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Development of solid-state electrolytes for sodium-ion battery–A short review

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ABSTRACT

All-solid-state sodium-ion battery is regarded as the next generation battery to replace the current commercial lithium-ion battery, with the advantages of abundant sodium resources, low price and high-level safety. As one critical component in sodium-ion battery, solid-state electrolyte should possess superior operational safety and design simplicity, yet reasonable high room-temperature ionic conductivity. This paper gives a comprehensive review on the recent progress in solid-state electrolyte materials for sodium-ion battery, including inorganic ceramic/glass-ceramic, organic polymer and ceramic-polymer composite electrolytes, and also provides a comparison of the ionic conductivity in various solid-state electrolyte materials. The development of solid-state electrolytes suggests a bright future direction: all solid-state sodium-ion battery could be fully used to power all electric road vehicles, portable electronic devices and large-scale grid support.

1. Introduction

Nowadays, the development of renewable energy sources, such as wind, solar, and nuclear energy sources, has become imperative, due to the limited resource constraints of the traditional fossil fuels [1]. However, these renewable sources could not deliver a regular power supply as the sources are variable in time and diffuse in space. Thus, the focus has been shifted to the electrical energy storage to smooth the intermittency of the energy sources. Rechargeable battery has the ability to store chemical energy and convert it into electrical energy with high efficiency [2]. Lithium-ion battery (LIB), as one typical rechargeable electrochemical battery, has dominated the markets of portable electronic devices, electric vehicles, and hybrid electric vehicles in the past decades, due to its high output voltages, high energy densities, and long cycle life; even though the high cost and the shortage of lithium resources are inhibiting the application of LIB in large-scale energy storage [3–9].

Sodium-ion battery (SIB) is one promising alternative to LIB, with comparable performance to that of LIB, abundant sodium resources and low price of starting materials [10–13]. As Na atom is heavier and larger than those of Li atom, the gravimetric and volumetric energy density of Na-ion battery are expected to not exceed those of the Li analogues [14]. However, energy density would not be considered as the critical issue in the field of large-scale grid support, for which the operating cost and the battery durability are the most important aspects [15,16]. Furthermore, the abundant resources and the much lower price of the starting materials are presented as the obvious advantages of SIB over the LIB, in the industrial applications, such as portable electronic devices, hybrid and all electric road vehicles. As known, battery performance strongly depends on the selected materials, and the challenges for the current SIB (Fig. 1 (a)) with the widely used organic liquid electrolyte materials are the leakage, volatilization and the high flammability of the organic liquid solutions. In view of the safety issue, all-solid-state SIB (Fig. 1 (b): rigid battery and Fig. 1 (c): flexible battery) is regarded as the next generation battery, as it employs solid-state electrolytes rather than liquid organic electrolyte, which exhibits a superior thermal/chemical stability, lower flammability, improved durability, and enhanced electrochemical stability [2,17–20]. Moreover, the battery cell design would be simplified with solid electrolyte, as it does not need the additional containment or separator components for battery assembling, and usually provides a good mechanical performance.

Generally, solid-state electrolytes could be categorized into inorganic ceramic/glass-ceramic electrolyte, organic polymer electrolyte, and ceramic-polymer composite electrolyte. Inorganic electrolyte is more suitable for rigid battery design (Fig. 1 (b)) which could be operated

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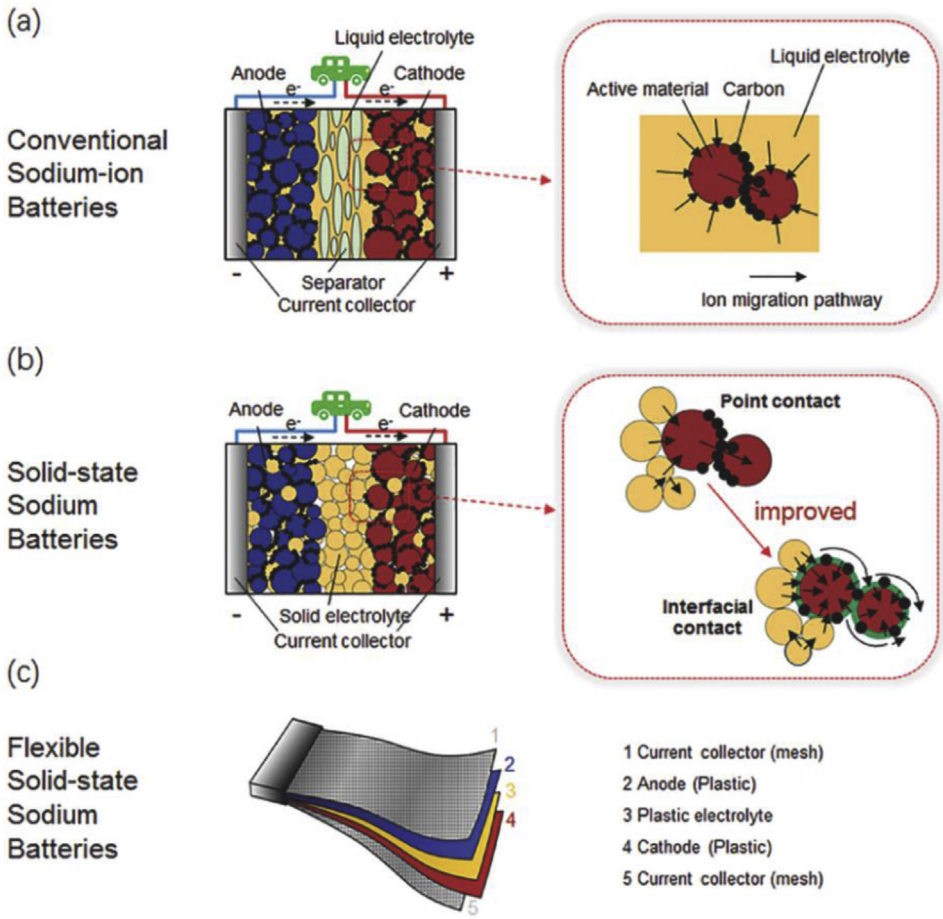

Fig. 1. Schematic representations of sodium-ion battery with (a) organic liquid electrolytes, (b) inorganic solid electrolytes, and (c) flexible polymer/plastic electrolytes (Reprinted with the permission from Ref. [18].).

