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Polymer electrolytes for lithium polymer batteries

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In this review, state-of-the-art polymer electrolytes are discussed with respect to their electrochemical and physical properties for their application in lithium polymer batteries. We divide polymer electrolytes into the two large categories of solid polymer electrolytes and gel polymer electrolytes (GPE). The performance requirements and ion transfer mechanisms of polymer electrolytes are presented at first. Then, solid polymer electrolyte systems, including dry solid polymer electrolytes, polymer-in-salt systems (rubbery electrolytes), and single-ion conducting polymer electrolytes, are described systematically. Solid polymer electrolytes still suffer from poor ionic conductivity, which is lower than $10^{-5} \text{ S cm}^{-1}$. In order to further improve the ionic conductivity, numerous new types of lithium salt have been studied and inorganic fillers have been incorporated into solid polymer electrolytes. In the section on gel polymer electrolytes, the types of plasticizer and preparation methods of GPEs are summarized. Although the ionic conductivity of GPEs can reach $10^{-3} \text{ S cm}^{-1}$, their low mechanical strength and poor interfacial properties are obstacles to their practical application. Significant attention is paid to the incorporation of inorganic fillers into GPEs to improve their mechanical strength as well as their transport properties and electrochemical properties.

1. Introduction

Since the lithium-ion battery was first produced by the Sony Corporation in 1990, it has attracted much attention of researchers during the past two decades. Nowadays, lithium-ion batteries have rapidly taken over the entire market of electronic

products such as mobile telephones, notebooks, personal computers (PCs), and digital cameras, owing to their desirable features including light weight, high energy densities, high open-circuit potentials, minimal memory effects, fast charging, low self-discharge rates, and environmental friendliness, *etc.*^{1–4} Moreover, they also exhibit excellent prospects for applications in electric vehicles (EV), hybrid electric vehicles (HEV), aviation technology and energy storage apparatus.⁵ A conventional lithium-ion battery comprises two electrodes, an anode and a cathode, and an electrolyte system, as shown in Fig. 1. It

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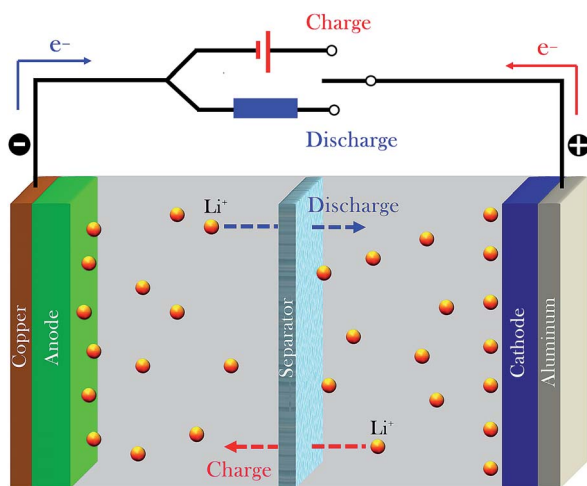


Fig. 1 Schematic of the working mechanism of a lithium-ion battery.

usually contains a separator to prevent physical contact between the anode and cathode. The electrolyte is one of the key components, which act as the ion transport pathway. The cell capacity, working temperature range, safety issues and cyclability of lithium-ion batteries are influenced significantly by the selected electrolyte. According to their physical state, electrolytes can be classified into liquid electrolytes and solid electrolytes. Liquid electrolytes are widely used in lithium-ion batteries because of their high ionic conductivity. However, safety problems associated with lithium metal anodes, the reaction of volatile and flammable organic solvents and the leakage of electrolytes have hindered the commercialization of any lithium-ion battery based on a liquid electrolyte. Solid electrolytes include inorganic solid electrolytes (such as conductive ceramics and glasses) and polymer electrolytes. Among these, polymer electrolytes have attracted ever-

increasing interest in the field of batteries such as lithium-ion batteries, fuel cells,^{6–8} vanadium redox flow batteries,^{9–12} etc.

Polymer electrolytes offer several advantages over liquid electrolytes and inorganic solid electrolytes, such as enhanced resistance to variations in the volume of the electrodes during the charge/discharge process, improved safety features, excellent flexibility and processability.^{13,14} Moreover, dendrite growth could be minimized or even suppressed in solvent-free polymer electrolytes under certain conditions.¹⁵ In 1973, polymer electrolytes were first studied by Fenton *et al.*,¹⁶ who found that the polymer salts formed by complexation between polyethylene oxide (PEO) and alkali metal salts had the property of ionic conductivity. Since then, there have been substantial research efforts toward new polymer electrolytes and theoretical modelling of their ion transfer mechanism, the physical and chemical properties of the electrolyte/electrode interface, etc.^{14,17–19} Initially, a solid polymer electrolyte (SPE) was defined as a polymer matrix swollen with lithium salts, which is now called a dry solid polymer electrolyte. PEO and its derivatives are the best candidates for use as polymer matrices. A PEO matrix dissolves lithium salts by coordination between the lithium ions and the ether oxygens in the polymer chains. However, in the past two decades little progress has been made in the commercialization of lithium-ion batteries based on a dry solid polymer electrolyte, in which poor ion transfer represents a seemingly insurmountable barrier. In order to improve the ionic conductivity and/or the Li^+ transference number, other solid polymer electrolyte systems including polymer-in-salt systems (rubbery electrolytes) and single-ion conducting polymer electrolytes have been developed. In addition, strategies such as modification of the polymer matrix, the search for new types of lithium salt and the incorporation of inorganic fillers into SPEs have been studied. In particular, attempts to improve the ionic conductivity of SPEs by incorporating a certain amount of plasticizer or solvent into SPEs have led us into the



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area of gel polymer electrolytes (GPE). Some of the key advantages of solid polymer electrolytes with respect to solvent-containing gels are their improved electrochemical stability and thermal stability. In general, the ionic conductivity of GPE can reach $10^{-3} \text{ S cm}^{-1}$, which is two orders of magnitude higher than that of SPE. However, the gain in ionic conductivity is often at the cost of a loss of mechanical strength. The incorporation of inorganic fillers into GPEs has proved to be a very effective way to improve their mechanical strength as well as their transport properties and electrochemical properties.

In this review, we first state the performance requirements and ion transfer mechanisms of polymer electrolytes. In the following, polymer electrolytes are divided into two main categories: solid polymer electrolytes and gel polymer electrolytes. In the section on solid polymer electrolytes, the classes of dry solid polymer electrolytes, rubber electrolytes, and single-ion conducting polymer electrolytes are described systematically and strategies to improve their ionic conductivity are introduced. In the section on gel polymer electrolytes, the types of plasticizer and preparation methods are summarized and then the strategy to improve their mechanical strength is described in detail.

2. Performance requirements and ion transfer mechanisms of polymer electrolytes

2.1. Performance requirements

In a lithium polymer battery, a polymer electrolyte is sandwiched between the anode (lithium metal, carbon, *etc.*) and the composite cathode, acting as both electrolyte and separator. The polymer membrane plays a crucial role in the performance of lithium polymer batteries. From the point of view of practical applications, a polymer electrolyte for lithium polymer batteries should inherently possess the following properties:^{20,21}

(1) High ionic conductivity. It should be a good ionic conductor and electronic insulator, so that ion transport can be facilitated and self-discharge can be minimized.¹⁴ Ionic conductivity is the determining factor of the internal impedance and electrochemical behavior at different charge/discharge rates. In general, the ionic conductivity of aprotic organic solvents that contain lithium salts can reach 10^{-2} to $10^{-3} \text{ S cm}^{-1}$. Polymer electrolytes should possess conductivities that approach or exceed $10^{-4} \text{ S cm}^{-1}$ at ambient temperature to achieve rapid charge/discharge.

(2) Appreciable Li^+ transference number. If possible, the Li^+ transference number is close to unity in an electrolyte system. A large Li^+ transference number can reduce concentration polarization of electrolytes during the charge/discharge process and thus produce higher power density.²² Reducing the mobility of anions can greatly increase the Li^+ transference number. Two approaches have been reported to effectively reduce the mobility of anions. One is to anchor anions to the polymer backbone, which is a common method for obtaining single-ion conducting polymer electrolytes.^{23–26} The other is the

introduction of anion receptors that selectively complex with anions in electrolytes.^{27,28}

(3) Good mechanical strength. The mechanical strength of a polymer electrolyte is the most important factor that needs to be taken into account in the large-scale manufacture of lithium-ion batteries. Polymer electrolytes should not be brittle like certain ceramics, but able to relax elastically when stress arises in the process of manufacture, cell assembly, storage and usage. Some feasible approaches have been introduced to increase the dimensional stability of electrolyte membranes, such as adding inorganic fillers, crosslinking, physical support by a polyolefin membrane, *etc.*

(4) Wide electrochemical stability window. The electrochemical window is defined as the difference between the potentials of the oxidation reaction and the reduction reaction. For an electrolyte, the primary requirement is to be inert to both electrodes, which means that the oxidation potential must be higher than the embedding potential of Li^+ in the cathode and the reduction potential must be lower than that of lithium metal in the anode. Thus, polymer electrolytes should have an electrochemical window of up to 4–5 V *vs.* Li/Li^+ to be compatible with both electrode materials.

(5) Excellent chemical and thermal stability. Polymer electrolytes should be inert to battery components such as the anode, cathode, cell separator, current collectors, additives and cell packaging materials. Excellent thermal stability ensures the safe use of a battery even in the cases of electrical (shorting, overcharge) or thermal (flame) abuse.

2.2. Ion transfer mechanisms

In the past three decades, there has been much interest in the mechanism of ionic conduction in polymer electrolytes.^{17,29–32} For solid polymer electrolytes, the polymer matrix should first have the ability to dissolve/complex lithium ions. Polymers with sequential polar groups such as $-\text{O}-$, $=\text{O}$, $-\text{S}-$, $-\text{N}-$, $-\text{P}-$, $\text{C}=\text{O}$, and $\text{C}\equiv\text{N}$ may dissolve lithium salts and form polymer-salt complexes.³ Furthermore, to facilitate the dissociation of inorganic salts in polymer hosts, the lattice energy of the salt should be relatively low and the dielectric constant of the host polymer should be relatively high.³ Typically, ionic conductivity is proportional to the effective number of mobile ions, the elementary electric charge, and the ion mobility. The effective number of mobile ions (free ions) depends on the degree of dissociation of the salt in the polymer host. It was generally accepted that ion transport in dry solid polymer electrolytes occurs only in amorphous regions above their glass transition temperature (T_g), with the segmental motion of chains playing a significant role in the ionic conductivity.^{17,32} The detailed mechanism of ionic conduction can be expressed as follows: lithium ions are located at suitable coordination sites (*e.g.*, $-\text{O}-$ in polyethylene oxide, $-\text{CN}$ in polyacrylonitrile, $-\text{NR}$ in polyamide, *etc.*) in polar chains of the polymer. The polymer chains undergo constant local segmental motion, which results in the appearance of free volumes. Lithium ions migrate from one coordination site to new sites along the polymeric chains or hop

from one chain to another through these free volumes under the effect of an electric field.

However, this old concept has been overturned recently by Bruce *et al.*, who reported that the ionic conductivity in static, ordered environments of the crystalline phase can be greater than that in the equivalent amorphous material above T_g .³³ They proposed that in the crystalline phase of $\text{P(EO)}_6\text{-LiX}$ ($\text{X} = \text{PF}_6$, AsF_6 , SbF_6) pairs of PEO chains fold to form cylindrical tunnels, within which the Li^+ cations are located and coordinated by ether oxygens, while the anions are located outside these tunnels in the inter-chain space and do not coordinate the cations, as shown in Fig. 2.³⁴ The Li^+ ions can migrate from one site to another along these cylindrical tunnels without the aid of segmental motion.³⁰ They also proposed that the modification of these stoichiometric crystalline complexes by replacing a few mol% of XF_6^- ions by monovalent ions with very different shapes and sizes such as $\text{N(SO}_2\text{CF}_3)_2^-$ or anions with different charges such as SiF_6^{2-} can increase the ionic conductivity by 1.5–2 orders of magnitude.^{30,33,35,36} However, the opposite results were reported by Henderson *et al.* after examining the ionic conductivity of the same crystalline SPEs, $\text{P(EO)}_6\text{-LiX}$ ($\text{X} = \text{PF}_6$, AsF_6 , SbF_6).^{37,38} Results of comparable ionic conductivities in amorphous and crystalline diblock copolymers have also been reported by Sun *et al.*³¹ It seems that the ion transfer mechanism of polymer electrolytes is still unclear and needs more research endeavour. Macroscopic studies of ionic conductivity upon variations in temperature may provide valuable information on the ion transfer mechanism.

It is reported that the dependence on temperature of the ionic conductivity of a polymer electrolyte often follows two dominant conduction mechanisms: the Vogel–Tamman–Fulcher (VTF) type and the Arrhenius type.^{20,39,40} The empirical VTF type can be expressed by eqn (1):

$$\sigma = \sigma_0 T^{-\frac{1}{2}} \exp\left(-\frac{B}{T - T_0}\right) \quad (1)$$

where σ_0 is the pre-exponential factor, which is related to the number of charge carriers, B is the pseudo-activation energy for the conductivity, and T_0 is the equilibrium glass transition temperature ($T_0 \approx T_g - 50$ K). The VTF equation was devised early in the 20th century for describing the diffusion process in glassy and disordered materials.³⁹ For polymer electrolytes, plots of σ versus $1/T$ are typically nonlinear, which is indicative of a mechanism of conductivity that involves an ionic hopping motion coupled with relaxation/breathing and/or segmental motion of polymeric chains.²⁰ VTF behaviour is generally observed in SPEs above the T_g , GPEs, ionic liquids, *etc.*⁴⁰

The Arrhenius equation can be expressed by eqn (2):

$$\sigma = \sigma_0 \exp\left(\frac{-E_a}{kT}\right) \quad (2)$$

where E_a is the activation energy, which can be calculated from nonlinear least-squares fitting of the data from plots of $\log \sigma$ versus $1/T$. Materials that exhibit linear Arrhenius variations indicate that ion transport occurs *via* a simple hopping mechanism decoupled from polymer chain breathing.³⁹

3. Solid polymer electrolytes

3.1. Dry solid polymer electrolytes

Solid polymer electrolytes (SPE), which comprise a polymer matrix and a lithium salt, are now called dry solid polymer electrolytes (dry-SPE). Lithium salts are dissolved in a polymer matrix to provide ionic conductivity. Taking into consideration the ability to dissolve lithium salts and electrochemical stability, polyethers appear to be the best candidates for serving as polymer matrices. Polyethers dissolve salts by complexation of the metal ions *via* binding interactions between the ether oxygens and the metal ions. Among these, PEO is the most promising candidate as a solid solvent for lithium salts owing to its flexible ethylene oxide segments and ether oxygen atoms, which have a strong donor character and thus readily solvate Li^+ cations. More importantly, it is commercially available in a relatively pure state at a very reasonable cost.

Other polymer matrices with a low T_g have also been investigated, including polypropylene oxide (PPO),^{41–44} poly[bis(methoxy-ethoxy-ethoxy)phosphazene] (MEEP),^{45–48} polysiloxane (PSi),^{49–53} *etc.*, which remain completely amorphous at ambient temperature. PPO is commonly used as a polymer matrix for ionic conduction, similarly to PEO. The solvation of lithium ions in MEEP is attributed to both the ether oxygens and the nitrogen atoms in the polymer backbone.⁴⁸ MEEP can be crosslinked by gamma irradiation and a MEEP- LiCF_3SO_3 electrolyte exhibited a room-temperature conductivity 2.5 orders of magnitude higher than that of PEO-based electrolytes.⁴⁷ Polysiloxanes possess a highly flexible $[\text{Si-O}]_n$ backbone and each monomer unit has two sites for crosslinking or functional side chains, so they are promising components for comb polyelectrolytes.

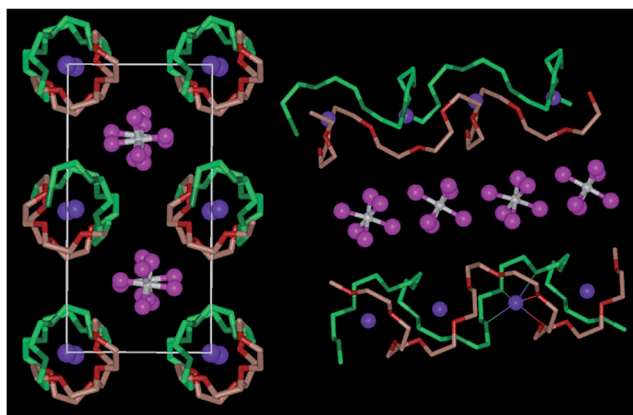


Fig. 2 Crystalline structure of $\text{P(EO)}_6\text{-LiAsF}_6$ polymer electrolyte. Left: View of the structure along the chain axis showing rows of lithium ions perpendicular to the page. Right: View of the structure showing the relative positions of the chains and their conformations (hydrogens are not shown). Blue spheres, lithium; white spheres, arsenic; pink spheres, fluorine; light green, carbon in chain 1; dark green, oxygen in chain 1; light red, carbon in chain 2; dark red, oxygen in chain 2. Thin lines indicate coordination around the Li^+ cations. Reprinted with permission from ref. 33. Copyright 2001 Nature Publishing Group.

In polymer electrolytes, the most widely used lithium salts are LiClO_4 , LiBF_4 , LiPF_6 , LiAsF_6 , LiCF_3SO_3 , $\text{LiN}(\text{CF}_3\text{SO}_2)_2$, *etc.* The mobility of the ions and their dissociation constants are in the following order:^{54,55}

Mobility of ions: $\text{LiBF}_4 > \text{LiClO}_4 > \text{LiPF}_6 > \text{LiAsF}_6 > \text{LiCF}_3\text{SO}_3 > \text{LiN}(\text{CF}_3\text{SO}_2)_2$.

Dissociation constants: $\text{LiN}(\text{CF}_3\text{SO}_2)_2 > \text{LiAsF}_6 > \text{LiPF}_6 > \text{LiClO}_4 > \text{LiBF}_4 > \text{LiCF}_3\text{SO}_3$.

The ionic conductivities of some typical dry-SPEs are listed in Table 1. It is noticeable that dry-SPEs usually display very low ionic conductivity at ambient temperature, which excludes them from practical applications.

