REVIEW

The critical role of inorganic nanofillers in solid polymer composite electrolyte for Li⁺ transportation

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Abstract

Compared with commercial lithium batteries with liquid electrolytes, all-solid-state lithium batteries (ASSLBs) possess the advantages of higher safety, better electrochemical stability, higher energy density, and longer cycle life; therefore, ASSLBs have been identified as promising candidates for next-generation safe and stable high-energy-storage devices. The design and fabrication of solid-state electrolytes (SSEs) are vital for the future commercialization of ASSLBs. Among various SSEs, solid polymer composite electrolytes (SPCEs) consisting of inorganic nanofillers and polymer matrix have shown great application prospects in the practice of ASSLBs. The incorporation of inorganic nanofillers into the polymer matrix has been considered as a crucial method to achieve high ionic conductivity for SPCE. In this review, the mechanisms of Li⁺ transport variation caused by incorporating inorganic nanofillers into the polymer matrix are discussed in detail. On the basis of the recent progress, the respective contributions of polymer chains, passive ceramic nanofillers, and active ceramic nanofillers in affecting the Li⁺ transport process of SPCE are reviewed systematically. The inherent relationship between the morphological characteristics of inorganic nanofillers and the ionic conductivity of the resultant SPCE is discussed. Finally, the challenges and future perspectives for developing high-performance SPCE are put forward. This review aims to provide possible strategies for the further improvement of ionic conductivity in inorganic nanoscale filler-reinforced SPCE and highlight their inspiration for future research directions.

KEYWORDS

all-solid-state lithium batteries, inorganic nanofillers, Li⁺ transportation, solid polymer composite electrolyte
1 INTRODUCTION

Secondary batteries play a paramount role in energy storage and supply, especially in electric vehicles, portable devices, and grid energy-storage applications. Among various types of secondary batteries, lithium-storage battery systems have multiple advantages over the other battery systems, such as higher energy density, higher working voltage, better cycling performance, and lower self-discharge rate. Therefore, this system is considered as one of the most advanced power sources, which has dominated the current energy-storage field. Since the commercialization of liquid electrolyte-based lithium-ion batteries (LIBs) in the 1990s, the development of LIBs has gained unprecedented advances in noticeably changing the daily lives of humans for nearly three decades. However, substantial advances of LIBs have encountered the performance bottleneck in recent years. In the current situation, the limited practical energy density (100–220 Wh·kg⁻¹) is the major issue setting their further development in commercialization, which hardly satisfies the ever-increasing demand from advanced electrical applications and technologies.

Hence, new lithium-based batteries with higher energy density and larger power density are urgently needed. On the basis of this design concept, electrode materials with higher capacity and wider voltage window are critical for achieving the objectives aforementioned. Recently, the appearance of lithium metal obviously presents potential opportunities in terms of anode material design, owing to its attractive theoretical specific capacity (3860 mAh·g⁻¹), low density (0.59 g·cm⁻³), and negative redox potential (−3.04 V vs. standard hydrogen electrode). In considering of matching the lithium metal anode and fostering substantial efforts for the development of lithium metal batteries (LMBs), high-voltage layered oxides, for example, LiNi₀.₈Co₀.₁Mn₀.₁O₂ (NCM811), are selected as large-capacity cathodes, therefore obtaining a large capacity and performing better when compared with commercial LIBs. Nevertheless, the wider application of high-energy LMBs encounters obstacles due to the safety concern originating from the flammable organic solvents in traditional liquid electrolytes. With the presence of highly active lithium metal, such organic solvents may cause battery explosion once thermal runaway occurs during the charge–recharge process, owing to the general volatilization and combustibility of organic solvents, which will limit the long-term durability of LMBs. Besides, during electrochemical cycling, non-uniform electrochemical stripping and electrochemical deposition of lithium in liquid electrolytes tend to form lithium dendrites on the surface of the lithium anode, which, in turn, triggers the risk of a short circuit by penetrating through the separator. In addition, the existing commercial separators are electrochemically unstable at high voltage in the liquid electrolyte, hindering the incorporation with high-voltage cathode materials.

For accessing the high energy density and safe LMBs, replacement of conventional liquid electrolytes with solid-state electrolytes (SSEs) has been recognized as an attractive approach. Compared with the liquid one, SSEs possess the merits of inflammability, higher thermal stability, better electrochemical stability, no leakage, and lower explosion risk. Moreover, the favorable mechanical strength is promising for suppressing the lithium dendrite growth with uniform Li⁺ electrodeposition and preventing the shuttle effect of active materials. Moreover, the thickness of SSEs is easy to be controlled, which benefits the achievement of a higher energy density battery system. Therefore, the above features endow all-solid-state lithium batteries (ASSLBs) with the safer application, higher energy density, longer cycle life, fewer packaging, and state-of-charge monitoring circuit requirements, which are expected to break through the bottleneck concerns of the current energy-storage technology.

In general, ASSLBs can be primarily classified into three categories: solid inorganic electrolytes (SIEs), solid polymeric electrolytes (SPEs), and composite electrolytes (SPCEs). Among them, SIEs show high Li⁺ conductivity (10⁻⁴ to 10⁻² S·cm⁻¹), united transference number, broad electrochemical window, and high mechanical strength. Nonetheless, poor interfacial contact with electrodes results in high impedance and polarization during cycling, which counteracts the beneficial effects of SIEs. On the contrary, SPEs present remarkable processability, flexibility, and favorable interfacial contact with electrodes, but possess inferior thermal and electrochemical stability and unsatisfactory behaviors in suppressing lithium dendrite growth, encountering the main obstacle of low ionic conductivities (≤10⁻⁴ S·cm⁻¹). The aforementioned drawbacks of SIEs and SPEs demonstrate that the single-component system is not suitable for the commercial utilization of LMBs. The SPCEs derived from the incorporation of SPE and inorganic nanofillers combine the merits of both SPE and SIE such as appropriate mechanical strength, intimate contact with electrodes, and high ionic conductivity. Therefore, SPCE shows great application prospect in the practice of ASSLBs.

Generally, polymer matrix, lithium salts, and inorganic nanofillers together constitute the major structure of SPCE. Numerous typical ion-conducting polymer matrices including poly(ethylene oxide) (PEO), polycarbonate, poly(methyl methacrylate), polyacrylonitrile (PAN), poly(vinylidene fluoride) (PVDF), poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP), and polysiloxane have been developed and characterized. The application of
lithium salts (LiN\((\text{CF}_3\text{SO}_2)\)\(_2\) (LiTFSI), LiN\((\text{SO}_2\text{F})_2\) (LiFSI), and LiClO\(_4\)) offers SPCE high electrochemical stability and promotion to form a stable SEI.\(^{51-55}\) The inorganic nanofillers include LISICON-type, perovskite-type, garnet-type, sulfide, oxides, and some other ceramics.\(^{30,56-58}\) The presence of inorganic nanofillers can disorder the crystallization of polymer matrix and facilitate the dissociation of lithium salts, thus increasing the ionic conductivity of SPCE.\(^{59,60}\) Moreover, some nanofillers may provide a highly efficient pathway for Li\(^+\) transportation.\(^{34}\) In brief, the integration of inorganic nanofillers into a polymer matrix is an effective approach that can simultaneously realize the enhancement of all required mechanical and electrochemical properties.

