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Polymer Electrolytes: State of the Art

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Polymers are defined as large molecules or macromolecules, which consist of repeated subunits. The polymers may be synthetic plastics or natural biopolymers such as protein, DNA, and so on. In the past 20 years, polymers have been tailored as electron or ion conductors. When appropriate salt is added into some polymers, their ionic conductivity can be improved to the value that can be used as electrolyte. In the past three decades, many researchers have endeavored to develop new polymer electrolytes (PEs) due to their potential application in electrochemical/electrical power generation, storage, and conversion systems. As a result, a lot of new PEs have been found, characterized, and tried to be applied in electrochemical/electrical devices. Particularly, Li ion-conductive PEs have been of interest for application in Li batteries due to their high energy density. In this chapter, the state-of-the-art development of Li ion-conductive PEs is described.

1.1 Introduction

PE was first introduced in 1973 [1]. Since then, the research on PE has been eagerly performed by many researchers, especially in the early 1980s, due to the recognition of PEs in industrial applications.

PE is a membrane composed of salts dissolved in a polymer [2]. Some polymer matrixes such as polyethylene oxide (PEO) and poly(methyl methacrylate) (PMMA) can dissolve salts and form salt-polymer complexes due to the interaction between oxygen atom in the polymer chain and cation in the salt. This solvent-free and ion-conductive system has been expected to be widely applied in electrochemical devices like rechargeable solid-state batteries, especially rechargeable Li ion batteries. In recent years, PEs have other prospective applications in advanced electrochemical, electrochromic, and electronic devices such as fuel cells, supercapacitors, electrochemical sensors, analog memory devices, and electrochromic windows [3–7]. Figure 1.1 shows the structure of commercial Li ion batteries using graphite and LiCoO_2 as an anode and cathode, respectively. Li ions only exist in the cathode side when the batteries are constructed. The Li

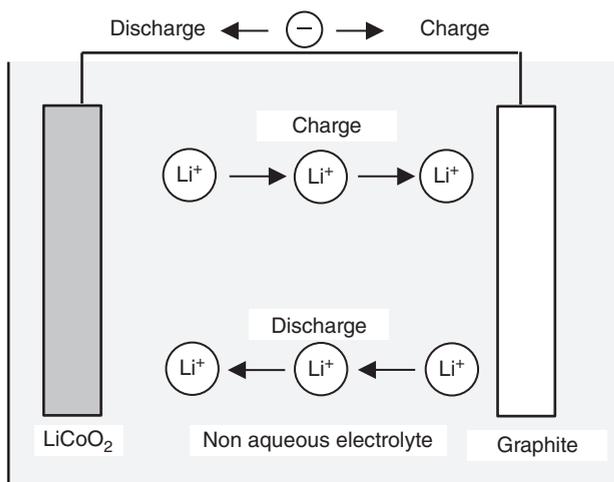


Figure 1.1 Li battery.

ions move from cathode to anode in a charge process. In a discharge process, Li ions migrate to the opposite direction. The electrolyte does not get involved in battery reactions in the Li batteries and just acts as Li ion-conductive media. In general, the electrodes of Li batteries are prepared by mixing three components, i.e. active material, binder, and conductive material. Poly(vinylidene fluoride) (PVdF) has been used as a binder thus far. As a conductive material, acetylene black and Ketjen black have been normally employed. These three components are mixed and added into a solvent *N*-methyl-2-pyrrolidone (NMP) to make a slurry. The slurry is painted onto Cu (for anode) or Al (for cathode) foil, which is used as a current collector. As for the electrolytes, nonaqueous electrolytes have been used so far due to narrow electrochemical window of aqueous electrolytes. The nonaqueous electrolytes are composed of Li salt (usually LiPF_6) dissolved into organic solvents, which are a mixture of acyclic solvent with low viscosity like dimethyl carbonate (DMC) and ethyl methyl carbonate (EMC) and cyclic solvent with high dielectric constant like ethylene carbonate (EC). However, flammability of these nonaqueous organic solvents sometimes has caused serious safety issues such as fire hazard and leakage of electrolyte [8–10]. Contrary to the nonaqueous electrolytes, solid polymer electrolytes (SPEs) can solve the issue of leakage. Additionally, PEs possess much lower flammability than the organic electrolytes due to low vapor pressure. The PEs should have the following physical, chemical, and electrochemical properties [11]:

- (1) High ionic conductivity at operating temperature (normally room temperature), while electronic conductivity can be negligible.
- (2) Sufficient mechanical strength at the operating temperature for self-supported cell.
- (3) High electrochemical decomposition voltage (wide electrochemical window).
- (4) High cationic or anionic transference number.

- (5) Environmental benign, non-hygroscopic, low cost, and ease of preparation.
- (6) Stability against chemical and electrochemical reactions with both electrodes (cathode and anode) during preparation and operation of the battery.
- (7) Thermal expansion coefficient matches with that of the electrodes to ensure good contacts between PE and electrodes.

Table 1.1 summarizes a comparison of properties of conventional nonaqueous electrolyte and PE. Ceramic electrolyte, which is another type of solid electrolyte, is also compared. The ceramic electrolytes possess excellent safety due to their nonflammable nature although structural flexibility is very low and conductivity is low because of high grain boundary resistance. PEs normally possess high conductivity and structural flexibility as well as relatively wide electrochemical window.

PEs can be categorized into three groups based on their physical state and composition: (i) Solid polymer electrolyte (SPE), (ii) gel polymer electrolyte (GPE), and (iii) composite polymer electrolyte (CPE) [12, 13]. Also, PEs can be divided into two groups by polymer source, i.e. synthetic polymer and natural polymer (Figure 1.2). Synthetic polymers such as PEO and polycarbonate have been used as polymer matrix. Natural polymers like chitosan are usually low cost, eco-friendly, biodegradable, and abundant. Therefore, researches on natural polymer for PEs have been eagerly performed in recent years.

Table 1.1 Comparison of various properties among nonaqueous, polymer, and ceramics electrolytes.

	Nonaqueous electrolyte	Polymer electrolyte	Ceramics electrolyte
Conductivity	High	Middle	Low
Safety	Low	High	High
Structural flexibility	Middle	High	Low
Electrochemical window	Middle	Middle	Wide

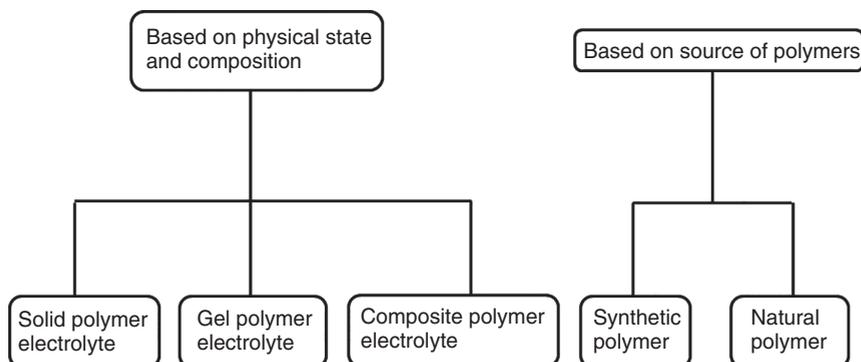


Figure 1.2 Classification of polymer electrolytes.

1.2 Solid Polymer Electrolyte

SPE is composed of host polymer matrix(es) and Li salts. The salts are dissolved into the polymer matrix(es) and provide ionic conduction. The research on SPEs commenced three decades ago [14]. The PEO-based SPE was investigated first and has been most widely researched so far [1]. The ether oxygen atoms in the PEO matrix complex with Li ion [15] and dissolve the Li salts. It is widely believed that the cation transport is related to the complexing segmental motion of PEO chain [16, 17] (Figure 1.3). Other polymer hosts such as PVdF, poly(vinylidene fluoride–hexafluoropropylene) (PVdF–HFP), PMMA, poly(vinyl chloride) (PVC), poly(acrylonitrile) (PAN), poly(acrylic acid) (PAA), poly(ethyl methacrylate) (PEMA), and so on also contain oxygen, nitrogen, chlorine, or fluorine atom, which can form a complex with Li ion, and the segmental motion would cause ion conduction. Table 1.2 summarizes repeat unit of polymer

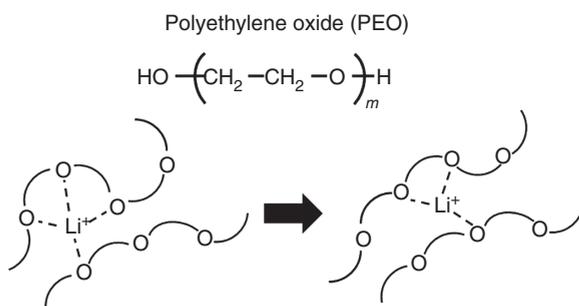
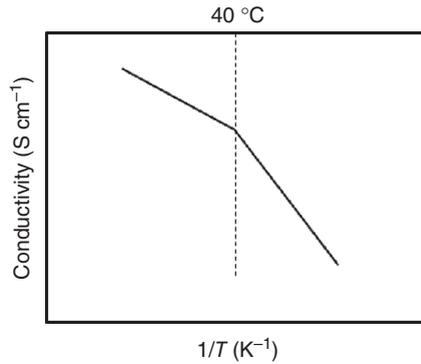


Figure 1.3 Segmental motion-assisted Li ion conduction in PEO-based polymer.