A dry-SPE is a typical ion-coupled system, in which ion transport only occurs in amorphous regions above the T_g assisted by the segmental motion of chains. Ion transfer in an ion-coupled system is decided by two factors: one is the proportion of the amorphous phase in the polymer matrix, and the other is the T_g . The most commonly used approaches to increase the ionic conductivity in an ion-coupled system are the modification of the polymer matrix by copolymerization, crosslinking, blending, *etc.* These approaches help to prevent crystallization and reduce the T_g , thus increasing the mobility of the polymer chains. A detailed discussion of such structural modifications can be found in the literature.^{61–67}

Dry-SPEs can also act as separators to insulate the positive electrode from the negative electrode. For this purpose, they are required to possess suitable physical properties in terms of mechanical robustness, elasticity and thermal stability.⁶⁸ Although the ionic conductivity of PEO-based SPEs can be increased by using PEO derivatives with a low molecular weight, freestanding films that have a certain degree of dimensional stability cannot be prepared from such derivatives because they are in a waxy state at room temperature. The incorporation of crosslinkable moieties into the polymer matrix is a widely used strategy for preparing dimensionally stable solid polymer electrolytes from oligomeric waxy polymers.^{68–74}

3.1.1. Organic/inorganic hybrid copolymers. Recently, organic/inorganic hybrid copolymers have been studied

extensively. Polyhedral oligomeric silsesquioxanes (POSS) are some of the most intriguing examples of nanostructured organic/inorganic hybrid building blocks, which contain nano-sized silicon/oxygen cores surrounded by organic groups at each corner.⁷⁵ The general formula of POSS is $(\text{R-SiO}_{1.5})_n$, where R is a range of organic functional groups, n is commonly 6, 8 or 10 and the ratio of Si/O is 1.5. Unreactive organic substituents make the POSS nanostructure easily incorporated into common polymers *via* copolymerization, grafting or blending.⁷⁶ POSS can provide additional free volume to a polymer matrix owing to a steric effect, which results in high chain mobility of the polymer. Lee *et al.*^{77,78} synthesized a series of organic/inorganic hybrid branched and linear graft copolymers comprising polyethylene glycol methyl ether methacrylate (PEGMA), 3-(3,5,7,9,11,13,15-heptaisobutylpentacyclo[9.5.1.13.9.15.17.13]octasiloxane-1-yl)propyl methacrylate (MA-POSS), and ethylene glycol dimethacrylate (EGDMA). An electrolyte of a branched graft copolymer coordinated with a LiTFSI salt has a higher ionic conductivity than that of its linear graft counterpart, owing to its increased chain mobility. The maximum ionic conductivity was obtained for hybrid branched copolymers containing 21 mol% MA-POSS. Composite electrolytes containing an organic/inorganic hybrid star-shaped polymer, P(PEGMA-*r*-MA-POSS), PEG-functionalized POSS, and LiTFSI in various blended compositions were studied by Lee *et al.*^{79,80} The composite electrolytes exhibited an ionic conductivity of $4.5 \times 10^{-5} \text{ S cm}^{-1}$ at 30 °C, and were electrochemically stable up to 4.2 V vs. Li/Li⁺.

The ionic conductivities of some dry-SPEs based on modified polymer matrices are listed in Table 2. The ionic conductivity was increased by 1–2 orders of magnitude with these modified polymer matrices.

3.2. Polymer-in-salt system

The attempt to increase the ionic conductivity of dry-SPEs by increasing the salt concentration leads us into the area of polymer-in-salt electrolyte systems. A polymer-in-salt system is defined as a small amount of a high-molar-mass polymer mixed with lithium salt(s) (exceeding 50 wt% salts). In a polymer-in-salt system, it is required that the salt or salt mixture must have a low T_g so that a rubbery material rather than a glass is formed when the polymer is added. Polymer-in-salt systems are also known as rubbery electrolytes, which were discovered by Angell *et al.*^{89,90} Rubbery electrolytes possess the combined merits of polymer electrolytes (*i.e.*, excellent mechanical properties) and glasses with fast ion conduction (*i.e.*, only cationic motion). Rubbery electrolytes based on a polyacrylonitrile matrix (PAN) and its copolymers have been extensively studied, because the interaction between Li⁺ ions and nitrile groups is regarded as very suitable for the stabilization of highly conducting amorphous ionic clusters.^{91–94} An ionic conductivity of up to $10^{-4} \text{ S cm}^{-1}$ at ambient temperature has been achieved for polymer-in-salt electrolytes of PAN–LiAlCl₄.⁹² The Li⁺ transference number in polymer-in-salt electrolytes is also expected to be high.⁹⁵

Based on the type of salt, rubbery electrolytes can be divided into single-salt systems,^{96–98} binary salt systems,^{88,91} and ternary

Table 1 Ionic conductivities of some typical dry solid polymer electrolytes

Polymer electrolyte	Conductivity (S cm^{-1})	Temperature (°C)	Ref.
P(EO) ₂₀ /LiBF ₄	6.32×10^{-7}	27	56
P(EO) ₂₀ /LiClO ₄	2.78×10^{-7}	27	56
PEO/5 wt% LiPF ₆	1.20×10^{-6}	25	57
PEO/11.1 wt% LiAsF ₆	1.43×10^{-4}	25	58
P(EO) ₂₀ /LiCF ₃ SO ₃	1.88×10^{-9}	27	56
PEO/15 wt% LiCF ₃ SO ₃	1.00×10^{-6}	RT ^a	59
P(EO) ₂₄ /LiN(CF ₃ SO ₂) ₂	3.84×10^{-4}	50	60
P(PO)/10 mol% LiClO ₄	$>10^{-4}$	50	41
MEEP/10 wt% LiCF ₃ SO ₃	1.00×10^{-5}	25	45
MEEP/25 wt% LiCF ₃ SO ₃	2.70×10^{-5}	30	47
P(Si) ₃₂ /LiN(CF ₃ SO ₂) ₂	4.50×10^{-4}	25	49

^a Room temperature.

Table 2 Ionic conductivities of some dry-SPEs based on modified polymer matrices

Polymer electrolyte	Type of polymer matrix	Conductivity (S cm ⁻¹)	Ref.
(PEO- <i>b</i> -(PMMA- <i>ran</i> -PMAALi))/[LiBOB]	Block copolymer	1.26×10^{-5} (21 °C)	81
(PEO-PS)/[LiTFSI]	Block graft copolymer	$>10^{-4}$ (60 °C)	82
(PEO-PMMA)/[LiCF ₃ SO ₃]	Blend polymer	2.02×10^{-5} (30 °C)	61
(PEO-ENR50)/[LiCF ₃ SO ₃]	Blend polymer	1.40×10^{-4} (25 °C)	83
(PEO-P(VDF-TrFE))/[LiClO ₄]	Blend polymer	7.00×10^{-4} (RT) ^a	84
(PEO-PMAA)/[LiClO ₄]	Blend polymer	10^{-6} (RT)	85
(PEO-PPC)/[LiClO ₄]	Blend polymer	6.83×10^{-5} (RT)	86
(PEO-PSi)/[LiCF ₃ SO ₃]	Crosslinked polymer	7.40×10^{-5} (24 °C)	87
P(EO-PO)/[LiTFSI]	Random copolymer	10^{-3} (80 °C)	44
P(EO-MEEGE)/[LiTFSI]	Comb-type copolymer	10^{-4} (30 °C)	65
P(EO-TEC)/[LiClO ₄]	Comb-type copolymer	$>10^{-4}$ (30 °C)	62
P(EO-PO)/[LiTFSI]	Comb-type copolymer	$10^{-5.5}$ (20 °C)	66
(PEGMA-(MA-POSS)-EGDMA)/[LiTFSI]	Organic/inorganic hybrid branched copolymer	1.60×10^{-4} (60 °C)	77
(PEGMA-(MA-POSS)-EGDMA)/[LiTFSI]	Organic/inorganic linear grafted copolymer	5.60×10^{-5} (60 °C)	77
(SPP13-(PEG-POSS))/[LiTFSI]	Organic/inorganic blend polymer	4.50×10^{-5} (30 °C)	79
((PPG-PEG-PPG)-D2000)/[LiClO ₄]	Organic/inorganic blend polymer	6.23×10^{-5} (30 °C)	88

^a Room temperature.

salt systems⁹⁹. Wang *et al.*^{100,101} studied a single-salt system comprising a PAN matrix, a PC solvent and LiTFSI. Impedance studies show that the conductivity of the electrolyte is strongly dependent on the salt content. A transition from a “salt-in-polymer” to a “polymer-in-salt” electrolyte is observed with an increase in salt content (up to a mole ratio of LiTFSI/PAN of 4 : 1). Zygadlo-Monikowska *et al.*¹⁰² incorporated a salt mixture of LiBF₄-LiDFOB (1 : 1) into an acrylonitrile/butyl acrylate copolymer (poly(AN-*co*-BuA)) to fabricate a polymer-in-salt electrolyte. Values of ionic conductivity of 10^{-5} S cm⁻¹ at room temperature were obtained for this binary salt system, which are nearly three orders of magnitude higher than those for the system with a single LiBF₄ salt. Łasińska *et al.*⁹⁶ have studied ageing effects in polymer-in-salt electrolytes composed of poly(AN-*co*-BuA) copolymer, LiTFSI or a mixture of LiI-LiTFSI salts. An increase in T_g and a decrease in ionic conductivity were observed in the course of their prolonged storage under an argon atmosphere. Also, precipitation of the salt was observed in electrolytes containing more than 84 wt% salt. The binary salt system comprising poly(AN-*co*-BuA) and 65 wt% salt mixture (16 wt% LiI + 84 wt% LiTFSI) exhibited high ionic conductivity and was more stable than the system with only LiTFSI salt. Fan *et al.*⁹⁵ prepared and characterized a rubbery electrolyte based on a ternary salt system containing LiClO₄-LiNO₃-LiOAc and PEO. LiOAc is a key component in this salt mixture, which is responsible for the increase in the T_g . An ambient-temperature conductivity of as high as 10^{-3} S cm⁻¹ can be obtained in a material with a large rubbery temperature range (20–130 °C).

Attempts have been made to explain the mechanism of ion transport in polymer-in-salt systems. It has been well accepted that an efficient ion transport mechanism should be associated with a high degree of ion aggregation in a polymer-in-salt electrolyte. There is also some agreement as to how ion clusters/aggregates are transported in these electrolytes.^{98,103–105} Mishra *et al.*¹⁰³ attributed the increase in conductivity with an increase in salt concentration to the formation of a percolation path in the polymer matrix. Forsyth *et al.*^{98,105} proposed a model for the

PAN/LiCF₃SO₃ electrolyte, which showed that the connectivity percolation of the ionic clusters was decoupled from the segmental motion of the bulk system. Bushkova *et al.*¹⁰⁴ believed that when a critical cluster concentration had been achieved all separate single clusters came into contact with each other, thus forming an infinite cluster and promoting a fast cationic transport process in the entire electrolyte.

Although polymer-in-salt systems have a higher ionic conductivity than dry-SPEs, they have the disadvantage of poor mechanical properties with an increase in the salt concentration. To solve this problem, networked polymer electrolytes have been developed. Walker *et al.*¹⁰⁶ synthesized two types of tunable network based on PEG (polyethylene glycol) loaded with LiTFSI and PEG-PDMS (polydimethylsiloxane) *via* crosslinking chemistry. Even at high salt loadings, both networks maintained rubber-like characteristics, which were stable over a range of temperatures (30–90 °C). The PEG network with the highest salt loading (EO/Li = 1 : 1) exhibited the highest ionic conductivity of 6.7×10^{-4} S cm⁻¹ at 30 °C. Lee *et al.*¹⁰⁷ prepared networked polymer electrolytes consisting of poly(hydroxyethyl methacrylate) (P(HEMA)), LiCF₃SO₃, and HCl. As a networked structure of P(HEMA) was obtained, the high ionic conductivity of the polymer-in-salt electrolyte was maintained and the mechanical properties were improved.

3.3. Single-lithium-ion conducting polymer electrolyte

Solid polymer electrolytes composed of a polymer matrix and a lithium salt are so-called bi-ionic conductors. In bi-ionic conductors, cations bind to polar groups of the polymer matrix; as a result, anions move faster and contribute more to the ionic conductivity than cations. The migration of anions toward the anode causes serious concentration polarization, which results in a substantial decay in conductivity or a time-dependent increase in cell impedance.¹⁰⁸ In general, the Li⁺ transference numbers (t_{Li^+}) for bi-ionic conducting systems fall far below a value of 0.5. In order to minimize polarization, two

approaches have been adopted to reduce the mobility of anions. The first is to anchor anions to the polymer backbone, which is a common method for obtaining a single-ion conducting polymer electrolyte. The other is the addition of an anion receptor that preferentially interacts with anions.

3.3.1. Polymeric lithium salts. In the past three decades, many efforts have been devoted to synthesizing polymeric lithium salts for achieving single-ion conduction. The properties of some typical single-ion conductors based on polymeric lithium salts with various anionic structures are listed in Table 3. These polymeric lithium salts can be divided into three types: (1) homopolymers, (2) copolymers, and (3) organic-inorganic hybrid polymers.

3.3.1.1 Homopolymer type of polymeric lithium salt. Lithium poly(2-acrylamido-2-methylpropanesulfonic acid) (LiPAMPS, Fig. 3(a)) homopolymer has been synthesized by Cui *et al.*¹¹¹ based on 2-acrylamido-2-methylpropanesulfonic acid (AMPS) using electrospinning technology. AMPS has been used to fabricate single-ion conductors owing to its structural characteristics, which include both a sulfonic acid group and a double bond. The double bond gives AMPS the ability to polymerize radically with itself or with other vinyl monomers. As a strong acid group, the sulfonic acid group is chemically attached to the polymer backbone after polymerization, so the polymer has a high dissociation ability to yield mobile cations. After introducing ethylene carbonate and dimethyl carbonate as plasticizers, the resulting LiPAMPS single-ion conducting polymer electrolyte exhibited an ionic conductivity of $2.12 \times 10^{-5} \text{ S cm}^{-1}$ at 20 °C, high thermal stability (304 °C), good dimensional stability and electrochemical stability (4.4 V vs. Li^+/Li). Fedkiw *et al.*¹¹⁷ prepared a nanocomposite single-ion conductor by dispersing LiPAMPS-graft-fumed silica particles into solvent(s). The highest room-temperature conductivity of $3.0 \times 10^{-6} \text{ S cm}^{-1}$ was obtained by dispersing 7.5 wt% filler in PC. Lithium poly(4-styrenesulfonyl(trifluoromethylsulfonyl)imide) (LiPSTFSI, Fig. 3(b)) polyelectrolytes containing a $-\text{SO}_2-\text{N}^--\text{SO}_2-\text{CF}_3$ anionic group associated with a lithium cation and attached to a polystyrene chain have been prepared by Meziane *et al.*²⁴ A single-ion conducting polymer electrolyte comprising LiPSTFSI and PEO polymer exhibited a Li^+ transference number that was close to unity and a high ionic conductivity (about $10^{-5} \text{ S cm}^{-1}$).

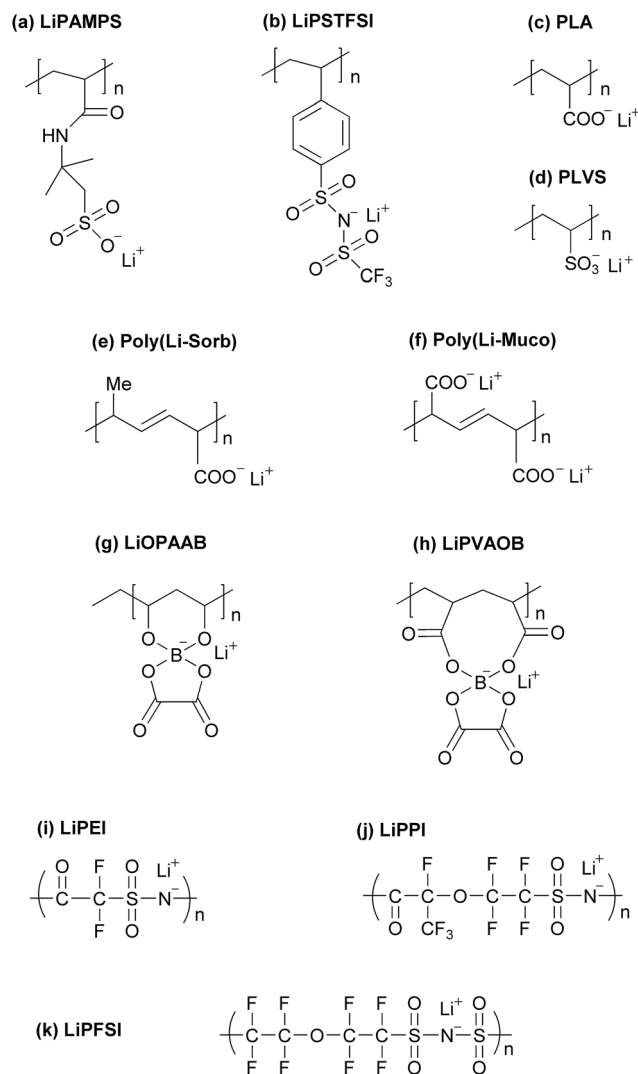


Fig. 3 Structures of homopolymer type of polymeric lithium salt.