under aggressive environment, as it possesses high elastic moduli, good thermal/chemical stability, wide electrochemical window, high ionic conductivity and low electronic conductivity [17,20–25]. On the other hand, solid polymer electrolyte could provide various geometries, high flexibility, and requires low-cost and simplified production processing, even though its ionic conductivity is lower than that of the inorganic solid electrolyte [26–29]. Besides, solid polymer electrolyte has the ability to easily form the effective electrode-electrolyte contact when assembling battery cells, which could improve the electrochemical performance and cycle life of the batteries [30–33]. Taking the advantages of both inorganic solid electrolyte and the organic polymer electrolyte, enhanced thermal/electrochemical stabilities and improved mechanical properties could be achieved in the ceramic-polymer composite electrolyte [30,34]. However, competitive ionic conductivity, one of the most important properties in electrolyte materials, is still yet obtained in the above mentioned solid-state electrolyte materials at room temperature, in comparison with the conventional organic liquid electrolyte materials ($\sim 10^{-2}$ S/cm). In 2017, J-J. Kim et al. gave a general review on the inorganic ceramic and glass-ceramic sodium-ion-conducting electrolytes, though the progress in solid-state organic polymer electrolyte and ceramic-polymer composite electrolyte was not included [20]. This paper gives a comprehensive review on the recent progress in the solid-state electrolytes for SIB, including inorganic, organic and composite electrolyte materials, and provides a comparison of the ionic conductivity in various solid-state electrolyte materials.

2. Inorganic solid electrolyte

Inorganic ceramic/glass-ceramic solid electrolyte consists of local symmetrical skeleton structure and mobile ions. The mobile ions may hop from one site to the adjacent one within the skeleton via point defect movements (Fig. 2), and generating the ion conduction [35]. Thus, the ionic conductivity of inorganic solid electrolyte is strongly dependent on the number of mobile ions/vacancies, the available hopping sites/vacancy sites, and the energy barrier for hopping [18,36–38]. The ion conduction presents an Arrhenius-type thermally activated process in both ceramic and glass-ceramic phases, as the mobile ions would be activated at higher temperature. It is noted that the ionic conductivity

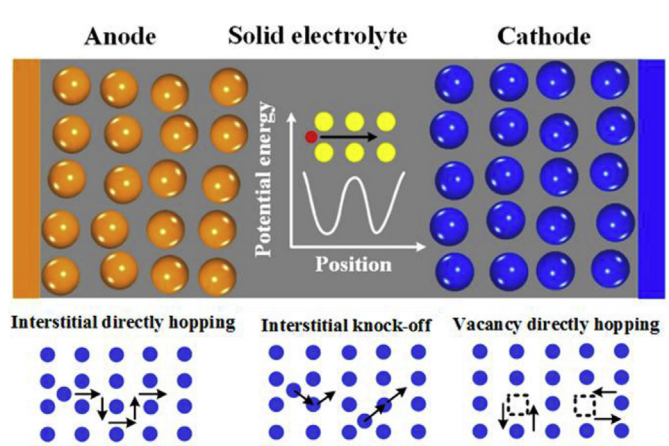

Fig. 2. Schematic representations of various mobile-ion-diffusion types within the solid-state inorganic electrolyte (Reprinted with the permission from Ref. [35]).

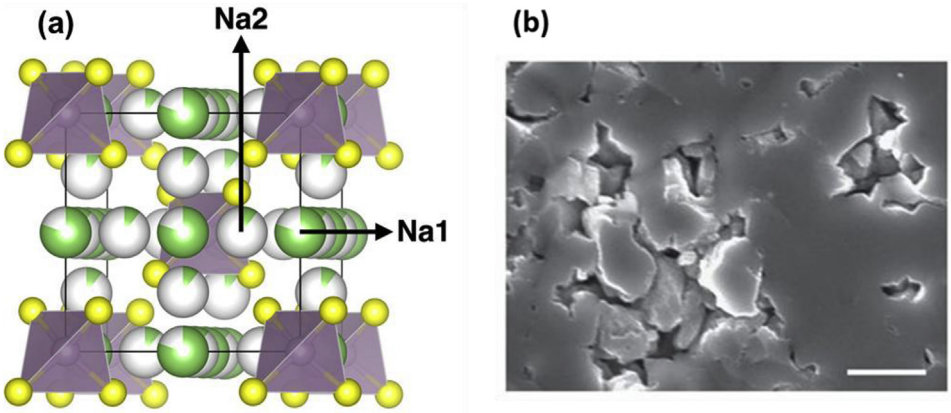

Fig. 3. (a) Cubic Na_3PS_4 crystalline structure (Reprinted with the permission from Ref. [49].), and (b) Cross-sectional SEM images of Na_3PS_4 glass-ceramic pellet (scale bar: 5μm. Reprinted with the permission from Ref. [17].).

varies from bulk grains to grain boundaries even within the same electrolyte material, due to the quite different local defect environment. In this section, the sulfide-based and oxide-based inorganic electrolyte compounds for SIB are mainly discussed and the total ionic conductivity instead of that of the individual bulk grain or grain boundary is compared among different electrolyte materials.

2.1. Sulfide-based inorganic electrolyte

Sulfide-based inorganic electrolyte is one of the attractive solid-state electrolytes, as it possesses a fast Na-ion conduction at room temperature and requires a relatively low temperature for synthesis. Furthermore, only a cold-pressing treatment is enough to form a good contact between the sulfide-based electrolyte and the electrode materials when assembling battery cells since it is soft, further reducing the industrial production cost [17,39–42].

Na_3PS_4 is a typical sulfide-based inorganic electrolyte. With a 3D pathway along the Na1 and Na2 sites in the open framework (Fig. 3(a)), cubic Na_3PS_4 (I43 m: $a_0 = 6.9965$ Å) ceramic electrolyte owns a high conductivity at room temperature (~10^{-4} S/cm) and a wide electrochemical window (5 V). The glass-ceramic phase of Na_3PS_4 exhibits an even higher total ionic conductivity, of 2.0–4.6 $\times 10^{-4}$ S/cm, at room temperature and a lower activation energy for hopping (19–27 kJ/mol) [17,40]. This is because the intimate contacts among grains could be achieved in the Na_3PS_4 glass-ceramic phase (Fig. 3(b)), which effectively suppresses the grain boundary resistance in the corresponding solid electrolyte material [17]. It is found that cation-substitution or anion-substitution in Na_3PS_4-based compounds could further facilitate the Na ion conduction, as additional point defects would be generated via the element doping or substitution. For Na_3PS_4—Na_4SiS_4 glass-ceramic electrolyte, high ionic conductivity of 7.4×10^{-4} S/cm has been achieved at room temperature [41], while for tetragonal Na_3SbS_4 (P421c: $a_0 = 6.9520$ Å, $c_0 = 7.0757$ Å) superionic conductor, a room-temperature ionic conductivity of up to 3×10^{-3} S/cm could be achieved, which is significantly higher than other sulfides with the cubic structure [43]. Fig. 4 summarizes the reported ionic conductivity at different temperatures in the cation-substituted and anion-substituted Na_3PS_4 inorganic solid electrolyte, and Arrhenius-type conductivity against temperature could be observed in all the presented electrolyte materials [40,43–47].

