Chapter 11
Tailoring Performance of Polymer Electrolytes Through Formulation Design

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Abstract The flammable organic solvent-based electrolytes used in lithium batteries impose serious safety concerns and temperature restrictions. A switch to solid polymer electrolytes can significantly increase chemical/mechanical stability, improve safety, reduce cost, and advance manufacturability, if only issues such as low conductivity and transference, limited operating temperature range, and insufficient mechanical strength can be overcome. To this end, significant research efforts have been directed to understand the mechanism of lithium ion motion in polymer matrices and to modify the chemistry, architecture, and morphology of the poly(ethylene oxide) polymer typically used in polymer electrolytes. Furthermore, the incorporation of nanoparticles into polymer electrolytes has created new opportunities for simultaneous improvement of conductivity and of mechanical properties. The performance of such composite polymer electrolytes can be modulated by the judicious surface chemical modification of the nanoparticles and/or by the addition of organic solvents or ionic liquids. The examples highlighted here point to the importance of formulation design for the improvement of the performance characteristics of multi-component systems such as polymer electrolytes.

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11.1 Introduction

Polymer electrolytes are widely utilized in electrochemical devices such as lithium-ion batteries, fuel cells, and supercapacitors for energy storage and conversion [1–8]. In this chapter, we focus on different additives and their effects on polymer electrolyte performance for lithium-ion batteries. A battery is composed of two electrochemically active electrodes [9] separated by an ion-conductive, electronically insulating electrolyte medium [10]. Rechargeable batteries find widespread use because of their repeated charge and discharge capability [11].

The electrolyte is one of the critical components of the lithium-ion battery. It facilitates ion transport and blocks electron conduction between the two electrodes [12]. Desirable properties of electrolytes are: high ionic conductivity and cation mobility, low electronic conductivity, good mechanical strength, thermal and chemical stability, and interfacial contact with electrodes, and large electrochemical stability window [13, 14]. Organic solvent-based electrolytes and ionic liquid-based electrolytes are two classes of electrolytes that have been well studied but they exhibit several drawbacks [15]. Organic solvent-based electrolytes have problems that include intrinsically poor cycling efficiency and flammability [16]. For ionic liquid-based electrolytes, a challenge is their relatively high viscosity which limits the attainable ionic conductivity [17–19]. Polymer electrolytes [20, 21] have thus been considered with an aim to overcome such limitations. The archetype polymer electrolyte is based on poly(ethylene oxide) (PEO) with lithium salt dissolved in it [22]. However, the semi-crystalline structure of PEO presents inherent problems as a polymer matrix for Li^+: (1) not sufficiently high ionic conductivity, especially in ambient temperature; (2) insufficient mechanical strength; and (3) dendrite growth at the interface between electrode and electrolyte, which might cause internal short circuits [2].

In order to overcome these limitations of polymer electrolytes, several avenues have been explored. One promising line of investigation involves the introduction of nano-sized additives, as shown in Fig. 11.1 [23], in order to minimize the concentration of PEO crystalline domains without diminishing the PEO flexibility and mechanical stability over a wide temperature range [24, 25]. Inert oxide ceramics are the most common additives [26]. The effects of such additives have been analyzed in terms of Lewis acid–base interactions [24] between the surface groups of the fillers and active sites on the polymer chains.

Even though ternary systems incorporating nano-additives are promising, e.g., due to simultaneous improvement of conductivity and mechanical strength [24–27], composite polymer electrolytes (CPEs) are still away from desirable performance, e.g., room temperature conductivity higher than 10^{-3} S/cm [28]. For applications in electrochemical devices such as lithium-ion batteries [4, 12], research on CPEs is directed toward the formulation of modified ternary (polymer + lithium salt + nanoparticle) systems.

Different schemes have been reported for modifying each component in CPEs. Here, we focus on two avenues of modification: (1) surface chemical modification

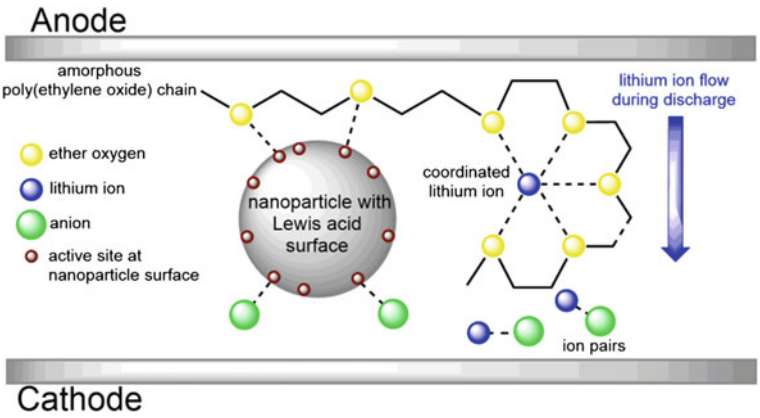

Fig. 11.1 Schematic of composite polymer electrolytes in the context of lithium-ion batteries

of nanoparticles, e.g., functionalization by oligomer groups or by ionic liquids; (2) physical modification via the addition of components such as organic solvents or ionic liquids. Section 11.2 discusses Li^+ transport mechanisms and factors that affect it in polymer-based electrolytes. Section 11.3 addresses the effect of nanoparticles on CPE properties and performance. Section 11.4 discusses nanoparticle chemical modification. Section 11.5 is concerned with the physical addition of a fourth component to CPEs. The purpose of Sects. 11.4 and 11.5 is to exemplify how different formulation modifications of CPEs have been designed and implemented, and to inspire ideas on novel CPE design for further CPE performance improvement.

