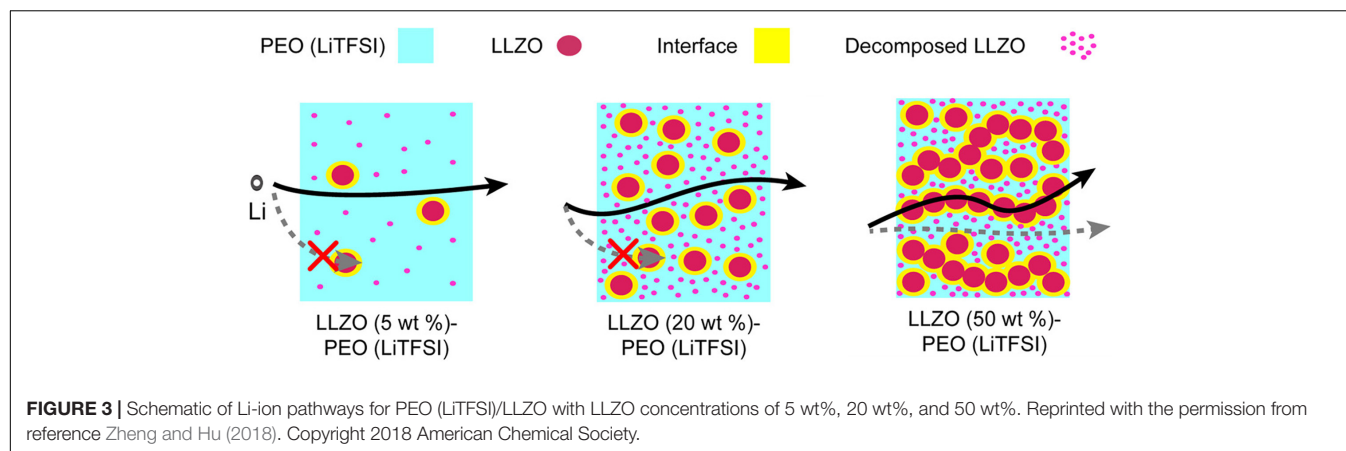
filler, polymer, and polymer/active filler interface. Many studies have shown the new  $\text{Li}^+$  pathways created by the active fillers such as LLZO (Murugan et al., 2007; Tao et al., 2017), LLTO (Le et al., 2015; Liu et al., 2015), and LATP (Goodenough et al., 1976; Aono, 1990; Chen X. C. et al., 2019; Peng et al., 2020), are the main reasons for the increase in ionic conductivity. These pathways, together with Li-ion concentration and ion mobility, determine the ionic conductivity of HSEs.

To understand the  $\text{Li}^+$  diffusion pathway, Zheng et al. (2016) took advantage of high-resolution  $^6\text{Li}$  NMR to investigate  $\text{Li}^+$  ion transportation in different phases of an HSE. The method builds on the basis that  $^6\text{Li}$  replaces  $^7\text{Li}$  during  $\text{Li}^+$  transport. Using a composite electrolyte with a mixture of PEO/ $\text{LiClO}_4$  polymer matrix and LLZO (50 wt%), the authors confirmed the presence of three ways of Li-ion transport ( $\text{Li}^+$  in the polymer phase, ceramic phase, and polymer-ceramic interface) within the material. Furthermore, by evaluating changes in the  $^6\text{Li}$  amount before and after electrochemical cycling tests revealed that  $\text{Li}^+$  diffusion in PEO-based electrolyte with LLZO (50 wt%) active filler preferred the pathway through the LLZO ceramic phase (Grey and Dupré, 2004; Bhattacharyya et al., 2010; Ilott et al., 2014). Yang et al. (2017) utilized a similar method to investigate the  $\text{Li}^+$  pathway in the electrolyte of PAN/ $\text{LiClO}_4$ /LLZO nanowire. The results showed a strong interaction between LLZO nanowires and the PAN polymer chains. Cycle tests demonstrated that the  $\text{Li}^+$  preferred to diffuse through the PAN-nanowire interface instead of the polymer or ceramic phase in HSEs with a low concentration of LLZO filler. In another study of PEO/ $\text{LiClO}_4$ /LATP HSEs, it has been shown that the ionic conductivity started to decrease beyond 4 vol% of LATP filler. The decrease was attributed to the agglomeration of nanoparticles that decreases volume ratio of the interface. Roman et al. studied the particle size effects on the ionic conductivity and found that the ionic conductivity increases as the particle size decreases, which is consistent with the prediction of the continuum percolation

