

Fillers for Solid-State Polymer Electrolytes: Highlight

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The current solid polymer electrolytes suffer from poor conductivity, low mechanical and electrochemical stability toward the lithium electrodes. To improve the performance of solid polymer electrolytes, the addition of nanoparticle fillers to the polymer electrolyte is being extensively investigated. In this paper, a brief review on the state of art of solid fillers for lithium battery electrolytes is presented.

Key Words: Secondary battery, Lithium, Fillers, Nanocomposite, Solid-state electrolyte

Introduction

A solid state electrolyte (SPE) can be defined as a solid solution of the conducted ions. Ions can be transported inside and through the host under the effect of an electric field by interactions with the host molecules.¹ SPEs are expected to contribute to the realization of lithium battery systems with much improved safety, energy density, and design flexibility. Moreover, the lithium dendrite formation on metal lithium anodes can be prevented mechanically and morphologically if highly stable and highly conducting SPEs are materialized, and thus lithium metal batteries, the most desirable battery system with the highest energy density, can be brought into the market.²

Among the SPEs so far reported, PEO-LiX is the most intensively studied electrolyte systems. Unfortunately, most of the SPEs based on PEO-LiX exhibits low ionic conductivities at ambient temperatures ($\sigma < 10^{-7}$ S cm⁻¹) because of their crystallization tendencies.³⁻⁵ To improve the ionic conductivity of SPEs, a concept of gel polymer electrolytes (GPE) was introduced.⁶ The conductivity PEO-LiX increased significantly by incorporating a liquid plasticizer into a SPE, but at

the sacrifices of mechanical strength and the compatibility of the electrolyte with lithium.

In Table 1, various types of lithium battery electrolytes are summarized.

Recently, a new strategy to overcome the disadvantages of SPEs is being intensively studied. Instead of liquid plasticizers, nanosized ceramic powders or molecular sieves were dispersed directly into the polymer hosts to gain mechanical strength and to improve ionic conductivities.⁷ These innovated electrolytes are known as composite polymer electrolytes (CPEs), in which the added solid particles, known as fillers, incorporate into the host polymer.⁸ This strategy was more encouraged by Z. Gadjourova *et al.*⁹ who proved that the conductivity in a static and ordered environment of the crystalline phase could be greater than that in the equivalent amorphous material above T_g . The study also showed that in a crystalline phase, ion transport is dominated by the cations, indicated by Li^+ transference number in the case of lithium battery polymer electrolytes.

In a conventional SPE, relaxation and segmental motion of the solvent chains are regarded as the key factors in enabling ion transport, suggesting that a sufficient conductivity can be

Table 1. Physical and electrochemical properties of various electrolytes for lithium batteries.

Property	Organic carbonate-based electrolytes	Ionic liquid-based electrolytes	Solid polymer electrolytes (SPE)	Polymer gel electrolytes (GPE)
mechanics	low flexibility and stability	low flexibility and stability	high flexibility and stability	moderate flexibility and stability
electrochemical and chemical stability	moderate	either low or moderate	high	moderate
thermal stability	low	high	high	moderate
conductivity	high	either high or moderate	very low	moderate
lithium selective transference	high	low	high	high

Table 2. Highest ionic conductivity and Li⁺ transference number reported.

Class of polymer electrolyte (Polymer-LiX)	Section	Highest value reported ^a		
		Conductivity (S cm ⁻¹)	Li ⁺ transference number	
PEO-based SPEs		10 ⁻⁷		
poly[bis(methoxyethoxyethoxy)phosphazene]-based SPEs	2.1	1.7 × 10 ⁻⁵	0.3 ²⁸	
SPEs containing	Inert oxide ceramic	2.1	3.8 × 10 ⁻⁴ ³³	0.8 ²⁹
	Treated SiO ₂	2.2	2.3 × 10 ⁻⁵ ⁴⁵	0.25 ⁴²
	Molecular sieves or zeolite	2.3	1.4 × 10 ⁻⁵ ⁵⁰	0.5 ⁵²
	Rare-earth ceramics	2.4	3.8 × 10 ⁻⁴ ⁵⁵	0.7 ⁵⁵
	Solid super acid	2.5	2.1 × 10 ⁻⁵ ⁶⁰	0.8 ⁶¹⁻⁶²
	Ferroelectric material	2.6	2.6 × 10 ⁻⁵ ^{65 b}	0.4 ^{64 c}
	Carbon	2.7	2.0 × 10 ⁻⁴ ^{68 b}	n/r
	Cellulose nanocrystals	3	10 ⁻⁵ ⁶⁹	0.3 ⁶⁹
Active fillers	4	3 × 10 ⁻⁴ ⁷²	0.4 ⁷⁷	
Nanogel composite electrolyte	5	4.0 × 10 ⁻³ ⁹⁰	0.7 ^{87 b}	