Table 1.2 Polymer host generally used in polymer electrolytes.

Polymer host	Repeat unit	Example of polymer electrolyte	Ionic conductivity at room temperature (S cm^{-1})	References
PEO	$-(\text{CH}_2\text{CH}_2\text{O})_n-$	(PEO-HBP)–LiTFSI– BaTiO_3	2.6×10^{-4}	[18]
PVdF	$-(\text{CH}_2\text{CF}_2)_n-$	PVdF–PEO–LiTFSI	5.4×10^{-4}	[19]
PVdF–HFP	$-[(\text{CH}_2\text{CF}_2) - (\text{CF}_2\text{CFCF}_3)]_n-$	P(VdF–HFP– SiO_2 –LiTFSI)	4.3×10^{-3}	[20]
PMMA	$-[(\text{CH}_2\text{C}(-\text{CH}_3) - \text{COOCH}_3)]_n-$	PMMA– LiClO_4 –DMP– CeO_2	7.3×10^{-6}	[21]
PVC	$-(\text{CH}_2\text{CHCl})_n-$	PVC– $\text{Li}_2\text{B}_4\text{O}_7$ –DBP	2.83×10^{-6}	[22]
PAN	$-[\text{CH}_2\text{CH}(-\text{CN})]_n-$	PAN– LiClO_4 – Al_2O_3	5.7×10^{-4}	[23]
PAA	$-[\text{CH}_2\text{CH}(-\text{COOH})]_n-$	PAA– LiClO_4 – Sb_2O_3	2.15×10^{-4}	[24]
PEMA	$-[(\text{CH}_2\text{C}(-\text{CH}_3) - \text{COOCH}_2\text{CH}_3)]_n-$	PEMA–LiTf–IL	1.17×10^{-4}	[25]

Figure 1.4 Schematic Arrhenius plot of PEO–LiClO₄ polymer electrolyte.



hosts and examples of PEs. The structural flexibility directly relates to the ionic conductivity. In other words, the amorphous phase in the SPEs supports ionic conduction. The continuous segmental motion of the amorphous chain occurs above the glass transition temperature (T_g) [26]. T_g of the PEs should be lower than room temperature. Moreover, increase in the amorphous regions with raised temperature improves the ionic conductivity. Figure 1.4 depicts a schematic Arrhenius plot of PEO–polystyrene (PSt)-LiClO₄ PE [27]. An inflection point around 40 °C can be observed in this plot. This corresponds to a phase transition from crystalline to amorphous phase of the polymer host. Due to the phase transition, the activation energy of ionic conduction is lowered considerably. However, mechanical strength of the SPE system is related to the movement of polymer chain. Increase in the amorphous regions implies that the polymer chains move actively, which enhances the ionic conductivity, but decreases the mechanical strength. This adverse effect leads to difficulty in construction of self-supported polymer batteries.

In order to solve this problem, many efforts have been devoted to develop novel polymer matrixes containing amorphous state, including blending of polymers, cross-linking, copolymerization, and so on. These approaches can lower crystallinity or T_g of the SPE systems and increase the ionic conductivity and mechanical strength [28–30].

Blend PEs are prepared by mixing two or more kinds of molecular chains (Figure 1.5). The chains are mixed with/without any chemical bonding between them. This blended polymer chain destroys the regularity of one polymer chain and prevents its rearrangement, resulting in formation of amorphous structure. Tanaka et al. prepared a polymer blend comprising of PEO and polyethylene imine (PEI). The ionic conductivity of [(8 : 2) PEO/PEI]–LiClO₄ was $\sim 10^{-4}$ S cm⁻¹ at 30 °C [31]. This high ionic conductivity is considered to

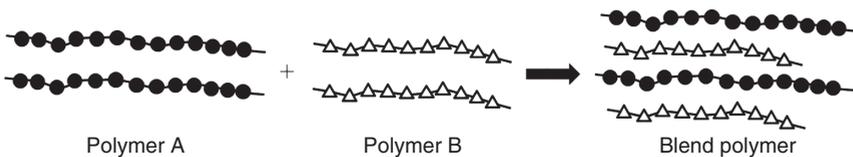


Figure 1.5 Schematic image of blend polymer.

be due to mixing of PEO with PEI that hindered their crystallization and led to more useful matrices.

Block copolymer electrolytes (BCEs) have been proposed as a novel SPE to satisfy both the ionic conductivity and the mechanical strength [32]. The most common structures researched are the diblock and triblock copolymers. A lithium salt-solvating polymer is used to ensure continuous ionic conduction pathways, and another polymer host, which forms a polymer framework of the SPEs, is chosen to provide the mechanical strength to the SPEs [33]. Polymer films with good mechanical strength can be obtained without sacrificing the ionic conductivity. Thus, a balance of the salt-solvating polymer and the framework polymer is important. Niitani et al. reported novel PSt–poly(ethylene glycol) (PEG) methyl ether methacrylate (PME)–PSt–LiClO₄ triblock copolymers (Figure 1.6) [34, 35]. The triblock SPE exhibited high ionic conductivity of $2.0 \times 10^{-4} \text{ S cm}^{-1}$ without plasticizer. The PSt block was used to improve mechanical properties, while the PEO moiety increased the ionic conductivity. An all-solid-state battery of LiCoO₂/SPE/Li cell demonstrated excellent charge–discharge property at room temperature. This concept can also increase Li ion transference number. Bouchet et al. reported a single-ion PE based on poly[lithium 4-styrenesulfonyl(trifluoromethylsulfonyl) imide] [P(STFSILi)–PEO–P(STFSILi)] polyanionic triblock copolymers [36]. This material demonstrated high Li ion transference number (>0.85), excellent mechanical strength, and good ionic conductivity ($1.3 \times 10^{-5} \text{ S cm}^{-1}$ at 60 °C). The battery tests exhibited good power and cycling performances at 60 °C.

Cross-linking PEs show good ionic conductivity at ambient temperature and fully amorphous feature (Figure 1.7) [37]. However, the cross-linking polymer generally exhibits low elasticity and brittleness as well as low processability [38]. A cross-linked high molecular weight poly(oxyethylene) has been reported as a

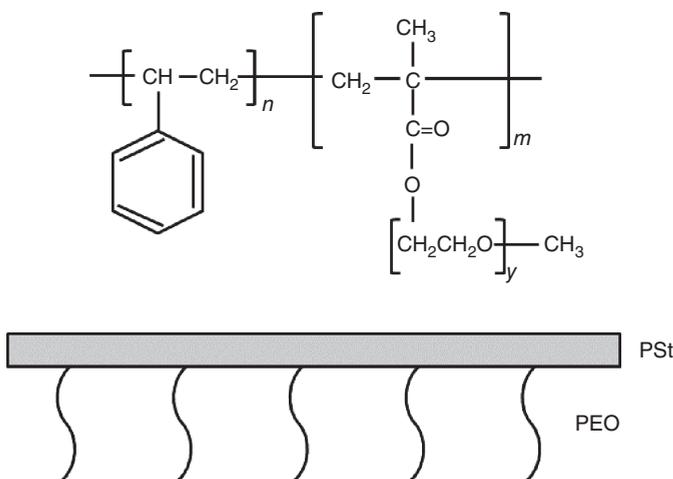


Figure 1.6 Schematic image of novel nanostructure-controlled SPE and its synthetic scheme.

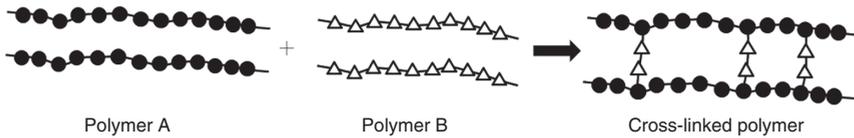


Figure 1.7 Schematic image of the cross-linked polymer.

new SPE, which demonstrated favorable ionic conductivity and good mechanical strength [39].