model (Roman, 1990). Zheng and coworkers did a systematic investigation on the compositional dependence of the three main factors for ionic conductivity, including ion mobility, ion transport pathways, and active ion concentration (Zheng and Hu, 2018). As shown in PEO ( $\text{LiTFSI}$ )/LLZO, with LLZO concentrations of 5 wt%, 20 wt%, and 50 wt% system in Figure 3, although active ion concentration increases with the addition of more ceramic filler, the actual fraction of  $\text{Li}^+$  participating in the conduction does not show the same trend. At low contents of LLZO (5 and 20 wt%), with the increase of LLZO content, ion mobility increases, and ion transport is primarily through the PEO phase. At high LLZO content (50 wt%), a percolated network is formed by LLZO, through which most of the ion transport occurs. The 50 wt% LLZO composite showed notably lower ionic conductivity compared to the other composites, due to LLZO aggregation blocking the ion transport pathway though PEO and the high activation energy required for a Li-ion to move from one discrete LLZO particle to another or to the PEO phase. In general, the battery performance increases with increasing the loading of the fillers, when the loading ratio is small. Once the filler loading reaches certain level, the performance will not improve any more or even deteriorates due to filler aggregation.

## PREPARATION OF HYBRID SOLID ELECTROLYTES

Hybrid solid electrolytes have been widely studied as promising electrolytes systems due to the synergetic effects of each component, which provide new opportunities to develop high-performance batteries with improved safety (Shim et al., 2014; Yue et al., 2016; Zhang et al., 2018). For HSEs, various preparation methods including casting, electrospinning, and *in situ* polymerization are utilized. Optimization of the preparation method is critical for enabling HSEs to achieve high



performance characteristics such as good interfacial contact and the formation of ion-conduction pathways (Kim J.-K. et al., 2015; Manthiram et al., 2017; Liu et al., 2018). As such, the various fabrication methods employed in the preparation of HSEs are discussed in the following sections.

## Casting

Casting is one of the common techniques used to prepare polymer films and their composites, and is applied in a variety of fields (Zhu et al., 2012, 2014). In a typical preparation method, a polymer is dissolved in a suitable solvent together with a salt and inorganic material to prepare a slurry and is then cast on a substrate to fabricate the HSE film. The films can be obtained after drying the slurry in a (vacuum) oven under certain conditions. For example, a facile tape casting method was performed by Chen et al. to prepare a thin solid electrolyte with improved interfacial contact between the HSE and the electrode, achieving a high-performance solid-state battery. As a result, the cell with such a structural design could deliver an initial capacity of 125 mAh/g at a current density of 0.1 C for the fabricated Li//LiFePO<sub>4</sub> cell at room temperature (Chen X. et al., 2019).