^ameasured at room temperature. ^bat 30 °C. ^cat 70 °C. n/r: not reported.

obtained only when the polymer is over its amorphous state.¹⁰ The addition of a filler to a polymer improve was found to improve the ionic conductivity by reducing the crystallization tendency.^{11,12} In addition, Jiang *et al.* also indicated that the presence of a ceramic filler significantly enhanced cation transference number and interfacial stability between the electrolyte and lithium metal electrode.^{13,14}

In general, inorganic fillers may be classified into two groups: active and passive. The active group consists of materials that participate in the ionic conduction process, while the inactive group consists of materials that do not involve in the lithium transport process. However, in all cases, the particle size and the characteristics of the fillers play vital roles in the electrochemical properties of the electrolytes.

During the last two years, CPEs have attracted great interest. Achievements made in this period strongly suggest that CPEs are the most promising next generation electrolytes for lithium batteries.

In this paper, a brief review of fillers for CPEs was presented. For a convenient comparison, the highest conductivity and Li⁺ transference number for various electrolyte systems were listed in Table 2.

Inactive Inorganic Fillers

Inert oxide ceramics. As conventional compounds, oxide ceramic fillers including Al₂O₃,¹⁵ TiO₂,¹⁶ ZrO₂^{17,18} have been of major interest in the study of inorganic fillers for SPEs.

The first study on the fillers for lithium battery polymer electrolytes was carried out with Al₂O₃.¹⁹ According to Croce *et al.*, either TiO₂ or Al₂O₃ dispersed in PEO-LiClO₄ (10 wt.%) forms complexes with the basic oxygen atoms in the PEO chains and acts as cross-linking centers for PEO segments, thereby reducing the reorganization tendency of the polymer chain and promoting preferred Li⁺ transport at the boundaries of the filler particles.²⁰ Indeed, below the melting temperature

of PEO, the conductivity of PEO-based nanocomposite electrolytes was reported to be strongly dependent on the thermal history.²¹ Such functional fillers are called somewhere as "solid plasticizers".^{14,22} However, in fact, the role of ceramic fillers seems to be quite different from that of liquid plasticizers, which significantly change the dynamics of polymer chain and thus promote the segmental conductivity.^{23,24} In contrast, the T_g values of the PEO-based electrolyte systems were not noticeably changed by the addition of ceramic fillers, preserving the initial amorphous structures. Lewis acid-base type interactions between filler surface groups and cations/anions appear to be responsible for conductivity enhancement (acidic > basic > neutral > weakly acidic).²⁵

Most of the studies have focused on the synthesis of nanosized fillers because the mechanical strength and the electrochemical performance of the electrolytes are expected to increase with the decreasing size of fillers. In fact, Krawiec *et al.* showed that the conductivity of PEO-LiBF₄ system increased with the decreasing size of Al₂O₃ filler particle.²⁶ On the contrary, micron-sized titanium oxide consisting of Ti₂O₃, TiO, and TiO₂ prepared by ball milling was also found to remarkably reduce the interface resistance between the polymer and the lithium electrode, thereby resulting in the increased conductivity.²⁷

It was shown in 1984 that poly[bis(methoxyethoxyethoxy)phosphazene] (MEEP)/lithium salt electrolyte system exhibited higher conductivity (1.7 × 10⁻⁵ S cm⁻¹ at room temperature) than that of PEO-lithium salt electrolyte system.²⁸ The conductivity of the poly[bis(methoxyethoxyethoxy)phosphazene] (MEEP)/lithium salt electrolyte system further increased to about by five times by incorporating 2.5 wt.% α-Al₂O₃.²⁹ Similar to the case of PEO-based composite electrolyte, the conductivity enhancement was explained in terms of Lewis acid-base interaction between the filler, polymer, and salt. Other polymer-salt complex systems comprising either nanosized Al₂O₃ or nanosized ZnO filler, such as PAN-LiClO₄-