11.2 Polymer-Based Electrolytes

First, we review key molecular mechanisms and phenomena influencing the motion of Li ions (and their counter-ions) in a polymer matrix, and we outline several major challenges that conventional polymer electrolytes are facing to become an efficient alternative to conventional organic solvent electrolytes. We use PEO-based polymer electrolytes to illustrate these issues as the overwhelming majority of polymer electrolytes investigated to date are PEO-based. In addition to a large number of experimental studies, PEO-based electrolytes have also been studied by molecular simulation [29–41], and therefore these systems provide good case studies to illustrate the full complexity of understanding and design of efficient polymer electrolytes.

11.2.1 Mechanism of Li^+ Motion in PEO-Based Polymer Electrolytes

PEO is the quintessential polymer electrolyte owing largely to its effectiveness at dissolving lithium salts due to strong Li^+-ether oxygen binding. Quantum chemistry (QC) and molecular dynamics (MD) simulation studies [29, 42] of PEO have revealed that Li^+ cations are very strongly coordinated by an average of six ether oxygen atoms as shown in Fig. 11.2. Coordination of Li^+ usually involves a single PEO chain, with occasional coordination by two polymer chains.

The nature of ether–-Li^+ interactions strongly affects the mechanism of Li^+ mobility in PEO-based solid polymer electrolytes (SPEs). This can be understood by comparing the mechanism of Li^+ diffusion in oligoethers with that in organic solvents. Li^+ motion in organic liquid electrolytes (typically carbonates) occurs by a combination of vehicular (with a solvent shell) and structural (exchange of solvent shell) diffusion [43]. In contrast, simulations reveal that Li^+ diffusion in pentaglyme + Li[bis[(trifluoromethyl) sulfonyl]imide] (TFSI) [43] salt occurs entirely by a vehicular mechanism, i.e., a pentaglyme/Li^+ complex diffuses long distances before Li^+ exchanges between complexing molecules. The residence time of Li^+ with a pentaglyme is around 50 ns, compared to $\sim$1 ns in carbonate, or 3–10 ns in ionic liquids [44]. While the lack of an efficient structural diffusion mechanism has relatively little influence on Li^+ motion in pentaglyme because of the fast center-of-mass diffusion of the low molecular weight (MW) solvent, the situation is different in higher molecular weight (MW) PEO. Because the center-of-mass diffusion of PEO is negligible, a Li^+ cation must change coordinating PEO chains, i.e., it will undergo "jumps" between PEO chains [45]. Compared with pentaglyme, Li^+ transport is considerably slower in the PEO-based SPE, while the diffusion of TFSI is reduced relatively little, indicative of the relative independence of anion motion from that of the polymer. This leads to a significantly lower transference number in the polymer electrolyte as a much greater fraction of charge is carried by the anion due to the very slow Li^+ motion. Furthermore, the PEO chain center-of-mass motion is considerably slower than that of the cation, intimating that the vehicular mechanism, which is so important in the oligoethers, does not contribute significantly to Li^+ motion in the SPE. Instead, Li^+ motion in the PEO-based electrolytes resembles diffusion along PEO chain contours with occasional inter-chain jumps on a time scale of $\sim$100 ns [41].

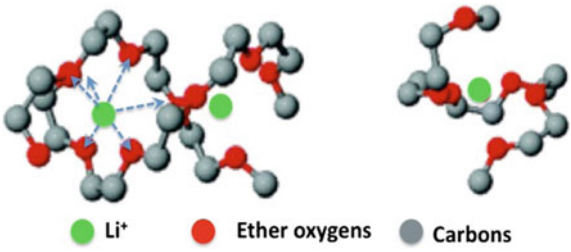

Fig. 11.2 Representative configurations of Li^+ coordination by PEO

Simulation [29] and experimental studies [46, 47] of linear PEO-based electrolytes also showed strong dependence of the Li^+ and anion motion on salt concentration. While the anion motion remains much faster than that of Li^+ for all salt concentrations, the translational dynamics of both ions decrease dramatically with increasing salt concentration, suggesting strong coupling with local polymer relaxations. The slowing of polymer segmental dynamics with increasing salt content is due to the strong binding between ether oxygens and Li^+, which greatly restricts conformational motion. As a result, a maximum in PEO-based electrolyte conductivity is observed for Li:EO molar ratio $\sim$1:10 due to two counter-acting effects: Ionic conductivity increases with increasing salt concentration due to the increase in the number of charge carriers, while increasing salt concentration slows down polymer dynamics, thereby decreasing also the Li^+ transport [29, 48].