Copolymer is a polymer prepared from at least two different types of monomers. PVdF-HFP is the most common copolymer researched as PE. The PVdF-HFP copolymer is prepared by copolymerization of PVdF and HFP (Figure 1.8). The copolymer exhibits better features compared with the mono-polymers alone, which could be attributed to the synergistic effects in the combined structure. Also, PVdF has received much attention due to good electrochemical stability and high dielectric constant [40, 41]. The presence of strong electron-withdrawing fluorine atoms (C–F) promotes dissociation of salts and increases the concentration of charge carriers, leading to high ionic conductivity. Jiang et al. reported ionic conductivity of PVdF-based SPEs of above 10^{-4} S cm^{-1} at room temperature [41].

Other polymer hosts also have been researched. The potential of PMMA as a polymer host was reported by Iijima et al [42]. The PMMA-based SPEs showed low mechanical integrity and high brittleness [43]. Blending of PMMA with PVC has also been researched [44, 45]. PVC is also an attractive polymer host due to its low cost and easy processing. GPEs based on PVC with plasticizers have been widely researched. Poly(vinyl alcohol) (PVA) is nontoxic and cost effective and possess good tensile strength, good mechanical strength, good optical properties, high temperature resistance, high abrasion resistance, good flexibility, biocompatibilities, high hydrophilicity, and excellent chemical and thermal stabilities [46–50]. PVA contains a large amount of polar hydroxyl group, leading to high hydrophilicity. This provides other advantages like ease in preparation and high dielectric constant. Due to these superior properties, PVA has received considerable research interest as electrolytes for fuel cells and electrical double layer capacitors [51]. A PAN-based PE has some outstanding characteristics such as high thermal stability and high ionic conductivity [52]. PAN is superior over PVdF with respect to mechanical stability [53]. The –CN groups in PAN can interact with cations. Structures of these polymer hosts are shown in Figure 1.9.

Additionally, natural polymer such as chitosan [54], rice starch [55], and corn starch [56] has also been studied. These have an advantage as novel polymer hosts due to being low cost, biodegradable, eco-friendly, and abundant.

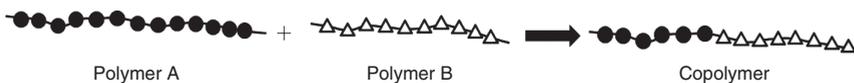


Figure 1.8 Schematic image of the copolymer.

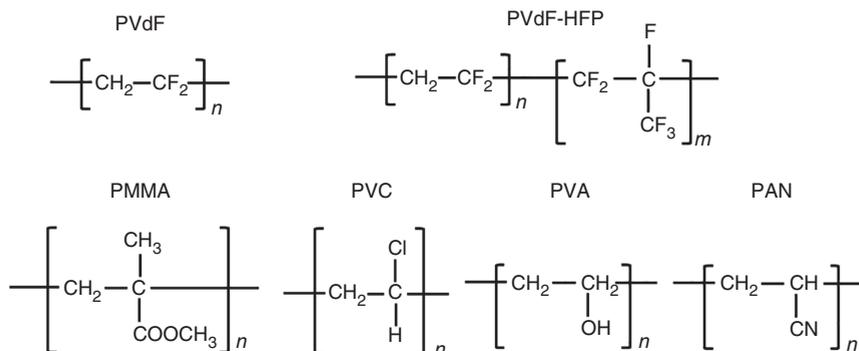


Figure 1.9 Structure of polymer hosts.

1.3 Gel Polymer Electrolyte

GPE is also known as plasticized PE, which was first introduced by Feuillade and Perche in 1975 [57]. GPE contains a plasticizer or gelled polymer matrix, which is swollen by addition of the plasticizers [58], and can be prepared by simply heating a mixture of polymer and Li salt with solvent. By introducing a plasticizer and/or solvent, the ion transport is not dominated by the segmental motion of polymer chains but occurs in the swollen gelled phase or liquid phase. In general, when the polymer is composed of interconnected micropores, the ionic conductivity of GPEs mainly depends on the properties of trapped liquid electrolyte. On the contrary, ion transport mainly occurs in the swollen gelled phase if the polymer does not contain many interconnected pores. The GPEs should possess good mechanical strength, capability of holding a liquid electrolyte, high ionic conductivity, and electrochemical stability toward both cathode and anode. Many kinds of polymer matrix such as PEO [59], PMMA [60], PAN [61], PVC [62], PVdF [63], and P(VdF-HFP) copolymer [64] have been widely studied as a framework for GPEs.

Plasticizers, which are usually low molar-mass organics, organic solvents, or ionic liquids (ILs), largely affect the properties of GPEs. A plasticizer can increase the content of the amorphous phase in a PE and promote segmental motion [65]. In addition, it can also promote dissociation of ion pairs. As a result, the number of charge carriers is increased, leading to enhanced ionic conductivity [59]. PEG has been widely used as a low molar-mass plasticizer. It was reported that the ionic conductivity of PEO-LiCF₃SO₃ complex increased with the decrease of molecular weight of PEG and with the increase of PEG content [66]. However, the hydroxyl end groups in PEG react with electrode materials such as lithium metal. Therefore, various modified forms of PEG were synthesized by replacing active oxygen atoms in PEG with monomethoxy (MMPEG), dimethoxy (DMPEG) groups, or lithium (LPEG) ions [67]. The LPEG plasticizer can improve the compatibility of the PE with lithium metal anode [13]. On the contrary, in some polymer systems such as PEO-PMMA, no significant improvement of ionic conductivity by addition of PEG was reported. The plasticizer must be chosen carefully depending on the polymer host used. Other low molar-mass

plasticizers such as polyethylene glycol dimethyl ether (PEGDME) [68], borate ester such as PEG borate ester [69], tris(2-(2-methoxyethoxy)ethyl) borate (B_2), and tris(2-(2-(2-methoxyethoxy)ethyl) borate (B_3) [70], phthalates such as dibutyl phthalate (DBP) [71], dimethyl phthalate (DMP) [65], dioctyl phthalate (DOP) [72], succinonitrile (SN) [73], and so on have also been studied. The ionic conductivity of the PEs containing these plasticizers is summarized in Table 1.3.

The organic solvents usually used as plasticizer are polar and nonvolatile solvents such as EC, propylene carbonate (PC), diethyl carbonate (DEC), and DMC. The solvents help to solvate ions and facilitate their transportation. Therefore, high dielectric constant and low viscosity are required for the solvents. Individual solvent is difficult to meet all the requirements; thus, a mixture of the solvents usually has been employed. The mixture of solvents is more efficient to enhance the ionic conductivity compared with a single solvent, which is due to the combined action of dielectric constant and viscosity [75]. The ionic conductivity of some GPEs using the plasticizers is tabulated in Table 1.4. The ionic conductivity can be increased to $\sim 10^{-3} \text{ S cm}^{-1}$ by the addition of suitable solvents. Choi et al. studied the ionic conductivity of PAN polymer swollen by 1 M LiPF_4 in EC/DMC (1 : 2 wt%), EC/DMC (1 : 1), EC/EMC (1 : 1), EC/DEC (1 : 1), and EC/DMC/DEC (1 : 1 : 1) [61]. The order of ionic conductivity was EC/DMC/DEC (1 : 1 : 1) > EC/DMC (1 : 1) > EC/EMC (1 : 1) > EC/DEC (1 : 1) > EC/DMC (2 : 1).

ILs have attracted considerable interest as a novel plasticizer. They are room temperature molten salts, which are composed of a bulky organic cation and a large delocalized inorganic anion. The ILs possess some unique properties such as high chemical and thermal stabilities, nonflammability, negligible volatility, and high electrochemical stability [83–85]. Due to these unique properties, the incorporation of room temperature ionic liquids (RTILs) into PEs can overcome inherent limitations of the ionic conductivity in SPEs as proposed by Passerini

Table 1.3 Ionic conductivity of various polymer electrolytes with plasticizers.