Table 3 Properties of some typical single-ion conductors based on polymeric lithium salts with various anionic structures

Anionic structure	Conductivity (S cm^{-1})	Temperature ($^{\circ}\text{C}$)	Ref.
$-\text{COO}^-$	2.00×10^{-6}	20	109
$-(\text{CF}_2)_3\text{COO}^-$	10^{-8}	25	110
$-\text{SO}_3^-$	2.00×10^{-7}	20	109
$-\text{SO}_3^-$	2.12×10^{-5}	20	111
$-\text{CF}_3\text{SO}_3^-$	10^{-8}	Room temperature	112
$-\text{CF}(\text{CF}_3)\text{SO}_3^-$	10^{-7}	25	113
$-\text{C}_6\text{H}_5\text{SO}_3^-$	3.00×10^{-8}	25	114
$-\text{C}_6\text{H}_5\text{SO}_3^-$	1.50×10^{-7}	30	115
$-\text{OB}^-\text{O}(\text{C}_2\text{O}_4)$	6.11×10^{-6}	25	26
$-\text{OB}^-\text{O}(\text{C}_2\text{O}_4)$	2.30×10^{-6}	25	25
$-\text{SO}_2\text{N}^-\text{SO}_2\text{CF}_3$	7.60×10^{-6}	25	116

Itoh *et al.*¹¹⁸ prepared two types of polyanionic lithium salt, poly(lithium acrylate) (PLA, Fig. 3(c)) and poly(lithium vinyl-sulfonate) (PLVS, Fig. 3(d)) with a carboxylic group and a sulfonic group, respectively. They found that the structure of functional groups in polyanionic lithium salts has a significant effect on the electrochemical and thermal properties of polymer electrolytes. The addition of a Lewis acid, boron trifluoride diethyl ether ($\text{BF}_3 \cdot \text{OEt}_2$), increases both the ionic conductivity and the Li^+ transference number of PEO/PLA and PEO/PLVS blended polymer electrolytes. Itoh *et al.*¹¹⁹ prepared poly-(lithium carboxylate)-type salts, poly(lithium sorbate) (poly(Li-Sorb), Fig. 3(e)) and poly(lithium muconate) (poly(Li-Muco), Fig. 3(f)), as crystalline polyanionic lithium salts and investigated the properties of polymer electrolytes composed of these polymeric salts and polyethers (PEO and P(EO/PO)). These single-ion conducting polymer electrolytes exhibited a relatively high Li^+ transference number (0.45–0.88), great mechanical strength, and good electrochemical and thermal stabilities. Zhu *et al.*^{25,26} synthesized a new type of single-ion conductor, lithium oxalate polyacrylic acid borate (LiOPAAB, Fig. 3(g)) and lithium

polyvinyl alcohol oxalate borate (LiPVAOB, Fig. 3(h)), based on polyacrylic acid (PAA) or polyvinyl alcohol (PVA), boric acid (H_3BO_3), lithium hydroxide (LiOH) and oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$). After absorbing the solvent PC, the single-ion conductor exhibited an ambient-temperature ionic conductivity of up to $10^{-6} \text{ S cm}^{-1}$ and an electrochemical window of up to 7.0 V (vs. Li^+/Li), which is very attractive for high-voltage lithium-ion batteries with high energy density. Watanabe *et al.*¹²⁰ synthesized polymeric lithium salts of a perfluorinated polyimide anion, poly(2-oxo-1-difluoroethylene sulfonylimide lithium) (LiPEI), and poly(5-oxo-3-oxa-4-trifluoromethyl-1,1,2,2,4-pentafluoropentylene sulfonylimide lithium) (LiPPI). Both polyimide salts have a structure similar to those of dissociable imide salts such as LiTFSI, with a strong electron-withdrawing group adjacent to the anionic sites (as seen in Fig. 3(i) and (j)). Electron-withdrawing groups in polyimide anions promote ionic dissociation, which increases the number of charge carriers. Both polyimide salts were compatible with a polyether matrix P(EO-PO) and exhibited a Li^+ transference number that was close to unity. The ionic conductivity of polymer electrolytes containing LiPPI reached $10^{-5} \text{ S cm}^{-1}$ at 30°C , which is two orders of magnitude higher than that of electrolytes containing LiPEI. Such a difference in ionic conductivity between LiPPI and LiPEI was caused by a variation in the dissociation ability of these polymeric lithium salts. Another lithium salt of a polyimide anion, lithium poly(perfluoroalkylsulfonyl)imide (LiPFSI, Fig. 3(k)), has been reported by Shi *et al.*¹²¹ A PEO/LiPFSI blended single-ion polymer electrolyte exhibited excellent electrochemical properties in terms of ionic conductivity, Li^+ transport number and electrochemical stability. A $\text{LiFePO}_4/\text{Li}$ cell based on a PEO/LiPFSI polymer electrolyte displayed high capacity and excellent long-term cycling stability.

3.3.1.2 Copolymer type of polymeric lithium salt. Single-ion conducting polymer electrolytes based on the copolymer type of polymeric salts have been reported.^{109,112,116,122} Bouchet *et al.*¹²² synthesized a new single-ion polymer electrolyte based on self-assembled polyanionic BAB triblock copolymers (P(STFSILi)-*b*-PEO-*b*-P(STFSILi), Fig. 4(a)) to finely tune the mechanical properties, ionic conductivity and Li^+ transference number at the same time. This multifunctional single-ion polymer electrolyte exhibited an ionic conductivity of $1.3 \times 10^{-5} \text{ S cm}^{-1}$ at 60°C , a Li^+ transference number that was close to unity, excellent mechanical properties and an electrochemical stability window of up to 5 V versus Li^+/Li . Zhou *et al.*¹¹⁶

synthesized a single-ion conducting polymer electrolyte, Li [PSTFSI-*co*-MPEGA] (Fig. 4(b)), by copolymerization of the two monomers, lithium (4-styrenesulfonyl) (trifluoromethanesulfonyl)imide (LiTFSI) and methoxypolyethylene glycol acrylate (MPEGA). The ionic conductivity of the Li[PSTFSI-*co*-MPEGA] copolymer electrolyte was higher by 1–3 orders of magnitude than those of the blended electrolytes. By optimizing the ratio of EO/ Li^+ for this copolymer electrolyte, a maximum ionic conductivity of $7.6 \times 10^{-6} \text{ S cm}^{-1}$ at 25°C was obtained.

3.3.1.3 Organic-inorganic hybrid polymeric salts. Organic-inorganic hybrid polymers are kinds of composite material that possess complementary and optimized performance between organic and inorganic materials. Currently, organic-inorganic hybrid materials include polysiloxanes, organic aluminate polymers, organoboron polymers, borosiloxane polymers, *etc.*

Polysiloxane-based hybrid materials are promising candidates as polymer electrolytes owing to their highly flexible backbone, which imparts a low T_g . Siska *et al.*¹²³ studied poly-electrolytes with trifluoromethylsulfonamide anions and short oligoether side chains attached to a polysiloxane backbone, as shown in Fig. 5(a). A lithium-ion conducting polymer electrolyte exhibited a room-temperature ionic conductivity of $1.2 \times 10^{-6} \text{ S cm}^{-1}$ and a T_g of -67°C . Subsequently, in order to increase the dissociation of ion pairs, they used perfluoroethersulfonate side chains instead of trifluoromethylsulfonamides in the same electrolyte system (Fig. 5(b)).^{50,124} Colby *et al.*¹²⁵ synthesized single-ion conductors with cyclic carbonates and lithium tris-(perfluorophenyl)(2,3,5,6-tetrafluoro-4-(2-(2-(vinyl)oxy)ethoxy)ethoxy)phenyl)borate side chains, as shown in Fig. 5(c). Although the introduction of borate anions can lower the ion association energy, the ambient-temperature ionic conductivity was only $10^{-7} \text{ S cm}^{-1}$.

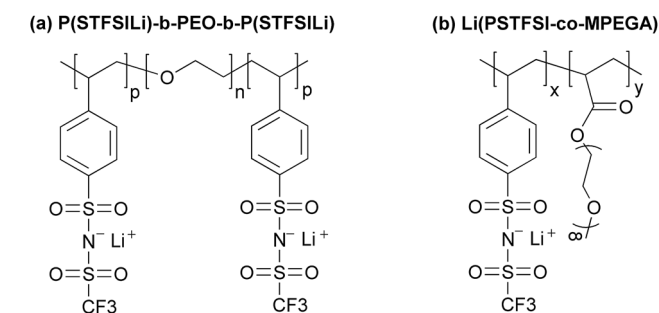


Fig. 4 Structures of copolymer type of polymeric lithium salt.^{116,122}

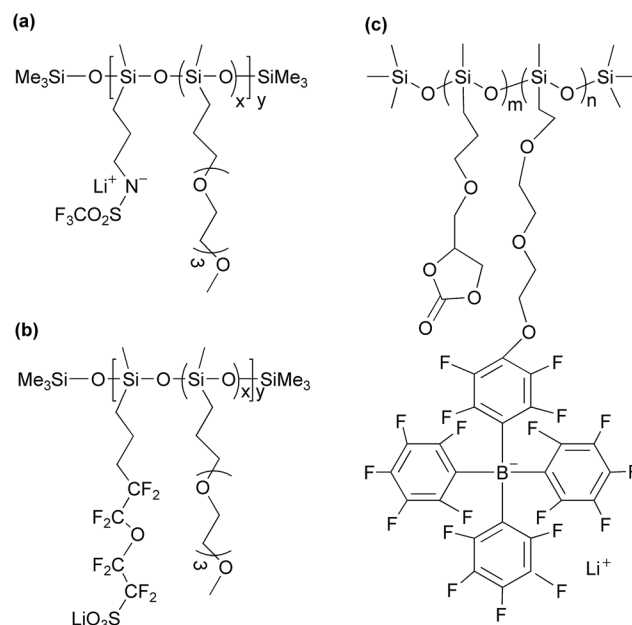
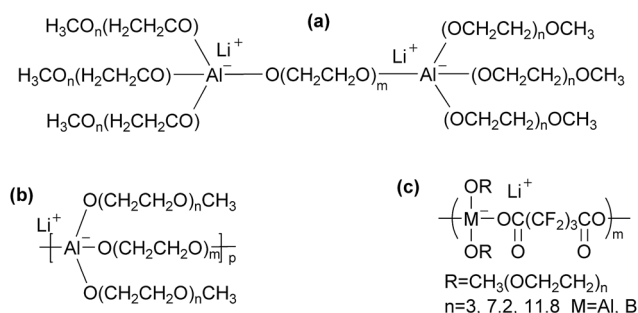
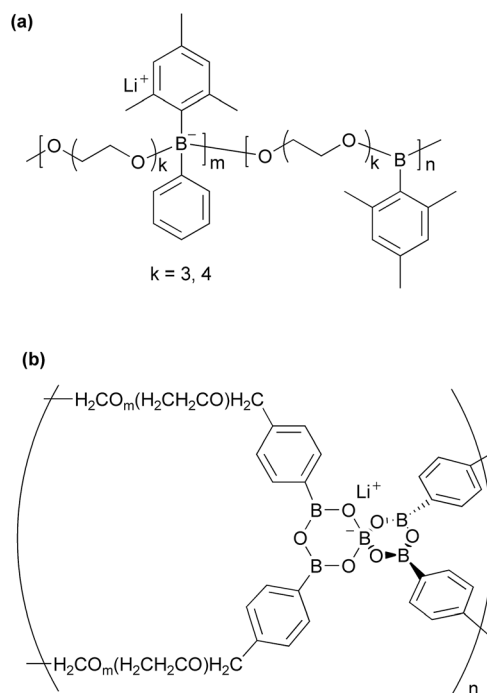


Fig. 5 Structures of polysiloxane type of organic-inorganic hybrid polymers.^{50,123,124}

Matsumi *et al.*^{129,130} synthesized organoboron hybrid polymers composed of alternating oligoethylene oxide and organoboron units (boric esters or alkylboranes). The organoboron polymers were subjected to reaction of the polymers with organolithium reagents with the aim of immobilizing the anions on the polymer chains as borate anions. The structure of the obtained single-ion conducting polymer electrolyte is shown in Fig. 7(a). After reaction of the polymers with phenyllithium, ionic conductivities of 9.45×10^{-7} to 8.22×10^{-7} S cm⁻¹ and a Li⁺ transference number of 0.78–0.82 were observed. When using pentafluorophenyllithium or naphthyllithium as the organolithium reagent, the conductivity increased by one order of magnitude owing to the increased degree of dissociation of the lithium borate unit in the presence of an electron-withdrawing substituent. Nishihara *et al.*¹³¹ synthesized a new class of organoborate polymers, poly(lithium tetraarylpentaborates) (Fig. 7(b)). By incorporating hexaethylene glycol ($m = 6$), the ionic conductivity of organoborate polymers can reach 5.0×10^{-5} S cm⁻¹ at 60 °C, which is ascribed to the improved diffusion of lithium borate.

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3.3.2. Anion receptors. The immobilization of anions on a polymer is the most common approach for creating a single-ion conductor. However, it is noticeable that the ionic conductivity of single-ion conducting polymer electrolytes is generally lower than that of dual-ion conducting systems because of the decreased number of mobile carrier ions. In recent years, an alternative method has been proposed, in which an anion receptor is introduced into electrolytes to enhance their ionic conductivity and/or cation transference number. In these systems, although anions are trapped by an anion receptor, the interaction between the anions and the anion receptor promotes the further dissociation of lithium salts, which might lead to an increase in both ionic conductivity and Li^+ transference number at the same time. Currently, anion receptors can be divided into two groups: Lewis acid type and calixarenes.

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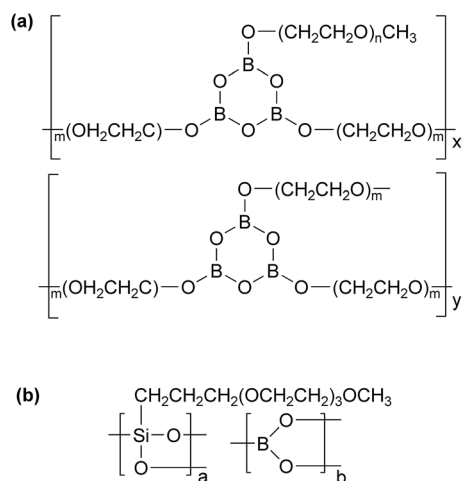


Fig. 8 Structures of anion receptors based on Lewis acids.^{133,135}

The other type of anion receptor comprises calixarenes. One of the most significant properties of calixarenes is the ease of monitoring their structure and functionality during synthesis, which leads to high selectivity for complexation of the desired anion. Scrosati *et al.*^{136,137} studied the addition of calix[4]arene (C4P) (Fig. 9(a)) as an anion acceptor in PEO–LiX complexes. A high value of the transference number of 0.77 was achieved for a sample with a low calixarene content (25 mol%), and this number reached unity for a sample with 100 mol% calixarene. They also studied composite electrolytes containing a calix[6]pyrrole (C6P) (Fig. 9(b)) derivative as an anion complexing agent for I^- , BF_4^- and CF_3SO_3^- anions.^{138,139} Siekierski *et al.*¹⁴⁰ studied the effect of a calyx[6]pyrrole anion receptor on the physico-chemical and ion transport properties of solid polymer electrolytes based on PEO doped with LiCF_3SO_3 and LiTFSI salts. The effect of an anion receptor on the properties of the electrolyte depends on the coordinating properties of the anion. In systems containing LiCF_3SO_3 , significant changes in properties are observed upon addition of a receptor. In contrast, in systems containing LiTFSI no interaction with the receptor and no significant change in conductivity were observed. Stephan *et al.*¹⁴¹ investigated the influence of calix[2]-*p*-benzo[4]pyrrole (CBP) (Fig. 9(c)) on the electrochemical properties of PEO-based electrolytes. The Li^+ transference number was found to increase from 0.23 to 0.78 on incorporating CBP into the polymer electrolyte. However, the incorporation of CBP did not increase the ionic conductivity below 60 °C although it improved the interfacial properties.

3.4. Search for new lithium salts

The properties of lithium salts affect the performance of rechargeable lithium polymer batteries. Traditional inorganic lithium salts have certain drawbacks: for instance, LiClO_4 is potentially explosive in contact with organics, LiAsF_6 contains arsenic, which may form poisonous compounds, and LiBF_4 and LiPF_6 could easily be hydrolyzed to toxic and corrosive HF in a moist atmosphere.¹⁴² Organic lithium salts containing sulfonate anions, such as lithium triflate (LiCF_3SO_3 , LiTf), lithium

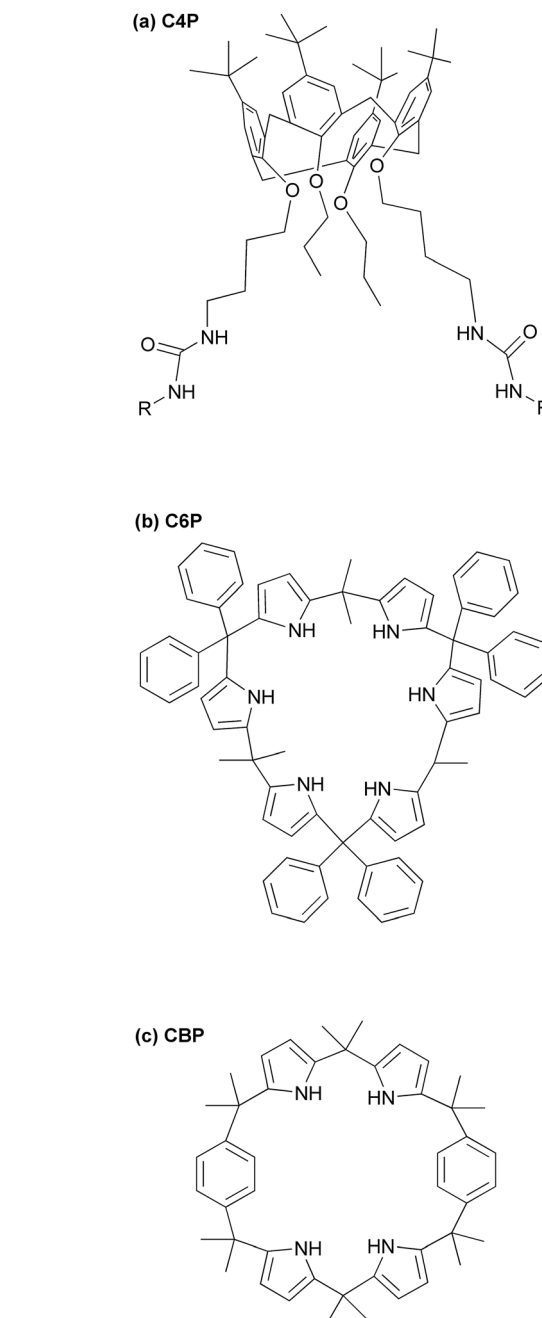


Fig. 9 Structures of anion receptors based on calixarene derivatives.^{136–139}

perfluoroethylsulfonate ($\text{LiC}_2\text{F}_5\text{SO}_3$), and lithium perfluorobutylsulfonate ($\text{LiC}_4\text{F}_9\text{SO}_3$), *etc.*, have become the salts of choice because they are highly resistant to oxidation, thermally stable, nontoxic, and insensitive to ambient moisture compared with inorganic lithium salts.^{55,143,144} The major drawback of these lithium sulfonate salts is their poor ionic conductivity. In order to increase the ion pair dissociation effect, lithium imide salts with a larger anionic radius, such as lithium bis(trifluoromethane)sulfonimide ($\text{LiN}(\text{CF}_3\text{SO}_2)_2$, LiTFSI) and lithium bis(perfluoroethylsulfonyl)imide ($\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$, LiBETI), *etc.*, have been developed, which could offer higher

conductivity of Li^+ .¹⁴⁵ However, they are corrosive toward aluminum current collectors, which makes them unsuitable for lithium polymer electrolytes. Therefore, the search for more reliable lithium salts is still a research focus in recent years. New types of lithium salts such as borate salts, phosphate salts, functionalized sulfonate and functionalized imide salts, and dilithium salts, *etc.*, have been widely studied.