Chemical stability of the electrolyte materials is practically important to the lifetime of the assembled battery cells. However, the phosphorous in Na_3PS_4-based solid electrolyte is unstable with oxygen in air, and the sulfide-based inorganic electrolyte materials tend to decompose through hydrolysis by the moisture in air [48]. Thus, improved chemical stability of the sulfide-based electrolyte under ambient air is suggested in the future research work.

2.2. Oxide-based inorganic electrolyte

In contrast to the sulfide-based electrolyte materials, oxide-based inorganic electrolyte materials possess superior chemical stability in ambient air and thus could be used to improve the solid-state battery performance with long-term cycling life and high-power density.

2.2.1. β-Alumina electrolyte

β-Alumina electrolyte is historically the first fast ion conductor used in commercial Na—S and Na-metal chloride batteries, especially at elevated temperatures (~300 °C) [50,51]. It is a layered compound with alternating layers of spinel block and conduction planes (Fig. 5). The Na ion conduction exists only within its conduction planes, and the ion conductivity is almost zero in the vertical direction of the structure [50–52]. There are two distinct crystal structures: one is β-alumina phase (Na_2O $11Al_2O_3$, hexagonal symmetry: P63/mmc with lattice constants a = 0.559 nm, c = 2.261 nm); and the other one is β″- alumina phase (Na_2O $5Al_2O_3$, rhombohedral symmetry: R3m with lattice constants a = 0.560 nm, c = 3.395 nm) [53]. Compared to β-alumina, rhombohedral β″-alumina phase exhibits a higher ionic conductivity due to its higher Na ion concentration (in the conduction plane) and the larger unit cell (1.5 times longer in c axis over the β-alumina phase) [54]. It is reported that β″-alumina single crystal possesses an extremely high ionic conductivity of 1 S/cm at 300 °C, which is 4 times higher than that of its

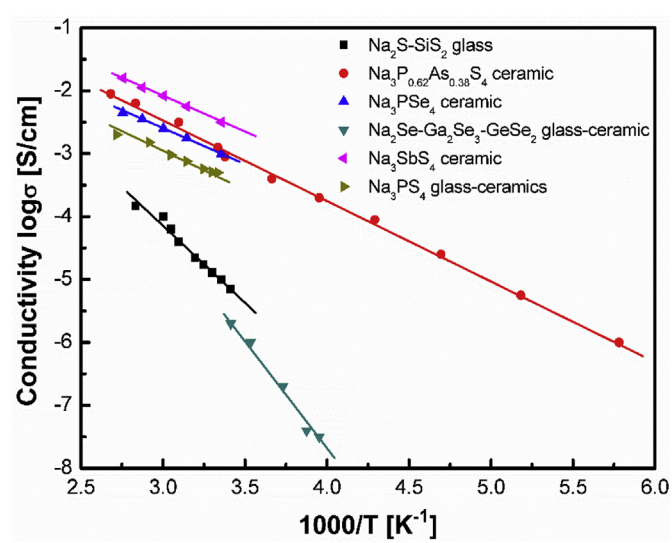

Fig. 4. Conductivity of various cation-substituted and anion-substituted Na_3PS_4 inorganic electrolytes.

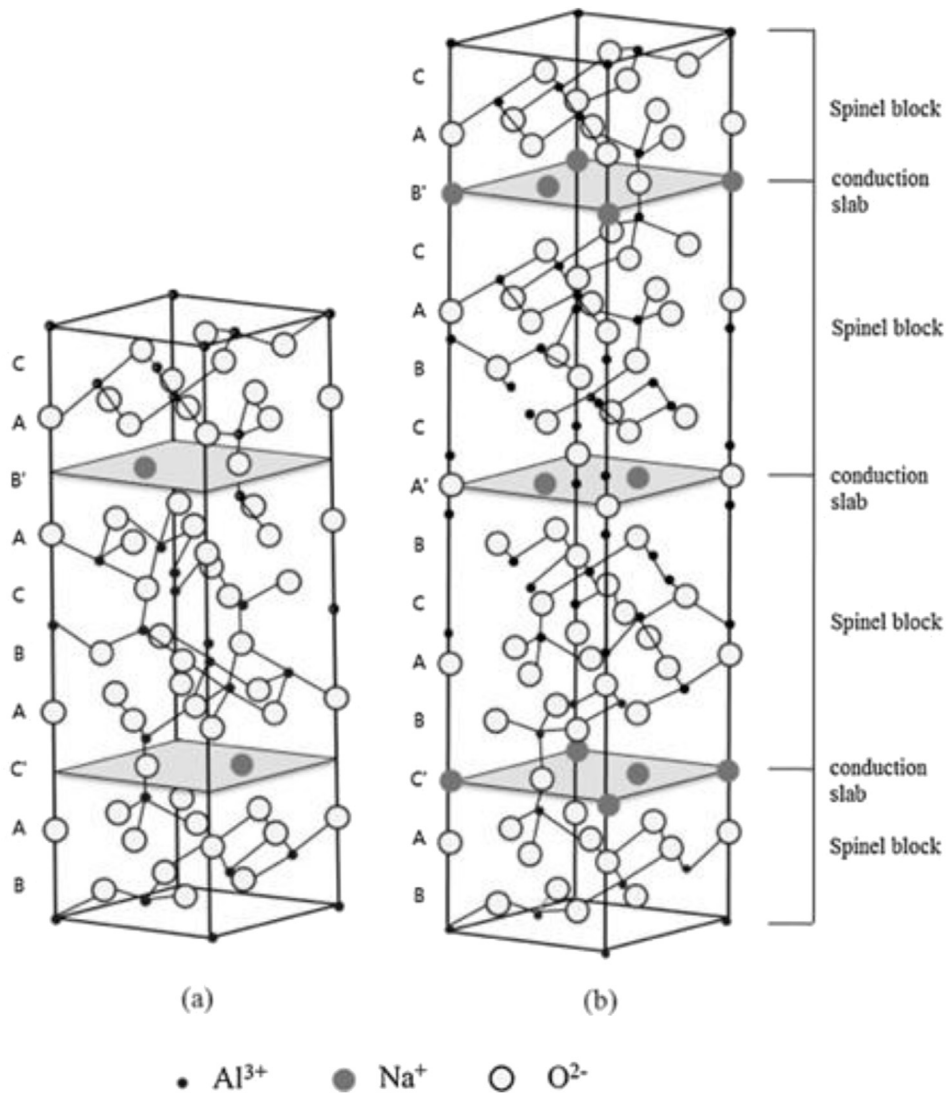

Fig. 5. (a) Na^+-β-alumina and (b) Na^+-β''-alumina structures (Reprinted with the permission from Ref. [56]).

polycrystalline phase (0.22–0.35 S/cm at 300 °C, but only 2.0×10^{-3} S/cm at room temperature) [1].