Polymer	Ionic conductivity (S cm^{-1})	Temperature ($^{\circ}\text{C}$)	References
(PEO) ₁₅ /LiTFSI/10 wt% PEGDME	$>10^{-3}$	50	[59]
(PEO) ₂₀ /LiCF ₃ SO ₃ /50 wt% PEGDME	1.2×10^{-4}	30	[68]
30 wt% PVA/10 wt% LiClO ₄ /60 wt% DMP	1.5×10^{-4}	29	[65]
17.5 wt% PVA+7.5 wt% PMMA/8 wt% LiClO ₄ /67 wt% DMP	6×10^{-5}	30	[74]
PEO/15 wt% LiCF ₃ SO ₃ /15 wt% PEG	1.7×10^{-5}	RT	[72]
PEO/15 wt% LiCF ₃ SO ₃ /20 wt% DOP	7.6×10^{-4}	RT	[72]
(PEO) ₂₀ /LiBOB/24 mol% SN	$>6 \times 10^{-4}$	60	[73]
PEO/13 wt% LiCF ₃ SO ₃ /10 wt% DBP	1.6×10^{-4}	27	[71]
(PEO) ₂₀ /LiTFSI/100 wt% PEG borate ester	1.36×10^{-5}	30	[69]
PSi/15 wt% LiCF ₃ SO ₃ /40 wt% borate ester B_2	3.70×10^{-5}	RT	[70]
PSi/15 wt% LiCF ₃ SO ₃ /40 wt% borate ester B_3	1.60×10^{-4}	RT	[70]

Table 1.4 Ionic conductivity of various polymer electrolytes with organic solvents.

Polymer	Ionic conductivity (S cm ⁻¹)	Temperature (°C)	References
P(VdF-HFP)/1.0 M LiPF ₆ /EC + DEC	1.0 × 10 ⁻³	RT	[76]
P(VdF-HFP)/1.0 M LiPF ₆ /EC + DMC + DEC	1.43 × 10 ⁻³	RT	[64]
PVdF/1.0 M LiPF ₆ /EC + DMC + DEC	1.0 × 10 ⁻³	RT	[77]
30 wt% PVC/8 wt% LiClO ₄ /62 wt% PC	6.70 × 10 ⁻⁶	30	[62]
PEO/15 wt% LiCF ₃ SO ₃ /20 wt% EC	8.12 × 10 ⁻⁵	RT	[78]
(PEO) ₁₆ /LiClO ₄ /40 wt% EC	2.67 × 10 ⁻⁴	RT	[79]
4.5 wt% PMMA/46.5 wt% LiClO ₄ /30 wt% PC + 19 wt% EC	5.0 × 10 ⁻⁴	RT	[80]
PAN/1 M LiPF ₆ /EC + DMC + DEC	>1.0 × 10 ⁻³	RT	[61]
PAN/1 M LiBF ₄ /EC + DEC	2.80 × 10 ⁻³	RT	[81]
PVdF/1.0 M LiPF ₆ /EC + DMC	1.00 × 10 ⁻³	RT	[63]
7.5 wt% PVC/5 wt% LiBF ₄ /42 wt% EC + 28 wt% PC	8.60 × 10 ⁻⁵	RT	[82]

et al. in 2003 [86]. Since then, many groups have devoted much effort to study GPEs containing ILs. Many types of IL comprising cations based on pyridium, imidazolium, piperidinium, quaternary ammonium, and so on and anions based on [BF₄]⁻, [PF₆]⁻, [N(CF₃SO₂)₂]⁻, [CF₃SO₃]⁻, [C₄F₉SO₃]⁻, [N(CN)₂]⁻, [CF₃CO₂]⁻, [CF₃CONCF₃SO₂]⁻, and so on have been investigated. In most cases, the ILs contain the same anion as salts such as IL containing [PF₆]⁻ anion in LiPF₆. This is because the solubility of the salt into the IL incorporating the same anion is much higher than in a system of different anions. Passerini et al. studied a series of ILs containing pyrrolidinium-based cations and TFSI anions [87–94]. The structure of *N*-alkyl-*N*-methyl-pyrrolidinium bis(trifluoromethanesulfonyl) imide (PYR_{1A}TFSI, A = C_{*n*}H_{2*n*+1}, 1 < *n* < 10) is depicted in Figure 1.10. The commonly used ILs for PEs are PYR₁₃TFSI (1-propyl-1-methylpyrrolidinium bis(fluorosulfonyl) imide) and PYR₁₄TFSI (1-butyl-1-methylpyrrolidinium bis(trifluorosulfonyl) imide). The ionic conductivity of PEO/LiTFSI/PYR₁₃TFSI PE is ~10⁻⁴ S cm⁻¹ at 20 °C, which is about two orders of magnitude higher than that without the IL [86]. It was reported that the PYR₁₃TFSI also improved the ionic conductivity of PVdF-based polymer. The GPE composed of P(VdF-HFP)/LiTFSI/PYR₁₃TFSI showed high ionic conductivity of 2.7 × 10⁻⁴ S cm⁻¹ [95]. Also, incorporation of PYR₁₄TFSI plasticizer into P(VdF-HFP)/LiTFSI PE showed a good ionic conductivity of 4.0 × 10⁻⁴ S cm⁻¹ and high thermal stability [96]. An interesting study was performed by Winter et al. [83, 84]. They conducted in situ UV photoradiation of a complex of PRO/LiTFSI/PYR₁₄TFSI using benzophenone as a cross-linking agent to obtain high conductive PEs with high mechanical properties.

ILs containing 1-alkyl-3-methylimidazolium cation have also been used as a plasticizer in GPEs. The structure of 1-alkyl-3-methylimidazolium

Figure 1.10 Structure of *N*-alkyl-*N*-methyl-pyrrolidinium bis(trifluoromethanesulfonyl) imide.

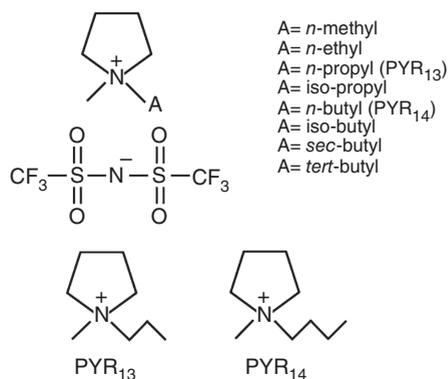
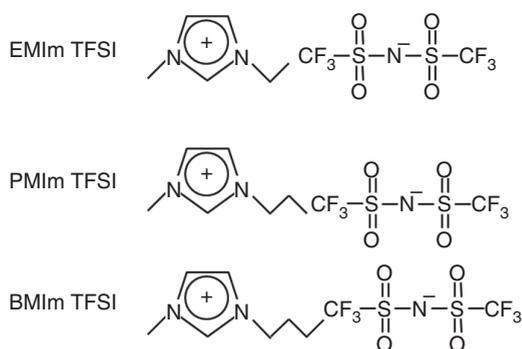


Figure 1.11 Structure of 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide.



bis(trifluoromethylsulfonyl) imide IL is depicted in Figure 1.11. The alkyl group in the cation affects the ionic conductivity of GPEs. EMImTFSI, PMImTFSI, and BMImTFSI were employed as plasticizers to form GPEs based on P(VdF-HFP) matrix [97]. All these GPEs revealed a high ionic conductivity in the range of 2.4×10^{-3} to $4.5 \times 10^{-3} \text{ S cm}^{-1}$. The GPE containing EMImTFSI showed the highest conductivity. Also, effects of anion on conductivity of PEO-based GPE were studied using ILs containing BMIm cation [98]. In the study, three different anions (TFSI^- , BF_4^- , and CF_3SO_3^-) and BMIm cation were employed. The PEO/LiTFSI/BMImTFSI electrolyte showed the highest ionic conductivity and good electrochemical stability [99].

As expected, compatibility between ILs and polymer is critical to determine the properties of GPEs. It was reported that quaternary ammonium-based ILs were more compatible than imidazolium-based ILs with PEO-PMMA copolymer [100]. This is thought to be due to preferable interaction between IL and polymer matrix.

The GPEs comprising polymeric lithium salts and ILs have been proposed as novel GPEs. Lithium poly(2-acrylamido-2-methyl propanesulfonate) (PAMPSLi, Figure 1.12) is used as the polymeric lithium salt. The PAMPSLi-PVdF copolymer was combined with 1-ethyl-3-methylimidazolium tricyanomethanide (EMImTCM). The ionic conductivity of PAMPSLi-PVdF

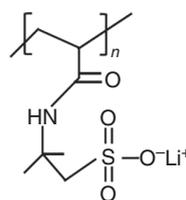


Figure 1.12 Structure of PAMPSLi.

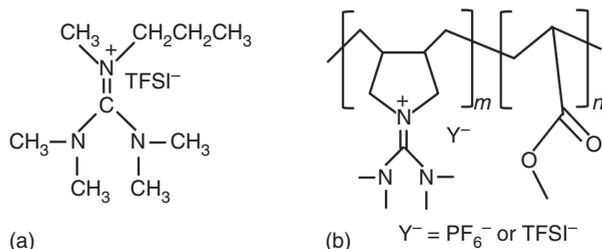


Figure 1.13 Structure of (a) guanidinium IL and (b) guanidinium-based PIL.

copolymer with EMImTCM IL was $5.43 \times 10^{-3} \text{ S cm}^{-1}$, which was four times higher than that of homopolymer system of PAMPSLi-PVdF [101].