3.4.1. Borate salts. Since 1995, a series of nontoxic, thermally, chemically, and electrochemically stable, and especially inexpensive borate salts based on organoborate anions with aromatic or aliphatic diols or carboxylic acids have been studied by Gores *et al.*^{146–150} In 2002, Xu *et al.*¹⁵¹ introduced lithium bis(oxalate) borate (LiBOB) as an electrolyte solute for lithium-ion batteries. Since then, LiBOB has been in the spotlight because of its thermal stability, excellent ionic conductivity, and ability to form protective solid electrolyte interphase (SEI) layers on graphite electrodes, *etc.*^{142,152,153} The structure of LiBOB is shown in Fig. 10(a). The bulky anion BOB^- favors the delocalization of charge and a reduction in anion–cation reactions, which leads to a high degree of dissociation of the salt. Wu *et al.*¹⁵³ reported that the ionic conductivity of PEO/LiBOB is one or two order(s) of magnitude higher than that of PEO/ LiClO_4 . However, the main drawback is that the SEI formed with LiBOB is more resistive, which consequently reduces the power and rate capability of the cell, especially in low-temperature conditions. Zhang *et al.*¹⁵⁴ designed and synthesized a new borate salt, lithium oxalyldifluoroborate (LiDFOB), as shown in Fig. 10(b). This salt was found to have the combined advantages of LiBOB and the low-temperature performance of LiBF_4 owing to its chemical structure, which comprises half the molecular moieties of LiBOB and LiBF_4 . The values of ionic conductivity in an electrolyte solution containing PC/EC/EMC (1 : 1 : 3) follow the order $\text{LiBF}_4 > \text{LiDFOB} > \text{LiBOB}$. Abraham *et al.*¹⁵² made a comparison of the impedances of full cells containing $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ /graphite electrodes and electrolytes with LiPF_6 , LiBF_4 , LiBOB and LiDFOB salts. The impedance data showed the following trend: $\text{LiBOB} > \text{LiBF}_4 > \text{LiDFOB} > \text{LiPF}_6$. In 2007, LiDFOB salt was first incorporated into a P(VDF-HFP)-based gel polymer electrolyte with a mixture of EC/DEC as a plasticizer and Sb_2O_3 as a filler.^{155,156} An ionic conductivity of $9.1 \times 10^{-5} \text{ S cm}^{-1}$ was obtained for a Sb_2O_3 -free

membrane. Compared with LiBOB, LiDFOB has higher solubility in linear carbonates and is less sensitive to impurities. Another borate salt, tetrakis(pentafluorobenzenethiolato)borate (LiTPSB, Fig. 10(c)), with a weakly coordinating anion has been designed by Aoki *et al.*¹⁵⁷ Because LiTPSB salt is insoluble in PVDF, polymer electrolytes were prepared by hot pressing a mixture of LiTPSB and PVDF or P(VDF-HFP). The ionic conductivity was largely dependent on the salt content for PVDF/LiTPSB polymer electrolytes. The ionic conductivity increased as follows: $\text{P(VDF-HFP)}/\text{LiTPSB (60/40)} > \text{PVDF}/\text{LiTPSB (50/50)} > \text{PVDF}/\text{LiTFSI (75/25)}$.

3.4.2. Phosphate salts. Lithium tris(perfluoroethyl)trifluorophosphate ($\text{Li}[\text{PF}_3(\text{CF}_3\text{CF}_2)_3]$, LiFAP) has been proposed as a potential alternative to LiPF_6 . LiFAP salt is obtained *via* partial replacement of the fluorine atoms in LiPF_6 by perfluoroalkyl groups. Steric shielding of the phosphorus atom by the hydrophobic perfluoroalkyl groups leads to superior stability towards hydrolysis. The delocalization of the negative charge owing to the strongly electron-withdrawing nature of the perfluorinated alkyl groups leads to weak coordination to the Li^+ ions and the salt thus acts as a solid plasticizer to increase the ionic conductivity.¹⁵⁸ LiFAP salt was synthesized and introduced into electrolytes for lithium-ion batteries by Schmidt *et al.*¹⁵⁹ In 2008, LiFAP salt was first incorporated as an electrolyte salt in a polymer skeleton by Aravindan *et al.*¹⁶⁰ P(VDF-HFP)-based polymer electrolytes having a mixed solvent of EC/DEC and LiFAP salt exhibited an ionic conductivity of $6.69 \times 10^{-4} \text{ S cm}^{-1}$ at ambient temperatures.^{160,161} Aravindan *et al.*¹⁴² made a comparison between the performance of P(VDF-HFP) nanocomposite membranes impregnated with LiBOB, LiDFOB and LiFAP. Galvanostatic cycling profiles clearly indicated the improved performance of chelateborate-based anions, *i.e.*, BOB and DFOB, when compared with fluoroalkyl groups (FAP).

3.4.3. Functionalized sulfonate salts. Another research trend in new types of lithium salt relates to functionalized sulfonates. Lithium perfluorosulfonate salts have been tailored to provide either a solvating and/or plasticizing effect or polar functions. Adding these extra functionalities to the organic anion may result in a good combination of ionic conductivity and cation transference number. Paillard *et al.*^{162,163} studied a broad family of aryl-substituted lithium perfluorosulfonate salts, and polymer electrolytes based on these new salts exhibited high cation transference numbers and fairly good ionic conductivities, as shown in Table 4. This new family of lithium salts exhibits high chemical and thermal stability. S2 and S3 exhibit good stability to reduction and a wide electrochemical stability window, whereas S6 and S7 have outstanding stability to oxidation.

Sanchez *et al.*¹⁶⁴ synthesized three kinds of functionalized sulfonate molecular salts, as shown in Fig. 11. Both symmetrical salts ($R_1 = R_2$) when dissolved in PEO networks ($\text{O/Li} = 30$) exhibited a conductivity of $3 \times 10^{-5} \text{ S cm}^{-1}$ at 21°C . However, the conductivity of the asymmetrical salt ($R_1 \neq R_2$) is one order of magnitude lower than those of the symmetrical salts. High Li^+ transference numbers of 0.45 ± 0.05 and 0.58 ± 0.05 were found for CNrfSO_3Li ($R_1 = R_2 = \text{CNCH}_2\text{CH}_2$) and $\text{CH}_3\text{ORfSO}_3\text{Li}$ ($R_1 = R_2 = \text{CH}_3\text{OCH}_2\text{CH}_2$) at 80°C , respectively.

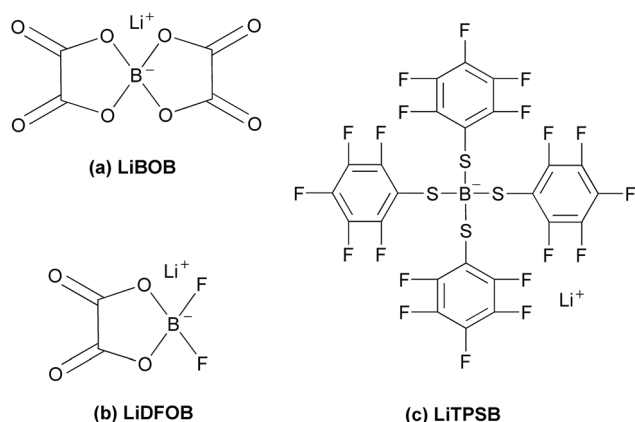
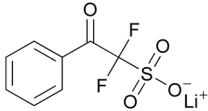
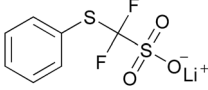
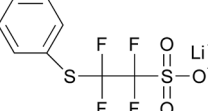
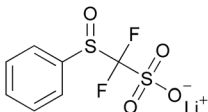
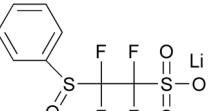
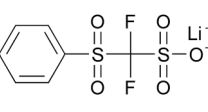
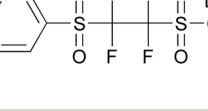
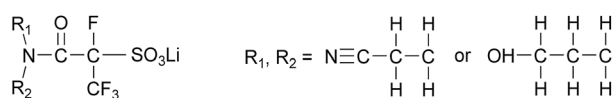


Fig. 10 Structures of borate salts: (a) LiBOB, (b) LiDFOB and (c) LiTPSB.

Table 4 Cation transference numbers and cationic conductivities of PEO-based solid polymer electrolytes comprising aryl-containing lithium perfluorosulfonates¹⁶⁵

Symbol	Formula	Concentration	T ⁺	σ (70 °C) (S cm ⁻¹)
S1		O/Li = 30	0.49	8.7×10^{-5}
		O/Li = 20	0.41	9.4×10^{-5}
		O/Li = 12	0.44	5.7×10^{-5}
S2		O/Li = 30	0.54	1.2×10^{-4}
		O/Li = 20	0.52	2.0×10^{-4}
		O/Li = 12	0.55	4.0×10^{-5}
S3		O/Li = 30	0.48	1.8×10^{-4}
		O/Li = 20	0.52	2.0×10^{-4}
		O/Li = 12	0.47	8.5×10^{-5}
S4		O/Li = 30	0.39	1.1×10^{-4}
		O/Li = 20	0.39	9.8×10^{-5}
		O/Li = 12	0.43	6.0×10^{-5}
S5		O/Li = 30	0.35	—
		O/Li = 20	0.36	1.1×10^{-4}
		O/Li = 12	—	8.1×10^{-5}
S6		O/Li = 30	0.47	8.8×10^{-5}
		O/Li = 20	0.37	1.7×10^{-4}
		O/Li = 12	0.42	5.0×10^{-5}
S7		O/Li = 30	0.35	8.6×10^{-5}
		O/Li = 20	—	1.2×10^{-4}
		O/Li = 12	0.41	1.1×10^{-5}

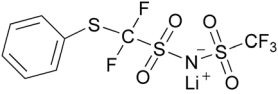
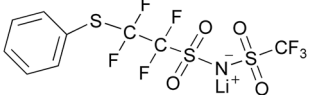
**Fig. 11** Structures of functionalized sulfonate molecular salts.¹⁶⁴

3.4.4. Functionalized imide salts. Important improvements have been achieved by designing new imide salts that exhibit a higher percentage of salt dissociation and electrochemical stability. The TFSI⁻ anion has a delocalized negative charge and very low basicity, which leads to good salt dissociation, less ion pairing, and high ionic conductivity in PEO-based electrolytes.^{60,165} As an alternative to LiTFSI, Reibel *et al.*¹⁶⁶ prepared lithium bis(4-nitrophenyl)sulfonylimide (LiNPSI), in which the charge delocalization of the anion is due both to the mesomeric effect of the sulfonyl groups and the negative inductive effect of the aromatic groups. A polymer electrolyte based on LiNPSI displayed more stability towards a lithium electrode than an electrolyte based on LiTFSI and its maximum ionic conductivity was 2.1×10^{-4} S cm⁻¹ at 66 °C. Shembel *et al.*¹⁶⁷ synthesized new lithium salts of *N,N*-disubstituted imides of an alkane iminosulfinic acid $C_xH_yS(NSO_2Ar)_2Li$ (Ar is an aromatic group and C_xH_y can be methane, ethane, butane,

propane, pentane, hexane, heptane, octane, nonane, or other alkanes), and these organic lithium salts possessed good discharge characteristics and stability during cycling. Sanchez *et al.*¹⁶⁸ synthesized a wide range of aryl-substituted perfluorosulfonimide salts *via* a general multi-step synthesis method, and made a preliminary electrochemical investigation of two lithium salts hosted by a PEO homopolymer. The molecular formulas, cation transference numbers and cationic conductivities of polymer electrolytes based on two lithium salts are listed in Table 5. Both salts display high cation transference numbers, which are more than twice that of LiTFSI, and high cationic conductivities.

3.4.5. Dilithium salts. Dilithium salts represent another research trend for lithium polymer electrolytes. Because of the presence of two lithium ions per molecule, these salts require lower concentrations than commonly used salts to achieve comparable ionic conductivities at ambient temperatures. Chakrabarti *et al.*¹⁶⁹ prepared a new class of dilithium (DL) salts (DL-1, DL-2 and DL-3) with structural features similar to those of LiTFSI, as shown in Fig. 12. The interesting feature of this class of salts is that the negative charge on the nitrogen atom is delocalized by two sulfone groups, similarly to LiTFSI, which makes the lithium ion highly mobile. Hence, these salts are expected to display low interionic attractions between the cation

Table 5 Cation transference numbers and cationic conductivities of polymer electrolytes comprising aryl-substituted perfluorosulfonimides and a PEO matrix¹⁶⁸

Symbol	Formula	Concentration	T ⁺	σ (70 °C) (S cm ⁻¹)
Salt 1		O/Li = 30	0.21	3.6×10^{-4}
		O/Li = 20	0.26	5.8×10^{-4}
		O/Li = 10	—	—
Salt 2		O/Li = 34.8	0.25	2.1×10^{-4}
		O/Li = 23.2	0.20	2.9×10^{-4}
		O/Li = 13.4	0.19	2.2×10^{-4}

and anion (*i.e.*, low lattice energy), which leads to high ionic conductivity. A PEO-based film with DL-1 salt exhibited the best ionic conductivity of 2.19×10^{-6} S cm⁻¹ at 30 °C, which is not high enough for practical applications. Creager *et al.*^{170–172} studied a series of dilithium salts based on new bis[(perfluoroalkyl)sulfonyl]diimide dianions (CF₃SO₂N(Li)SO₂(CF₂)_xSO₂N(Li)SO₂CF₃, *x* = 2, 4, 6, 8). They found that SPEs based on these dilithium salts and a PEO host exhibited lower ionic conductivities compared with those based on LiTFSI salt, because of the diminished contribution of the anions in the dimeric salts to the overall conductivity of the SPE. Moreover, the length of the perfluoroalkylene linkage has a significant influence on the ionic conductivity, which is related to the content of fluorine-containing anions and the anion size.¹⁷⁰ Dilithium salts containing carboxyl groups have also been investigated. Heishi *et al.*¹⁷³ reported that the use of the lithium oxalate salt with discrete carboxyl groups (LiOOC-COO-Li) as a polymer electrolyte is a promising method for increasing the lithium transference number.

3.5. Addition of inorganic fillers

3.5.1. Ceramic fillers. The addition of ceramic fillers to SPEs has proved to be one of the most effective ways to increase their ionic conductivity without affecting their mechanical

strength and/or interfacial stability.¹⁷⁴ In general, ceramic fillers for applications in SPEs can be classified into two categories. One is inert fillers, which means that nanoparticle fillers can influence the ion transport mechanisms in polymers in a variety of indirect ways such as acting as “plasticizers”, inhibiting polymer crystallization, increasing the free volume and speeding up segmental dynamics.^{175,176} Inert ceramic fillers include micro/nanoparticles, Al₂O₃,^{177–182} SiO₂,¹⁸³ TiO₂,^{179–182} ZrO₂,¹⁸⁴ MMT,^{56,185–188} molecular sieves,^{189,190} ferroelectric materials, *etc.* The other category is active fillers, which means that nanoparticles can directly participate in ion transport by providing either an increase in free Li⁺ concentrations, surface conduction of Li⁺, or anion attraction, or as a Li⁺ source.¹⁷⁶ Active ceramic fillers include γ -LiAlO₂, LiAlO₃, Li₃N, LiN₂O₃, *etc.* The ionic conductivities, Li⁺ transference numbers, and electrochemical stability windows of some typical composite polymer electrolytes are listed in Table 6.

In a pioneering work, Weston *et al.*¹⁷⁷ studied the effect of inert α -Al₂O₃ (300 mesh) on the properties of a PEO/LiClO₄ electrolyte. Although the effect of α -Al₂O₃ on the conductivity and Li⁺ transference number was negligible, the mechanical stability was improved above 100 °C. Nano-sized fillers are more effective for reducing crystalline and interfacial resistance than micron-sized fillers.^{195,196} Groce *et al.* reported that the incorporation of nano-sized TiO₂, Al₂O₃, or SiO₂ into a PEO/LiClO₄ electrolyte not only enhanced the interfacial stability, mechanical stability and electrochemical stability but also improved the transport properties at ambient temperature.^{179–183,192,197} The addition of 4 wt% Al₂O₃ nanoparticles to a poly[bis(2-methoxyethyl)amino]_{1-x}(*n*-propylamino)_x-phosphazene] (BMEAP)-LiCF₃SO₃ electrolyte led to a sharp increase in conductivity by almost two orders of magnitude compared with the filler-free electrolyte.¹⁷⁸ Zhou *et al.*^{198–203} developed a new type of composite electrolyte by dispersing fumed silica into PEO with a low to moderate *M_w*. Unlike the composite based on high-*M_w* PEO, a solid-like structure was formed by the filler (fumed silica) instead of PEO chains. Composites that comprise fumed silica, low-*M_w* PEO and lithium salts are promising materials for rechargeable lithium batteries in terms of their high conductivity ($>10^{-3}$ S cm⁻¹ at room temperature), mechanical strength (elastic modulus $>10^5$ Pa) and interfacial stability toward lithium metal (potential window up to 5.5 V). Molecular sieve fillers such as zeolite¹⁹⁰ and ZSM-5 (ref. 189) have been

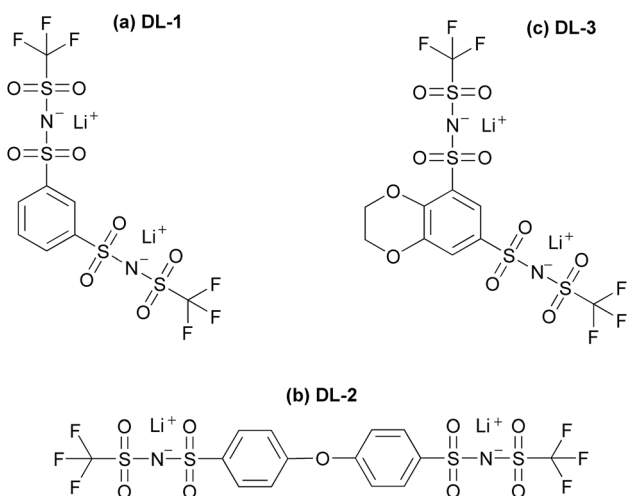
**Fig. 12** Structures of dilithium salts (a) DL-1, (b) DL-2 and (c) DL-3.¹⁶⁹

Table 6 Ionic conductivities, Li^+ transference numbers, and electrochemical stability windows of some typical composite polymer electrolytes