Al_2O_3 ,³⁰ PEG-LiClO₄-Al₂O₃,³¹ (UV-cured cyclic phosphazene)-LiClO₄-Al₂O₃,³² and PEO-LiClO₄-(organic acid)-Al₂O₃,³³ PEO-LiN(SO₂CF₃)₂-ZnO,³⁴ were also investigated. The ionic conductivity and the lithium ion transference numbers of a conventional SPE. PEO-LiX was considerably increased by the addition of a ceramic oxide filler (about 2.5 - 15 wt.%). Even though the incorporation of a nanosized ceramic filler was able to increase the conductivity of PEO-LiX up to more than 10³ times, this conductivity value is still far from the desired for the practical application.²⁹

Treated SiO₂. Silica, a well-known material as a heterogeneous catalyst support, has also been expected to enhance the ionic conductivity of polymer electrolytes because the surface hydroxyl groups can be easily modified for a specific need.

It was reported that the conductivity of SPE comprising treated SiO₂ as a filler was much higher than that containing untreated SiO₂.^{35,36} Capiglia *et al.* were able to improve the conductivity of PEO-LiClO₄ by incorporating SiO₂ particles, which was treated at 900 °C to remove surface hydroxyl groups on SiO₂.³⁷ Contrary to this, hydrophilic silica was also found to enhance the stability of lithium metal/polymer electrolyte interface.³⁸ A nanocomposite system, PUA (polyurethane acrylate)-LiN(SO₂CF₃)₂ containing 20 wt.% hydrophilic silica, resulted in an improved performance of lithium battery cell at moderate temperature, suggesting that the addition of nano-SiO₂ powders is capable of greatly improving the interfacial stability between the Li anode and the electrolyte.³⁹

From these results, it is likely that the performance of the SPEs can be improved by incorporating either the thermally treated silica or untreated functionalized SiO₂. Liu *et al.*⁴⁰ found that surface-functionalized SiO₂ by 2-[methoxy(polyethylenoxy)-propyl] trimethoxysilane could be better dispersed into the PEO matrix than untreated SiO₂. The presence of polymeric moieties on the SiO₂ surface was proven to improve the Li⁺-polymer interfacial stability. In a routine of immobilizing short-chained polymer plasticizers onto the silica fillers in GPEs,^{35,41} poly(ethylene) glycol was grafted onto pristine SiO₂ nanoparticle surface using toluene 2,4-diisocyanate as a bridging molecule.⁴² The fillers were then employed in a PEO-LiBF₄ system to obtain all-solid-state electrolytes. However, Lewis acid-base interactions between the polymer backbone and the fillers were weaker, leading to a decrease in Li⁺ transference number. This can be attributed to the smaller number of OH groups on the silica surface compared with that on the unmodified silica.

The room temperature ionic conductivity of PEO-LiClO₄ increased by more than two times when a functionalized SiO₂ (Degussa-Huls, R805, ~12 nm) possessing two surface silanol (Si-OH) groups and an octyl (Si-C₈H₁₇) group was used as a filler after thermal treatment. Interestingly, thermal-induced segregation of silica particles was not observed and this could be responsible for the enhancement of conductivity.⁴³ In another paper, the addition of commercially available mesoporous SBA-15 as fillers into a PEO-LiClO₄-based SPE was found to improve the mechanical, electrochemical, and physicochemical properties of the electrolyte.⁴⁴

In summary, silicone-based fillers enhanced the mechanical strength, conductivity, and electrochemical properties of the SPEs, especially by stabilizing the interfacial interaction between the electrolyte and the electrodes. Moreover, functionalized silicone-based fillers could be dispersed homogeneously in the electrolyte systems. Unfortunately, despite their high designability, silicone-based filler-containing SPEs exhibit insufficient conductivity and Li⁺ transport at room temperature for practical application. Nonetheless, the cell performance with these electrolyte systems was found stable up to thousands of stable cycles at 60 °C.³⁹