However, the fabrication of the highly conductive β''-Al_2O_3 single crystal is too expensive at industry scale. On the other hand, polycrystalline β''-alumina could be synthesized via high-temperature solid-state reaction (~1600 °C), solution combustion and sol-gel methods [50, 55]. It is still challenging to achieve homogeneous and pure products of β''-alumina polycrystals, since the synthesized β''-alumina is often mixed with β-alumina phase. Additionally, the remnant $NaAlO_2$ phase accumulated along the β''-alumina grain boundaries makes the polycrystalline product susceptible to the H_2O and CO_2 attack from atmosphere, diminishing its chemical stability in air [51]. The poor chemical stability, β/β''-alumina mixture and the 2D ionic conduction hinder the β-Alumina's application in solid-state SIB, and therefore the current research focus has been shifted to NASICON-type electrolyte.

2.2.2. NASICON electrolyte

NASICON (**NA S**uper **I**on **CON**ductor) is regarded as the most promising oxide-based electrolyte with suitable 3D tunnels for Na ion migration, to overcome the restrictions of β-Alumina electrolyte. The strong covalent framework of NASICON is of great practical importance, and high thermal and chemical stabilities are demonstrated [57–59]. Goodenough and Hong reported the first NASICON compound, $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$ ($0 \leq \times \leq 3$, abbreviated as NZSP), which was a solid solution between $NaZr_2P_3O_{12}$ and $Na_4Zr_2Si_3O_{12}$ [60,61]. Now the NASICON term is used to describe a special crystalline structure with a general composition formula of AMP_3O_{12}, where the A site can be occupied by monovalent cations (e.g. Li^+, Na^+, K^+), divalent cations (e.g. Mg^{2+}, Ca^{2+}, Ba^{2+}, Cu^{2+}, Co^{2+}), trivalent cations (e.g. Al^{3+}, Y^{3+}) and tetravalent cations (e.g. Ge^{4+}; Zr^{4+}; Hf^{4+}); and the M sites can be occupied by divalent cations (e.g. Cd^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}), trivalent cations (e.g. Al^{3+}, Ga^{3+}, Y^{3+}), tetravalent cations (e.g. Ti^{4+}; Si^{4+}; Zr^{4+}) and pentavalent cations (e.g. V^{5+}; Nb^{5+}; Sb^{5+}) [23]. In $NaA'MP_3O_{12}$ ionic conductors, A' sites could be either vacant or filled to maintain the electric neutrality, and therefore greatly affecting the amount of the mobile Na ions as well as the interaction between the mobile Na ions and the immobile skeleton atoms.

Depending on various chemical compositions and synthesis methods, the phase structure of NASICON could be further classified into rhombohedral (R3c), monoclinic (C2/c), triclinic, orthorhombic and corundum-like symmetry. Take the rhombohedral and monoclinic phase (often treated as a rotationally distorted rhombohedral) structures as examples (Fig. 6), ZrO_6 octahedra and PO_4 tetrahedra share the common corners in the 3D framework of NASICON and the mobile Na ions could migrate within the interconnected channels from Na(1) sites to Na(2) sites in rhombohedral phase or to Na (2)/Na(3) sites in monoclinic phase

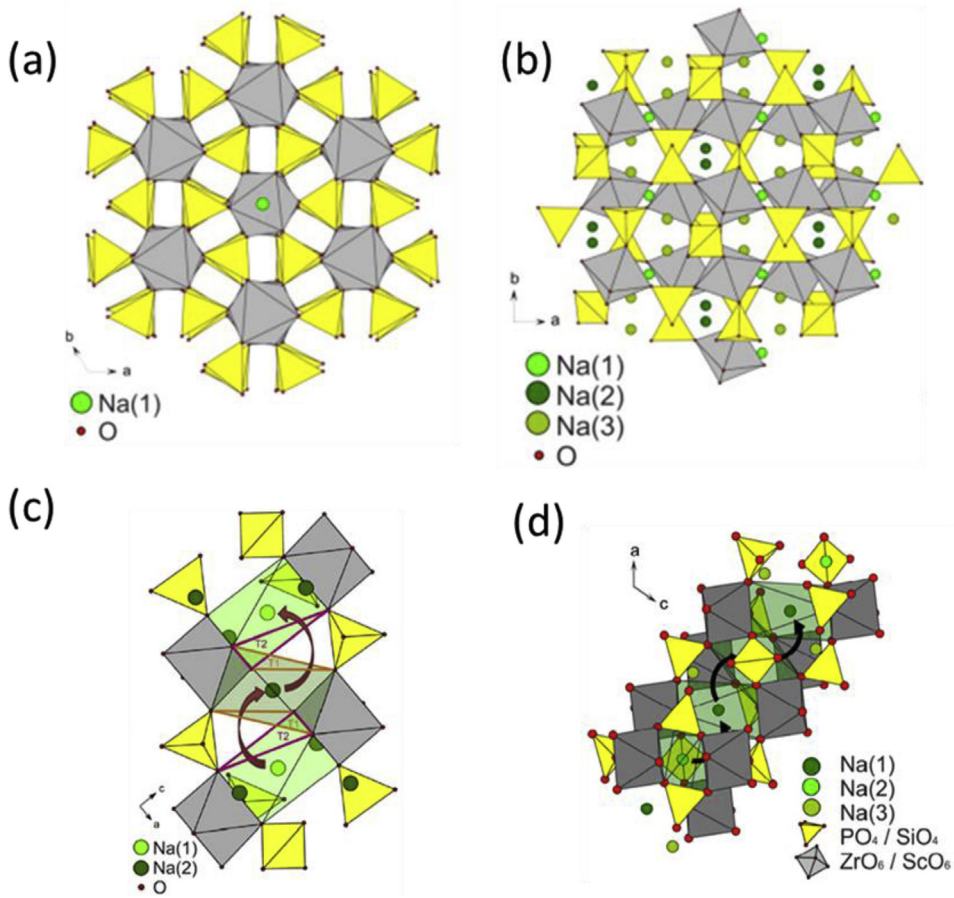

Fig. 6. NASICON-type (a) rhombohedral (R3c) structure and (b) monoclinic (C2/c) structure (the yellow tetrahedra and the grey octahedra correspond to SiO_4/PO_4 and ZrO_6 units, respectively); Na ion conduction pathway in NASICON-type (c) rhombohedral and (d) monoclinic structure (Reprinted with the permission from Refs. [24,62].).