Composition of the sample	Conductivity (S cm^{-1})	Electrochemical window (V)	Li^+ transference number	Temperature ($^{\circ}\text{C}$)	Ref.
BMEAP/10 wt% LiCF_3SO_3 /4 wt% Al_2O_3	10^{-5}		0.38 (60 $^{\circ}\text{C}$)	Room temperature	178
$\text{P}(\text{EO})_8/\text{LiClO}_4$ /10 wt% Al_2O_3	10^{-5}	5.0	0.30 (91 $^{\circ}\text{C}$)	31	179
$\text{P}(\text{EO})_8/\text{LiClO}_4$ /10 wt% TiO_2	$>10^{-5}$	5.0	0.6 (45–49 $^{\circ}\text{C}$)	31	180
$\text{P}(\text{EO})_8/\text{LiClO}_4$ /10 wt% TiO_2	2.3×10^{-5}		0.5–0.6	30	182
PEO/PPC/10 wt% LiClO_4 /3 wt% TiO_2	1.4×10^{-5}	4.5	0.62	Room temperature	86
$\text{P}(\text{EO})_8/\text{LiClO}_4$ /1.4 wt% BaTiO_3	10^{-5}	4.0	0.37 (70 $^{\circ}\text{C}$)	25	191
$\text{P}(\text{EO})_{16}/\text{LiClO}_4$ /10 wt% SiO_2	$\approx 10^{-5.5}$	5.0		30	183
$\text{P}(\text{EO})_8/\text{LiN}(\text{CF}_3\text{SO}_2)_2$ /5 wt% SiO_2	1.4×10^{-4}		0.20	43	192
$\text{P}(\text{EO})_{20}/\text{LiBF}_4$ /10 wt% sulphated ZrO_2	10^{-7}		0.68 (100 $^{\circ}\text{C}$)	Room temperature	184
$\text{P}(\text{EO})_{10}/\text{LiClO}_4$ /10 wt% ZSM-5	10^{-5}		0.35 (70 $^{\circ}\text{C}$)	25	189
$(\text{PEO-PMMA})_{15}/\text{LiClO}_4$ /1 wt% MMT	5.3×10^{-8}			Room temperature	185
PEO/7 wt% LiClO_4 /1.2 wt% MMT	1.0×10^{-5}			Room temperature	186
$\text{P}(\text{EO})_{20}/\text{LiBF}_4$ /10 wt% $\gamma\text{-LiAlO}_2$	3.0×10^{-7}		0.26	30	182
$\text{P}(\text{EO})_{20}/\text{LiCF}_3\text{SO}_3$ /10 wt% $\gamma\text{-LiAlO}_2$	2.9×10^{-6}		0.29	30	182
PEO/ LiCF_3SO_3 /92 wt% Li_3N	1.2×10^{-4}			30	193
$\text{P}(\text{EO})_{10}/\text{LiCF}_3\text{SO}_3$ /91.2 vol% 1.2 Li_2S –1.6 LiI – B_2S_3	3.5×10^{-5}			25	194
PE/ LiCF_3SO_3 /84.3 vol% 1.2 Li_2S –1.6 LiI – B_2S_3	4.8×10^{-5}			25	194

incorporated into a PEO/LiX polymer complex to increase the ionic conductivity and Li^+ transference number. MMT was employed by Choudhary *et al.*⁵⁶ to increase the ionic conductivity of PEO/LiX electrolytes. Sengwa *et al.*¹⁸⁸ reported that a maximum conductivity value of more than $10^{-5} \text{ S cm}^{-1}$ at room temperature was obtained for a (PEO-PMMA)/ LiCF_3SO_3 /PEG/MMT composite electrolyte containing 3 wt% MMT. Ferroelectric materials such as BaTiO_3 , PbTiO_3 and LiNbO_3 have been added to polymer electrolytes together with various lithium salts (LiClO_4 , LiBF_4 , LiPF_6 , LiCF_3SO_3 and LiTFSI).²⁰⁴ The ionic conductivity and Li^+ transference number of the composite polymer electrolytes were increased by adding these ferroelectric materials.^{191,204} This phenomenon was explained on the basis of the spontaneous polarization of the ferroelectric material owing to its particular crystal structure. In addition to the ion transfer properties, the lithium/electrolyte interface stability was also greatly improved.¹⁹¹ Takeda *et al.*²⁰⁵ studied the cycling performance of a cell comprising $\text{Li}/\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ electrodes and a composite polymer electrolyte with BaTiO_3 , TiO_2 , and Al_2O_3 fillers. The best result was observed for the electrolyte with a BaTiO_3 filler. Furthermore, the good cycling performance that was observed in a cell comprising $\text{Li}/(\text{PEO-LiTFSI-BaTiO}_3)/\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ was explained by the improved interfacial stability between the electrolyte and the electrodes.

Croce *et al.* studied the effect of micron-sized $\gamma\text{-LiAlO}_2$ or crystalline zeolite (molecular sieve) on the performance of a PEO-based electrolyte. The addition of a $\gamma\text{-LiAlO}_2$ or crystalline zeolite filler can effectively control the morphology and growth of the passivation layer on a Li electrode.²⁰⁶ Moreover, a $\gamma\text{-LiAlO}_2$ filler can greatly reduce the crystallization rate and increase the ionic conductivity and lithium/electrolyte interface stability.^{207,208} Li_3N is a promising conductor of Li^+ with an ionic conductivity of the order of $10^{-3} \text{ S cm}^{-1}$ at ambient temperature.²⁰⁹ Mixed-phase electrolytes consisting of Li_3N ,

LiCF_3SO_3 , and PEO polymer have been constructed by Skaarup *et al.*¹⁹³ to combine the advantages of crystalline and polymeric ionic conductors. They also reported that mixed-phase electrolytes that contained Li^+ -conducting sulphide glass (1.2 Li_2S –1.6 LiI – B_2S_3) and non-conducting polyethylene materials were found to yield room-temperature ionic conductivities that were about three orders of magnitude higher than those of PEO-based polymer electrolytes.¹⁹⁴ These results suggest that a non-conducting polymer can be chosen to impart superior mechanical, chemical, and thermal properties and applied in solid-polymer lithium batteries. PEO/ LiBF_4 / Li_3N composite electrolytes containing 5–50% Li_3N exhibited an increase in conductivity by an order of magnitude at ambient temperature.²¹⁰

In contrast to the above results, Vogel *et al.*²¹¹ reported that the presence of TiO_2 nanoparticles hardly affected the behavior of a PEO/ LiClO_4 electrolyte. Ganesan *et al.*²¹² also reported that the addition of Al_2O_3 nanoparticles to a PEO/ LiBF_4 electrolyte led to a decrease in the mobility of Li^+ cations and BF_4^- anions and the overall conductivity, which was related to both nanoparticle-induced changes in the dynamical properties of the polymer and interactions between the nanoparticles and ions. Johansson *et al.*²¹³ studied the influence of SiO_2 and Al_2O_3 on the performance of polymer electrolytes based on PEO and amorphous PEO. No great effect was seen on the ionic conductivity upon the addition of nanoparticles to the amorphous system. However, a highly crystalline system can become partially amorphous upon the addition of nano-sized particles, which results in larger increases in ion conduction.

3.5.2. Roles of ceramic fillers in SPEs. Much effort has been devoted to explaining the roles of ceramic fillers in SPEs. Wiczorek *et al.*²¹⁴ analyzed the effects of AlBr_3 , AlCl_3 , and $\alpha\text{-Al}_2\text{O}_3$ fillers on the conductivity and ultrastructure of polyether/ LiClO_4 electrolytes using Lewis acid–base theory. In these

composite polymer electrolyte systems, the polyether matrix and ClO_4^- anions act as Lewis base centers, AlBr_3 and AlCl_3 are known to be strong Lewis acids, and in $\alpha\text{-Al}_2\text{O}_3$ Lewis acid centers (Al) and Lewis base centers (O) coexist. Because the Li^+ cation is known to be a kind of hard acid, there is a possibility that various acid-base interactions may occur in these composite systems. The final ultrastructure and hence the conductivity of composite systems are the results of an equilibrium between various Lewis acid-base reactions. Croce *et al.*²¹⁵ proposed a model to account for the role of ceramic fillers in enhancing the transport properties of PEO-based composite electrolytes. They concluded that inorganic fillers mainly play two important roles in the polymer matrix. One is to act as crosslinking centers for PEO segments and X^- anions, which reduces the tendency of PEO to undergo reorganization and thus promotes structural modification of the polymer chains, and the expected effect is the promotion of Li^+ transfer at the surface of the ceramic fillers. The other role is to act as centers of Lewis acid-base interaction for the ionic species in the electrolyte, which reduces ionic coupling, and the expected effect is the promotion of salt dissociation *via* the formation of a type of 'ion-ceramic complex', as shown in Fig. 13. They also reported that when the superacid ZrO_2 was added to a PEO/ LiBF_4 complex, the transport properties, in particular the Li^+ transference number, were greatly improved, which can be ascribed to specific Lewis acid-base interactions between the surface states of the ceramic and both the anion of the lithium salt and the PEO chains.^{186,216} Ganesan *et al.*²¹⁷ studied the origin of the increase in the low-temperature conductivity of polymeric materials with added TiO_2 . They concluded that the addition of nanoparticle fillers modifies polymer conformations and polymer segmental dynamics and thereby influences the ion mobility of polymer electrolytes.

Wang *et al.*²¹⁸ interpreted the effects of nano- Al_2O_3 particles on the ionic conductivity and transference number of a PAN/ LiClO_4 electrolyte based on Lewis acid-base theory, as shown in Fig. 14. When acidic nanoscale Al_2O_3 ceramic is added, the stronger polarizability of the H^+ ions of the acidic groups than that of the Li^+ ions toward the nitrile groups of PAN and the higher affinity of ClO_4^- anions toward the surface acidic groups of Al_2O_3 than that of cations help to separate $\text{Li}^+\text{-ClO}_4^-$ ion pairs. Such competition results in an increase in free Li^+ ions in the composite electrolyte and increases the ionic conductivity. When basic nanoscale Al_2O_3 is added, the interaction between the polar O atoms of Al_2O_3 and the Li^+ ions helps to dissociate both $\text{Li}^+\text{-ClO}_4^-$ ion pairs and $\text{R-C}\equiv\text{N}\cdots\text{Li}^+$ bonds, which results in free ClO_4^- anions. The Li^+ cations interact with polar O atoms *via* transient hydrogen bonding, and can migrate in the vicinity of the filler grains. When neutral nanoscale Al_2O_3 is added, although both interactions described above can occur, the anions can reassociate with the Li^+ cations to form new ion pairs, which leads to a lower concentration of charge carriers.

A combination of molecular dynamics and Monte Carlo simulations was used by Wick *et al.*²¹⁹ to obtain insight into lithium ion transport in PEO/ LiClO_4 polymer electrolytes next to both acidic and basic treated model solid surfaces of alumina at 323, 348, and 373 K. The ionic conductivities were not

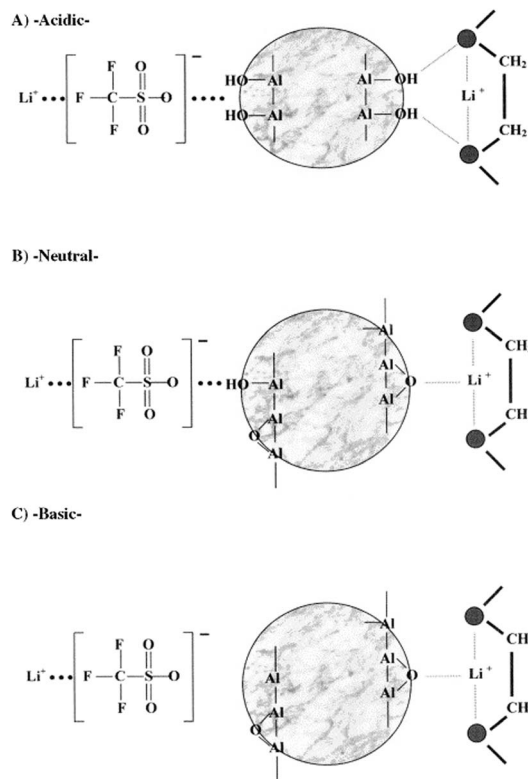


Fig. 13 Schematic of the surface interactions between three forms of dispersed nano-sized Al_2O_3 ceramic and a PEO/ LiCF_3SO_3 electrolyte complex. (A) Al_2O_3 acidic, (B) Al_2O_3 neutral, and (C) Al_2O_3 basic. Reprinted with permission from ref. 215. Copyright 2001 Elsevier Science Ltd.

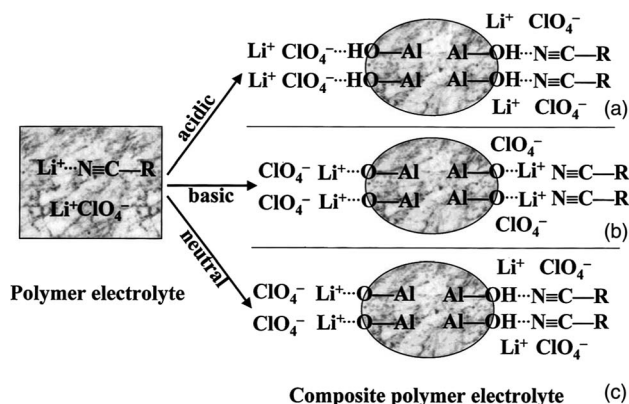


Fig. 14 Schematic demonstration of the dissociation effects of (a) Lewis acidic, (b) Lewis basic, and (c) neutral surface groups on nano-scale Al_2O_3 particles. Reprinted with permission from ref. 218. Copyright 2003 The Electrochemical Society, Inc.

significantly affected by the alumina surfaces, but the diffusivities were found to be increased at 323 K when acid-treated alumina was present. Close to the alumina surfaces, the diffusivity was significantly lower than further away owing to higher polymer density and strong binding between the ions and the alumina surface.

3.5.3. Other fillers. As well as ceramic fillers, other materials such as cellulose, carbon materials, *etc.*, have been employed as fillers in SPEs. Cellulose, which is an organic component of the primary cell wall of green plants with the formula $(C_6H_{10}O_5)_n$, has been investigated as a biomass filler for the preparation of a composite polymer electrolyte.^{220–224} Its fibers can be used as a reinforcing agent in polymer electrolytes to deliver greater mechanical strength for applications as separators in lithium-based batteries. Ahmad *et al.*²²² used cellulose from kenaf as reinforcing fibers in lithium-ion-conducting composite polymer electrolytes based on natural rubber grafted with poly(methyl methacrylate) (PMMA) and $LiCF_3SO_3$. Although the addition of cellulose involved a slight decrease in conductivity, the mechanical performance was greatly improved (a tensile strength of 10.9 MPa and a Young's modulus of 995 MPa). Samir *et al.*²²⁰ studied the thermomechanical behavior, ionic conductivity and electrochemical stability of nano-composite polymer electrolytes containing high- M_w PEO, cellulosic whiskers and LiTFSI. The results showed that the filler provided a significant reinforcing effect without affecting the Li^+ transference number, and a high level of ionic conductivity was retained with respect to that of polymer electrolytes without the filler. They also reported that the main effect of the cellulosic whiskers was thermal stabilization of the storage modulus of the composites above the melting point of the PEO–LiTFSI complexes.²²³ In 1999, Appetecchi *et al.*²²⁵ first proposed that the addition of carbon powders could increase the conductivity and interfacial stability of polymer electrolytes. Ibrahim *et al.*^{226,227} reported that the incorporation of amorphous carbon nanotubes into a plasticized PEO-20 wt% LiPF₆-15 wt% EC composite polymer electrolyte increased the conductivity significantly to $10^{-3} S cm^{-1}$. Zhou *et al.*²²⁸ reported an enhancement in the ionic conductivity and mechanical properties of a PEO/LiClO₄ electrolyte on adding functionalized multiwalled carbon nanotubes (MWCNTs). The increase in the ionic conductivity is attributed to a decrease in the crystallinity of PEO induced by the functionalized MWCNTs and an increase in salt dissociation owing to Lewis acid–base interactions among the functionalized MWCNTs, PEO and LiClO₄. Lee *et al.*⁷⁸ used PEG-grafted graphene oxide (PGO) as a filler in a composite polymer electrolyte containing the organic/inorganic hybrid branched graft copolymer PEGMA-(MA-POSS) and LiClO₄ salt. The ionic conductivity of the composite polymer electrolyte with 0.2 wt% PGO was found to be $2.1 \times 10^{-4} S cm^{-1}$ at 30 °C. The thermal and mechanical stabilities of the composite polymer electrolyte were also improved by introducing the PGO filler.

4. Gel polymer electrolytes

Gel polymer electrolytes (GPEs) are obtained by incorporating a certain amount of liquid plasticizer and/or solvent into a polymer–salt system. This concept was first proposed in 1975 by Feuillade *et al.*,²²⁹ who studied the process of plasticizing a polymer matrix with an aprotic solution containing an alkali metal salt. Owing to the introduction of a liquid plasticizer and/or solvent constituent, the transport of lithium ions is not

dominated by the segmental motion of polymer chains, but occurs in the swollen gelled phase or liquid phase. Generally speaking, when the bulk of the membrane is composed of connected micropores, the ionic conductivity of GPEs mainly depends on the properties of the trapped liquid electrolyte. Otherwise, if the membrane is homogeneous or does not contain many connected pores, the transfer of Li^+ mainly occurs in the swollen gelled phase. From the point of view of practical applications, a GPE should possess the properties of great mechanical strength, capability of holding a liquid electrolyte, high ionic conductivity, and electrochemical stability toward both electrodes. Many kinds of polymer matrix such as polyethylene oxide (PEO),^{169,230,231} polyvinyl chloride (PVC),^{232,233} polyacrylonitrile (PAN),^{234–236} poly(methyl methacrylate) (PMMA),^{237,238} polyvinylidene fluoride (PVDF),^{239–241} and poly(vinylidene fluoride-hexafluoropropylene) (P(VDF-HFP)) copolymer,^{242,243} *etc.*, have been widely studied as frameworks in gel polymer electrolytes. Table 7 displays the structures and physical properties of commonly used polymer matrices for GPEs. In our group, poly(propylene carbonate maleate) (PPCMA) was synthesized and employed as a polymer matrix in GPEs, and was considered to be a promising candidate material for lithium-ion batteries.²⁴⁴

Usually, GPEs based on a single polymer matrix cannot fulfill all the above listed requirements. For example, PAN-based electrolytes undergo severe passivation upon contact with lithium metal anodes,²⁴⁷ PMMA-based electrolytes exhibit low mechanical strength, PVC-based electrolytes display low ionic conductivity and compatibility towards lithium metal anodes, and PVDF-based electrolytes including P(VDF-HFP) exhibit poor interfacial properties with lithium metal anodes and a reaction between lithium and fluorine results in the formation of LiF, which is responsible for safety hazards.²⁴⁸ The commonly used methods for improving the properties of polymer matrices are blending, copolymerization, crosslinking, and compounding, which have been described in detail in reviews.^{22,245,246,249} In the following sections, the types of plasticizer and preparation methods for GPEs are summarized. The strategy of the addition of inorganic fillers with the aim of improving the mechanical strength and interfacial stability is described in detail.