Along with the incorporation of diverse inorganic nanofillers, this review will discuss the mechanisms of Li\(^+\) transportation variation in the polymer matrix (Scheme 1). On the basis of the recent reports, an in-depth analysis will be made on respective contributions of the polymer chains, passive inorganic nanofillers, active inorganic nanofillers, and corresponding morphological characteristics in affecting the Li\(^+\) transport process of SPCE. This review aims to provide possible strategies to solve the problems of ionic conductivity in SPCE with inorganic nanoscale filler reinforcement and highlight their inspiration for future research directions.

## 2 | Li\(^+\) Transport Mechanisms

### 2.1 | Polymer chains

As mentioned in Section 1, various polymers have been applied as the polymer matrices to constitute SPCE. The incorporation of polymers can significantly improve the interface contact of SPCE, which is conducive to minimizing the resistance at the electrode–electrolyte...
interface. Besides, the existing polymer processing technology enables the polymer matrix easier to manufacture and more cost-effective than SIE. As a result, SPCE is more suitable for large-scale manufacturing processes. Considering this situation, it is necessary to thoroughly comprehend the ion conduction among the polymer chains to adapt to the demand of industrialization.

Generally speaking, ionic species in a liquid electrolyte will migrate in response to an external electric field. Being attributed to the strong positive electrochemical nature and small size, Li⁺ coordinates and diffuses in concert with the solvent molecules. Yet, in the polymer matrix, the mechanism of ion conduction is more complex due to the lack of simple structure–properties correlations. Typically, Li⁺ coordinates with the polar groups on the polymer backbone by a hydrophilic interaction. When the temperature is above the glass transition temperature (T_g), the segmental motion of polymer chains in amorphous regions promotes Li⁺ hopping along with the adjacent coordination sites. Meanwhile, the presence of local free volume also assists this Li⁺ hopping process. Therefore, the short-range ion hopping, together with the long-range motions of polymer chains, realizes the Li⁺ conduction in SPE. Hence, it is obvious that T_g and the dissociation ability of lithium salts in polymers chains significantly influence the ionic conductivity in SPE. Yet, if the interaction between Li⁺ and polymer chains is extremely strong, it will translate into a major contributing factor to limit ionic conductivity in SPE.

It has been reported that the mobility of Li⁺ in SPE can also decouple from the segmental relaxation of polymer chains. Oligomeric PEO molecules arrange in ordered helices with specific PEO/salt ratios, whereas four EO sites coordinate with one Li⁺ averagely. Thus, Li⁺ is capable of moving through the helix tunnel of these small molecule crystalline polymer chains. With the assistance of complete ordering of helices, direct transport pathways are constructed to achieve the remarkably higher Li⁺ conductivity more easily than that in traditional crystalline electrolytes, which are dominated by the randomly oriented crystalline.

The introduction of multiple hydrogen bonds or π-conjugated groups into polymer chains is another way to design the Li⁺ channels. In general, the hydrogen bond can interact with polar groups in polymer chains, and thus decrease the interaction strength with Li⁺, leading to an increase of free Li⁺. Meanwhile, hydrogen bond interactions can disrupt the regular arrangement of conducting segments and reduce the crystallinity of the polymer, leading to the improvement of ionic conductivity. Besides, π–π stacking interaction generated from the π-conjugated groups can construct Li⁺ channels through the spontaneous induction of phase segregation. Therefore, designing effective aligned ion channels will improve ionic conductivity, especially in the polymer matrix full of flexible terminal chains.

Even so, the simple SPE still suffers from undesirably low mobile ion concentrations, which is attributed to the poor ion-pair dissociation of polymer chains. To alleviate this phenomenon, incorporation of inorganic nanofillers into the polymer matrix to fabricate the SPCE may benefit the ion transportation. According to their ion transport characteristics, such nanofillers can be classified into two main categories: passive inorganic nanofillers and active inorganic nanofillers, which will be discussed in the following sections.

### 2.2 Passive inorganic nanofillers

Passive inorganic nanofillers are defined as nanosized nonconductive fillers. This kind of nanofillers did not significantly change the ion-conducting mechanism of polymers because they are Li⁺-insulated. Passive inorganic nanofillers influence the ion transport mechanisms of SPCE, mainly in a variety of indirect ways. First, small passive inorganic nanofillers are analogous to molecular plasticizers, which may increase the number of free volume in the polymer matrix and speed up the segmental dynamics, thus inhibiting the polymer crystallization and decreasing the T_g of polymer matrix. With the increasing passive inorganic nanofiller content up from 10 to 15 wt%, the amorphicity of polymer matrix at temperatures lower than T_g is achievable, thereby enhancing the ion conductivity. Second, according to the Lewis acid–base theory, the specific surface of passive nanofillers actively interacts with the ion pairs and promotes their further dissociation, which increases the number of free Li⁺ for participating in conduction. Third, the passive inorganic nanofillers provide additional sites on the surface for ion migration, making the acidic surface sites interact with anions, whereas basic surface sites attract cations. It should be noted that either the anion or cation attracted on the surface of passive nanofillers will hinder their mobility. In addition, passive nanofillers are capable of altering the polymer chains’ behaviors at their interface and create pathways for transporting Li⁺ independent of the segmental motion. However, larger or poorly dispersed passive inorganic nanofillers can oppositely affect the ion conduction by serving as excess cross-linking sites for polymer chains with polar groups and anions, which will also reduce the segmental dynamics, ultimately inducing the reduction of ion mobility and conductivity.

For example, the polar O atoms (Lewis basic site) on the surface of Al₂O₃ interact with Li⁺ and dissociate ion pairs of LiClO₄, bringing more extra charge carriers to...
migrate in the vicinity of nanofiller grains. However, the interaction between Li$^+$ and polar O atom on the surface of Al$_2$O$_3$ may increase the concentration of free anions, bringing about the decrease of Li$^+$ transference number. Therefore, passive inorganic nanofillers with Lewis acidic surface groups will more positively affect the improvement of ionic conductivity and Li$^+$ transference number. In addition, when the content of Al$_2$O$_3$ exceeds 20%, the aforementioned intermittent coordinations will constitute the continuous pathways for the transportation of charge carriers, which form the percolation network in SPCE.

Another example for this section is the Y$_2$O$_3$-doped ZrO$_2$ (YSZ) nanowires synthesized by Liu et al. YSZ nanowires are full of positive-charged oxygen vacancies in a low oxidation state, which enable a more consecutive ion-conducting pathway along with the interface and utilize it as the effective percolation network. The oxygen vacancies in YSZ nanowires are capable of serving as the Lewis acid sites, and they assist to construct a stronger affinity with ClO$_4^-$ and subsequently release more free Li$^+$. Consequently, the SPCE with YSZ nanowires exhibited the ionic conductivity of $1.07 \times 10^{-5}$ S·cm$^{-1}$ at 30°C and a high Li$^+$ transference number of 0.56, both of which are much higher than those of the conventional filler-free electrolytes (Figure 1).