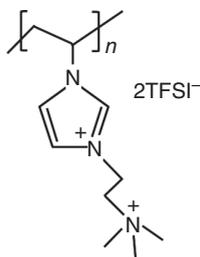


Figure 1.14 Structure of imidazolium-tetraalkylammonium-based PIL.

Also, polymeric ionic liquids (PILs) obtained by the polymerization of an IL monomer have attracted much attention as the polymer matrix in GPEs. The main advantages of the PIL-based GPEs are low flammability and high anodic stability. Guanidinium-based PILs containing different anions (PF_6^- and TFSI^-) were prepared by the polymerization of a guanidinium IL monomer with methyl acrylate (Figure 1.13). A quaternary GPE with a guanidinium PIL (matrix), a guanidinium IL, LiTFSI salt, and nano- SiO_2 particles showed high conductivity and wide electrochemical stability window [102]. Yin et al. synthesized a novel dicationic PIL and employed it for the GPE matrix (Figure 1.14) [103]. The novel GPE with dicationic PIL, poly(*N,N,N*-trimethyl-*N*-(1-vinylimidazolium-3-ethyl) ammonium bis(trifluoromethanesulfonyl)imide), 1,2-dimethyl-3-ethoxyethylimidazolium TFSI (IM(2o2)11TFSI) IL, and LiTFSI salt exhibited a low T_g (-54°C), high thermal stability (330°C), good ionic conductivity (about $10^{-4} \text{ S cm}^{-1}$ at $25\text{--}40^\circ\text{C}$), and high electrochemical stability. In another research using PIL, a less flammable GPE was prepared by the in situ polymerization of an IL monomer, 1-methyl-2-(2-acryloyloxyethyl)imidazolium tetrafluoroborate (MAHI- BF_4) [104].

1.4 Composite Polymer Electrolyte

CPEs were discovered in an attempt to overcome disadvantages and limitations of PEs. Generally, the CPEs are prepared by dispersing inorganic fillers such as insulative ceramic fillers (Al_2O_3 , SiO_2 , TiO_2 , etc.), ferroelectric ceramic fillers (BaTiO_3 , PbTiO_3 , LiNbO_3 , etc.), clay, carbon nanotubes (CNTs), and powder of fast ionic conductors into the polymer matrix [80, 105, 106], which can improve the mechanical properties and ionic conductivity of PEs [107–109]. Also, the fillers can increase the ionic conductivity by percolating interfacial effect, i.e. anions adsorb on the surface of fillers due to Lewis acid–base character and then

promote dissociation of ion pairs, leading to increase interfacial ionic conductivity. Another reason for improvement of ionic conductivity by the fillers is thought to be due to a reduction in the crystallinity of the polymer–salt system because the nanoparticles can reduce crystallinity [110–112]. Accordingly, particle size, content, and surface functional groups of fillers are critical factors to determine the properties of the CPEs.

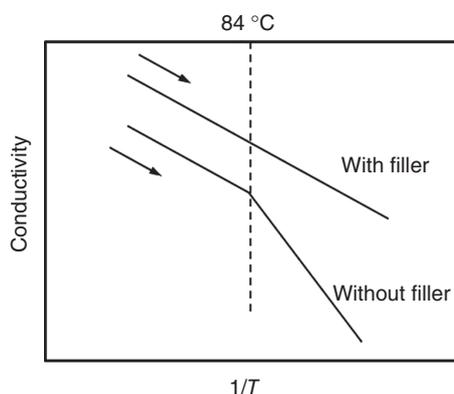
A novel PE that was PEO-based incorporated with inert ceramic fillers such as Al_2O_3 , TiO_2 , and SiO_2 was reported as a successful approach to enhance ionic conductivity [113, 114]. Figure 1.15 depicts an image of the Arrhenius plots of $\text{P}(\text{EO})_8\text{LiClO}_4 + 10 \text{ wt\%}$ ceramic nanoparticle electrolyte during cooling. In the filler-free electrolyte, an inflection point was observed around 84°C . This was attributed to the crystallization of PEO polymer. On the contrary, the inflection point did not appear in the electrolytes containing TiO_2 or SiO_2 filler. The fillers prevented the crystallization of PEO polymer and helped to keep high conductive amorphous phase. As a result, the filler containing PEO polymer exhibited high ionic conductivity.

The amorphous state of PEO polymer was stable over 60 days at 30°C by the addition of filler. The fillers stabilized the high conductive amorphous state at ambient temperature for a long time. Similar behavior was also observed in Al_2O_3 -added PEO- LiCF_3SO_3 composite electrolyte [72, 115].

The addition of fillers can also enhance the ionic conductivity of PEO-PVdF blend PE [116]. Yoon et al. fabricated a composite electrolyte based on PEO-PVdF- LiClO_4 -2 wt% silica aerogel. Highest conductivity of $1.7 \times 10^{-4} \text{ S cm}^{-1}$ was obtained at 30°C in the composite composed of PEO:PVdF = 3 : 1 and polymer:salt = 6 : 1. The ionic conductivity decreased with an increase of silica aerogel content owing to degradation of mobility caused by the aggregation of silica aerogel particles. The surface functional groups on the fillers affect properties of the CPEs. It was reported that addition of acid-modified nano- SiO_2 reduced the interfacial resistance and prevented dendrite formation of Li metal significantly [117].

Among the nanosized ceramic fillers, TiO_2 was thought to be the best candidate for the CPEs. Lin et al. studied the effects of particle size of TiO_2 on ion transport properties of PEO-based composite electrolytes [118]. It was

Figure 1.15 Arrhenius plots of the ionic conductivity of $\text{P}(\text{EO})_8\text{LiClO}_4$.



found that the ionic conductivity increased with a decrease in the particle size of TiO_2 . The conductivity of $1.40 \times 10^{-4} \text{ S cm}^{-1}$ was obtained for PEO–10 wt% LiClO_4 –5 wt% TiO_2 (3.7 nm) electrolyte. The transference number also increased from 0.21 to 0.51 by the addition of TiO_2 . This result indicated that nanosized TiO_2 particles in the PEO– LiClO_4 matrix formed a new pathway for Li ion transport. It is thought that TiO_2 – Li^+ interaction changed the Li ion environment and provided a fast Li ion-conducting pathway at the interface between the fillers and the polymer [119].

A highly conductive layer on the surface of filler particles is created by an interaction between the filler and cations. Therefore, ferroelectric ceramic fillers are expected to interact with the cations easily owing to the permanent dipole of the ferroelectric ceramic materials, resulting in enhancement in ionic conductivity [120]. Sun et al. studied electrochemical properties of composite electrolytes based on PEO, Li salts (LiClO_4 , LiBF_4 , LiCF_3SO_3 , and $\text{LiN}(\text{CF}_3\text{SO}_2)_2$), and ferroelectric ceramic materials (BaTiO_3 , PbTiO_3 , and LiNbO_3) [121]. The results showed that the ionic conductivity was greatly enhanced by only a small amount of ferroelectric filler addition. The highest ionic conductivity was obtained for 2 wt% ferroelectric BaTiO_3 addition. Also, it was found that the enhancement in ionic conductivity was affected by anions of the Li salt. The enhancement in conductivity was highest in ClO_4^- anion. On the contrary, no enhancement was observed in the composite with LiCF_3SO_3 salt. This enhancement of conductivity can be explained by the association tendency of anions with Li ions and the spontaneous polarization of the ferroelectric ceramics due to their particular crystal structure.

The usage of layered clays such as montmorillonite (MMT) and hecrite as fillers has also been reported [122, 123]. The layered clay can contain cations due to intercalation reaction. It was reported that the ionic conductivity of PEO–LiTFSI composite containing 10 wt% MMT was 3.22×10^{-4} and $2.75 \times 10^{-5} \text{ S cm}^{-1}$ at 60 and 25 °C, respectively [124]. Li-intercalated clay (bentonite) also increased the ionic conductivity about one order of magnitude when it was incorporated into PEO-based PE [125]. CNT has also been researched as fillers to enhance the ionic conductivity of PEs. The strong affinity between CNT's electron cloud and cation promotes salt dissociation, resulting in high conductivity. However, compositing CNTs with the PE may enhance the electronic conductivity due to high electronic conductivity of CNTs. Therefore, Tang et al. prepared CNT packaged in insulating clay for nanofiller. This hybrid nanofiller can block electron conduction in CNT and eliminate the risk of increased electronic conductivity of CPEs. This hybrid filler could increase the ionic conductivity of PEO– LiClO_4 electrolyte (Figure 1.16) [126]. The highest conductivity was obtained for PEO– LiClO_4 containing 10 wt% clay–CNT hybrid filler.