[24]. Compared with the rhombohedral phase, one additional migration channel is formed and more available vacancy sites are generated in the distorted NASICON-monoclinic phase. The Na ions migrate from one site to the adjacent site within the immobile skeleton through oxygen triangles T1 and T2, forming the bottlenecks for Na ion migration, and therefore the larger bottleneck size indicates the lower energy barrier for the Na ion migration (Fig. 2).

The NASICON-type inorganic electrolyte's ionic conductivity varies even by orders of magnitude with different chemical compositions, due to the quite different interaction between the mobile ions and the skeleton atoms [24,30,34]. Besides the various chemical compositions, the specific phase structure (e.g. rhombohedral, monoclinic and orthorhombic symmetry), the lattice parameters, the size of the structural bottleneck (oxygen triangles T1 and T2) and the Na concentration also effect the ionic conduction in the electrolyte [22–25,62–65]. It is found that the monoclinic NASICON could further facilitate the Na ion migration than the rhombohedral phase; the larger bottleneck size indicates the wider conduction path for Na ion to travel; and the optimum Na concentration is around 3.3 mol per unit formula [22–25,62–65]. In addition, proper chemical compositions and suitable synthesis methods could lead to a higher density and further suppress the grain-boundary impedance of NASICON-type electrolyte. For NASICON-type NZSP ($Na_3Zr_2Si_2PO_{12}$) compound, which is regarded as the benchmark in NASICON-type electrolytes, the total ionic conductivity is 6.7×10^{-4} S/cm at room temperature and 0.2 S/cm at 300 °C [60,61]. Fig. 7 summarizes the recently reported ionic conductivity in the attractive NASICON-type electrolyte compounds. The room-temperature ionic conductivity of up to 10^{-3} S/cm has been achieved in the doped-NZSP

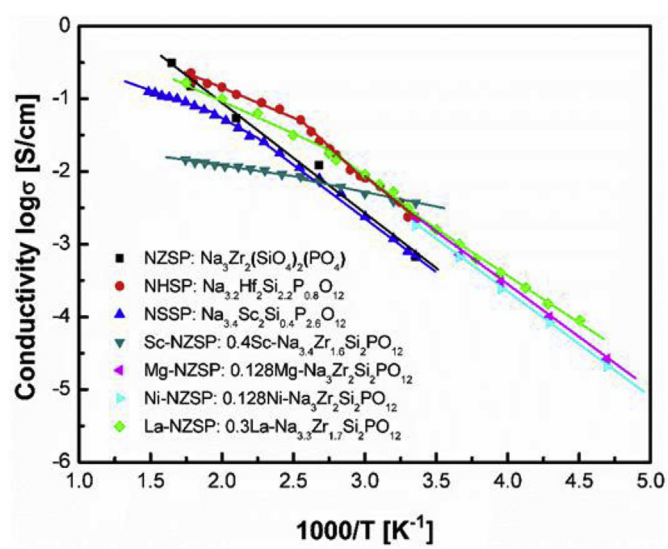

Fig. 7. Conductivity of various NASICON-type inorganic electrolytes.

and NHSP conductor, and the Arrhenius-type conductivity is presented in all the NASICON compounds [22,25,60,62,63,66]. The observed two different slopes (in NHSP, NSSP and La-NZSP) within the temperature range indicates different activation energy exists for Na ion conduction, i.e. low temperature activation energy and high temperature activation energy.

Unlike the sulfide-based electrolytes, where intimate electrode-electrolyte contact could be easily formed via the cold-pressing treatment, unstable electrode (especially, the metallic Na)-electrolyte interface and high interface impedance problems have been found in SIB with NASICON-type electrolytes. To further enhance the energy density and cycling life in SIB, Na metal is required to replace the carbon anode. However, the NASICON compounds could not be wetted by the metallic Na and Na dendrite often forms at the grain boundaries of NASICON-type electrolyte during the plating of sodium, causing the battery cell short-circuited [67,68]. Furthermore, the low electrode-electrolyte interface Na^+ conductivity ($<10^{-5}$ S/cm at room temperature) is another problem that greatly inhibits the practical application of NASICON-type electrolyte in SIB. Recently, Goodenough's group repoted that either the in situ formed interfacial interlayer (formed from the reaction with molten Na) or a dry polymer film could effectively improve the wetting of NASICON eletrolyte with the metalic Na, and a high cycling stability has been demonstrated in the resultant SIB at 65 $^{\circ}C$ [68]. The wetting of NASICON-type electrolyte with sodium metal should be further improved and a SIB with good performance at room temperature is desired in the future research work.

3. Organic polymer electrolyte

Organic polymer electrolytes have several advantages over the inorganic solid electrolyte, such as its high flexibility, the ability to easily form intimate electrode-electrolyte contact and the simple processability [30–33]. There are two types of polymer electrolyte materials: gel polymer electrolyte and solvent-free solid polymer electrolyte. The former one exhibits weaker mechanical properties but higher ionic conductivity, while the latter one is mechanically stronger and could be prepared into free-standing electrolyte membranes without adding other mechanical supports. In view of ion conduction mechanism, the former one is similar to the liquid electrolyte; whereas in the latter electrolyte, Na-salts are dissolved in the polymer host and Na ions could transport within the polymer hosts via the segmental motion of the polymer chains [38,69,70]. Fig. 8 presents the ion conduction phenomenon in solid polymer electrolytes: with low salt concentration, the polymer segmental motions governs the ion conduction, whereas with high salt concentration, mobile ions could self-diffuse within the polymer hosts, due to the diminished coupling between the polymer segmental motion and ion motion. Unlike the inorganic solid electrolyte materials, which presents a simple Arrhenius-type thermally activated conduction process, Vogel-Tammann-Fulcher model is often used to analyze the temperature-dependent conductivity in polymer-based electrolyte materials.

3.1. Gel polymer electrolyte

Gel polymer electrolyte is formed by incorporating liquid electrolyte solutions (sodium salts dissolved in propylene carbonate, PC, or ethylene carbonate, EC) into polymer matrix, and the gel matrix could improve the safety over the liquid solvent. The retained liquid solvent in the gel polymer matrix could facilitate the ion transportation, and therefore the ionic conductivity of gel polymer electrolyte is quite attractive ($\sim 10^{-3}$ S/cm at room temperature) [72]. Unlike the inorganic electrolyte where only one kind of mobile ions can transport under the external electric field, ions other than Na ions could be mobile and carry charges in gel polymer electrolyte. In some gel polymer electrolyte, the Na ion conduction could be only few percent of the total ion conduction. To describe the specific Na ion conduction in gel polymer electrolyte, transference/transport number, the portion of current carried by Na ions, is often studied. In this section, the ionic conductivity as well as the transference number in various gel polymer electrolyte materials are reviewed and compared (Table 1).