### 2.3 Active inorganic nanofillers

Normally, active inorganic nanofillers involve perovskite-structured, NASICON-structured, garnet-structured, and sulfide-type materials, possessing inherent high Li$^+$ conductivity, which is also able to directly apply as SIE for LMB. Introduction of active inorganic nanofillers into a polymer matrix can offer SPCE various advantages, including high electrochemical stability and flammability inhibition, which is capable of effectively improving the cycling performance of LMB.

According to the percolation model developed by Dietrich et al., the ionic conductivity can obtain enormous enhancement when the particle concentration is between the threshold concentrations of conductor–superconductor and conductor–insulator transitions. With the addition of active inorganic nanofillers, the highly conductive interface in SPCE should be taken into account. Hence, the overall region of ion migration in SPCE should contain interphases including nanofillers, polymer, and the interface between polymer and nanofillers. In this system, with the growing addition of active inorganic nanofillers, the agglomerated clusters of active inorganic nanofillers will be observed and bring about the dramatic reduction of the volume ratio of the interface (Figure 2). Ultimately, most of the bulk polymer phase cannot be converted to the highly conductive interfacial phase, leading to the obvious decrease of ionic conductivity. Therefore, it is expected that the ionic conductivity mechanism in this system is highly related to the interfacial regions between polymer chains and active inorganic nanofillers.

In contrast, some researchers proposed that the interfacial Li$^+$ originated from the active inorganic nanofillers’ surface under the formidable interactions with the polymer matrix. Moreover, these speculations also suggest that Li$^+$ diffusion in SPCE is...
inclined to move through neither the polymer phase nor the interfaces between polymer chains and nanofillers, but the crystal structure of active inorganic nanofillers. When Li$^+$ moves in the crystal structure, the Li$^+$ diffusion mechanisms mainly include simple vacancy mechanism, interstitial mechanism, and interstitial–substitutional exchange mechanism (Figure 3). For the vacancy mechanism, it normally relies on the Schottky defects, which create a large amount of vacancies available for Li$^+$ hopping through the crystalline. According to the interstitial mechanism, if the interstitial is larger than the Li$^+$ radius, the interstitial Li$^+$ will diffuse in the interstitial between the skeletons of molecules through successively displacing Li$^+$ in adjacent available sites. In addition, on the basis of a synergistic mechanism, high ionic conductivity can be achieved in some special structures such as crystalline garnet.

For example, a comparison between PEO-based SPCE with lithium lanthanum zirconium oxide (LLZO) and PAN-based SPCE with LLZO demonstrated that the Li$^+$ transport pathway is different in both cases. Li$^+$ prefers the pathway through the crystal structure of LLZO in the PEO matrix, whereas in the PAN matrix, it moves through the interface between PAN and LLZO, which is the main pathway for Li$^+$ (Figure 4). This diversity may due to the following reasons: on the one hand, the appropriate amount of LLZO forms the connected percolation network to support the Li$^+$ diffusion through the LLZO phase. On the other hand, the distinction of polymer matrix significantly improves the local environment of PAN chains with high ionic conductivity at the interfaces. Yet, a further increase in the amount of active inorganic nanofiller also leads to the lower ionic conductivity, which was attributed to their irregular agglomeration effect.

Therefore, the above analysis suggested that the variation of active inorganic nanofillers content in the SPCE results in the change of the Li$^+$ transport pathways. With the increasing fraction of active inorganic nanofillers, ion transport pathways gradually transit from polymer phase to interfaces between the polymer and inorganic nanofillers first, and subsequently to ceramic phase, which decreases the ion mobility but increases the active ion concentration.
### 3 | MORPHOLOGICAL EFFECTS OF INORGANIC NANOFillERS

#### 3.1 | Zero-dimensional (0D) inorganic nanofillers

The 0D nanofillers usually refer to the inorganic nanoparticles in the polymer matrix. In the work of Wu et al., fluorite Gd_{0.1}Ce_{0.9}O_{1.95} (GDC) and perovskite La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{2.55} (LSGM) with a high concentration of oxygen vacancies, but Li⁺-insulating, were applied to demonstrate the PEO-based SPCE, each with a Li⁺ conductivity above $10^{-4}$ S·cm⁻¹ at 30°C (Figure 5). The TFSI⁻ tends to form a bond with the surface of the crystal by the oxygen attachment, which is confirmed by the accumulation of electrons between the O atom of...
TFSI⁻ and the surface of oxide nanoparticles. The Li⁺ transportation mainly benefits from the adsorption of TFSI⁻ on the surface of oxide nanoparticles by weakening the interaction between Li⁺ and TFSI⁻, thus releasing more Li⁺ and leading to the largest improvement of Li⁺ conductivity in SPCE, which further alters the Li⁺ distribution. The stronger the TFSI⁻ binds to the surface of oxide nanoparticles, the weaker it interacts with the Li⁺.

On the one hand, the uniform distribution of nanoparticles contributes to the prevention of polymer crystallization and creates plentiful interface regions, with the merit of a larger specific surface area than micron-sized fillers. On the other hand, by acting as the cross-linking point in support of the whole SPCE structure, the nanoparticles are capable of creating a new Li⁺ transport pathway independent of the movement of the chain segment, thus bringing about the remodeling of crystallinity. Lin et al. introduced an in situ synthesis of monodispersed 12-nm diameter SiO₂ nanospheres in PEO electrolyte with LiClO₄, producing stronger chemical/mechanical interactions between nanospheres and polymer chains by in situ hydrolysis, which enormously suppresses the crystallization of PEO (Figure 6). In this study, the nanoscale and high monodispersity of SiO₂ furnish the maximized surface area, further enhancing the interactions between ClO₄⁻ and SiO₂ surface. Moreover, the decreasing crystallinity of the polymer matrix immensely improves the segmental motion of PEO chains, which further strengthens the binding of Li⁺ with ether groups on PEO chains. The above factors together conduce to the separation of LiClO₄ in the PEO matrix, and thus facilitate the polymer segmental motion for Li⁺ conduction (1.2 × 10⁻³ S·cm⁻¹ at 60°C and 4.4 × 10⁻⁵ S·cm⁻¹ at 30°C).

In another work, Zhang et al. took Li₆.75La₃Zr₁.₇₅Ta₀.₂₅O₁₂ (LLZTO) nanoparticles to trigger the structural modification of PVDF-based SPCE and obtained a high ionic conductivity of about 5 × 10⁻⁴ S·cm⁻¹ at 25°C (Figure 7). In this system, LLZTO nanoparticles and the partially dehydrofluorinated PVDF chains together form the complex with Li⁺ via Lewis acid–base interaction, effectively dissociating LiClO₄ and increasing the Li⁺ transference number for conduction. Moreover, the amorphous region of PVDF can accelerate the segmental motion of polymer chains and reinforce the interactions among LLZTO nanoparticles, whereas the F atoms of PVDF can reduce the crystallinity of the polymer matrix, together, promoting the ionic migration.