Inorganic ceramic solid electrolytes, namely, fast ceramic ionic conductors, are also considered as promising fillers because it can provide another pathway for ionic transport (Figure 1.17).

The CPEs with many Na superionic conductor (NASICON) type ionic conductors with the general formula of $\text{LiM}_2(\text{PO}_4)_3$ ($M = \text{Ti, Ge, Sr, Zr, Sn, etc.}$) (Figure 1.18) have been investigated in the past decade [127]. Among the

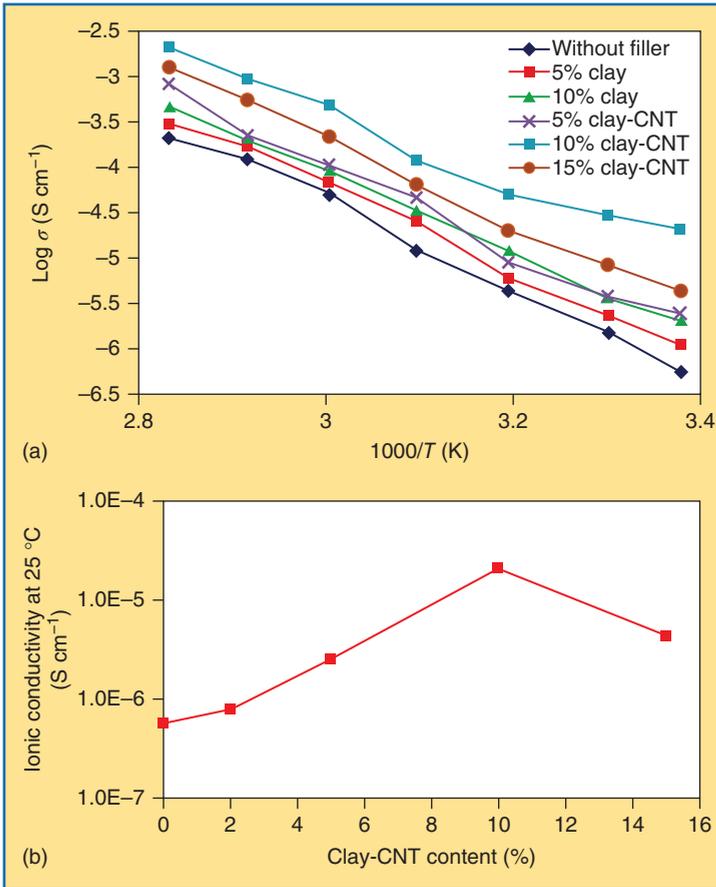


Figure 1.16 (a) Ionic conductivity of PEO-based composite electrolytes and (b) ionic conductivity of PEO-based composite electrolyte with various contents of the hybrid filler.

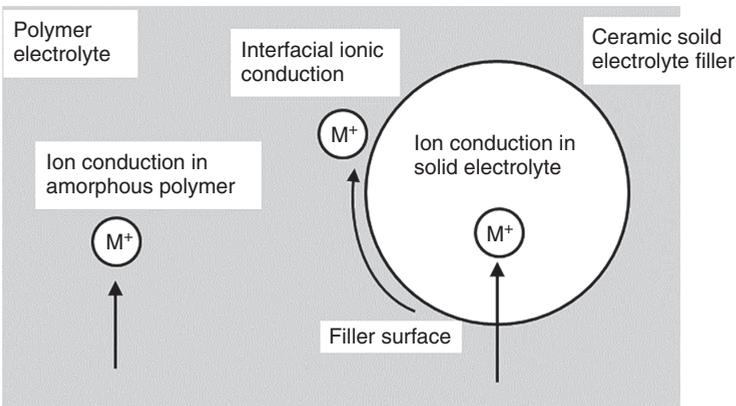


Figure 1.17 Three conduction pathway in composite electrolyte with inorganic solid electrolyte filler.

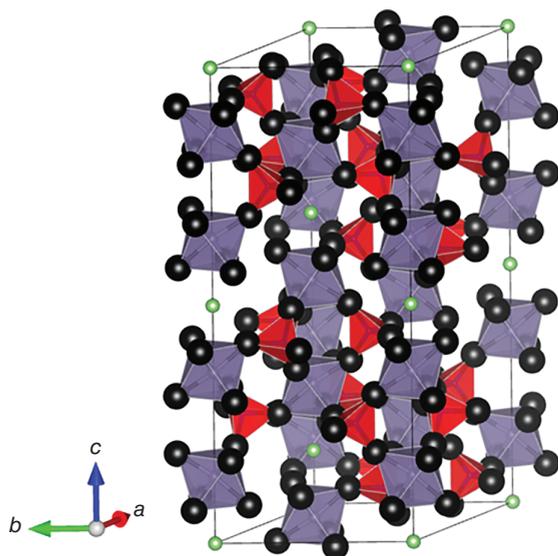


Figure 1.18 Crystal structure of NASICON-type solid electrolyte.

NASICON-type ionic conductors, $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$ (LAGP) has been of particular interest because of its wide electrochemical window and relatively high ionic conductivity. Solvent-free composite electrolyte comprising LAGP and PEO– LiClO_4 has been studied [128]. The electrolyte possessed high mechanical strength and is free standing. By addition of ion-conductive LAGP powder into the PEO– LiClO_4 PE, the ionic conductivity was improved. The all-solid-state $\text{LiFePO}_4/\text{Li}$ cell assembled with the composite electrolyte demonstrated a good cycle stability at 55°C . Garnet-type solid electrolytes, $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZ), and its derivatives have also been paid much attention as composite for solid electrolyte due to their high chemical stability, high ionic conductivity, and wide electrochemical window [129–131]. The structure of LLZ is depicted in Figure 1.19. The framework of LLZ garnet is composed of dodecahedral LaO_8 and octahedral ZrO_6 . The CPEs composed of LLZ and PEO– LiClO_4

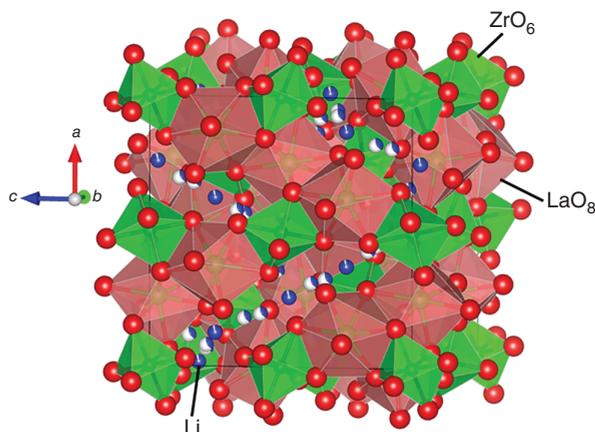


Figure 1.19 Structure of LLZ.

matrix showed high ionic conductivity of $4.42 \times 10^{-4} \text{ S cm}^{-1}$ [132]. Furthermore, the charge and discharge properties of Li/LiNi_{0.6}Co_{0.2}Mn_{0.2}O₂ cell using the composite electrolyte were better than those of pure PEO membrane.

The sulfide electrolytes have extra high ionic conductivity and wide electrochemical window. The addition of sulfide electrolytes into the polymer matrix has also been studied. Li₁₀GeP₂S₁₂ (LGPS) was incorporated into PEO-LiTFSI matrix [133]. The composite electrolyte with 1 wt% LGPS exhibited the highest conductivity of 1.21×10^{-3} and $1.18 \times 10^{-5} \text{ S cm}^{-1}$ at 80 and 25 °C, respectively.

1.5 Summary

Recent researches on PEs for Li battery are described. The battery using PEs has a lot of advantages such as their structural flexibility and high safety. The researches on PEs have focused on the increase in ionic conductivity and improving mechanical strength, but a compatibility of the PEs with electrode materials, which is another critical property, has not been extensively studied. The compatibility, particularly the interface between electrode materials and the PEs during electrochemical reactions, should be studied in nanoscale. The characterization of the interface and a development of the characterization technique for this type of study will promote the development of Li batteries using PEs.