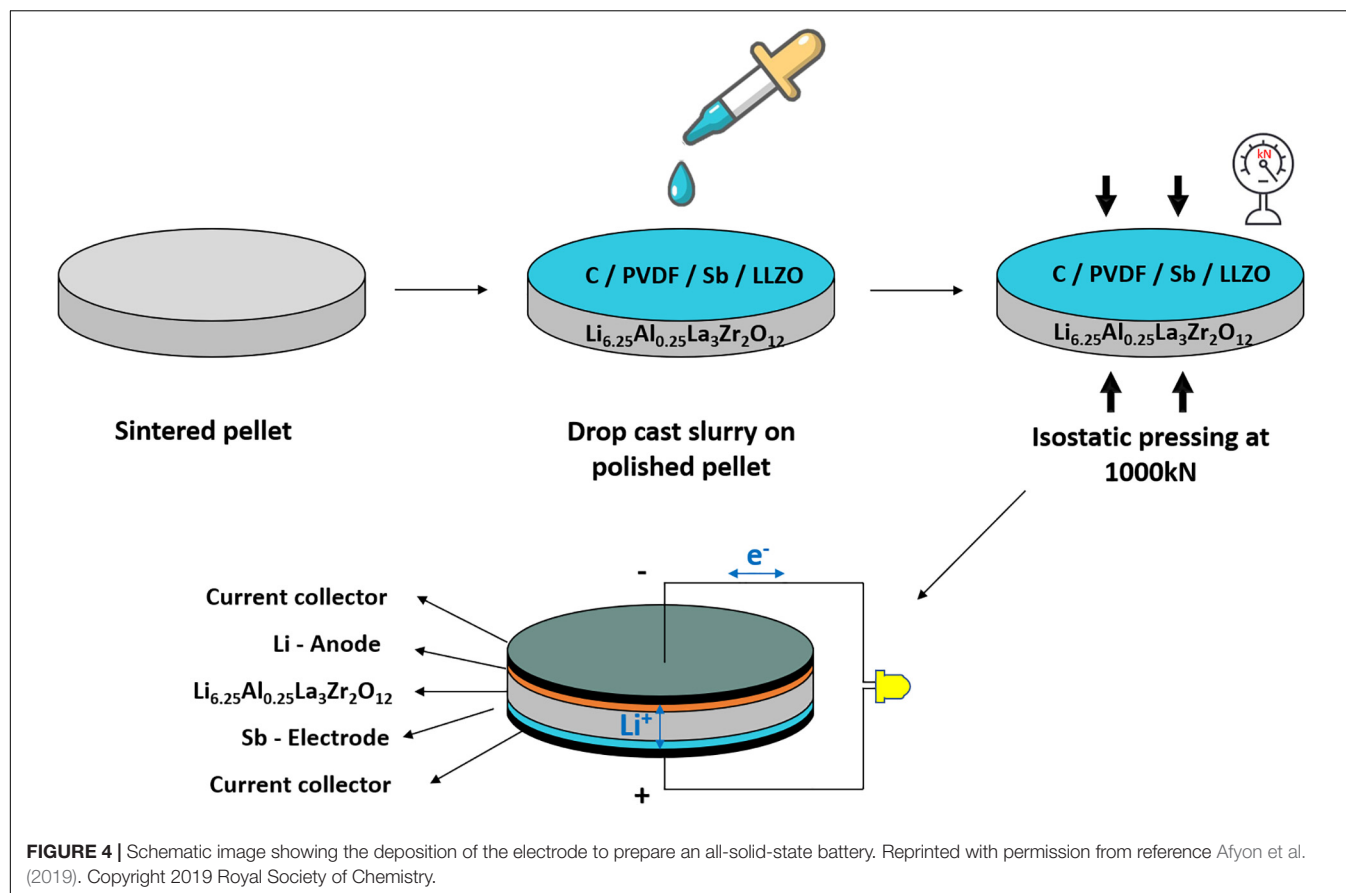
To further solve the interfacial issue, isostatic processing, in which equal pressure is applied in all directions on the substrate, has been recognized as a promising method. By using this approach, good mechanical contact, as well as the enhancement of ionic transference, could be assured. For example, Afyon et al. (2019) utilized garnet-type solid electrolytes of LLZO for assembling solid-state battery cells and composite electrodes as well. Generally, LLZO was prepared based on a modified sol-gel synthesis-combustion approach. Sub-micron-sized particles were obtained at 650°C (Afyon et al., 2019). The resultant LLZO electrolyte pellets had relative densities of ~87% and ionic conductivities of  $\sim 0.5 \times 10^{-3}$  S/cm at room temperature. A composite of antimony nanoparticles, carbon black, LLZO electrolyte powder, and PVDF was tape-casted onto sintered thin LLZO pellets with a thickness of 300–400  $\mu\text{m}$ . The dried solid-state electrodes were then pressed at a force of 1000 kN onto the solid electrolyte to ensure good contact at the interface of electrode/LLZO. Additionally, this method is scalable, as shown in Figure 4.

## Electrospinning

Electrospinning has been recognized as one of the promising approaches to produce functional one-dimensional (1D) nanomaterials, which provide unique properties including high surface-to-volume ratio, good flexibilities, and large porosity (Zhu et al., 2015, 