Therefore, the complex structure of LLZTO with PVDF is in favor of the more efficient ionic hopping in available sites.
3.2 One-dimensional (1D) nanofillers

1D nanofillers refer to nanorods, nanotubes, or nanofibers, which can generate different effects than 0D nanofillers due to their extension in a certain direction. Liu et al.109 designed an SPCE of PAN–LiClO₄ incorporated with 15 wt% Li₀.₃₃La₀.₅₅₇TiO₃ (LLTO) nanowires, which exhibited an ionic conductivity of 2.4 × 10⁻⁴ S·cm⁻¹ at room temperature (Figure 8). The high ionic conductivity is ascribed to the fast ion transport on the surfaces of 1D LLTO nanowires, which act as the conductive network in the PAN matrix. As a perovskite-type Li⁺ conductor, the

FIGURE 6 (A) A schematic illustration of interaction mechanisms among PEO chains and SiO₂. Two possible interaction mechanisms are shown, including chemical bonding between the ends of PEO chains with hydroxyl groups on SiO₂ surfaces and mechanical wrapping of PEO chains during the growth of SiO₂ spheres. (B) Arrhenius plots of ionic conductivity of PEO electrolyte with SiO₂ nanospheres. Reproduced with permission: Copyright 2016, American Chemical Society.105 PEO, poly(ethylene oxide); SPCE, solid polymer composite electrolyte; SPE, solid polymeric electrolyte

FIGURE 7 (A) Reaction schemes consistent with the chemical signatures detected by Raman, FTIR, and ¹H NMR. (B) Possible complex structures in the PVDF/LLZTO–SPCE, where blue clusters denote LLZTO. (C) Conductivities of the PVDF-based SPCE as a function of the weight percentages of LLZTO at different temperatures. (D) Arrhenius plots of the PVDF-based polymer electrolytes and LLZO disk. Reproduced with permission: Copyright 2017, American Chemical Society.106 FTIR, Fourier-transform infrared; LLZTO, Li₆.₇₅La₂Zr₁.₇₅Ta₀.₂₅O₁₂; PVDF, poly(vinylidene fluoride); NMR, nuclear magnetic resonance; SPCE, solid polymer composite electrolyte
surface region of LLTO is full of vacancies that allowed Li⁺ to hop from one vacancy to another. Thus, Li⁺ can diffuse quickly over the surface area of LLTO nanowires, resulting in increased ion mobility. Such a mechanism of Li⁺ replacing the nearby vacancies in LLTO nanowires will reduce the activation energy in the PAN electrolyte. Therefore, both the density and mobility of Li⁺ get improvement on the 1D LLTO nanowire surfaces in SPCE.

By utilizing 1D nanofillers, SPCE is capable of reducing the polymer crystallinity, increasing the effective migration concentration of Li⁺, as well as improving the electrochemical stability of polymers.

Chen et al.110 added Ca–CeO₂ nanotubes to PEO electrolyte by electrospinning and subsequent high-temperature treatment to obtain ionic conductivity and transference number of 1.3 × 10⁻⁴ S·cm⁻¹ and 0.453 at 60°C, respectively (Figure 9). The Ca–CeO₂ nanotubes provide an effective percolation network to act as continuous ionic conduction pathways, whereas their hollow structure offers enough contact area with PEO chains. Moreover, with the contribution of chain relaxation and segmental motion, Ca–CeO₂ nanotubes accelerate the LiTFSI ion pairs to dissociate and bring more free Li⁺, bringing about the reduced resistance, increased transference number, and electrochemical stability at high voltage.111 In this process, the Ca–CeO₂ nanotubes suppress the reorganization of PEO chains and reduce the crystallization degree of the PEO matrix, thereby increasing the dipole moment of PEO chains.112,113 On the one hand, Ca–CeO₂ nanotubes possess a mass of oxygen vacancies with positive potential, which guarantee a strong immobilization with TFSI⁻ groups.114 On the other hand, Ce and Ca atoms also enable the positively charged surface of Ca–CeO₂ nanotubes to absorb the TFSI⁻ groups through −SO₂−Ce−O− and −O−Ca−CF₃− bonding.86,115 Hence, synergetic effects offered by both oxygen vacancy and dopants enhance the separation of Li⁺ from LiTFSI. Meanwhile, the features of hollow structure and large surface area furnish Ca–CeO₂ nanotubes with more active sites for LiTFSI in PEO electrolytes, fostering the rapid Li⁺ migration with the formation of continuous 3D pathways. Consequently, more free Li⁺ will move through the interface between Ca–CeO₂ nanotubes and PEO matrix via interacting with the EO units on PEO chains.

Nevertheless, 1D nanofillers are hard to control their uniform dispersion, which is less able to effectively promote the concentration gradient reduction to distinctly prevent lithium dendrite. Moreover, in an external electric field, Li⁺ usually migrates in a vertical direction to the surface of the electrode.96 Considering this situation, Zhai et al.116 presented an ice templating-based method to fabricate vertically aligned and connected Li₁⁺ₓAlₓTi₂⁻ₓ(PO₄)₃ (LATP) conductors in the PEO electrolyte, where vertically aligned ion-conductive LATP fillers form the fast pathways for Li⁺ transport, whereas the polymer matrix provides flexibility and mechanical support for SPCE (Figure 10). The connected LATP nanofillers immensely improve the ionic conductivity to 0.52 × 10⁻⁴ S·cm⁻¹. These results demonstrated that the rational design of vertically aligned LATP nanofillers makes an important contribution to the conductivity increase due to the direct channels formed by aligned structure for Li⁺ transportation. Meanwhile, the 1D nanofillers parallel to the surface of the electrode are not conducive to Li⁺ transport substantially but only take effect as cross-linking sites for polymer chains.14,116

3.3 Two-dimensional (2D) nanofillers

Unlike the aforementioned nanofillers, 2D nanofillers such as nanosheets are rarely applied in SPCE.96 One of the reasons is that it is difficult for 2D nanofillers to form
consecutive paths analogous to nanowires. The other one is that the nanosheets may be located in a position parallel to the electrode surface if the size is extremely large, which will lead to a longer and more convoluted Li\(^+\) transportation pathway. In addition, the polymer crystallinity is incapable of reducing efficiently if the 2D nanofillers are excessively large. Yet, the above problems can be effectively avoided by reducing the size

**Figure 9** (A) A schematic illustration of the mechanism for enhanced Li\(^+\) transport in PEO-based electrolyte with Ca–CeO\(_2\) nanotubes. (B) Arrhenius plots of PEO/LiTFSI and PEO/LiTFSI/Ca–CeO\(_2\) electrolytes. (C) Impedance spectra from 30°C to 90°C. Reproduced with permission: Copyright 2020, Wiley.\(^{110}\) PEO, poly(ethylene oxide)