References

- 1 Fenton, D.E., Parker, J.M., and Wright, P.V. (1973). *Polymer* 14: 589.
- 2 Ramesh, S. and Lu, S.C. (2012). *J. Appl. Polym. Sci.* 126: 484–492.
- 3 Bruce, P.G. (1995). *Solid State Electrochemistry*. Cambridge University Press.
- 4 Kim, J.H., Kang, M.S., Kim, Y.J. et al. (2004). *Chem. Commun.* 14: 1662–1663.
- 5 MacCallum, J.R. and Vincent, C.A. *Polymer Electrolytes Reviews*, vol. 2. Elsevier.
- 6 Scrosati, B. *Applications of Electroactive Polymers*. London: Chapman Hall.
- 7 Vincent, C.A. (1987). *Prog. Solid State Chem.* 17: 145–261.
- 8 Kotobuki, M., Suzuki, Y., Sato, Y. et al. (2011). *J. Power Sources* 196: 9815–9819.
- 9 Hoshina, K., Yoshima, K., Kotobuki, M., and Kanamura, K. (2012). *Solid State Ionics* 209–210: 30–35.
- 10 Kotobuki, M. and Koishi, M. (2015). *Ceram. Int.* 41: 8562–8567.
- 11 Thangadurai, V. and Weppner, W. (2005). *J. Power Sources* 142: 339–344.
- 12 Bloise, A.C., Tambelli, C.C., Franco, R.W.A. et al. (2001). *Electrochim. Acta* 46: 1571–1579.
- 13 Stephan, A.M. (2006). *Eur. Polym. J.* 42: 21–42.
- 14 Wright, P.V. (1975). *Br. Polym. J.* 7: 319–327.
- 15 Golodnitsky, D., Strauss, E., Peled, E., and Greenbaum, S. (2015). *Electrochim. Acta* 162: A2551–A2566.

- 16 Meyer, W.H. (1998). *Adv. Mater.* 10: 439–448.
- 17 Wright, P.V. *Electrochim. Acta* 43: 1998 1137–1998 1143.
- 18 Itoh, T., Ichikawa, Y., Uno, T. et al. (2003). *Solid State Ionics* 156: 393–399.
- 19 Goren, A., Costa, C.M., Tamano Machiavello, M.N. et al. (2015). *Solid State Ionics* 280: 1–9.
- 20 Kim, J.K., Cheruvally, G., Li, X. et al. (2008). *J. Power Sources* 178: 815–820.
- 21 Rajendran, S., Mahendran, O., and Kannan, R. (2002). *J. Phys. Chem. Solids* 63: 303–307.
- 22 Ramesh, S., Yin, T.S., and Liew, C.W. (2011). *Ionics* 17: 705–713.
- 23 Chen-Yang, Y.W., Chen, H.C., Lin, F.J., and Chen, C.C. (2002). *Solid State Ionics* 150: 327–335.
- 24 Kam, W., Liew, C.W., Lim, J.Y., and Ramesh, S. (2014). *Ionics* 20: 665–674.
- 25 Ramesh, S., Uma, O., Shanti, R. et al. (2014). *Measurement* 48: 263–273.
- 26 Fullerton-Shirey, S.K. and Maranas, J.K. (2009). *Macromolecules* 42: 2142–2156.
- 27 Sun, H.Y., Sohn, H.-J., Yamamoto, O. et al. (1999). *J. Electrochem. Soc.* 146 (5): 1672–1676.
- 28 Acosta Luque, J.-L. and Bergas, E.M. (1996). *Solid State Ionics* 91: 75–80.
- 29 Khurana, R., Schaefer, J.L., Archer, L.A., and Coates, G.W. (2014). *J. Am. Chem. Soc.* 136: 7395–7402.
- 30 Porcarelli, L., Gerbaldi, C., Bella, F., and Nair, J.R. (2016). *Sci. Rep.* 6: 19892.
- 31 Tanaka, R., Sakurai, M., Sekiguchi, H. et al. (2001). *Electrochim. Acta* 46: 1709–1715.
- 32 Soo, P.P., Huang, B., Jang, Y.-I. et al. (1999). *J. Electrochem. Soc.* 146: 32–37.
- 33 Sadoway, D.R. (2004). *J. Power Sources* 129: 1–3.
- 34 Niitani, T., Shimada, M., Kawamura, K., and Kanamura, K. (2005). *J. Power Sources* 146: 386–390.
- 35 Niitani, T., Shimada, M., Kawamura, K. et al. (2005). *Electrochem. Solid-State Lett.* 8: A385–A388.
- 36 Bouchet, R., Maria, S., Meziane, R. et al. (2013). *Nat. Mater.* 12: 452–457.
- 37 Nishimoto, A., Agehara, K., Furuya, N. et al. (1999). *Macromolecules* 32: 1541–1548.
- 38 Wen, Z., Itoh, T., Uno, T. et al. (2003). *Solid State Ionics* 160: 141–148.
- 39 Matoba, Y., Ikeda, Y., and Kohjiya, S. (2003). *Solid State Ionics* 147: 403–409.
- 40 Gopalan, A.I., Santhosh, P., Manesh, K.M. et al. (2008). *J. Membr. Sci.* 325: 683–690.
- 41 Jiang, Z., Carroll, B., and Abraham, K.M. (1997). *Electrochim. Acta* 42: 2667–2677.
- 42 Iijima, T., Toyoguchi, Y., and Eda, N. (1985). *Electrochemistry* 53: 619–621.
- 43 Liew, C.W., Durairaj, R., and Ramesh, S. (2012). *J. Mater. Res.* 27: 2996–3004.
- 44 Rhoo, H.J., Kim, H.T., Park, J.K., and Hwang, T.S. (1997). *Electrochim. Acta* 42: 1571–1579.
- 45 Croce, F., Persi, L., Scrosati, B. et al. (2001). *Electrochim. Acta* 46: 2457–2461.
- 46 Dasenbropck, C.O., Ridgway, T.H., Seliskar, C.J., and Heineman, R.W. (1998). *Electrochim. Acta* 43: 3497–3502.

- 47 Yang, J.M., Wang, Z.W., and Yang, C.C. (2008). *J. Membr. Sci.* 322: 74–80.
- 48 Yang, C.C. and Wu, G.M. (2009). *Mater. Chem. Phys.* 114: 948–955.
- 49 Lu, Y., Wang, D., Li, T. et al. (2009). *Biomaterials* 30: 4143–4151.
- 50 Qiao, J., Okada, T., and Ono, H. (2009). *Solid State Ionics* 180: 1318–1323.
- 51 Hirankumar, G., Selvasekarapandian, S., Kuwata, N. et al. (2005). *J. Power Sources* 144: 262–267.
- 52 Tsutsumi, H., Matsuo, A., Takase, K. et al. (2010). *J. Power Sources* 90: 33–38.
- 53 Tatsuma, T., Taguchi, M., Iwaku, M. et al. (1999). *J. Electroanal. Chem.* 472: 142–146.
- 54 Osman, Z. and Arof, A.K. (2003). *Electrochim. Acta* 48: 993–999.
- 55 Khanmirzaei, M.H. and Ramesh, S. (2013). *Int. J. Electrochem. Sci.* 8: 9977–9991.
- 56 Teoh, K.H., Ramesh, S., and Arof, A.K. (2012). *J. Solid State Electrochem.* 16: 3165–3170.
- 57 Feuillade, G. and Perche, P. (1975). *J. Appl. Electrochem.* 5: 63–69.
- 58 Saikia, D., Chen-Yang, Y.W., Chen, Y.T. et al. (2008). *Desalination* 234: 24–32.
- 59 Kim, Y.T. and Smotkin, E.S. (2002). *Solid State Ionics* 149: 29–37.
- 60 Ramesh, S. and Ang, G.P. (2010). *Ionics* 16: 465–473.
- 61 Choi, S.W., Kim, J.R., Jo, S.M. et al. (2005). *J. Electrochem. Soc.* 152: A989–A995.
- 62 Rajendran, S., Babu, R., and Sivakumar, P. (2009). *J. Appl. Polym. Sci.* 113: 1651–1656.
- 63 Choi, S.W., Jo, S.M., Lee, W.S., and Kim, Y.R. (2003). *Adv. Mater.* 15: 2027–2032.
- 64 Li, Z.H., Cheng, C., Zhen, X.Y. et al. (2009). *Electrochim. Acta* 54: 4403–4407.
- 65 Rajendran, S., Sivakumar, M., and Subadevi, R. (2004). *Solid State Ionics* 167: 335–339.
- 66 Ito, Y., Kanehori, K., Miyauchi, K., and Kudo, T. (1987). *J. Mater. Sci.* 22: 1845–1849.
- 67 Yang, L., Lin, J., Wang, Z. et al. (1990). *Solid State Ionics* 40-41: 616–619.
- 68 Kim, H., Oh, B., and Kang, Y. (2000). *Polym. Bull.* 44: 509–515.
- 69 Chakrabarti, A., Filler, R., and Mandal, B.K. (2010). *Solid State Ionics* 180: 1640–1645.
- 70 Karatas, Y., Banhatti, R.D., Kaskhedikar, N. et al. (2009). *J. Mater. Chem. B* 113: 15473–15484.
- 71 Johan, M. and Fen, L. (2010). *Ionics* 16: 335–338.
- 72 Klongkan, S. and Pumchusak, J. (2015). *Electrochim. Acta* 161: 171–176.
- 73 Wu, X.-L., Xin, S., Seo, H.-H. et al. (2011). *Solid State Ionics* 186: 1–6.
- 74 Rajendran, S. and Mahendran, O. (2001). *Ionics* 7: 463–468.
- 75 Bandara, L.R.A.K., Dissanayake, M.A.K.L., and Mellander, B.E. (1998). *Electrochim. Acta* 43: 1447–1451.
- 76 Yan, P., Huang, Z., Lin, Y. et al. (2015). *Ionics* 21: 593–599.
- 77 Kim, J.R., Choi, S.W., Jo, S.M. et al. (2004). *Electrochim. Acta* 50: 69–75.
- 78 Johan, M.R., Shy, O.H., Ibrahim, S. et al. (2011). *Solid State Ionics* 196: 41–47.