2016a,e; Li et al., 2018a,b; Zhu J. et al., 2019). The open porous structure and nanosized fibers may provide good ion transport path, benefiting the electrochemical performance of the prepared cells. The basic setup of electrospinning is shown in Figure 5A, which includes a syringe, a syringe pump, a high-voltage supplier, and a collector (Zhu et al., 2016c). Zhu et al. designed and prepared a PEO-based HSE with 1D ceramic LLTO nanofibers, showing a good ionic conductivity of  $2.4 \times 10^{-4}$  S/cm at room temperature (Zhu P. et al., 2019). Briefly, LLTO precursor nanofibers were first fabricated via electrospinning using poly(vinylpyrrolidone) as the polymer matrix followed by heat-treatment. The effect of treatment temperature on the morphology of the prepared LLTO has also been studied. As can be seen from Figures 5B,C, the average diameter of the LLTO nanofibers treated at 800°C is around 110 nm with a good fibrous shape. Figure 5D shows the TEM images of the individual LLTO nanofibers. The high-resolution TEM image indicates a lattice spacing of  $\sim 0.27$  nm, as shown in Figure 5E, which is ascribed to the (110) plane of LLTO. The resultant LLTO calcined at 800°C was mixed with PEO to prepare the LLTO/PEO solid-state composite electrolyte using acetonitrile as the casting solvent. It exhibits a high ionic conductivity of  $2.4 \times 10^{-4}$  S/cm at room temperature and a large electrochemical stability window of up to 5.0 V vs. Li/Li<sup>+</sup>.