Poly(vinylidene fluoride) (PVdF) is a commonly used gel polymer matrix, due to its high electrochemical stability. With the addition of hexafluoropropylene (HFP) unit, the crystallinity of PVdF could be reduced and the semi-crystalline P(VdF-HFP) exhibits higher flexibility as compared to PVdF [73]. Generally, the ionic conductivity of P(VdF-HFP) gel polymer electrolyte is $2 \sim 4 \times 10^{-3}$ S/cm, and the transference number is around 0.3. The addition of ceramic particles or plasticizer could further increase the transference number, but the large amount of ceramic fillers would degrade the mechanical properties of the gel polymer electrolyte [38,74–76]. Besides, poly(methylmethacrylate) (PMMA), poly(acrylonitrile) (PAN) and some co-polymers (Table 1) have also been studied as the gel polymer matrix for SIB, which exhibits higher ionic conductivity than P(VdF-HFP) [16,77–79]. By introducing photo-initiators, the co-polymer gel electrolyte could be cured via the UV light at ambient temperature, which could greatly reduce the production time and cost [16]. However, the gel polymer electrolyte could not ultimately eliminate the safety issue of the incorporated liquid solutions and the leakage/volatilization problem of the liquid solvent still remains. Stable gel polymer electrolytes with high safety is strongly desired for SIB in the future research work.

3.2. Solvent-free solid polymer electrolyte

In solvent-free solid polymer electrolyte, Na salts are dissolved by the polymer chains (e.g. the sequential oxyethylene group: —CH_2—CH_2—O— and the polar groups: —O—, —H—, —C—H—), instead of the additional liquid solvent, which ultimately solves the leakage/volatilization problem of the organic solvent. The Na ions could

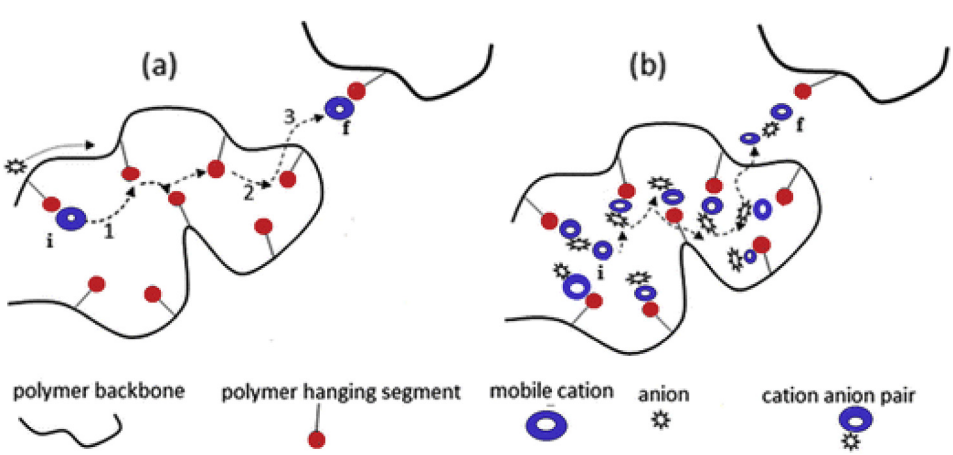

Fig. 8. Schematic representations of ion conduction phenomenon in solvent-free solid polymer electrolyte: (a) with low salt concentration, and (b) with high salt concentration (Reprinted with the permission from Ref. [71]).

Table 1
Room-temperature ionic conductivity and transference number of various gel polymer electrolytes.

Gel Polymer Electrolyte	Room-Temperature Ionic Conductivity σ, S/cm	Transference Number	*Ref.*
PVdF-HFP/Glass Fiber + $NaClO_4$-PC	4.60×10^{-3}	–	[80]
PVdF-HFP + $NaCF_3SO_3$-EC-PC + SiO_2	4.10×10^{-3}	0.43	[74]
PVdF-HFP + $NaClO_4$-EC	0.60×10^{-3}	0.30	[81]
PVdF-HFP + EMI-triflate + $NaCF_3SO_3$	5.74×10^{-3}	0.23	[72]
PVdF-HFP + $NaCF_3SO_3$-PC-EC	2.50×10^{-3}	0.62	[76]
BEMA-PEGMA + TiO_2 + $NaClO_4$-PC	5.10×10^{-3}	0.53	[16]
METEPP-MMA-TFMA + $NaClO_4$-PC-EC	6.29×10^{-3}	–	[77]
PMMA + $NaClO_4$-PC-EC + SiO_2	3.40×10^{-3}	0.23	[78]
PAN + $NaClO_4$-PC-EC	4.50×10^{-3}	–	[79]

transport in the solvent-free polymer hosts via the segmental motion of the polymer chains, and the conduction mechanism is related to the ion hopping along with the polymer chain relaxation, therefore strongly dependent on the amount of mobile charged carriers and temperature (Fig. 8) [70,82]. Compared with the gel polymer electrolyte, the ionic conductivity in solvent-free polymer electrolyte is much lower (only $10^{-9} \sim 10^{-6}$ S/cm at room temperature), but the conductivity would increase with temperature ($10^{-4} \sim 10^{-3}$ S/cm above 80 °*C*). Furthermore, it has been found that the amorphous phase of the polymeric host could facilitate the fast ion conduction, i.e. the larger degree of amorphicity, the higher ionic conductivity in solvent-free polymer electrolyte.

Poly(ethylene oxide) (PEO) is a popular polymer host for solid polymer electrolyte, due to its good electrochemical stability, mechanical properties, and the capability to solvate different metal salts. Fig. 9 summarizes the conductivity in PEO-based polymer electrolyte with various sodium salts and additives, whose Na^+ transference numbers are in the range of 0.2–0.53 [27–29,83–87]. The appropriate anions (e.g. FSI: $[(FSO_2)_2N]^-$ and TFSI: $[(CF_3SO_2)_2N]^-$) in the sodium salts would facilitate the cation (Na) ion conduction in the PEO host, as it could interact with the PEO chains, effectively reducing the crystallinity of PEO and increasing the number of free Na^+ ions [88]. Furthermore, the less "free" anions (due to the interaction with polymer chains) could enhance the