Molecular sieves and zeolites. Molecular sieves, microporous materials with high BET surface areas and two-dimensional intersection channels, especially aluminosilicate molecular sieves (zeolites), have been evaluated as fillers for CPEs. Compared with those of traditional nanofillers, certain types of molecular sieves were shown to possess much stronger Lewis acid centers in their frameworks and inside the channels, which might contribute to the prevention of the crystallization tendency of the polymer host more effectively, thus resulting in a higher degree of conductivity and Li⁺ transference number enhancement.⁴⁵⁻⁴⁸ The addition of a molecular sieve was found to decrease the crystallinity of PEO as well as increasing the amount of PEO spherulites, thus resulting in a significantly enhanced ionic conductivity and electrochemical stability up to 4.5 V. Remarkably, in comparative studies, zeolite fillers like ZSM-5 appeared to a better choice than the ceramic fillers, solid super acid, layered materials, and mesoporous materials.^{49,50}

In a study by Xi *et al.*, several ordered mesoporous silica (OMS) fillers were synthesized, characterized, and applied for PEO-LiClO₄-based nanocomposite polymer electrolytes.⁵¹ As reported, because of their mesoporous channels, OMS was capable of functioning as physical cross-linking centers for the polymer chains, thus strengthening the mechanical stability of the system. In addition, the conductivity, Li⁺ transference number, electrochemical stability of the PEO-LiClO₄-based electrolytes were significantly improved by the addition of OMS fillers. Further improvement in electrochemical properties of these electrolyte systems was also observed when OMS was modified using ionic liquids.⁵² Room temperature conductivities of 10⁻⁵ S cm⁻¹ and Li⁺ transference numbers of 0.3 - 0.5 were achieved with PEO-based electrolytes containing 10 - 15 wt.% of molecular sieve or zeolite. Obviously, these values are encouraging, but still far from those required for practical lithium batteries.

Rare-earth oxide ceramics. Solid-state synthesis: inorganic ingredients are mixed and thermally calcinated at high temperature to form ceramic fillers directly. Subsequently, the solids are grinded to a specified grain size. Using this technique, D. Shanmukaraj *et al.* prepared nanosized SrBi₄Ti₄O₁₅ ferroelectric filler and applied for the PEG-LiClO₄. Room temperature conductivity of 0.64 × 10⁻⁷ S cm⁻¹ was achieved at the concentration of 12.5 wt.% SrBi₄Ti₄O₁₅.⁵³

Indirect synthesis: a homogeneous gel is prepared first, then dried, and heated to form foamy flakes, which give very fine powder consisting of small sized particles after grinding. In the last step, the powder is decomposed at a very higher

temperature to obtain electrolyte fillers. CPE containing 10 wt.% nanosized $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ ferroelectric fillers, prepared by an indirect synthesis, showed a maximum conductivity of $0.75 \times 10^{-6} \text{ S cm}^{-1}$ at room temperature, which is about 10 times higher than that with $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ prepared from a direct synthesis.⁵⁴

Through a combination of the above two methods, $\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$ fibers and mats were fabricated, then dispersed (20 wt.%) into PEO- $\text{LiN}(\text{SO}_2\text{CF}_2\text{CF}_3)_2$ mixture containing 12.5 wt.% Li^+ in PEO.⁵⁵ Surprisingly, these nanocomposite electrolytes showed a maximum ionic conductivity of $5.0 \times 10^{-4} \text{ S cm}^{-1}$ at room temperature and Li^+ transference number of 0.7, which are far above those of previously mentioned filler-containing electrolytes. Moreover, the interfacial stability of the electrolytes in contact with lithium-ion and lithium-metal anodes was further improved when the ceramic fibers were coated by PEO. Although the above SPEs systems exhibit sufficiently high room temperature conductivity for lithium batteries, no cell test result was reported in the study.