## Spray Coating

Spray coating is a facile and scalable processing method to manufacture composite electrolyte films. Pandian et al. (2018) used aqueous spray coating to fabricate composite electrolyte films with high ceramic loadings (>50 vol% ceramic). In the spray coating process, slurry containing the polymer electrolyte and ceramic particles are delivered through the spray nozzle onto the substrate and forms a thin layer of composite. The thin layer is allowed to dry on the heated substrate before the next layer is delivered. The spraying-drying procedure is



repeated until the desired thickness is reached. This method creates a film that is large, crack-free and three-dimensionally uniform, even with very high ceramic loadings. The thickness can be precisely controlled from a few micrometers to hundreds of micrometers. Comparatively conventional casting methods lead to crack formation when the ceramic loadings are high, due to segregation of the ceramics during drying. Furthermore, using aqueous slurry is a green process that is less expensive, more environmentally friendly which makes it attractive for commercialization.

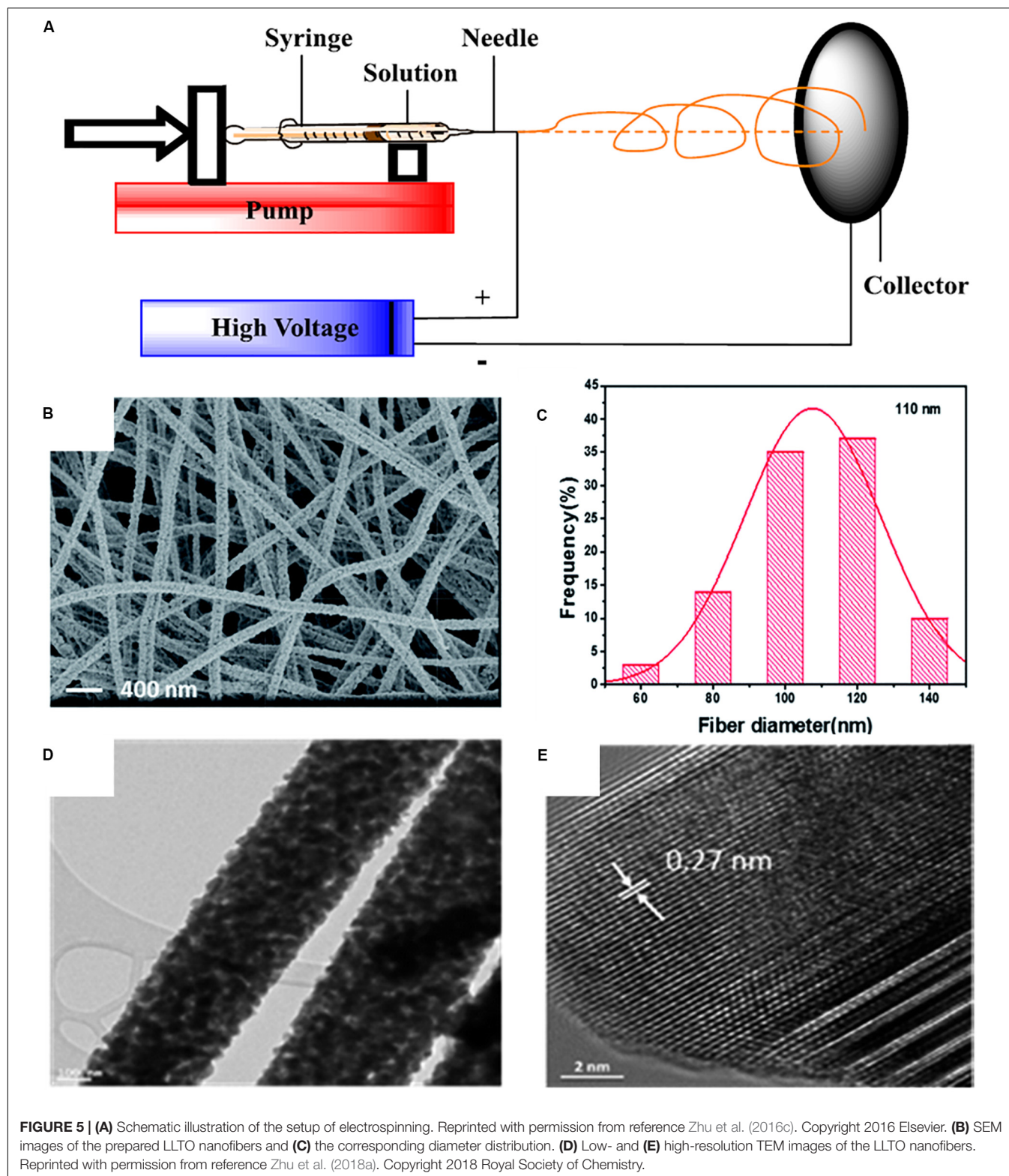
### In situ Polymerization

*In situ* polymerization to prepare HSEs provides several advantages including solvent-free preparation and improved contact with electrodes (Zhou et al., 2015, 2017; Suk et al., 2016; Chen et al., 2018a; Duan et al., 2018). Generally, a precursor containing a curable monomer, an initiator, lithium salts, and other additives is cured under certain conditions (i.e., thermal, UV irradiation, etc.) to synthesize HSEs. For example, Zhou et al. synthesized a solid-state electrolyte based on nitrile materials for achieving high-performance LIBs. **Figure 6** exhibits the synthesis route. Briefly, *in situ* polymerizing the cyanoethyl polyvinyl alcohol (PVA-CN) was performed to prepare this hierarchical structure, which was dissolved in succinonitrile (SN) and then mixed with two lithium salts (LiTFSI and  $\text{LiPF}_6$ ) at a weight ratio of 5:1 to generate a slurry. The prepared slurry was further

poured into a PAN nanofiber membrane and put into a cell. After heating the cell at  $70^\circ\text{C}$  for 6 h, a crosslinked 3D framework structure filled by SN-based solid electrolyte could be fabricated. In this work,  $\text{LiPF}_6$  was used as an initiator for the polymerization of PVA-CN, and LiTFSI could provide charge carrier due to its low dissociation and large anionic radius. A conductivity of  $4.49 \times 10^{-4} \text{ S/cm}$  could be achieved. The assembled cells used  $\text{LiFePO}_4$  and lithium foil as the cathode and the anode, respectively, with the above-mentioned solid thin film as the electrolyte. An initial discharge capacity of 147 mAh/g for such cells achieved at a current density of 0.1 C. A capacity retention of 97% was obtained even at the 100th cycle, indicating a relatively stable electrochemical performance (Zhou et al., 2015).