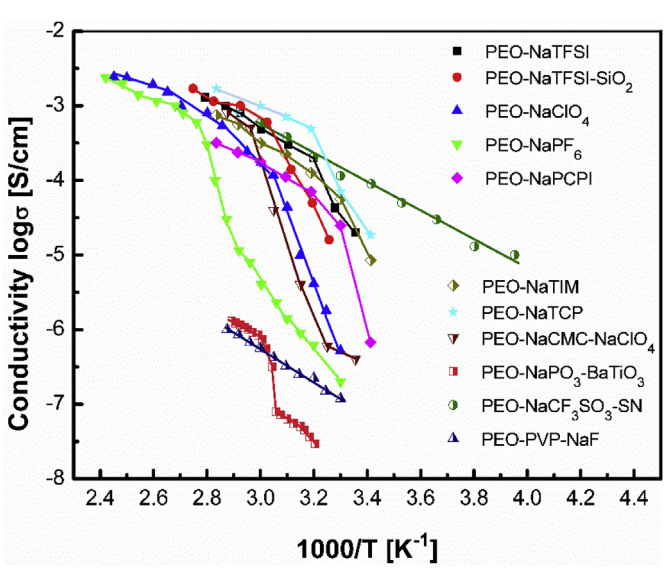

Fig. 9. Conductivity of PEO-based solvent-free solid polymer electrolytes.

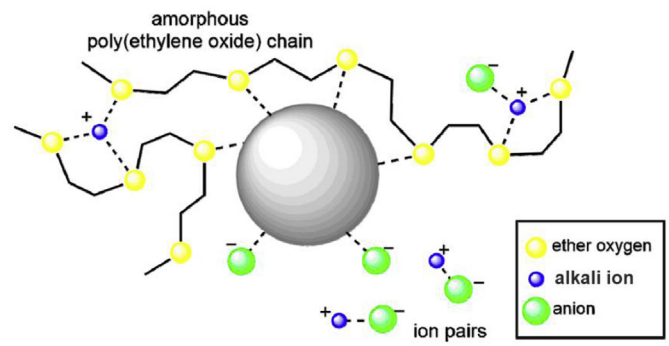

Fig. 10. Schematic representations of the interactions within PEO polymer, alkali salt and a ceramic nanoparticle (Reprinted with the permission from Ref. [90].).

cation/Na^+ transference number. The additives, such as polymer blends (Polyvinylpyrrolidone, PVP), plasticizers (succinonitrile, SN), and inorganic ceramic fillers (TiO_2, SiO_2 and $BaTiO_3$), could also improve the ionic conductivity in the PEO-based polymer electrolyte, since they could reduce the crystallinity of the polymeric PEO [26,28,29,31,83,89]. As shown in Fig. 10, the introduced ceramic nanoparticles could interact with both the ether oxygens in the PEO chains and the oxygens from the anions in the alkali salts via the oxygen vacancies on the ceramic surface. The interaction with the polymer chains could hinder the crystallization and increase the amorphous fraction of PEO; while the interaction with alkali salts would immobilize the anions and release more "free" cations/alkali ions [90]. In contrast to the ceramic fillers which could also improve the mechanical strength of the polymeric membrane, the other additives, i.e. plasticizers and polymer blends, are detrimental to the mechanical performance of the polymer electrolyte materials. So far, competitive ionic conductivity and mechanical properties have yet been obtained in the PEO-based solid polymer electrolyte simultaneously, even though attractive ionic conductivity has been demonstrated in PEO-plasticizer/gel electrolyte.

4. Ceramic-polymer composite electrolyte

Besides the passive ceramic fillers (e.g. SiO_2, TiO_2, ZrO_2, $BaTiO_3$), active ceramic fillers (e.g. NASICON-type ceramic fillers) have also been incorporated into the polymer hosts, forming the ceramic-polymer composite electrolyte. Taking the advantages of both inorganic ceramic electrolyte and the organic polymer electrolyte, enhanced ionic conductivity, good mechanical property and high chemical/thermal stability could be achieved in the composite electrolyte simultaneously [30,34,91]. In PEO-based polymeric membranes, a large enhancement of Young's modulus and yield-point stress has been achieved with the addition of the nanosized ceramic particles (TiO_2 and Al_2O_3) [92]. The PEO-NASICON composite membranes are demonstrated highly flexible and thermally stable even up to 150°*C* [30].

The ion conduction is very complex in ceramic-polymer composite electrolyte. Compared with the ceramic-free polymer electrolytes, the ion movement could be further facilitated in the polymer host with the addition of ceramic fillers, due to the reduced crystallinity of the polymer host. The mobile ions could also transport within the introduced active ceramic fillers and the ceramic-polymer interfaces, both of which provide even faster conduction pathways over the polymer matrix [91,93–95]. As discussed in Section 2, the room-temperature ionic conductivity of the active ceramics is in the level of $10^{-3} \sim 10^{-4}$ S/cm, while the inherent conductivity of the ceramic-polymer interface is estimated to be higher than 1×10^{-4} S/cm [96]. It is found that the composite's conductivity is strongly dependent on the amount of the added ceramic fillers [30,34]. According to the effective medium theory model, the composite's conductivity would continuously increase with the amount of the ceramic fillers, if the ceramic fillers could form into percolation clusters (with