- 79 Qian, X., Gu, N., Cheng, Z. et al. (2002). *Mater. Chem. Phys.* 74: 98–103.
- 80 Meneghetti, P., Qutubuddin, S., and Webber, A. (2004). *Electrochim. Acta* 49: 4923–4931.
- 81 Min, H.-S., Ko, J.-M., Kim, D.-W., and Power, J. (2003). *Sources* 119–121: 469–472.
- 82 Vivkraman, P. and Ramamurthy, S. (2006). *Mater. Lett.* 60: 3431–3436.
- 83 Wetjen, M., Kim, G.-T., Joost, M. et al. (2013). *Electrochim. Acta* 87: 779–787.
- 84 Kim, G.T., Appetecchi, G.B., Carewska, M. et al. (2010). *J. Power Sources* 195: 6130–6137.
- 85 Rupp, B., Schmuck, M., Balducci, A. et al. (2008). *Eur. Polym. J.* 44: 2986–2990.
- 86 Shin, J.-H., Henderson, W.A., and Passerini, S. (2003). *Electrochem. Commun.* 5: 1016–1020.
- 87 Appetecchi, G.B., Montanino, M., Zane, D. et al. (2009). *Electrochim. Acta* 54: 1325–1332.
- 88 Shin, J.-H., Henderson, W.A., and Passerini, S. (2005). *J. Electrochem. Soc.* 152: A978–A983.
- 89 Shin, J.-H., Henderson, W.A., and Passerini, S. (2005). *Electrochem. Solid-State Lett.* 8: A125–A127.
- 90 Shi, J.-H., Henderson, W.A., Scaccia, S. et al. (2006). *J. Power Sources* 156: 560–566.
- 91 Tizzani, C., Appetecchi, G.B., Carewska, M. et al. (2007). *Aust. J. Chem.* 60: 47–50.
- 92 Shi, J.-H., Henderson, W.A., Tizzani, C. et al. (2006). *J. Electrochem. Soc.* 153: A1649–A1654.
- 93 Appetecchi, G.B., Kim, G.T., Montanino, M. et al. (2011). *J. Power Sources* 196: 6703–6709.
- 94 Kim, G.T., Jeong, S.S., Xue, M.Z. et al. (2012). *J. Power Sources* 199: 239–246.
- 95 Ye, H., Huang, J., Xu, J.J. et al. (2007). *J. Electrochem. Soc.* 154: A1048–A1057.
- 96 Li, L.B., Wang, J.J., Yang, P.X. et al. (2013). *Electrochim. Acta* 88: 147–156.
- 97 Raghavan, P., Zhao, X., Choi, H. et al. (2014). *Solid State Ionics* 262: 77–82.
- 98 Kim, Y.H., Cheruvally, G., Choi, J.W. et al. (2007). *Macromol. Symp.* 249–250: 183–189.
- 99 Choi, J.-W., Cheruvally, G., Kim, Y.-H. et al. (2007). *Solid State Ionics* 178: 1235–1241.
- 100 Egashira, M., Todo, H., Yoshimoto, N., and Morita, M. (2008). *J. Power Sources* 178: 729–735.
- 101 Cha, E.H., Lim, S.A., Park, J.H. et al. (2008). *J. Power Sources* 178: 779–782.
- 102 Li, M.T., Yang, L., Fang, S.H. et al. (2012). *Polym. Int.* 61: 259–264.
- 103 Yin, K., Zhang, Z.X., Li, X.W. et al. (2015). *J. Mater. Chem. A* 3: 170–178.
- 104 Lee, Y.-S. and Kim, D.-W. (2013). *Electrochim. Acta* 106: 460–464.
- 105 Kumar, B. (2004). *J. Power Sources* 135: 215–231.
- 106 Adebahr, J., Byrne, N., Forsyth, M. et al. (2003). *Electrochim. Acta* 48: 2099–2103.
- 107 Appetecchi, G.B. and Passerini, S. (2000). *Electrochim. Acta* 45: 2139–2145.

- 108 Michael, M.S., Jacon, M.M.E., Prabakaran, S.R.S., and Radhakrishna, S. (1997). *Solid State Ionics* 98: 167–174.
- 109 Slane, S. and Salomon, M. (1995). *J. Power Sources* 55: 7–10.
- 110 Krawiec, W., Scanlon, L.G. Jr., Fellner, P. et al. (1995). *J. Power Sources* 54: 310–315.
- 111 Croce, F., Appetecchi, G.B., Persi, L., and Scrosati, B. (1998). *Nature* 394: 456–458.
- 112 Jayathilaka, P.A.R.D., Dissanayake, M.A.K.L., Albinsson, I., and Mellander, B.-E. (2002). *Electrochim. Acta* 47: 3257–3268.
- 113 Croce, F., Persi, L., Ronci, F., and Scrosati, B. (2000). *Solid State Ionics* 135: 47–52.
- 114 Scrosati, B., Croce, F., and Persi, L. (2000). *J. Electrochem. Soc.* 147: 1718–1721.
- 115 Pitawala, H.M.J.C., Dissanayake, M.A.K.L., and Seneviratne, V.A. (2007). *Solid State Ionics* 178: 885–888.
- 116 Yoon, M.Y., Hong, S.K., and Hwang, H.J. (2013). *Ceram. Int.* 39: 9659–9663.
- 117 Liu, S., Imanishi, N., Zhang, T. et al. (2010). *J. Power Sources* 195: 6847–6853.
- 118 Lin, C.W., Hung, C.L., Venkateswarlu, M., and Hwang, B.J. (2005). *J. Power Sources* 146: 397–401.
- 119 Adebahr, J., Best, A.S.>, Byrne, N. et al. (2003). *Phys. Chem. Chem. Phys.* 5: 720–725.
- 120 Shanmukaraj, D., Wang, G.X., Murugan, R., and Liu, H.K. (2008). *J. Phys. Chem. Solids* 69: 243–248.
- 121 Sun, H.Y., Yakeda, Y., Imanishi, N. et al. (2000). *J. Electrochem. Soc.* 147: 2462–2467.
- 122 Huang, G., Li, Y., Han, L. et al. (2011). *Appl. Clay Sci.* 51: 360–365.
- 123 Walls, H.J., Riley, M.W., Singhal, R.R. et al. (2003). *Adv. Funct. Mater.* 13: 710–717.
- 124 Zhang, Y., Zhao, Y., Gosselimk, D., and Chen, P. (2015). *Ionics* 21: 381–385.
- 125 Moreno, M., Quijada, R., Santa Ana, M.A. et al. (2011). *Electrochim. Acta* 58: 112–118.
- 126 Tang, C., Hackenberg, K., Fu, Q. et al. (2012). *Nano Lett.* 12: 1152–1156.
- 127 Zhu, Y., Zhang, Y., and Lu, L. (2015). *J. Power Sources* 290: 123–129.
- 128 Jung, Y.C., Lee, S.M., Choi, J.-H. et al. (2015). *J. Electrochem. Soc.* 162: A704–A710.
- 129 Kotobuki, M., Munakata, H., Kanamura, K. et al. (2010). *J. Electrochem. Soc.* 157: A1076–A1079.
- 130 Kotobuki, M., Kanamura, K., Sato, Y., and Yoshida, T. (2011). *J. Power Sources* 196: 7750–7754.
- 131 Kotobuki, M., Kanamura, K., Sato, Y. et al. (2012). *J. Power Sources* 199: 346–349.
- 132 Choi, J.-H., Lee, C.-H., Yu, J.-H. et al. (2015). *J. Power Sources* 274: 458–463.
- 133 Zhao, Y., Wu, C., Peng, G. et al. (2016). *J. Power Sources* 301: 47–53.