**Figure 10** A schematic illustration of vertically aligned and connected LATP channels for enhancing ionic conduction. (A) Ceramic particles are randomly dispersed in the PEO matrix, where ion transport is blocked by the PEO matrix with low conductivity. In contrast, vertically aligned and connected structure exists to facilitate Li\(^+\) transport. (B) Ionic conductivities of the three structures at different temperatures. Reproduced with permission: Copyright 2017, American Chemical Society.\(^{116}\) LATP, Li\(_{1+x}\)Al\(_x\)Ti\(_{2−x}\)(PO\(_4\))\(_3\); PEO, poly(ethylene oxide)
of 2D nanofillers or designing a direct way for Li⁺ penetration. Furthermore, the reduced size of 2D nanofillers is able to provide a larger effective interface than that of 0D nanofillers, which enables the high ionic conductivity to be obtained.

Chen et al. fabricated SPCE by inserting poly(ethylene carbonate) (PEC)-based electrolytes into the interlayer of intercalated lithium montmorillonite (LiMNT; Figure 11). The SPCE presents high ionic conductivity of $3.5 \times 10^{-4}$ S·cm⁻¹ and a high ionic transference number of 0.83 at 25°C. The high swelling capacity of montmorillonite clays renders PEC insert in the interlayer of LiMNT to easily form an intercalated SPCE. The parallel surfaces of nanoflake LiMNT comprising a silica tetrahedral sheet have obvious negative charges, whereas the edge-shared faces consisting of alumina octahedral groups are positively charged. This distinction in surfaces enables the selective immobilization of charged species. Therefore, when SPE is inserted into the interlayer of LiMNT, FSI⁻ will rather approach the edges of LiMNT, while Li⁺ is inclined to move into the intercalation space. Meanwhile, the carbonate groups in PEC with substantial lone-pair electrons interact with free Li⁺, whereas LiMNT also provides immobilized counter ions, together resulting in the formation of high Li⁺ transference numbers in an electric field. In brief, the electrostatic interactions among PEC, LiMNT, and LiFSI effectively order Li⁺ into the intercalation space, which conduces to shortening the transport distance of free Li⁺, reducing the ionic coupling, and affording a high-speed freeway for Li⁺ transport.

Shi et al. constructed a layer of mesoporous silica around the surface of MXene-Ti₃C₂ to obtain the individual 2D sandwich structure with low electrical conductivity, which offers the poly(propylene oxide) elastomer (ePPO)-based SPCE a high ionic conductivity of $4.6 \times 10^{-4}$ S·cm⁻¹ (Figure 12). Such high Li⁺ transportation is ascribed to numerous Lewis acid–base interactions between MXene-mSiO₂ and LiTFSI. The massive presence of functional groups including –F of MXene-Ti₃C₂ and –OH of silica in mesopores and surface is beneficial to the extensive formation of Lewis acid–base interactions. As a result, interfaces between MXene-mSiO₂ and ePPO form the highways for Li⁺ transport.
Three-dimensional (3D) nanofillers

Most of the 3D nanofillers are network structures, which are prepared as a whole, being different from those constructed by nanofibers. The development of 3D nanofillers becomes important and significant in the future understanding of electrochemical performance for the 3D ion-conducting network-based SPCE. Fu et al. designed a 3D ceramic network based on garnet-type Li6.4La3Zr2Al0.2O12 (LLZO) nanofibers to create continuous Li+ transport channels in PEO-based SPCE, which exhibits reasonably high ionic conductivity of 2.5 × 10−4 S·cm−1 at room temperature (Figure 13).

Bae et al. fabricated a 3D nanostructured hydrogel-derived pre-percolated Li0.33La0.55TiO3 (LLTO) framework for high-performance SPCE (Figure 14). The SPCE with LLTO framework shows a high ceramic content (44 wt%) and exhibits an improved Li+ conductivity to 8.8 × 10−5 S·cm−1 at room temperature. Such pre-percolated LLTO framework avoids the agglomeration of particles and enhances the conductivity with a higher degree of percolation. In this system, the pre-percolated LLTO network actually constructs a continuous interphase along with the 3D interconnected structure, which acts as a pathway for Li+ conduction. However, the ionic conductivity of this SPCE is not superior to that of the 3D network constructed by 1D nanofibers.

Lin et al. developed an ultrafine and well-distributed SiO2 aerogel-reinforced SPCE with a large internal surface area of SiO2 by incorporating the strong SiO2 aerogel backbone (Figure 15). First, the nonconductive but highly porous SiO2 aerogel occupies a minimal volume of SPCE, to expand the Li+ conducting phase. Moreover, the ultrasmall and well-interconnected domains of SiO2 with acidic –OH surface maximize the Lewis acid–base interaction with TFSI−, increasing LiTFSI dissociation and thus forming a continuous highly conductive pathway through the whole SPCE film. By virtue of the above effects, such an interconnected network with successive regions of high TFSI− adsorption further boosts ionic conductivity to 0.6 mS·cm−1 at 30°C. The acidic SiO2 aerogel and the high surface area with uniformly distributed pores together play a key role in facilitating more pronounced Lewis acid–base interaction for TFSI− adsorption and enable the further dissociation of LiTFSI in SPCE for favorable ion transport.
From the aforementioned examples, it can be concluded that different morphological structures of inorganic nanofillers have their own way of affecting Li⁺ conduction. The construction of continuous and direct ion conduction pathways will be an appealing strategy to enhance Li⁺ migration. Simultaneously, combining both the crystal structure and Lewis acid–base interface together to create a variety of ion transport paths is conducive to the overall improvement of electrochemical performance.

**FIGURE 13**  (A) A schematic illustration of the hybrid solid polymer composite electrolyte (SPCE), where ceramic garnet nanofibers function as the reinforcement and Li⁺-conducting polymer functions as the matrix. The inner welded garnet nanofiber network provides a continuous ion-conducting pathway in the SPCE membrane. (B) Arrhenius plots of Li⁺ conductivity of SPCE. Reproduced with permission: Copyright 2019, Wiley.¹²³

**FIGURE 14**  (A) Ionic conductivity of LLTO framework, LLTO nanoparticle, and silica particle SPCE. (B) Percolation model (black dashed line) and conductivity data of SPCE with LLTO nanoparticles (blue) and framework (red). A schematic representation of possible conduction mechanism in SPCE with (C) agglomerated nanoparticles and (D) three-dimensional continuous framework. Reproduced with permission: Copyright 2018, Wiley.¹²⁴ LLTO, Li₀.₅₅La₀.₃₅TiO₃; PEO, poly(ethylene oxide); SPCE, solid polymer composite electrolyte
SURFACE FUNCTIONALIZATION

With the introduction of inorganic nanofillers, some interfacial problems also appear gradually, for instance, the agglomeration of inorganic nanofillers and the relatively poor polymer–ceramic interface contact, which make the further improvement of ionic conductivity a challenge. To optimize this interphase performance, numerous methods involving particle size reduction and orderly design of nanofillers are attempted. Yet, such poor interfacial compatibility still impedes the utilization of SPCE, because only the physical interactions are exploited in this process. It has been reported that the inorganic nanofillers can act as a source of charge carriers by grafting suitable functional groups on the surface, which would be a critical strategy to ameliorate this problem.