Solid superacid. Sulfated metal oxide ceramics, solid super acids, including $\text{SO}_4^{2-}/\text{ZrO}_2$, $\text{SO}_4^{2-}/\text{Fe}_2\text{O}_3$, and $\text{SO}_4^{2-}/\text{TiO}_2$, are being used as catalysts for a variety of chemical reactions.⁵⁶⁻⁵⁸ As the solid super acids possess strong acidic centers to interact with the oxygen atoms of PEO, they can also find application as fillers for CPEs.⁵⁹

In an early study,⁶⁰ nanosized $\text{SO}_4^{2-}/\text{ZrO}_2$ was reported to effectively reduce the crystallinity of PEO in PEO_{12} - LiClO_4 - $\text{SO}_4^{2-}/\text{ZrO}_2$ system, thus resulting in enhanced ionic conductivity and Li^+ transference number. The decomposition voltage of the system increased by about 0.1 - 0.2 V compared with that of PEO_{12} - LiClO_4 . The highest room temperature ionic conductivity of $2.1 \times 10^{-5} \text{ S cm}^{-1}$ was attained with 7 wt.% of $\text{SO}_4^{2-}/\text{ZrO}_2$.

Using a PEO- LiBF_4 -sulfated- ZrO_2 electrolyte system, Croce *et al.* achieved a surprisingly high Li^+ transference number of 0.8, which is about two times higher than that obtained with ceramic-free electrolyte, and they also expected that a value approaching unity could finally be obtained soon.⁶¹⁻⁶²

Ferroelectric materials. Despite the high density of functional groups, PEOs have relatively low dielectric constant ($\epsilon = 5$), and thus the dissociation of an electrolyte salt is limited.⁶³ For this reason, electroceramic fillers are introduced into the polymer electrolyte matrixes to increase the polarity of the polymer backbone and to increase the charge separation and conductivity. The addition of a small amount of ferroelectric BaTiO_3 (1.4 wt.%), a widely used capacitor material with high dielectric constant ($10^3 - 10^5$), was found to enhance the lithium interface stability and the conductivity of PEO- LiClO_4 SPE, especially at temperatures higher than 70 °C.⁶⁴

A PEO-based polymer electrolyte system employing $\text{LiN}(\text{SO}_2\text{C}_2\text{F}_5)_2$ as an electrolyte and BaTiO_3 (10 wt.%) as the ferroelectric filler showed excellent cell performance without a significant loss of initial capacity upon charging to 3.9 V at 80 °C.⁶⁵ In the extent study, it was also reported that solid-PEO solution of a salt mixture of LiPF_6 (1 wt.%) and $\text{LiN}(\text{SO}_2\text{C}_2\text{F}_5)_2$ (9 wt.%) with dispersed BaTiO_3 fillers exhibited enhanced cell performance upon charging at 4.2 V.⁶⁶ Similar results of the studies with BaTiO_3 fillers were also obtained using the

$\text{LiN}(\text{SO}_2\text{C}_2\text{F}_5)_2$ -PEO-based polymer electrolyte.⁶⁷

However, it seems that much work needs to be done to improve the conductivity at room temperature for both solid super acid-containing and electroferric material-containing SPEs to be used as lithium battery electrolytes for practical purposes.

Carbon. Carbon is an important anode material in Li-ion batteries. In an early study of PEO-based composite cathodes, Appetecchi *et al.* recognized that the addition of a small volume fraction (< 1.5%) of carbon with moderately high surface area ($\sim 60 \text{ m}^2 \text{ g}^{-1}$) led to excellent performance of composite lithium polymer electrolytes in terms of conductivity and interfacial stability.⁶⁸ Although the mechanism of the conductivity enhancement in the composite electrolyte is still unclear, the room temperature ionic conductivity of $2.0 \times 10^{-4} \text{ S cm}^{-1}$ reported for SPEs is really promising and meaningful with the addition of such an inexpensive material.

Cellulose Nanocrystals

Nanocomposite polymer electrolytes based on poly(oxyethylene) and cellulose nanocrystals were studied by Samir *et al.*^{69,70} The addition of 6 - 10 wt.% of nanocrystalline cellulose filler (whiskers) to a PEO- $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ polymer system reinforced the mechanical properties of the system without affecting the lithium transference number. However, the ionic conductivity was not improved by the addition of the fillers. In contrast, it is also admitted that the hydroxyl groups of the cellulose fillers led to the electrolyte instability in contact with lithium electrodes.