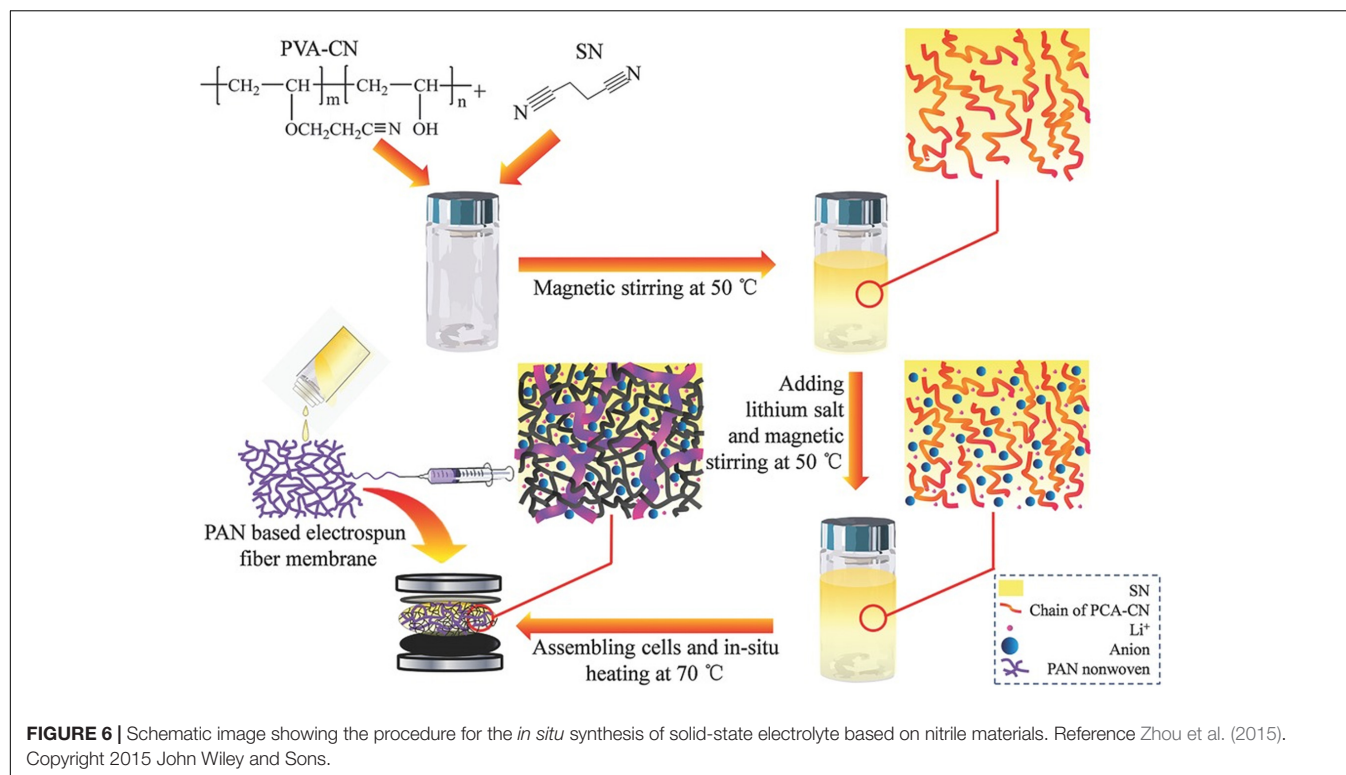
### Hybrid Methods

The above approaches can be combined to prepare unique composite solid electrolytes that take advantage of the benefits of each technique (Yan et al., 2019, 2020). For instance, Yan et al. used electrospinning to manufacture  $\text{Li}_{6.28}\text{La}_3\text{Al}_{0.24}\text{Zr}_2\text{O}_{12}$  (LLAZO) nanofibers, which were then modified with silane functional groups (denoted as s@LLAZO) with different reaction times. The goal was to investigate the effect of silane functionalization on eliminating agglomeration of LLAZO during the casting process. In this study, a new type of hybrid solid electrolyte composed of s@LLAZO nanofibers and poly(ethylene glycol) diacrylate (PEGDA) was prepared



and developed (Figure 7). As a result, the silane coupling agent could eliminate the agglomeration effect, which ensured high ionic conductivity and large lithium transference number of the s@LLZAO-PEGDA electrolyte, demonstrating a wider

electrochemical stability window and better cycling stability for the cells with such electrolytes.  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$  was also fabricated to be used as the cathode material for the cells. The high voltage cells with an HSE of s@LLZAO-PEGDA with



$\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$  exhibited a stable capacity of 110 mAh/g after 250 cycles at a current density of 0.5 C at room temperature and with a high capacity retention of 97%. The excellent capacity retention was due to the good ionic conductivity of  $3.9 \times 10^{-4}$  S/cm and large transference number of 0.61 for the prepared hybrid electrolytes (Yan et al., 2020).

In another example, Palmer et al. (2020) used a novel spray coating – partially sintering method to create a three-dimensionally interconnected ceramic network using a doped LATP ceramic (LIGCG<sup>TM</sup>). The ceramic network is then backfilled with a crosslinkable PEO-based polymer electrolyte to form the composite. The resulting composite has a very high ceramic loading (77 wt% or 61 vol%) and an ionic conductivity of  $3.5 \times 10^{-5}$  S/cm at 20°C with an activation energy of 0.43 eV. X-ray tomography verified that the composite is a bicontinuous structure with a connected ceramic phase and a connected polymer phase. The main ion transport pathway is through the ceramic network as the ionic conductivity scales proportionally with the volume fraction of the ceramic network. Owing to the interconnected structure of the ceramic and the polymer, the composite electrolyte exhibits much improved mechanical strength compared to the neat polymer electrolyte and decreased brittleness compared to the neat ceramic electrolyte.