Until now, surface modification is mainly employed in 0D inorganic nanofillers. This is due to two following reasons: (1) the high surface energy of 0D nanofillers makes it more thermodynamically favorable for them to agglomerate to reduce surface energy; (2) a big gap of the surface energy domains the wetting of different interphases, resulting in the poor compatibility between 0D nano-fillers and polymer; (3) the morphology of 0D nanofillers is simpler than that of the other 0D nanofillers, which is conducive to the control of surface modification. Therefore, surface modification is suitable for 0D
inorganic nanofillers to improve the interface environment.

To construct a chemical cross-linking point, Tang et al.\textsuperscript{130} prepared PPO–PEO–PPO triblock copolymers based on SPCE containing enhanced framework, which exhibited high ionic conductivity of 1.32 mS·cm\(^{-1}\) at 20°C (Figure 16). This system is generated from the cross-linked structure of copolymers and surface-modified SiO\(_2\) nanoparticles, which brings about the effective solvation of LiPF\(_6\) and the encapsulation of organic solvents. In general, the matrix structure of SPCE consists of duplicated aromatic urethane groups (–O–CO–NH–Ar–NH–CO–O–), the ether groups (–O–), and the SiO\(_2\) nanoparticle clusters, together, providing the diversity of functionality and microphase separation of polymer segments. The introduction of SiO\(_2\) nanoparticle clusters can increase the cross-linkable nodes of SPCE and reduce the crystallization of PEO, which will generate a more amorphous phase in PEO and PPO chains, supplying more pathways for Li\(^+\) transportation. In addition, the polar urethane segments offer a complementary hydrogen bonding system and rigid aromatic groups in SPCE, whereas the nonpolar PEO and PPO segments are regarded as flexible and mobile linkages. Such strong complementary hydrogen bonding in urethane groups is considered to be the driving force for the microphase separation.\textsuperscript{131} In particular, this system shows no macrophase separation, because the hard and soft segments of the polymer matrix are covalently linked, which form the hard

![Image](https://example.com/image.png)

**FIGURE 16** A schematic illustration of (A) three-dimensional framework in SPCE, (B) Arrhenius plots of ionic conductivity versus inverse temperature of SPCE with PEO of \(M_w = 500\) and \(M_w = 1000\). (C) Transport paths of Li\(^+\) in the polymer segments and in the internal channels. Reproduced with permission: Copyright 2020, Elsevier.\textsuperscript{130} CNPE, carbon nanotube paste electrode; PEO, poly(ethylene oxide); SPCE, solid polymer composite electrolyte.
and soft domain in SPCE with self-assembled aggregation. Moreover, the PEO and PPO segments are twisted together in a tangled mass due to the self-complementarity of diverse copolymerized chains between two SiO₂ nanoparticle clusters, which resulted from the formation of multiple hydrogen bonds. Therefore, it is reasonable to believe that the two-phase microstructure played a critical role in inhibiting the PEO crystallization and creating the elastomeric resiliency with elongation enhancement. It is supposed that this structure is conducive to promoting Li⁺ conductivity by creating 3D ion transport paths. Consequently, Li⁺ not only can transport among the polymer chains via coordination/dissociation with the ether oxygen, but it can also transfer from one polymer segment to another in the inner porous channels of the SPCE framework via diffusion.

In another research, Chai et al.¹³² utilized the copolymerization by γ-methyl-propylene trimethoxysilane (KH570) and vinylene carbonate to supply a 3D cross-linked network SPCE layer modified with Li₂La₃Zr₂O₁₂ (LLZO; Figure 17). As a flexible–rigid coupling skeleton, the SPCE is employed in buffering the volume expansion and solving the hurdle of uncontrollable dendritic lithium growth during cycling. The SPCE possesses a Li⁺ transference number of 0.752, which may due to the existence of a large amount of LLZO. Obviously, as a kind of Li⁺ conductor, only Li⁺ is able to pass through LLZO ceramic particles. During this process, Li⁺ can hop through the rich vacancies on the surface of LLZO, which contributes to constructing a fast pathway for diffusing Li⁺, resulting in an increased Li⁺ transference number.¹⁰⁹ Furthermore, on the basis of the Lewis acid theory, LLZO may act as anionic receptors, which will restrict the movement of anions.¹³³

To improve the uniform distribution of nanoparticles, Lee et al.¹³⁴ prepared the SPCE based on P(VdF-co-HFP) and core–shell-structured SiO₂ nanoparticles containing Li⁺. The ionic conductivity of the SPCE prepared with 20 wt% SiO₂ (Li⁺) powders is 1.4 × 10⁻³ S·cm⁻¹ at room temperature. A thin layer of poly(lithium 4-styrene sulfonate) surrounding a nano-sized SiO₂ core particle constitutes the unique core–shell morphology of these SiO₂ particles (Figure 18). Li⁺ is capable of dissociating with the assistance of core–shell-structured SiO₂ particles.

![Figure 17](image-url)
and forms a SiO$_2$ (Li$^+$) complex, thus enabling the SiO$_2$ particles to act as the charge carriers. Moreover, the incorporation of SiO$_2$ (Li$^+$) powders brings about a filler network, which furnishes mechanical integrity to the final formation of free-standing films. The core–shell-structured SiO$_2$ nanoparticles exhibit the characteristics of intrinsic single ion conduction, as the pendant group on the polymer shell can anchor the sulfonate anions. Therefore, it is plausible that the Li$^+$ dissociated from the SiO$_2$ (Li$^+$) particles is beneficial to the increase of Li$^+$ transport efficiency. Besides, the generation of a free volume at the interface of dispersed SiO$_2$ (Li$^+$) nanoparticles may also contribute to the improvement of ionic conductivity.

Huang et al.\textsuperscript{135} modified Li$_{6.4}$La$_3$Zr$_{1.4}$Ta$_{0.6}$O$_{12}$ (LLZTO) nanoparticles with the coating of polydopamine (PDA) to avoid aggregation, leading to a uniform dispersion in the PEO matrix (Figure 19). As a result, the SPCE showed the conductivity of 1.15 × 10$^{-4}$ S·cm$^{-1}$ at 30°C, which is higher than that of the PEO matrix with pure LLZO (6.34 × 10$^{-5}$ S·cm$^{-1}$). The modification of dopamine with dual wetting capability on the surface of both organic and inorganic nanoparticles constructs the formidable bonding between LLZTO and PEO, which will facilitate Li$^+$ transferring in the SPCE. PDA assists the homogeneous particles to distribute homogeneously in the PEO matrix, which introduces more effective percolation pathways for Li$^+$ migration.