Active Fillers for Lithium Batteries' CPEs

Although the addition of nonconducting fillers into the polymer matrix significantly improves the electrochemical properties of the electrolytes, the room temperature conductivity is still too low (mostly less than $10^{-4} \text{ S cm}^{-1}$) to be used in the practical applications. As an alternative, active fillers with very high lithium-ion conductivity were extensively explored.

The first study on the active filler was reported by Skaarup *et al.*, who investigated a CPE system, PEO- LiCF_3SO_3 containing Li_3N .⁷¹ It was reported that the incorporation of small amounts of Li_3N , increased the room temperature conductivity of PEO- LiCF_3SO_3 up to 1,000 times. Other early studies carried out with a filler having composition of $0.56\text{Li}_2\text{S}$ $0.19\text{B}_2\text{S}_3$ 0.25LiI and Li_3N , achieved the conductivities of 3×10^{-4} and $1.4 \times 10^{-4} \text{ S cm}^{-1}$, respectively.^{72,73} However, both of these active fillers are highly unstable and sensitive in terms of heat and environment. More disappointingly, Li_3N even has a poor electrochemical stability (2.5 V versus Li^+/Li).

Among the active fillers of ceramic type, γ - LiAlO_2 was most intensively investigated because γ - LiAlO_2 has larger defect-rich grain boundaries than inert ceramics, which might contribute to the ionic conduction.⁷⁴ Especially, the interface of $\text{Li}/(\text{PEO})_8\text{-LiClO}_4\text{-}\gamma\text{-LiAlO}_2$ showed the most stable electrochemical behavior, compared with the interface of $\text{Li}/(\text{PEO})_8\text{-LiClO}_4$ and $\text{Li}/\text{PAN-EC-PC-LiClO}_4$.⁷⁵

Li^- -conducting glass also attracted much interest in the last decade. Employing Li^+ -conducting glass, $14\text{Li}_2\text{O} \cdot 9\text{Al}_2\text{O}_3 \cdot 38\text{TiO}_2 \cdot 39\text{P}_2\text{O}_5$, which was shown to have the highest solid-state Li^- conductivity (around $10^{-3} \text{ S cm}^{-1}$),⁷⁶ Zhang *et al.* reported a PEO- $\text{LiN}(\text{SO}_2\text{C}_2\text{F}_5)_2$ -based electrolyte with a room temperature conductivity of $1.7 \times 10^{-4} \text{ S cm}^{-1}$, an Li^+ transference number of 0.4, and an electrochemical stability window to +5.1 V versus Li/Li^+ .⁷⁷ In another report, the addition of a glass powder of $0.4\text{B}_2\text{S}_3 \cdot 0.4\text{Li}_2\text{O} \cdot 0.2\text{Li}_2\text{SO}_4$ was found to suppress the charge resistance of Li/PEO-LiBF_4 interface by a factor of three.⁷⁸ Impressively, a Li^- transport number of 0.98 for a glass-polymer composite electrolyte containing 13 vol.% PEO- $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ and 87 vol.% $0.56\text{Li}_2\text{S} \cdot 0.19\text{B}_2\text{S}_3 \cdot 0.25\text{LiI}$ was reported by Cho *et al.*⁷⁹

In spite of these promising results, active fillers have not been successfully employed as all-solid-state electrolyte system for practical lithium battery, mostly because of the insufficient conductivity at room temperature. In some case, the reported electrolyte containing active fillers had even much lower ionic conductivity at room temperature than that of inactive filler-containing systems.⁸⁰

From Nanocomposite to Nanogel Composite Electrolytes

To enhance the conductivity of CPEs, the addition of liquid electrolytes was suggested in an expectation to combine the advantages of both gel and nanocomposite polymer electrolytes.⁸¹⁻⁸³ Nanogel composite electrolytes can be obtained either from a nanocomposite polymer electrolyte by incorporating a conventional liquid electrolyte (nanogel porous polymer electrolyte) into a porous structure of a nanocomposite polymer or from a GPE containing dispersed nanoparticles (homogeneous nanogel polymer electrolyte). As a whole, the addition of filler particles into the GPE increases the ionic conductivity, porosity, and liquid uptake, while reducing the risk of liquid leakage.