4.1. Plasticizers

Plasticizers can be low-molar-mass organics, organic solvents or ionic liquids (ILs). A plasticizer is reported to help increase the content of the amorphous phase in a polymer electrolyte and promote segmental motion.^{59,250} In addition, it can also promote the dissociation of ion pairs, which increases the number of charge carriers available for charge transport, leading to an increase in ionic conductivity.²³¹

4.1.1. Low-molar-mass organics. Polyethylene glycol (PEG) has been widely used as a plasticizer in PEO–salt complexes.^{59,251–253} Both the content and the molecular weight of PEG have a significant influence on the ionic conductivity. Ito *et al.*²⁵¹ reported that the conductivity of a PEO– $LiCF_3SO_3$ complex increased with a decrease in the molecular weight of PEG and with an increase in the PEG content. Kelly *et al.*²⁵² employed PEG as a plasticizer in

Table 7 Molecular formulas and physical properties of commonly used polymer matrices^{22,245,246}

Polymer matrix	Molecular formula	Glass transition temperature (°C)	Melting point (°C)
PEO	$\left(\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ -\text{C}-\text{C}-\text{O}- \\ \quad \\ \text{H} \quad \text{H} \end{array} \right)_n$	-64	65
PVC	$\left(\begin{array}{c} \text{H} \quad \text{Cl} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{H} \quad \text{H} \end{array} \right)_n$	80	220
PAN	$\left(\begin{array}{c} \text{H} \quad \text{CN} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{H} \quad \text{H} \end{array} \right)_n$	125	317
PMMA	$\left(\begin{array}{c} \text{H} \quad \text{COOCH}_3 \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{H} \quad \text{CH}_3 \end{array} \right)_n$	105	Amorphous
PVDF	$\left(\begin{array}{c} \text{H} \quad \text{F} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{H} \quad \text{F} \end{array} \right)_n$	-40	171
P(VDF-HFP)	$\left(\begin{array}{c} \text{H} \quad \text{F} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{H} \quad \text{F} \end{array} \right)_n \left(\begin{array}{c} \text{F} \quad \text{F} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{F} \quad \text{CF}_3 \end{array} \right)_m$	-90	135

a PEO-LiCF₃SO₃ system. When 65 mol% PEG was added, the ionic conductivity increased from $3 \times 10^{-7} \text{ S cm}^{-1}$ to $10^{-4} \text{ S cm}^{-1}$ at 40 °C. However, the hydroxyl end groups of PEG react with lithium metal, which makes the system unsuitable for lithium polymer batteries. Yang *et al.*²⁵³ synthesized various modified forms of PEG by replacing active hydrogen atoms with monomethoxy (MMPEG) or dimethoxy (DMPEG) units or lithium (LPEG) ions. An ionic conductivity of $10^{-5} \text{ S cm}^{-1}$ at 25 °C was obtained when using these modified forms of PEG as plasticizers in PEO-LiCF₃SO₃ electrolytes.²⁵³ In the case in which LPEG was used as a plasticizer, not only the ionic conductivity but also the compatibility between the polymer electrolyte and the lithium anode were improved.²⁴⁵ However, in some polymer-salt systems the addition of PEG can increase the extent of the crystalline phase of the polymer matrix, which counteracts the increase in conductivity. Sengwa *et al.*⁶¹ reported that the addition of PEG as a plasticizer to a (PEO-PMMA)/LiCF₃SO₃ complex had no significant effect on the ionic conductivity.

Other low-molar-mass organics including polyethylene glycol dimethyl ether (PEGDME),^{230,231} borate esters such as PEG borate ester,¹⁶⁹ tris(2-(2-methoxyethoxy)ethyl)borate (B₂), and tris(2-(2-(2-methoxyethoxy)ethoxy)ethyl)borate (B₃),⁵³ phthalates such as dibutyl phthalate (DBP),^{254,255} dimethyl phthalate (DMP),^{256,257} and dioctyl phthalate (DOP),⁵⁹ and succinonitrile (SN),^{153,258} *etc.*, have been employed as plasticizers in polymer-salt systems. Kim *et al.*²³¹ made a comparative study of the conductivities, cation transference numbers and salt diffusion coefficients of plasticized PEO/LiTFSI electrolytes containing three different plasticizers, ethylene carbonate (EC), propylene carbonate (PC) and PEGDME (*M_w* 400). Moreover, they found that the conductivity and salt diffusion coefficients of the

plasticized electrolytes followed the order of PEGDME > PC > EC. In other words, PEGDME is the best organic additive for PEO-based polymer electrolytes among the selected additives. The ionic conductivities of some typical plasticized polymer-salt electrolytes are listed in Table 8.

4.1.2. Organic solvents. The commonly used solvents are polar and non-volatile such as ethylene carbonate (EC), propylene carbonate (PC), diethyl carbonate (DEC), dimethyl carbonate (DMC), γ -butyrolactone (γ -BL), *etc.* The physical properties of these organic solvents are listed in Table 9.


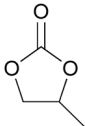
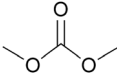
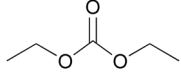

The solvents help to solvate Li⁺ ions and facilitate their transportation. Therefore, it is required that the solvents have a high dielectric permittivity but a low viscosity. Individual solvents often fail to meet all these requirements, so a mixture of solvents is often employed. Choi *et al.*²³⁴ prepared GPEs by swelling a PAN membrane in a 1 M solution of LiPF₄ in the following mixed solvents: EC/DMC (2 : 1, wt%), EC/DMC (1 : 1, wt%), EC/EMC (1 : 1, wt%), EC/DEC (1 : 1, wt%), and EC/DMC/DEC (1 : 1 : 1, wt%). The ionic conductivity decreased in the order of EC/DMC/DEC (1 : 1 : 1) > EC/DMC (1 : 1) > EC/EMC (1 : 1) > EC/DEC (1 : 1) > EC/DMC (2 : 1). The ionic conductivities of some typical GPEs based on different organic solvents are listed in Table 10. The addition of suitable organic solvents can increase the ionic conductivity to $10^{-3} \text{ S cm}^{-1}$. A mixture of solvents is more effective for increasing the ionic conductivity compared with a single solvent, which reflects the combined action of the viscosity and dielectric permittivity.²⁶⁰

4.1.3. Ionic liquids. Ionic liquids (ILs), or so-called “room temperature molten salts”, which comprise a bulky organic cation and a large delocalized inorganic anion, have attracted considerable interest as an alternative to organic solvents owing

Table 8 Ionic conductivities of some plasticized polymer–salt electrolytes

Composition of the sample	Ionic conductivity (S cm ⁻¹)	Temperature (°C)	Ref.
(PEO) ₂₀ /LiCF ₃ SO ₃ /50 wt% PEGDME	1.20 × 10 ⁻⁴	30	230
(PEO) ₁₅ /LiTFSI/10 wt% PEGDME	>10 ⁻³	50	231
(PEO) ₂₀ /LiTFSI/100 wt% PEG borate ester	1.36 × 10 ⁻⁵	30	169
PSi/15 wt% LiCF ₃ SO ₃ /40 wt% borate ester B ₂	3.70 × 10 ⁻⁵	Room temperature	53
PSi/15 wt% LiCF ₃ SO ₃ /40 wt% borate ester B ₃	1.60 × 10 ⁻⁴	Room temperature	53
PEO/13 wt% LiCF ₃ SO ₃ /10 wt% DBP	1.60 × 10 ⁻⁴	27	254
5 wt% PVC + 20 wt% PEMA/8 wt% LiClO ₄ /33.5 wt% EC + 33.5 wt% DBP	3.01 × 10 ⁻⁴	30	255
30 wt% PVA/10 wt% LiClO ₄ /60 wt% DMP	1.49 × 10 ⁻⁴	29	256
17.5 wt% PVA + 7.5 wt% PMMA/8 wt% LiClO ₄ /67 wt% DMP	0.60 × 10 ⁻⁴	30	257
PEO/15 wt% LiCF ₃ SO ₃ /20 wt% DOP	7.60 × 10 ⁻⁴	Room temperature	59
PEO/15 wt% LiCF ₃ SO ₃ /15 wt% PEG	1.71 × 10 ⁻⁵	Room temperature	59
(PEO) ₂₀ /LiBOB/24 mol% SN	>6 × 10 ⁻⁴	60	153

Table 9 Physical properties of some organic solvents commonly used in rechargeable lithium-ion batteries²⁵⁹

Solvent	Molecular formula	Molecular weight	Melting point (°C)	Boiling point (°C)	Dielectric permittivity	Viscosity at 25 C (mPa s)
EC		88.06	36.4	248	89.78	1.93
PC		102.09	-48.8	242	66.14	2.53
DMC		90.08	2.4	90	3.12	0.585
DEC		118.13	-43	126	2.82	0.748
γ-BL		86.09	-43.4	204	39.0	1.7

to several advantages: high chemical and thermal stability, non-flammability, negligible volatility, and especially high electrochemical stability and hydrophobicity in some cases.^{263–265} More importantly, some ILs with a certain combination of cation and anion have recently been reported to be electrochemically stable toward lithium metal.²⁶⁶ Many types of IL comprising cations based on pyridinium, imidazolium, piperidinium, quaternary ammonium, *etc.*, and anions based on [BF₄]⁻, [PF₆]⁻, [N(CF₃SO₂)₂]⁻, [CF₃SO₃]⁻, [C₄F₉SO₃]⁻, [N(CN)₂]⁻, [CF₃CO₂]⁻, [CF₃CONCF₃SO₂]⁻, *etc.*, have been investigated as liquid electrolytes for lithium-ion batteries. In most cases, the investigated ionic liquid electrolyte contains the same anion in both the Li salt and the ionic liquid. This is because the solubility of a Li salt in an ionic liquid incorporating the same anion is much higher than in systems with different anions. A coulombic cycling efficiency for Li plating/stripping of close to 100% has

been achieved with liquid electrolytes using these ILs as solvents.²⁶⁷

Recently, the incorporation of room-temperature ionic liquids (RTILs) into polymer electrolytes to overcome the inherent limitations to the ionic conductivity of dry-SPEs has been proposed by Passerini *et al.*²⁶⁸ They have studied a series of RTILs containing pyrrolidinium-based cations and TFSI anions.^{263,264,269–276} The structure of *N*-alkyl-*N*-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (PYR_{1A}TFSI, A = C_nH_{2n+1}, with *n* ranging from 1 to 10) is shown in Fig. 15.

During the charge/discharge cycles of rechargeable Li ion batteries, the charge is mainly carried by the lithium cations. However, the other ions in the polymer electrolyte such as PYR_{1A}⁺ and TFSI⁻ are also mobile and may accumulate on the surfaces of the electrodes. These ions may thus be adsorbed or decompose on the electrodes and form a passive film when

Table 10 Ionic conductivities of some typical GPEs plasticized by solvent(s)

Composition of the sample	Ionic conductivity (S cm ⁻¹)	Electrochemical window (V)	Temperature (°C)	Ref.
(PEO) ₁₆ /LiClO ₄ /40 wt% EC	2.67 × 10 ⁻⁴		Room temperature	261
PEO/15 wt% LiCF ₃ SO ₃ /20 wt% EC	8.12 × 10 ⁻⁵		Room temperature	262
30 wt% PVC/8 wt% LiClO ₄ /62 wt% PC	6.70 × 10 ⁻⁶		30	232
7.5 wt% PVC/5 wt% LiBF ₄ /42 wt% EC + 28 wt% PC	8.60 × 10 ⁻⁵		Room temperature	233
4.5 wt% PMMA/46.5 wt% LiClO ₄ /30 wt% PC + 19 wt% EC	5.00 × 10 ⁻⁴		Room temperature	237
68 wt% PMMA/12 wt% LiN(CF ₃ SO ₂) ₂ /20 wt% EC	1.20 × 10 ⁻⁴		Room temperature	238
59.5 wt% PMMA/10.5 wt% LiN(CF ₃ SO ₂) ₂ /30 wt% PC	2.00 × 10 ⁻⁴		Room temperature	238
PAN/1 M LiPF ₆ /EC + DMC + DEC (1 : 1 : 1, wt%)	>1.0 × 10 ⁻³	4.5	Room temperature	234
PAN/1 M LiBF ₄ /EC + DMC (1 : 1, vol%)	2.80 × 10 ⁻³	5.0	Room temperature	235
PAN/1.0 M LiPF ₆ /EC + DMC + DEC (0.25 : 1 : 1, vol%)	1.70 × 10 ⁻⁵		20	236
PVDF/1.0 M LiPF ₆ /EC + DMC (1 : 1, wt%)	1.00 × 10 ⁻³	4.5	Room temperature	239
PVDF/1.0 M LiClO ₄ /EC + PC (1 : 1, vol%)	>1.4 × 10 ⁻³	>4.5	20	240
PVDF/1.0 M LiPF ₆ /EC + DMC + DEC (1 : 1 : 1, wt%)	1.00 × 10 ⁻³	5.0	Room temperature	241
P(VDF-HFP)/1.0 M LiPF ₆ /EC + DEC (1 : 1, vol%)	1.00 × 10 ⁻³	4.5	Room temperature	242
P(VDF-HFP)/1.0 M LiPF ₆ /EC + DMC + DEC (1 : 1 : 1, wt%)	1.43 × 10 ⁻³		Room temperature	243
PPCMA/1.0 M LiClO ₄ /EC + DMC (1 : 1, vol%)	8.43 × 10 ⁻³		Room temperature	244

a current is passed. Therefore, both the ionic conductivity and the lithium ion transference number (t_{Li^+}) are critical for high-performance polymer electrolytes.^{268,277} Based on the ionic conductivity and t_{Li^+} , the conductivity of lithium ions can be calculated according to the following equation:

$$\sigma_{\text{Li}^+} = \sigma t_{\text{Li}^+} \quad (3)$$

where σ is the total conductivity of the electrolyte and σ_{Li^+} is the conductivity of lithium ions.²⁷⁷

The commonly used PYR_{1A}TFSI ILs in polymer electrolytes are PYR₁₃TFSI and PYR₁₄TFSI. The ionic conductivity of a PEO/LiTFSI/PYR₁₃TFSI polymer electrolyte reached 10⁻⁴ S cm⁻¹ at 20 °C, which is almost two orders of magnitude higher than that of the IL-free electrolyte.²⁶⁸ However, the Li⁺ transference number decreased with an increase in the mass fraction of PYR₁₃TFSI IL.²⁶⁸ Lithium metal batteries consisting of Li/LiFePO₄ electrodes and a polymer electrolyte based on PYR₁₃TFSI or PYR₁₄TFSI exhibited excellent reversible cyclability and exceptional electrochemical stability.^{271,272,274,275} A dimensionally stable, elastic, flexible, non-volatile GPE comprising P(VDF-HFP)/LiTFSI/PYR₁₃TFSI was obtained by using PYR₁₃TFSI as a plasticizer.²⁷⁸ This GPE displayed high electrochemical

stability and a high ionic conductivity of 2.7 × 10⁻⁴ S cm⁻¹ at room temperature. On further adding a small amount of EC to this GPE, increases in the ionic conductivity (5 × 10⁻⁴ S cm⁻¹ at room temperature), Li⁺ transport number, and Li⁺ transport kinetics were observed. Hofmann *et al.*²⁷⁹ prepared a GPE comprising PYR₁₃TFSI IL, organic carbonates, LiTFSI salt, and a P(VDF-HFP) matrix. The ionic conductivities of this GPE were in the range of 1 × 10⁻³ to 2 × 10⁻³ S cm⁻¹ at room temperature. The incorporation of a PYR₁₄TFSI plasticizer into a P(VDF-HFP)/LiTFSI polymer electrolyte produced a good freestanding membrane, which exhibited an ionic conductivity of 4.0 × 10⁻⁴ S cm⁻¹, a good electrochemical window, and a sufficient level of thermal stability. The lithium ion transference number and conductivity of lithium ions increased at first and then decreased with an increase in the mass fraction of the ionic liquid. The Li⁺ transference number reached a maximum value of 0.8 when 33.3 wt% PYR₁₄TFSI ionic liquid was added.²⁷⁷ Unfortunately, the trade-off between mechanical stability and ionic conductivity still existed when the IL content was increased. In the attempt to obtain room-temperature highly conductive polymer electrolytes without impairing their mechanical properties, *in situ* UV photoirradiation of the complex of PEO/LiTFSI/PYR_{1A}TFSI was performed using benzophenone (Bp) as a crosslinking agent.^{263,264}

A type of IL containing a 1-alkyl-3-methylimidazolium cation has been employed as a plasticizer in GPEs. The structure of 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide IL is shown in Fig. 16. Raghavan *et al.*²⁸⁰ used three different ILs, namely 1-ethyl-3-methylimidazolium TFSI (EMImTFSI), 1-propyl-3-methylimidazolium TFSI (PMImTFSI), and 1-butyl-3-methylimidazolium TFSI (BMImTFSI) as plasticizers to form GPEs based on a P(VDF-HFP) matrix. All these GPEs exhibited a high ionic conductivity in the range of 2.4 × 10⁻³ to 4.5 × 10⁻³ S cm⁻¹ at 25 °C. The GPE that used EMImTFSI IL as a plasticizer displayed the highest electrochemical properties. When assembled with Li/LiFePO₄ electrodes, the gel polymer battery that was obtained delivered a high discharge capacity

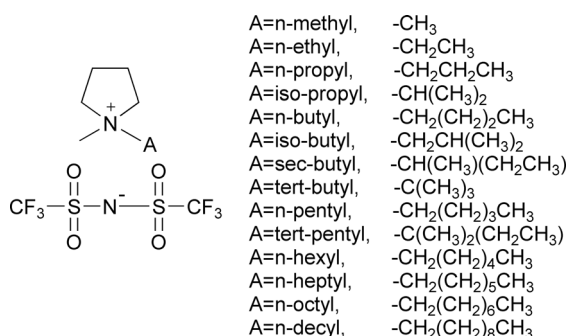


Fig. 15 Structure of N-alkyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (PYR_{1A}TFSI) ionic liquids.

($\sim 140 \text{ mA h g}^{-1}$) at 0.1C and exhibited a very stable discharge capacity under continuous cycling. Zhai *et al.*²⁸¹ reported that when BMImBF₄ IL was added to a P(VDF-HFP)/PMMA/LiClO₄ polymer electrolyte, the GPE exhibited a glass transition temperature of -87°C and a high ionic conductivity of $1.4 \times 10^{-3} \text{ S cm}^{-1}$ at 30°C .

Three kinds of ILs comprising the BMIm cation and different anions (TFSI⁻, BF₄⁻ and CF₃SO₃⁻) were employed to study the influence of the anion on the electrochemical properties of a PEO/LiTFSI electrolyte.²⁸² The best results were obtained for ILs with the TFSI⁻ anion. The PEO/LiTFSI/BMImTFSI electrolyte exhibited good electrochemical stability and significantly low interfacial resistance with the lithium electrode.²⁶⁶ The effect of the concentration of the IL salt solution on the properties of a P(VDF-HFP)/LiBF₄/BMImBF₄ electrolyte has been studied by Shalu *et al.*²⁸³ The melting temperature, glass transition temperature, degree of crystallinity, thermal stability, elastic modulus, and hardness gradually decreased with an increase in the content of the IL salt solution as a result of complexation between P(VDF-HFP) and the IL. The ionic conductivity of the GPE increased with an increase in the concentration of the IL salt solution.