To form a new interfacial ion transport channel, Wang et al.\textsuperscript{136} incorporated polymeric ionic liquid-functionalized mesoporous silica nanoplate (PIL-FMSiNP) into polymeric ionic liquid (PIL)-based SPE to obtain SPCE (Figure 20). Ionic conductivity of 1.82 × 10$^{-3}$ S·cm$^{-1}$ is obtained with PIL-FMSiNP at 8 wt% loading in SPCE at 130°C. The in situ grafting of PIL on the surfaces of nanoplates provides a high degree of compatibility between the nanoplates and PIL as well as a homogeneous dispersion of nanoplates in SPCE. The combination of modified PIL and mesoporous structure in the nanoplates increases their properties of ionic liquid immersion and retention, creating stable ion-conducting channels at the interfaces between nanoplates and polymer electrolyte. More importantly, abundant ionic channel junctions in the mesoporous PIL-FMSiNP supply shorter and continuous Li$^+$ diffusion pathways, thus facilitating Li$^+$ transfer through the SPCE. Consequently, Li$^+$ can move through the porous PIL-FMSiNP and the interfaces between nanoplates and polymer electrolyte simultaneously, allowing the achievement of high ion transfer efficiency. In addition, by creating large interfacial contacts between the electrodes and PIL/IL, the large surface area and high affinity generated from the high porosity and grafting ratio of PIL increase the immersion and accessibility, thereby ensuring the facile diffusion of Li$^+$ through the interface between the electrode and PIL/IL with the improvement of the cycling reliability.

Li et al.\textsuperscript{137} designed molecular brushes anchored to the surface of Li$_{6.4}$La$_3$Zr$_{1.4}$Ta$_{0.6}$O$_{12}$ (LLZTO) nanoparticles (MB-LLZTO) to prepare a PEO-based SPCE (Figure 21). The combination of MB-LLZTO and PEO offers an alteration of the Li$^+$ diffusion pathway with one magnitude enhancement in Li$^+$ ionic conductivity (3.11 × 10$^{-4}$ S·cm$^{-1}$ at 45°C), whereas the corresponding value of the SPCE with pristine LLZTO was 9.16 × 10$^{-5}$ S·cm$^{-1}$. The anchored organic chains at the LLZTO surface form a percolation network, which allows a large amount of Li$^+$ to be transferred in SPCE.

On the basis of the above analysis, it is obvious that surface modification endows inorganic nanofillers with three new functions: (1) constructing chemical cross-linking bonds between inorganic nanofillers and polymer chains; (2) promoting the uniform distribution of inorganic nanofillers in a polymer matrix; and (3) creating...
the novel interfacial ion transport channels. Such surface modification should be explored more in 1D, 2D, and 3D inorganic nanofillers. The above typical examples are listed in Table 1.

5 | CONCLUSION AND PERSPECTIVES

Over the past decades, ever-increasing attention has been paid to ASSLBs owing to their promising potential application value of commercialization, which have been considered as the next-generation LMB. As a substitution for liquid electrolyte, SSE is the core component to offer advanced battery performance and promote the commercialization of ASSLB. The incorporation of inorganic nanofillers into SPE to fabricate the SPCE is an effective way that not only improves ionic conduction but also supports the mechanical strength and electrochemical stability of the polymer matrix. This review focuses on the study and development of Li\(^{+}\) transport mechanisms of SPCE applied in ASSLBs. Transportation mechanisms of Li\(^{+}\) with polymer chains are analyzed at the beginning. Besides, the passive and active inorganic nanofillers are introduced and their difference in transporting Li\(^{+}\) in SPCE are also summarized and compared. Moreover, the improvement of Li\(^{+}\) transport process is elaborated with the morphology effects of inorganic nanofillers.

Inorganic nanofillers influence the ion transport mode in several ways. The most essential one is to reduce the polymer crystallization and speed up the segmental motivation with lower \(T_g\), hence, the ion conductivity...
gets enhanced. Another one is to create an extra pathway for transporting Li\textsuperscript{+} independent of the polymer chain motion. On the one hand, the specific surface of inorganic nanofillers provides a large amount of Lewis acid–base sites for anion or cation migration, and therefore promotes further transportation of free Li\textsuperscript{+} in SPCE. On the other hand, the ceramic phase of inorganic nanofillers offers the pathway for Li\textsuperscript{+} to transport through, which is based on several solid diffusion mechanisms. In particular, the morphological effect of inorganic nanofillers also plays an important role in the transportation of Li\textsuperscript{+} in SPCE. The uniform distribution of 0D nanofillers can create a large number of interface regions or ceramic phase as the pathway for Li\textsuperscript{+}. 2D nanofillers with a reduced size can provide a larger effective interface than 0D nanofillers, which have huge advantages in Li\textsuperscript{+} transportation. Effects of 1D and 3D nanofillers on Li\textsuperscript{+} transportation by realizing continuous interphase for Li\textsuperscript{+} conduction are different from those of 0D nanofillers or 2D nanofillers. Besides, suitable surface modification can improve the interfacial compatibility between inorganic nanofillers and polymer chains, making nanofillers act as a source of charge carriers with direct contribution in the transportation of Li\textsuperscript{+}.

Herein, some future research directions of SPCE are proposed to further improve the performance of ASSLBs, which are schematically illustrated as follows:

(1) Improving the room temperature ionic conductivity and Li\textsuperscript{+} transference number of SPCE, which are critical to maximizing the performance of ASSLBs. Most of the current ionic conductivity of SPCE is in the range of 10\textsuperscript{−5} to 10\textsuperscript{−4} S·cm\textsuperscript{−1}, which should get a further enhancement, equivalent to that of the liquid electrolytes (10\textsuperscript{−3} to 10\textsuperscript{−2} S·cm\textsuperscript{−1}).

(2) Carrying out further study on the mechanism of Li\textsuperscript{+} transportation in SPCE. More details of the ion transport process should be studied. Theoretical calculations should be employed more extensively in the study of Li\textsuperscript{+} transportation mechanism to confirm the experimental results and provide directions for the explorations of advanced SPCE.

(3) Developing more types of inorganic nanofillers with new structures and surface properties. Well-designed and controlled structures can establish a regular and effective Li\textsuperscript{+} transport model, whereas surface modification can offer inorganic nanofillers more unique functions.

(4) Optimizing the interface between electrolyte and electrode, which will promote the utilization of active materials in electrodes and reduce internal and interfacial resistance, enhancing the cycling performance and rate capability of ASSLBs.