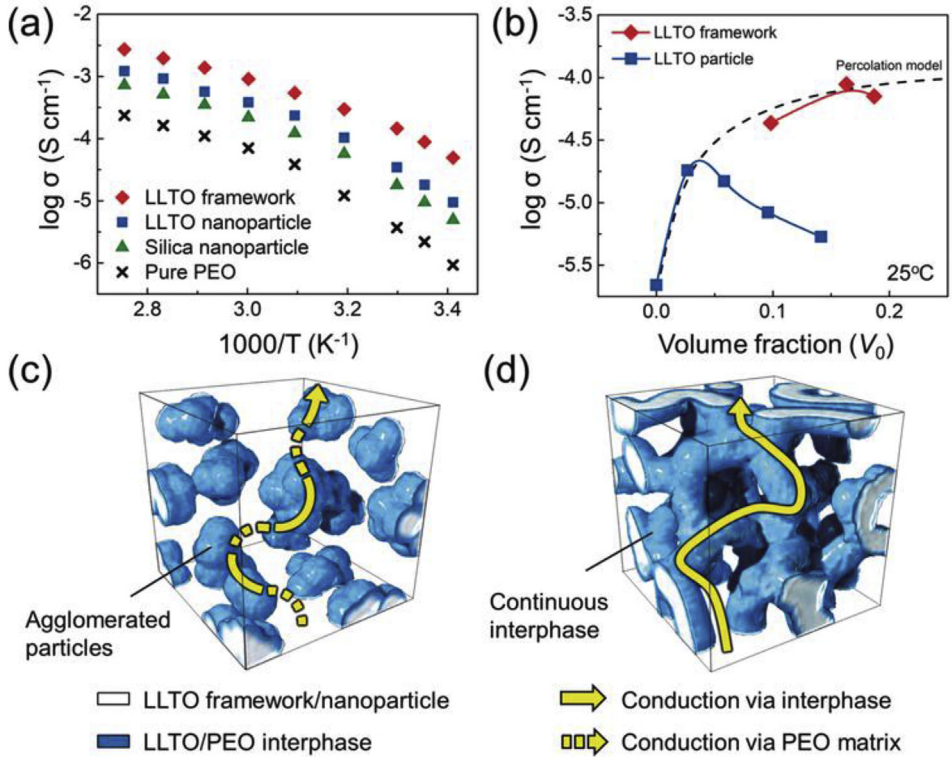

Fig. 11. (a) Ionic conductivity of composite electrolytes with active (LLTO) and passive ceramics (SiO_2) (pure PEO polymer is presented as a control group), and (b) conductivity comparison between the percolation model and experimental data. Schematic representation of conduction mechanism in composite electrolytes with (c) agglomerate nanoparticles and (d) continuous interphase (Reprinted with the permission from Ref. [99].).

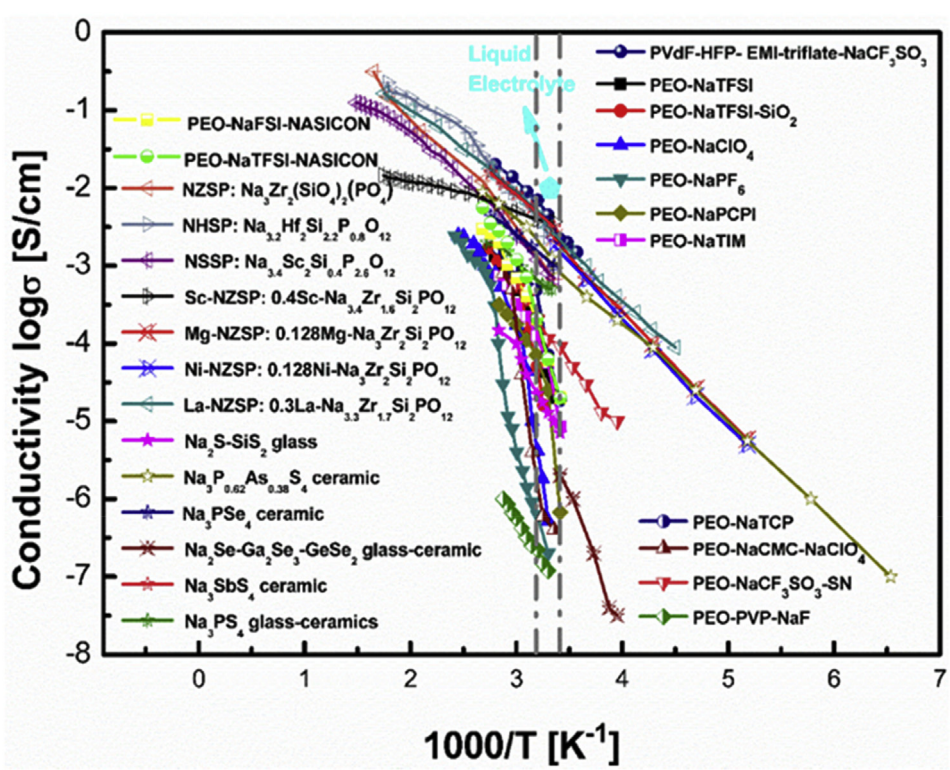

Fig. 12. Conductivity of various solid-state electrolytes for SIB. The room-temperature ionic conductivity in the conventional liquid electrolytes is also presented as a benchmark.

continuous ceramic-polymer interface) [97]. However, in most cases, the conductivity decreases after reaching certain amount of ceramic fillers, because of the aggressive agglomeration of the ceramic particles [98,30,34,87,96]. On the contrary, greatly enhanced ionic conductivity has been achived in the ceramic-polymer composite electrolyte with higher degree of percolation (continuous interphase), as shown in Fig. 11 [99].

In PEO-NaTFSI-NASICON ($Na_3Zr_2Si_2PO_{12}$ and $Na_{3.4}Zr_{1.8}Mg_{0.2}Si_2PO_{12}$ ceramic fillers) composite electrolyte membranes, the limitation amount for the NASICON fillers is 40–50 wt%. Room-temperature ionic conductivity of $4.4 \sim 6.0 \times 10^{-5}$ S/cm could be achieved at the limitation amount, which is higher than that in most PEO-based polymer electrolyte [30,34]. A brief summary and comparison of the reported ionic conductivity in various solid-state electrolytes is presented in Fig. 12 (the room-temperature ionic conductivity in liquid electrolyte, $\sim 10^{-2}$ S/cm, is highlighted as a benchmark). As shown, ionic conductivity in PEO-NASICON composite electrolyte is still far below that of the inorganic NASICON-based, Na_3PS_4-based solid electrolytes and the PVdF-based gel polymer electrolytes. So far, the research studies on the ceramic-polymer composite electrolytes for SIB is still in the infancy stage and further development is desired to further enhance the composite's ionic conductivity.

5. Perspectives and conclusion

Solid-state electrolytes can provide advantages of superior thermal stability, lower flammability, improved durability and battery design simplicity, over the conventional organic liquid electrolytes, even though the room-temperature ionic conductivity in solid electrolytes is still lower than that in liquid electrolytes. Among various solid-state electrolytes, the PVdF-based gel polymer provides higher ionic conductivities, even competitive to that in organic liquid electrolytes, but the leakage/volatilization problem of the incorporated liquid solvent could not be fully solved, degrading the durability of the gel polymer electrolytes. The inorganic electrolyte is more suitable for rigid battery design, as it possesses better thermal/chemical stabilities, higher mechanical strength and exhibits an obvious conductivity advantage over a wide temperature range. However, the chemical stability in sulfide-based inorganic electrolyte need to be further developed in the future research; while for NASICON-based inorganic electrolyte, its wetting with sodium metal should be enhanced, in order to improve the energy density and cycling life in the resultant SIB with metallic Na as anode. On the other hand, the solvent-free PEO-based solid polymer electrolytes and the flexible ceramic-polymer composite electrolytes are more befitting for the flexible battery cells. The high flexibility in electrolyte could also provide higher electrode compatibility, which reduces the electrode-electrolyte interface resistance and improves the electrochemical performance and cycle life of the battery cells. So far, the intrinsic conductivity performance in the polymer-based and ceramic-polymer composite electrolytes is still unsatisfied and greatly enhanced room-temperature ionic conductivity is strongly desired, which is also suggested as the future research direction.

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