Compatibility between the IL and polymer is an important factor that must be considered in the selection of an ionic liquid. Egashira *et al.*²⁸⁴ reported that quaternary ammonium-based ionic liquids appeared to be more compatible than imidazolium-based ILs with a PEO-PMMA branched copolymer, owing to preferable interaction between the IL and polymer matrix, which enabled the transport of Li⁺ in the ionic liquid phase. Fernicola *et al.*²⁸⁵ synthesized P(VDF-HFP)-based GPEs by mixing with LiTFSI salt and a piperidinium-based IL. The structure of *N*-butyl-*N*-ethylpiperidinium TFSI (PP₂₄TFSI) is shown in Fig. 17. The LiTFSI/PP₂₄TFSI mixture acted as a plasticizer, which suppressed the crystallinity of the polymer matrix. This kind of GPE exhibited an ionic conductivity of the order of $10^{-4} \text{ S cm}^{-1}$ at room temperature, and an increased Li⁺ transference number.

Novel GPEs comprising polymeric lithium salts and ILs have become a new research focus in recent years. Polymeric lithium salts including lithium poly(2-acrylamido-2-methylpropanesulfonate) (PAMPSLi, Fig. 3(a)) homopolymer and PAMPSLi-PVF copolymer combined with the ILs 1-ethyl-3-methylimidazolium tricyanomethanide (EMImTCM) and *N,N*-dimethyl-*N*-propyl-*N*-

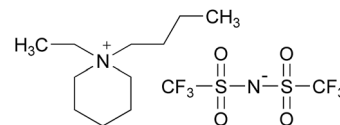


Fig. 17 Structure of the PP₂₄TFSI ionic liquid.

butylammonium tricyanomethanide (N1134TCM) have been obtained by Cha *et al.*²⁸⁶ The structures of EMIm⁺, N1134⁺ and TCM⁻ are shown in Fig. 18. The ionic conductivity of the copolymer system of PAMPSLi-PVF/EMImTCM ($5.43 \times 10^{-3} \text{ S cm}^{-1}$ at 25°C) was four times higher than that of the homopolymer system of PAMPSLi/EMImTCM ($1.28 \times 10^{-3} \text{ S cm}^{-1}$ at 25°C). The PAMPSLi/PVF polyelectrolyte with the EMImTCM IL exhibited a higher ionic conductivity ($5.43 \times 10^{-3} \text{ S cm}^{-1}$) than that of the polyelectrolyte with the N1134TCM IL ($2.48 \times 10^{-3} \text{ S cm}^{-1}$).

Ogihara *et al.*²⁸⁷ prepared GPEs containing polymeric lithium salts, namely, poly(3-sulfopropyl acrylate) lithium salt (PAC3SLi) and poly(2-acrylamido-2-methylpropanesulfonic acid) lithium salt (PAMPSLi), and the alkali metal ionic liquids EMLiSO₄ and MPyLiSO₄ or the typical ionic liquids EMImBF₄ and EMImTFSI. An AMIL is composed of three parts: a sulfate anion, an *N*-ethyl-imidazole (EIm) or *N*-methylpyrrolidine (MPy) cation, and a Li cation. The structures of the alkali metal ionic liquids EMLiSO₄ and MPyLiSO₄ are shown in Fig. 19. Typical ILs and AMILs are both capable of dissolving the negatively charged polyelectrolytes PAC3SLi and PAMPSLi to form homogeneous gels. A room-temperature ionic conductivity higher than $10^{-4} \text{ S cm}^{-1}$ was obtained by adjusting the amount of polyelectrolyte.

In recent years, polymeric ionic liquids (PILs) obtained by the polymerization of an ionic liquid monomer have attracted much attention as the polymer matrix in GPEs. The main advantages of PIL-based electrolytes are their lower flammability and exceptionally high anodic stability compared with conventional GPEs, which allow their use in safety-enhanced lithium batteries with high-voltage cathodes. Li *et al.*²⁸⁸ synthesized PILs containing guanidinium cations and different

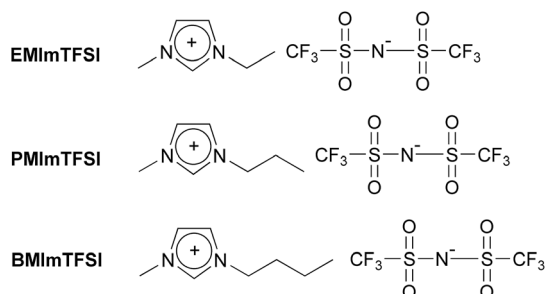


Fig. 16 Structures of 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ionic liquids.

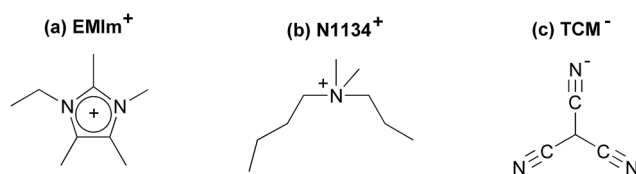


Fig. 18 Structures of (a) 1-ethyl-3-methylimidazolium cation (EMIm⁺), (b) *N,N*-dimethyl-*N*-propyl-*N*-butylammonium cation (N1134⁺), and (c) tricyanomethanide anion (TCM⁻).

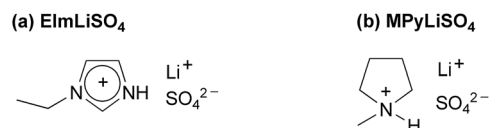


Fig. 19 Structures of the alkali metal ionic liquids (a) EMLiSO₄ and (b) MPyLiSO₄.

anions (PF_6^- and TFSI^-) by polymerization of a guanidinium ionic liquid monomer with methyl acrylate. The structures of a guanidinium-based PIL and a guanidinium IL are shown in Fig. 20. A quaternary GPE comprising a guanidinium-based PIL (matrix), a guanidinium ionic liquid, LiTFSI salt, and nano-sized SiO_2 remained chemically stable at a higher temperature (80°C) in contact with a lithium anode. In particular, the quaternary GPE exhibited a high conductivity of lithium ions, a wide electrochemical stability window and good lithium stripping/plating performance.

Yin *et al.*²⁸⁹ synthesized a novel imidazolium-tetraalkylammonium-based dicationic PIL, poly(*N,N,N*-trimethyl-*N*-(1-vinylimidazolium-3-ethyl)ammonium bis(trifluoromethanesulfonyl)imide), and employed it as an electrolyte matrix in GPEs. Ternary GPEs comprised the dicationic PIL, 1,2-dimethyl-3-ethoxyethylimidazolium TFSI (IM(2o2)11TFSI) IL, and LiTFSI salt. The structures of the IM(2o2)11TFSI ionic liquid and dicationic PIL are shown in Fig. 21. The PIL/ LiTFSI /IM(2o2)11TFSI electrolyte displayed a low glass transition temperature (-54°C), high thermal stability (330°C), good ionic conductivity (about 10^{-4} S cm^{-1} at $25\text{--}40^\circ\text{C}$), high electrochemical stability and good interfacial stability with lithium metal.

Lee *et al.*²⁹⁰ prepared a less flammable GPE by the *in situ* polymerization of an ionic liquid monomer, 1-methyl-3-(2-acryloyloxyhexyl)imidazolium tetrafluoroborate (MAHI-BF_4). The structure of poly(MAHI-BF_4) is shown in Fig. 22. When assembled with LiCoO_2/Li electrodes, the lithium polymer cell that was obtained delivered a discharge capacity of 134.3 mA h g^{-1} at room temperature and exhibited good capacity retention.

4.2. Preparation methods

Based on their physical state, GPEs can be divided into two types: homogeneous (uniform) and heterogeneous (phase-separated).²⁴⁶ In homogeneous GPEs, the gel phase is

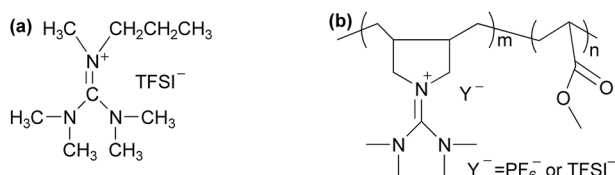


Fig. 20 Structures of (a) a guanidinium ionic liquid and (b) guanidinium-based polymeric ionic liquids.

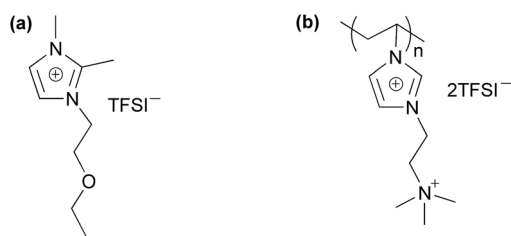


Fig. 21 Structures of (a) 1,2-dimethyl-3-ethoxyethylimidazolium TFSI (IM(2o2)11TFSI) ionic liquid and (b) an imidazolium-tetraalkylammonium-based dicationic PIL.

responsible for the transportation of ions. Homogeneous GPEs are usually prepared by casting and *in situ* polymerization methods. In contrast, heterogeneous gels comprise three phases: a liquid electrolyte, a gel electrolyte swollen by solvents and a polymer matrix. The preparation of heterogeneous gel electrolytes usually includes two stages: the formation of a porous polymer membrane, and its activation by uptake of the liquid organic electrolyte. Therefore, the membrane porosity, conductivity of the electrolyte, thickness of the membrane and extent to which the electrolyte wets the pores of the membrane are properties to be considered in the preparation of the membrane. The greater the porosity that the membrane possesses, the greater the amount of liquid electrolyte the membrane may take up, but an excessively open architecture of the membrane will lead to leakage of liquid, which will limit further increases in conductivity.²⁹¹ In order to obtain an ideal polymer electrolyte with high ionic conductivity and low leakage of liquid, membranes with high porosity and small pore sizes are suggested.²⁴⁰ Porous polymer membranes are usually prepared by extraction-activation methods, phase inversion methods, electrospinning technology, foaming technology, *etc.*

4.2.1. Casting method. In the early stages, GPEs were usually prepared by a solution casting method. In this process, a polymer matrix is dissolved in a low-boiling solvent (acetonitrile, tetrahydrofuran (THF), *etc.*) together with a non-aqueous lithium salt electrolyte, and the resulting slurry is cast on a substrate to form films.^{292,293} The GPEs that are obtained are usually tacky and have low mechanical strength. When used in practical cells, the films have to be hardened by either chemical or physical crosslinking. In addition to the need for crosslinking, the main drawback is that all the processes must be carried out in a moisture-free environment because a highly moisture-sensitive lithium salt is present at the initial stage. This critical environmental requirement adds to the cost and prevents its large-scale application.

4.2.2. *In situ* polymerization. Recently, a new procedure of *in situ* polymerization for synthesizing GPEs has been suggested. In this method, a precursor consisting of a curable monomer, a liquid electrolyte and an initiator is directly put into a lithium-ion battery and then cured under certain conditions (such as UV radiation, thermal radiation or electron beam radiation) to form a polymer network; at the same time, the liquid electrolyte solidifies evenly in the gaps in the network. The precursor needs to have a relatively low viscosity so that it can easily wet the electrodes and the separator, resulting in good contact and affinity between the electrodes and electrolyte. The commonly used initiators are organic peroxides, such as

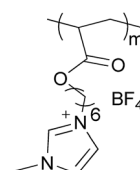


Fig. 22 Structure of poly(1-methyl-3-(2-acryloyloxyhexyl)imidazolium tetrafluoroborate).

bis(4-*tert*-butylcyclohexyl)peroxydicarbonate,^{294,295} benzoyl peroxide,^{296,297} and *t*-amyl peroxyphthalate,²⁹⁰ and azo compounds such as 2,2-azobisisobutyronitrile (AIBN).²⁹⁸

The monomers for the GPE are required to have a double bond at their end, a low molecular weight and oxide groups to provide good compatibility with the electrolyte and high mechanical strength. Currently, the commonly used polymerization monomers are of the acrylate type²⁹⁴ and sometimes oligomeric polyethers are used.^{299,300} Kim *et al.* reported that many macromonomers such as polyurethane acrylate²⁹⁷ and monomers such as tetraethylene glycol diacrylate,^{296,301} triethylene glycol dimethacrylate,³⁰² and di(trimethylolpropane) tetraacrylate²⁹⁴ could be used to obtain GPEs for lithium-ion polymer batteries. The obtained GPEs exhibited good electrochemical stability up to 4.5–4.8 V (vs. Li/Li⁺) and an ionic conductivity above 10^{−3} S cm^{−1} at room temperature. Oh *et al.*²⁹⁹ prepared a GPE by using copolymers of ethylene oxide (EO) and propylene oxide (PO) as macromonomers. This P(EO-PO)-based GPE had an ionic conductivity higher than 10^{−3} S cm^{−1} and better battery performance.

4.2.3. Extraction–activation method. The extraction–activation method was first proposed by Bellcore to facilitate industrial production.¹⁹ The process of the extraction–activation method can be divided into four stages. In the first stage, a mixture of a polymer, acetone, anode and cathode materials, and a plasticizer (*e.g.*, dibutyl phthalate (DBP)) is prepared and then cast on substrates to form films. In the second stage, the obtained plasticized films are laminated together with Al and Cu current collectors to form cells. In the third stage, the DBP plasticizer is extracted from the assembled cells using an appropriate solvent. In the last stage, after drying and packaging, the battery is activated by a liquid electrolyte. The ability to introduce the moisture-free liquid electrolyte at the last stage allows the manufacture of the cells in a completely open environment. However, the extraction of DBP is inconvenient and dangerous, because it involves the handling of a large amount of volatile solvents. Consequently, this method has rarely been used after the development of the following phase separation/inversion method.

4.2.4. Phase separation/inversion method. The phase separation/inversion method is a well-known technique for preparing microporous polymer membranes, which avoids the use of a plasticizer extraction process. Currently, the phase separation/inversion method can be roughly classified into four types:

(1) Evaporation-induced phase separation/inversion.^{242,303–305} In this process, a polymer is dissolved in a mixture of a volatile solvent such as *N*-methyl-2-pyrrolidone (NMP), acetone, tetrahydrofuran (THF), or *N,N*-dimethylformamide (DMF) and a high-boiling non-solvent such as ethanol, pentane, 1-butanol, or ethylene glycol (EG). The resulting solution is cast as films on substrates and the solvents are allowed to evaporate. Owing to the difference in the evaporation rate between the solvent and non-solvent, phase separation of the polymer from the solution occurs and results in the formation of a porous polymer membrane. Stephan *et al.*³⁰⁴ reported that the morphology and

porosity of P(VDF-HFP) copolymer membranes are related to the chemical structure of the non-solvents that are used.

(2) Non-solvent-induced phase separation/inversion.^{305–307} In this process, a polymer is dissolved in a solvent or mixture of solvents such as *N*-methyl-2-pyrrolidone (NMP), glycerol, or DMF and the resulting slurry solution is cast as films on substrates. A highly porous structure in a polymer matrix is formed after immersing the films in a bath of a non-solvent such as water owing to diffusive interchange between the solvent and non-solvent. A lotus root-like porous P(VDF-HFP)-based nanocomposite polymer membrane with a diameter in the range of 5–40 μm was obtained by using a mixed solution of NMP and glycerol as a solvent. The ionic conductivity of the nanocomposite gel polymer electrolyte was 1.21 × 10^{−3} S cm^{−1} at room temperature and its electrochemically stable potential was 5.52 V (vs. Li/Li⁺).³⁰⁷ Min *et al.*³⁰⁸ prepared a porous P(AN-MMA) membrane by using DMF as a solvent and water as a non-solvent, and found that both the pore size and pore volume could be controlled by changes in the evaporation time of the solvent before immersion in a bath of non-solvent.

(3) Vapor-induced phase separation/inversion. In this process, a polymer is dissolved in a solvent and the resulting slurry is cast as films on substrates. A highly porous structure in a polymer matrix is formed by exposing the films to water vapor, supercritical CO₂, *etc.* Pu *et al.*³⁰⁹ prepared a porous P(AN-MMA) membrane by water vapor-induced phase inversion, and found that the pore size was much more uniform across the cross-section of the membrane than that of a porous membrane prepared by a conventional water bath coagulation technique. Xu *et al.*³¹⁰ prepared microporous P(VDF-HFP) membranes by phase separation with supercritical CO₂ as a non-solvent. Factors such as the pressure of CO₂, polymer concentration and temperature have a significant influence on the membrane porosity and average pore size. Reverchon *et al.*³¹¹ reported that the structure of P(VDF-HFP) membranes can be changed from cellular to bicontinuous *via* increasing the pressure of CO₂ and decreasing the temperature.

(4) Thermally induced phase separation/inversion. In this process, a polymer is dissolved in a diluent at high temperature and then the solution is cooled to induce phase separation. The diluent is extracted by an extractant to yield a microporous structure. Compared with the other phase inversion processes, this method is more controllable because the factors that influence the porous structure are fewer. Gu *et al.*³¹² prepared a PVDF membrane using benzophenone as a diluent and found that the membrane structures were influenced by the quenching temperature. They also reported that the porosity was influenced by the diluents that were used.³¹³ Ji *et al.*³¹⁴ prepared a microporous PVDF membrane using a mixed diluent of dibutyl phthalate (DBP) and di(2-ethylhexyl) phthalate (DEHP). The microstructure of the membrane can be easily and conveniently controlled by adjusting the DBP/DEHP ratio in the diluent mixture. Cui *et al.*³¹⁵ prepared microporous P(VDF-HFP) membranes using sulfolane as a diluent and ethanol as an extractant. When immersed in a liquid electrolyte, the formed polymer electrolyte exhibited a maximum transference number of 0.55, a maximum ionic conductivity of 2.93 × 10^{−3} S cm^{−1} at

20 °C, and an electrochemical stability window of up to 4.7 V (vs. Li^+/Li).