(5) Promoting the application of SPCE in Li–S battery and Li–O\textsubscript{2}/air battery. Currently, most of the SPCEs

**FIGURE 20** (A) Conceptual illustrations of Li\textsuperscript{+} diffusion pathways and electrode–PIL/IL interface in PIL/IL(LiTFSI)/PIL-FMSiNP cell. (B) Temperature dependence of ionic conductivity for SPCE with 5 wt% of silica content. Reproduced with permission: Copyright 2017, Elsevier.\textsuperscript{136} CPE, carbon-paste electrode; PIL-FMSiNP, polymeric ionic liquid-functionalized mesoporous silica nanoplate; SPCE, solid polymer composite electrolyte.
are applied in low-voltage LiFePO₄ cathode and a few high-voltage cathodes such as NCM811 due to the low electrochemical stability of the polymer host. It is necessary to develop the high-voltage-resistant SPCEs with wide electrochemical windows to improve the interfacial compatibility with cathodes.

6) Using advanced characterization techniques to comprehensively investigate of Li⁺ transportation mechanism in SPCE during the charge-discharge process. An in-depth understanding of the atomic level for interfacial interaction between the polymer and inorganic nanofillers is needed. Moreover, interfacial electrochemical variation and microstructure evolution during Li⁺ transportation should be revealed more intuitively and clearly. To support the above research concepts, several in situ analysis techniques such as solid-state nuclear magnetic resonance (SS-NMR), cryogenic electron microscopy, and powder neutron diffraction should be combined with electrochemical characterizations and simulation methodologies. Recently, Zuo et al. systematically analyzed and summarized the contribution of the aforementioned in situ characterizations in revealing the structural issues of the electrode in lithium-based batteries. Hence, to obtain more information about the structural composition variation of SPCE during the cycling process, such application of in situ techniques in SPCE should be fully utilized and developed.

In summary, SPCE with appealing properties can satisfy the ever-increasing demand for safe LMB for industrialization. Researchers should exert more efforts to enhance the ionic conductivity and optimize the interface between SPCE and electrode. Therefore, the utilization of SPCE in ASSLBs is a promising strategy that is worth considering and developing in the next-generation LMB for a sustainable society.
| Structure type | Inorganic nanofiller composition | Polymer matrix composition | Ionic conductivity (S·cm\(^{-1}\)) | \(t_{Li}^+\) | Temperature (°C) | References | Year |
|---------------|---------------------------------|---------------------------|-------------------------------------|-----------|-----------------|------------|------|
| 0D            | Gd\(_{0.1}\)Ce\(_{0.9}\)O\(_{1.95}\) | PEO                       | 1.9 × 10\(^{-4}\)                  | 0.26      | 30              | [103]      | 2010 |
|               | La\(_{0.8}\)Sn\(_{0.2}\)Ga\(_{0.8}\)Mg\(_{0.2}\)O\(_{2.55}\) | PEO                       | 1.3 × 10\(^{-4}\)                  | 0.19      | NA              | [105]      | 2016 |
|               | SiO\(_2\)                        | PEO                       | 4.4 × 10\(^{-5}\)                  | NA        | 30              | [106]      | 2017 |
|               | Li\(_{0.75}\)La\(_{0.75}\)Ti\(_{0.25}\)O\(_{12}\)  | PVDF                      | 5 × 10\(^{-4}\)                   | NA        | 25              | [106]      | 2017 |
|               | Hollow SiO\(_2\)                 | TPGDA                     | 1.74 × 10\(^{-3}\)                 | 0.44      | Room temperature | [118]      | 2019 |
| 1D            | Li\(_{0.33}\)La\(_{0.55}\)Ti\(_{0.52}\)O\(_{3}\)  | PAN                       | 2.4 × 10\(^{-4}\)                  | NA        | 20              | [109]      | 2015 |
|               | Ca–CeO\(_2\)                     | PEO                       | 1.3 × 10\(^{-4}\)                  | 0.453     | 60              | [110]      | 2020 |
|               | Li\(_{1-x}\)Al\(_{x}\)Ti\(_{2-x}\)(PO\(_4\))\(_3\) | PEO                       | 0.52 × 10\(^{-4}\)                | NA        | Room temperature | [116]      | 2017 |
|               | Li\(_3\)La\(_{0.5}\)Zr\(_{1.5}\)O\(_{12}\)      | PEO                       | 2.39 × 10\(^{-4}\)                | NA        | Room temperature | [119]      | 2019 |
| 2D            | Intercalated lithium montmorillonite | PEC                     | 3.5 × 10\(^{-4}\)                  | 0.83      | 25              | [118]      | 2019 |
|               | MXene–mSiO\(_2\)                 | PPO                       | 4.6 × 10\(^{-4}\)                  | NA        | Room temperature | [121]      | 2020 |
| 3D            | Li\(_{0.35}\)La\(_{0.35}\)Zr\(_{1.4}\)Al\(_{0.6}\)O\(_{12}\)  | PEO                       | 2.5 × 10\(^{-4}\)                  | NA        | Room temperature | [123]      | 2016 |
|               | SiO\(_2\)                        | PEO                       | 8.8 × 10\(^{-5}\)                  | NA        | Room temperature | [124]      | 2018 |
|               | Surface functionalization         |                           | 0.6 × 10\(^{-3}\)                  | 0.38      | 30              | [125]      | 2018 |
|               | PPO–PEO–PPO-modified SiO\(_2\)    | PPO–PEO–PPO               | 1.32 × 10\(^{-3}\)                 | 0.44      | 20              | [130]      | 2020 |
|               | KH\(_{570}\)-Li\(_{3}\)La\(_{1}\)Zr\(_{3}\)O\(_{12}\) | PVCA                      | 3.39 × 10\(^{-4}\)                 | 0.752     | Room temperature | [132]      | 2018 |
|               | Poly(lithium 4-styrene sulfonate)-SiO\(_2\) | P(VdF-co-HFP)             | 1.4 × 10\(^{-4}\)                  | 0.48      | Room temperature | [134]      | 2013 |
|               | PDA-Li\(_{0.35}\)La\(_{0.35}\)Zr\(_{1.4}\)Ta\(_{0.6}\)O\(_{12}\) | PEO                       | 1.15 × 10\(^{-4}\)                | NA        | 30              | [135]      | 2019 |
|               | PIL–FMSiO\(_2\)                  | PIL                       | 1.82 × 10\(^{-3}\)                 | 0.56      | 130             | [136]      | 2017 |
|               | MB-Li\(_{0.35}\)La\(_{0.35}\)Zr\(_{1.4}\)Ta\(_{0.6}\)O\(_{12}\) | PEO                       | 3.11 × 10\(^{-4}\)                | 0.39      | 45              | [137]      | 2019 |

Abbreviations: PAN, polyacrylonitrile; PDA, polydopamine; PEC, poly(ethylene carbonate); PEO, poly(ethylene oxide); PIL, polymeric ionic liquid; PPO, poly(propylene oxide); PVDF, poly(vinylidene fluoride); P (VdF-co-HFP), poly(vinylidene fluoride-co-hexafluoropropylene); SPCE, solid polymer composite electrolyte; TPGDA, tripropylene glycol diacrylate.
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CONFLICT OF INTERESTS
The authors declare that there are no conflict of interests.

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