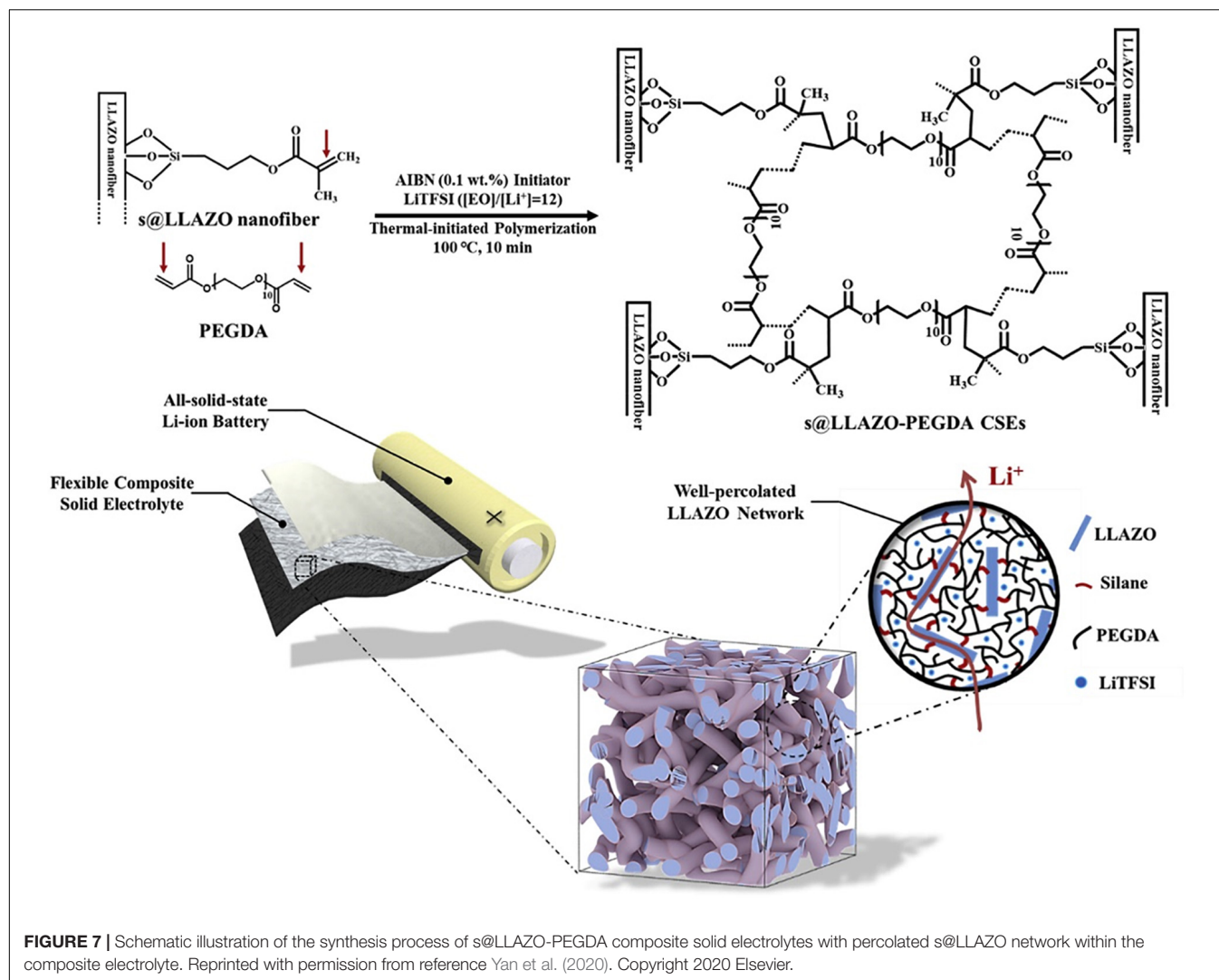
## CURRENT CHALLENGES AND PERSPECTIVES

In this review, we have highlighted three types of solid electrolytes; inorganic, polymer, and HSEs. HSEs can be the

most promising solid-state electrolytes for LIBs, attributed to their good mechanical properties, excellent processability, low flammability, wide electrochemical stability window, and ease of scalability. In particular, HSEs incorporating different matrix components and fillers, common processing methods, and ion transport mechanisms were discussed in details. In recent years, the performance of LIBs with composite solid electrolytes has been greatly enhanced. The improved properties of HSEs have come close to being adequate for their potential use in LIBs.

Looking to the future, solid-state LIBs may become even more important in personal portable electronics, electric vehicles, and stationary storage devices. To promote the practical application and commercialization of solid-state batteries, the performance of HSEs for LIBs still needs to be improved. Current issues of HSEs include unsatisfactory ionic conductivity ( $<10^{-3}$  S/cm at room temperature), poor interfacial stability, and high interfacial resistance, which greatly restrict the performance of these electrolytes.

Inorganic-type electrolytes allow for the realization of high power density LIBs, attributed to the high ionic conductivity of these electrolytes. However, inorganic-type electrolytes are brittle, have low adhesion to electrodes, and are difficult to manufacture, especially using current battery manufacturing processes, which limits their practical application. Polymer electrolytes are easy to process, are flexible and have good adhesion to electrodes, while their ionic conductivity is far from satisfactory. Therefore, HSEs developed by the mixing of an inorganic filler with a polymer matrix have attracted much attention. Many HSEs demonstrate better ionic conductivity than that of the polymer electrolyte matrix itself. Nonetheless, the



mixing of filler and matrix still needs improvement to increase ionic conductivity of composite electrolytes. Constructing a good dispersion method and strengthening the interaction between filler and the polymer may contribute to the improvement of ionic conductivity. Another factor is that insufficient investigation into the ion conduction mechanisms in HSEs is, restricting well-articulated development of novel fillers, polymers, and their composite. Continuous Li-ion transport channels between interconnected polymer matrix and filler are also in need of an in-depth study. In addition, the electrolyte/electrode interface has a great impact on the internal resistance of a battery. Significant advancements need to be made to improve the interfacial contact between the electrolyte and electrodes in order to achieve high performance of solid-state batteries.