GPEs obtained by a phase separation/inversion method simultaneously exhibit good electrochemical and mechanical properties. However, residual solvents or non-solvents cannot easily be removed, which affects electrochemical properties such as the electrochemical stability and safety of lithium polymer batteries.²³⁹

4.2.5. Electrospinning technology. Electrospinning is a novel and efficient fabrication process for preparing fibrous polymer membranes with fiber diameters in the range of tens of nanometers to several micrometers.^{239,241} The fully interconnected open porous structure provides good ion conduction channels and a large specific surface area. Fibrous membranes with porosities in the range of 30–90% and pore sizes from sub-micrometer to a few micrometers can easily be produced by adjusting the process parameters. A maximum ionic conductivity of $7.89 \times 10^{-3} \text{ S cm}^{-1}$ for fibrous PAN–PVDF membranes can be obtained by optimizing the electrospinning parameters, *i.e.*, the applied voltage, solution concentration, and PVDF content.³¹⁶ He *et al.* reported that the morphology of nano-fibrous PVDF–PMMA membranes was highly dependent on the solvent that was used during the electrospinning process.³¹⁷ PVDF–PMMA nanofibers with beads were formed in the electrospun membrane when *N,N*-dimethylformamide (DMF) was used as the solvent, whereas uniform PVDF–PMMA nanofibers without beads in the electrospun membrane were obtained with a DMF–acetone mixed solvent. Carol *et al.*²³⁶ prepared a non-woven membrane of PAN by electrospinning technology. The membranes had thin fibers with a diameter in the range of 0.88–1.26 μm , high porosity, and great mechanical strength. Huang *et al.*³¹⁸ prepared a cellulose–P(VDF–HFP) nanofiber membrane by coaxial electrospinning of a cellulose acetate core and a P(VDF–HFP) shell. The coaxial fibrous membrane displayed high tensile strength (34.1 MPa), high porosity (66%), excellent thermal stability (up to 200 °C), and high electrolyte compatibility (355% electrolyte uptake). GPEs based on these membranes exhibited a low interfacial resistance of 98.5 Ω and a high ionic conductivity of $6.16 \times 10^{-3} \text{ S cm}^{-1}$. Bi *et al.*³¹⁹ prepared nanofiber membranes with a core (PAN)–shell (PMMA) structure by coaxial electrospinning. The GPEs exhibited high ionic conductivities (4.4×10^{-3} to $5.1 \times 10^{-3} \text{ S cm}^{-1}$), good electrochemical stability (4.7–5.2 V vs. Li/Li^+), appropriate lithium ion transference numbers (0.46–0.50), and also good stability and compatibility with the lithium electrode. In our group, a chemically heterogeneous sandwiched nonwoven membrane composed of hydrophilic sulfonated poly(fluorenyl ether ketone) (SPFEK) nanofibers and hydrophobic beaded polyethersulfone (PES) nanofibers was prepared by a program-controlled co-electrospinning process.¹⁷⁴

4.2.6. Foaming technology. In the foaming process, a foaming agent and a polymer matrix are dissolved in a solvent, and the resulting slurry is coated on a substrate to form films. After evaporating the solvent, the films are heated at an elevated temperature to remove the foaming agent and form a porous structure within the polymer matrix. Zhang *et al.*³²⁰ prepared porous PVDF membranes by using salicylic acid as a foaming

agent for the first time. The pores in the PVDF polymer were evenly distributed with an average diameter of about 400 nm. When the film was gelled with a liquid electrolyte, an ionic conductivity of up to $4.8 \times 10^{-3} \text{ S cm}^{-1}$ at room temperature was obtained. The same group also prepared a porous P(VDF–HFP) polymer membrane by using urea as a foaming agent. The porous membrane exhibited a high porosity of 70.2%, and the obtained GPE displayed an ionic conductivity of up to $1.43 \times 10^{-3} \text{ S cm}^{-1}$ at room temperature.²⁴³

4.3. Introduction of inorganic fillers

The presence of a plasticizer in GPEs increases the ionic conductivity but at the cost of mechanical strength. Moreover, plasticizers are susceptible to various redox reactions on the electrodes, which leads to deterioration of the performance of lithium polymer batteries. The degradation of mechanical properties can be offset by chemical or physical crosslinking (light radiation,^{52,230,264} thermal radiation,^{174,263,295} or electron beam radiation) of the system or physically supported by polyolefin membranes such as polyethylene^{321–323} or polypropylene.^{298,300} In addition, the addition of inorganic fillers such as SiO_2 , TiO_2 , Al_2O_3 , or MgO , *etc.*, to GPEs proved to be one of the most efficient ways to improve their mechanical strength as well as their transport properties and electrochemical properties. The role of inorganic fillers in liquid electrolytes has been widely studied. Osińska *et al.*³²⁴ reported that thin layers of electrolyte adsorbed on the surfaces of filler grains can provide a sufficiently favorable transport environment for ions. Kumar *et al.*³²⁵ postulated the existence of space charge layers at the boundaries of ceramic grains dispersed in liquid electrolytes. These space charge layers tend to overlap with an increase in the concentration of ceramic grains, which leads to the formation of favorable ion transport pathways.

Tarascon *et al.*¹⁹ found that the addition of highly dispersed SiO_2 to a P(VDF–HFP) matrix significantly increased its solvent absorption ability and led to a considerable increase in its ionic conductivity. The same results were also observed by Caillon-Caravanier *et al.*³²⁶ Zalewska *et al.*³²⁷ reported that GPEs that were filled with sub-micron-sized SiO_2 exhibited a higher ionic conductivity than that of GPEs filled with nano-sized SiO_2 . Osińska *et al.*³²⁴ obtained the same results and proposed that the primary ion transport in GPEs filled with a large amount of sub-micron-sized modified SiO_2 (up to 50%) occurs at the boundaries of the filler grains *via* overlapping space charge layers of the silica grains. Wang *et al.*³²⁸ prepared a novel hierarchical mesoporous SiO_2 network and added it to P(VDF–HFP)-based gel electrolytes. GPEs containing the mesoporous SiO_2 network exhibited higher ionic conductivity and mechanical stability compared with samples without SiO_2 and with fumed SiO_2 . Yang *et al.*³²⁹ prepared highly ordered large mesoporous SiO_2 (m-SBA15) powders using a hard-template method. On incorporating an m-SBA15 filler into a P(VDF–HFP) membrane, the ionic conductivity is increased owing to its mesoporous structure and large specific surface area, which can trap a large amount of liquid electrolyte. The P(VDF–HFP)/m-SBA15 composite membrane is a strong candidate for applications in

$\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ lithium polymer batteries, which display a high coulombic efficiency of *ca.* 99%. It has been reported that the high surface energy of inorganic nanoparticles usually causes particle agglomeration and phase separation in polymer matrices.^{330,331} Surface modification of inorganic nanoparticles is an efficient way to improve their dispersibility and affinity with organic compounds. Walkowiak *et al.*³³² prepared various surface-modified forms of SiO_2 with vinylene, glycidyl, mercapto, chloropropyl, octyl, methacryl and amino functional groups. These modified SiO_2 fillers caused an increase in the specific conductivity of a gel by about two orders of magnitude (close to $10^{-2} \text{ S cm}^{-1}$ at 20°C) compared with a gel with unmodified SiO_2 . In a case in which bifunctional (hydrophilic/hydrophobic) SiO_2 was used as a filler, not only the conductivity but also the interfacial stability between lithium and the GPE were significantly improved.³³³ Li *et al.*³³⁴ studied the effects of fluorinated SiO_2 nanoparticles on the thermal and electrochemical properties of a composite PP nonwoven/P(VDF-HFP) separator. The incorporation of fluorinated SiO_2 led to an improvement in pore distribution, a high electrolyte uptake of 280 wt%, and a high ionic conductivity of $1.9 \times 10^{-3} \text{ S cm}^{-1}$. $\text{LiFePO}_4/\text{Li}$ cells that were assembled with these composite separators displayed remarkable C-rate performance, which indicated an enhancement in their chemical stability and discharge capacity. Liao *et al.*³³⁵ reported that SiO_2 and Al_2O_3 can be used as anti-thermal shrinkable nanoparticles in GPEs based on P(MMA-AN-VAc) and incorporated with an ionic liquid (PYR_{14}) and LiTFSI salt.

Li *et al.*³³⁶ disclosed that Al_2O_3 nanoparticles played the role of a solid plasticizer in a polymer matrix by reducing the degree of crystallization of the polymer matrix. The addition of Al_2O_3 nanoparticles to a P(VDF-HFP) matrix can also weaken the interaction between Li^+ ions and F atoms of the polymer units.³³⁷ However, an excess of Al_2O_3 nanoparticles leads to micro-phase separation between the polymer matrix and the filler and reduces both the ionic conductivity and the lithium ion transference number. The optimal amount of Al_2O_3 nanoparticles in a P(VDF-HFP) polymer matrix is reported to be 10 wt%, at which the ionic conductivity is $1.95 \times 10^{-3} \text{ S cm}^{-1}$ and the lithium ion transference number is 0.73. Hwang *et al.*³³⁸ studied the effect of $\alpha\text{-Al}_2\text{O}_3$ on the properties of PAN-based GPEs. The conductivity of PAN/ $\alpha\text{-Al}_2\text{O}_3$ nanocomposite films was inversely proportional to the size of the $\alpha\text{-Al}_2\text{O}_3$ particles and directly proportional to the amount of $\alpha\text{-Al}_2\text{O}_3$. The addition of $\alpha\text{-Al}_2\text{O}_3$ to the PAN electrolyte increased not only the ionic conductivity but also the electrochemical stability. It has been reported that the addition of fillers with Lewis acid surface groups usually leads to a reduction in ion pairing and therefore to an increase in conductivity.²¹⁵ Stolarska *et al.*³³⁹ prepared acidic Al_2O_3 by impregnating particles with aqueous solutions of sulphuric acid. When the modified Al_2O_3 was used as a filler in GPEs based on P(VDF-HFP), not only the ionic conductivity but also the interfacial stability and lithium transference number were increased. The Li^+ transference number increased with the fraction of acidic surface groups.

Kim *et al.*³⁴⁰ studied the effect of nanoscale TiO_2 (anatase) on the physical and electrochemical properties of GPEs based on

P(VDF-HFP). The liquid uptake, ionic conductivity, electrochemical stability and compatibility with lithium electrodes all improved upon incorporating the TiO_2 nanoparticles. The GPEs also exhibited much lower interfacial resistance between the polymer electrolyte and lithium metal electrode owing to the solid solvent role of the TiO_2 filler. When rutile TiO_2 nanoparticles were used as a filler, the transport properties of GPEs were greatly improved owing to the effective ion transport that was assisted by rutile TiO_2 .³⁴¹ In addition, the porous structure of polymer membranes has also been reported to be influenced by the TiO_2 content.³⁰⁵ Sarnowska *et al.*³⁴² studied the effect of micron-sized TiO_2 and Al_2O_3 fillers, both pure and modified with 4% H_2SO_4 , on the properties of gel electrolytes based on a P(VDF-HFP) polymer matrix. The Li^+ transference number increased upon the addition of the filler and increased with an increase in the fraction of acidic surface groups. In order to overcome the aggregation of TiO_2 nanoparticles in the polymer matrix, PMMA was grafted onto the surface of nano-sized TiO_2 particles to form a TiO_2 -PMMA nanohybrid.³⁴³ The nanocrystalline TiO_2 -PMMA hybrid can be well dispersed in a P(VDF-HFP) matrix and enhances a GPE membrane based on P(VDF-HFP) in terms of pore distribution, electrolyte uptake and ionic conductivity. An optimized GPE displayed an electrolyte uptake of up to 280 wt% and an ionic conductivity of $2.77 \times 10^{-3} \text{ S cm}^{-1}$ at room temperature (25°C), as well as high electrochemical stability up to 4.5 V (vs. Li/Li^+). More importantly, LiCoO_2/Li cells containing these GPEs exhibited good C-rate performance.

Stephan *et al.*¹³ first prepared and studied the electrochemical properties of composite polymer electrolytes based on P(VDF-HFP) incorporated with aluminum oxyhydroxide ($\text{AlO}[\text{OH}]_n$). The incorporation of $\text{AlO}[\text{OH}]_n$ as an inert filler not only reduces the crystallinity of the polymer matrix and acts as a 'solid plasticizer' that is capable of enhancing the transport properties, but also provides better interfacial properties towards a lithium metal anode. Aravindan *et al.*¹⁴² reported that the incorporation of 10% $\text{AlO}(\text{OH})_n$ in a polymer membrane resulted in a significant enhancement in its mechanical stability. They proposed that a Lewis acid-base interaction between the OH^- groups of $\text{AlO}(\text{OH})_n$ and the F atoms of the P(VDF-HFP) polymer promotes the dissociation of salts, which results in a larger number of mobile charge carriers for the transport of Li^+ ions, thereby increasing the ionic conductivity. Prosini *et al.*³⁴⁴ have studied the influence of different fillers on the compatibilities of intrinsically porous P(VDF-HFP) separators toward electrodes. Freestanding separators based on $\gamma\text{-LiAlO}_2$ exhibited good anode stability, whereas separators based on Al_2O_3 displayed good cathode stability. A MgO -based separator displayed the best anode and cathode compatibilities, and exhibited an ionic conductivity of about $4 \times 10^{-4} \text{ S cm}^{-1}$ after activation with a liquid electrolyte. Subramania *et al.*³⁴⁵ reported that a polymer electrolyte membrane based on P(VDF-HFP) incorporating ZrO_2 as a filler exhibited high ionic conductivity ($1.104 \times 10^{-2} \text{ S cm}^{-1}$ at room temperature), a high lithium transference number (0.942), good compatibility with electrode materials ($\text{carbon}/\text{LiMg}_{0.10}\text{Mn}_{1.90}\text{O}_4$), and a high discharge capacity (135 mA h g^{-1}).

The addition of montmorillonite clay to PMMA/LiClO₄/EC + PC GPEs led to a maximum ionic conductivity of 8×10^{-4} S cm⁻¹ at a clay content of 1.5 wt%, an increase in the glass transition temperature, and stable lithium interfacial resistance.²³⁷ Hwang *et al.*^{346,347} prepared a series of nanocomposite gel electrolyte materials comprising PAN or PVDF matrices, organophilic clay, a PC/EC cosolvent, and LiClO₄. The addition of organophilic clay enhanced the dimensional stability, electrochemical stability and plasticizer-maintaining ability of polymer electrolyte films. The nanocomposite electrolyte displayed a maximum ionic conductivity of up to 10^{-2} S cm⁻¹. Xiao *et al.*³⁴⁸ prepared modified carbon nanotubes (m-CNTs) by interactions between nitric and sulfuric acids and CNTs, and used them as additives in polymer electrolytes based on P(VDF-HFP). A GPE membrane doped with 2.2 wt% m-CNTs exhibited a high decomposition temperature of up to 450 °C, an electrochemical working window of 5.4 V (vs. Li/Li⁺), and an ionic conductivity of 4.88×10^{-3} S cm⁻¹ at room temperature. Cellulose nanocrystals (CNCs) have been employed to improve the mechanical properties of GPEs. Kelley *et al.*³⁴⁹ reported that the incorporation of CNCs increased the tensile modulus and tensile strength of a P(VDF-HFP) membrane.

5. Conclusions

The polymer electrolyte is the key component in lithium polymer batteries and serves as both the separator and the electrolyte. To be successfully used as a lithium polymer electrolyte, a polymer electrolyte should possess certain properties, namely, an ionic conductivity that approaches 10^{-4} S cm⁻¹ at ambient temperature, a Li⁺ transference number that is close to unity, great mechanical strength, an electrochemical window up to 4–5 V vs. Li/Li⁺, and excellent chemical and thermal stability.

A solid polymer electrolyte (SPE) comprising a polymer matrix and a lithium salt is also called a dry-SPE. Dry-SPEs usually possess very low ionic conductivity at ambient temperature, which excludes them from practical applications. The most commonly used approaches to increase the ionic conductivity of dry-SPEs are the modification of the polymer matrix by copolymerization, crosslinking, blending, *etc.* The ionic conductivity can be increased by 1–2 orders of magnitude with modified polymer matrices. The attempt to increase the ionic conductivity of dry-SPEs by increasing the salt concentration (in excess of 50 wt% salt) leads us into the area of polymer-in-salt electrolytes. An ionic conductivity of up to 10^{-4} S cm⁻¹ at ambient temperature could be achieved. Ion transport in polymer-in-salt systems is considered to be associated with a high degree of ionic aggregation in the polymer-in-salt electrolyte. An SPE composed of a polymer matrix and a lithium salt is a so-called bi-ionic conductor. In bi-ionic conductors, the migration of anions toward the anode causes serious concentration polarization. The immobilization of anions in the polymer is the most common approach for creating a single-ion conductor. However, the ionic conductivities of single-ion conducting polymer electrolytes are generally lower than those of dual-ion conducting systems because of the decreased number of mobile carrier ions. In recent years, an alternative

method has been employed, in which an anion receptor is introduced into electrolytes to increase their ionic conductivity and/or cation transference number. In these systems, although anions are trapped by an anion receptor, the interaction between the anion and anion receptor promotes the further dissociation of lithium salts, which might lead to an increase in both ionic conductivity and Li⁺ transference number at the same time.

The properties of the lithium salt affect the performance of rechargeable lithium polymer batteries. In the field of the development of new types of lithium salts, borate salts, phosphate salts, functionalized sulfonate and imide salts, dilithium salts, *etc.* have been investigated and displayed excellent properties when employed in polymer electrolytes. In the future, the ideal lithium salt should be inexpensive, easy to prepare and environmentally friendly. It should also fulfill the electrochemical requirements.

The strategy of adding inorganic fillers to SPEs is a very effective way of increasing the ionic conductivity as well as the mechanical and electrochemical stability of SPEs. Ceramic fillers play the roles of crosslinking centers and centers of Lewis acid–base interactions, thus influencing the conductivity of composite systems. Fillers can be inert or active ceramic materials, carbon materials, or cellulose, *etc.* However, the high surface energy of inorganic nanoparticles usually causes particle agglomeration and phase separation in polymer matrices, especially with nano-sized fillers. The surface modification of inorganic nanoparticles is very effective for improving their dispersibility and affinity with organic compounds.

Gel polymer electrolytes (GPEs) are obtained by incorporating a certain amount of a liquid plasticizer and/or solvent into the polymer–salt system. Plasticizers can be low-molar-mass organics, organic solvents or ionic liquids (ILs). Among these, ionic liquids are a very promising type of plasticizer owing to their inherent properties: high chemical and thermal stability, non-flammability, negligible volatility, and especially high electrochemical stability and hydrophobicity. Recently, a polymeric lithium salt combined with an IL exhibited an ionic conductivity higher than 10^{-4} S cm⁻¹ at room temperature. GPEs based on polymeric ionic liquids (PILs) exhibit high conductivity of lithium ions, high electrochemical stability and good interfacial stability toward lithium metal, which makes them very promising polymer electrolytes for applications in lithium metal batteries. Several approaches have been used to prepare these GPEs, including casting methods, *in situ* polymerization methods, extraction–activation methods, phase inversion methods, electrospinning technology, and foaming technology, *etc.* In the preparation of a porous polymer membrane, the porosity, pore size, and thickness of the membrane and its ability to hold a liquid electrolyte are properties that need to be taken into consideration. Although the ionic conductivity of GPEs is generally of the order of 10^{-3} S cm⁻¹, their low mechanical strength and poor interfacial properties are still obstacles to their application in commercial lithium polymer batteries. In addition to chemical or physical crosslinking of the system and physical support by polyolefin

membranes, another efficient way to improve the mechanical strength, as well as the transport properties and electrochemical properties, is the addition of inorganic fillers. In these composite GPEs, Li^+ transfer predominantly occurs in space charge layers at the boundaries of ceramic grains dispersed in liquid electrolytes.

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