Rutile TiO_2 nanoparticles were claimed to be more easily dispersed in the polymer solution than the anatase type. These materials were used as nanofillers for a PVdF-HFP-based nanocomposite porous polymer electrolyte swollen with 1M LiPF_6 in EC:DMC (1:1 v/v).⁸⁴⁻⁸⁵ The electrolyte system was reported to possess low liquid uptake and sufficient ionic conductivity. Such a high ionic conductivity was explained by the liquid medium within nanopores as well as effective ion transport supported by TiO_2 nanoparticles. Excellent electrochemical stability of the polymer electrolyte was also observed, and 30 - 40 wt.% TiO_2 was suggested as the optimum. Similar results were also reported with the electrolyte systems based on PVdF-HFP and a filler like TiO_2 , nanosized $\text{Al}(\text{OH})_n$, molecular sieves, or zeolites.⁸⁶⁻⁹⁵

Wu *et al.* carried out a comparative study with metal oxides and mesoporous zeolites as fillers, which were dispersed in the porous polymer matrix of PVdF-HFP-based electrolyte comprising EC:PC (1:1 v/v) mixture as the liquid plasticizer.⁹⁶ The addition of these solid fillers into the filler-free electrolytes increased the ionic conductivity twice, from $1.2 \times 10^{-3} \text{ S cm}^{-1}$ to $2.1 \times 10^{-3} \text{ S cm}^{-1}$, possibly because of the increased porosity and liquid uptake. More advantageously, these

electrolyte systems showed the electrochemical stability up to 5.5 V (versus Li/Li^-).

SiO_2 -containing poly(ethylene glycol) diacrylate (PEGDA)-based nanogel electrolytes were prepared with 1 M LiPF_6 in EC:DMC:DEC (1:1:1 by volume) solution as the liquid plasticizer.⁹⁷ Cyclic voltammograms of the system were reported up to 5 V, and the superior chemical stability was ascribed to the addition of SiO_2 . The nanosized SiO_2 was found to contribute to the rapid formation of compact and stable passive films, which stabilize the interface between the electrolyte and lithium electrode. With all liquid contents, the nanogel system exhibited a little higher conductivity than that of the corresponding GPE. A cell performance employing the above electrolyte system retained 97% initial discharge capacity after 30 cycles at 0.2 C rate, which was more stable than that of PEGDA-based GPE developed by Song *et al.*⁹⁸

In terms of practical application, an impressive cell performance was reported by Yang *et al.*⁹⁹ Nanogel polymer electrolytes of PVdF/PEGDA/PMMA containing $\text{LiPF}_6/\text{LiCF}_3\text{SO}_3$ (10/1, wt.%) were prepared employing several traditional ceramic fillers such as Al_2O_3 , BaTiO_3 , and TiO_2 . The cell performance of the system with Al_2O_3 filler maintained 95% of initial capacity after 100 cycles at C/2 rate.

Conclusions

In contrast to the ionic transport mechanism in SPEs and GPEs, in which the ion motion is coupled with the segmental relaxation of the polymer host, the ionic transport mechanism in CPEs can be explained as an indirect result of Lewis acid-base type interactions between the filler surface and the polymer host. Because of these interactions, the crystallinity can be reduced to a great extent, allowing Li^+ to move more freely either on the interface between the low-density polymer phase and the particles or on the surface of the particles. The addition of these solid fillers to the polymer electrolyte significantly increases the properties of the electrolytes in terms of ionic conductivity, mechanical stability, thermal and chemical stability, and stability of the interface between the electrolytes and lithium electrodes.

Nanogel composite electrolytes have been recognized as innovative alternatives due to their excellent electrochemical and mechanical properties comprising advantages of both CPEs and GPEs.

The presence of nanoparticle fillers in the GPEs is found to improve the liquid uptake, leading to an increase in ionic conductivity and a decrease in liquid leakage. Remarkably, nanogel composite electrolytes show superior ionic conductivities and electrochemical stability.

In conclusion, nanocomposite and nanogel composite electrolytes can be regarded as the most promising next generation electrolytes with superior properties, such as higher safety, much longer cycle life, higher energy density, and shorter charging time.

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