Our perspective on the future research directions of HSEs for solid-state LIBs is to develop safe, highly stable, and conductive composite polymer electrolytes. A fundamental understanding of the mechanisms of ion transport, the interfacial properties between the polymer and filler, and between the electrolyte

and electrodes may facilitate further molecular design to address these issues.

The future focus of HSE development should include:

- (i) Understand the underlying mechanisms of ion transport in HSEs. A variety of proposed mechanisms of ion transport through an HSE are discussed in section “Ion conduction mechanisms in hybrid solid electrolytes” in detail. As discussed, the dominant mechanism depends on several factors, including the type of filler (inert or active) and filler loading. By developing a deeper understanding of each mechanism and the molecular interactions that cause transition from one mechanism to another is instrumental in the rational design of new HSE materials. Designing HSE materials on the molecular level may allow for greater interactions between polymer and filler that may be essential in increasing the ionic conductivity of the HSEs. Computational simulations would assist in the investigation of ion transport mechanisms and the polymer-filler interactions.

- (ii) Improve the interfacial property between the polymer matrix and fillers, which is pivotal in obtaining a solid-state electrolyte with high conductivity and processability. The polymer-filler interface can influence the crystallinity and morphology of the polymer chain and provide a path for ion transportation through the HSE. Furthermore, with active fillers, controlling the interface between the active ceramic particle and the polymer is crucial for marrying the high conductivity of conductive ceramics with the flexibility of a polymer. Treatment and functionalization of filler's surfaces might provide significant enhancement of interfacial transport. A greater understanding of the structure-property relationships that control the polymer/filler interface may allow for the rational design of materials to create a stable interface. The nanostructure of HSEs could be investigated by TEM. In addition, typical polymer composite characterization techniques including, differential scanning calorimetry, rheology, broadband dielectric spectroscopy, and X-ray diffraction, would assist in gaining an in-depth understanding of the interfacial behavior between matrix and filler.
- (iii) The design and synthesis of novel polymer matrices would open new avenues for improving the performance of HSEs. The optimal combination of matrix and filler would allow for high ionic conductivity and stability to be achieved. Novel polymer electrolytes designed specifically for a composite system is a field that researchers have rarely explored. Single ion conducting polymers, namely polyelectrolytes where the anions are covalently tethered to the polymer backbone and the lithium ions are the only mobile species, shows potential of increasing the lithium transference number. Considerable improvements in battery performance has been achieved by the introduction of single ion conducting polymers and the optimization of the macromolecular architecture via random and block copolymerization with various monomers. Therefore, a promising direction for HSE development is the use of a single ion conducting polymer as the matrix material.
- (iv) Design of HSEs that are compatible with next-generation high energy density anodes and cathodes. In commercial LIBs, some commonly used cathode materials are lithium cobalt oxide, lithium iron phosphate (LFP), and lithium nickel manganese cobalt (NMC). The anode typically consists of graphite, but new anode materials of a significantly higher energy density are currently under investigation, including lithium metal. Both the anode and cathode require the solid electrolyte to exhibit a certain amount of flexibility and adhesion to ensure low

interfacial resistance at the electrode/electrolyte interface. While the use of a lithium metal anode requires a strong solid electrolyte to resist puncture by lithium dendrites. HSEs can provide both requirements of flexibility and mechanical strength that opens the avenue for the use of a lithium metal anode that is not realizable with liquid electrolytes.

- (v) Advanced simulations and computations would provide insight and a path to an in-depth understanding of ion transport, the interaction between polymer and filler, and interactions between electrode and electrolyte. By taking advantage of advanced computing simulations and calculations, researchers will be able to make informed decisions on new materials design and selection, and the potential combinations of fillers and polymers that may lead to improved performance of HSEs.

## AUTHOR CONTRIBUTIONS

LH wrote the manuscript with support from ML, JZ, TL, ZZ, XT, C-TH, PC, and XC. AS and TS helped supervise the project. All authors contributed to the article and approved the submitted version.

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**Conflict of Interest:** 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.

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