11.2.2 Influence of Polymer Architecture

Polyethers of comb-branch chain architecture have been investigated in efforts to develop polymer electrolytes that take advantage of the ability of oligoethers to coordinate Li^+ while, at the same time, preventing crystallinity due to use of short side chains, and allow for separate optimization of the backbone properties from those of the side chains [49]. The ideal comb-branch electrolyte might, for example, use a glassy backbone polymer, thereby leading to good mechanical properties, while Li^+ transport would be carried out by flexible ether (PEO) side chains (Fig. 11.3a). The use of relatively short side chains not only reduces/prevents PEO crystallinity, but may also facilitate the inter-chain hopping needed for large-scale Li^+ transport, due to sharing of Li^+ cations between side chains. Several polymer electrolytes formed from comb-branch polymer have been studied experimentally [50, 51] and in simulations [30], however, studies showed that the conductivity of the comb-branch electrolytes is very similar to that of the linear PEO electrolytes. Molecular simulations of the comb-branched systems revealed that Li^+ motion occurs primarily by hopping of the cation from one side chain to another [30]. However, a fraction of Li^+ cations are partially coordinated by the polyether backbone and, therefore, have very slow dynamics and do not contribute to conductivity. The slow dynamics of cations that are partially coordinated by the chain backbone can be correlated with conformational transitions of PEO segments: those that are closer to the backbone are significantly slower due to steric crowding. Hence, the Li^+ complexed by the slower segments exhibits the lowest mobility. Therefore, while the comb-branched PEO-based electrolytes investigated so far did not show improved Li^+ conductivity, they provided evidence of two promising trends: (1) the Li^+ that is not complexed by the backbone exhibits higher mobility than in the linear PEO electrolyte, indicating that the short side chains do promote inter-chain hopping, and (2) the Li^+ mobility, at least for those cations not complexed by the polymer backbone, is largely independent of the backbone motion.

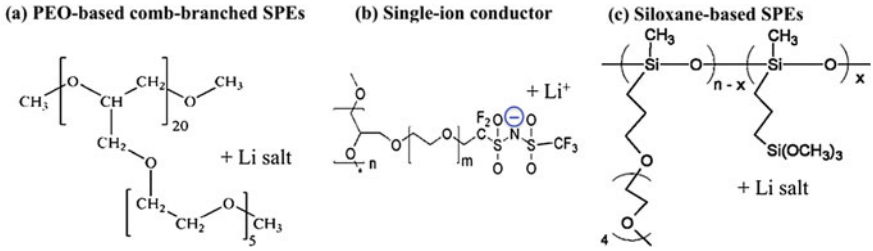

Fig. 11.3 Representative PEO-based polymer architectures considered for SPEs

One disadvantage of current PEO-based electrolytes is their low transference number due to relatively high anion mobility. Large-scale anion motion in comb-branch electrolyte can be eliminated by attaching the anions to the polymer (Fig. 11.3b), however, this has a deleterious effect on Li^+ mobility [52], because anions play an important role in the ability of Li^+ cations to undergo inter-chain jumps. While attaching the anion to the polymer has the advantage of improving transference number (all charge is carried by Li^+), further reducing the Li^+ mobility is a major disadvantage. Addition of a solvent/plasticizer [e.g., ethylene carbonate (EC)] to the single-ion conductor electrolytes showed dramatic improvement in ionic conductivity over the non-plasticized single-ion conductor. EC increases the rate of polymer conformational transitions, yet it is not directly involved in coordination and transport of Li^+ [53]. An experimental investigation [54] of a single-ion conductor made from blending PEO with a comb-branch polystyrene-based polyanion showed a low conductivity, but depending dramatically upon the polyanion structure. Such blending provides additional degrees of freedom in terms of composition and architecture design of polymer electrolyte [55].

Finally, there has been an interest in siloxane as a component for polymer electrolytes due to its conformational flexibility (and hence low glass transition temperature) and electrochemical stability. Because siloxane itself has limited ability to solvate Li^+, siloxane-based electrolytes contain ether groups for the purpose of solvating and transporting Li^+. Siloxane-ether oligomers [56–59] and comb-branch polymers with siloxane backbones and PEO side chains [60–63] (Fig. 11.3c) show indeed improved conductivity. However, these electrolytes do not exhibit adequate room temperature conductivity and mechanical stability for most applications.

11.2.3 Influence of Polymer Morphology

Microphase-separated copolymers consisting of PEO covalently linked to a different type polymer offer an attractive avenue to achieving both high ionic

conductivity and dimensional stability in polymer electrolytes [64]. Microphase-separated copolymers can also prevent the formation of semi-crystalline spherulites that reduce contact with electrodes [65]. It is important to note that added lithium salts modulate the degree of block segregation and can alter the resulting polymer organization and properties emanating from this [66, 67]. Copolymer electrolytes that provide nano-scale domains ion-rich and ion-lean can be advantageous [68]. The ion-rich domains play a primary role in ion transport and, to this end, the polymer segments localized there should be mobile, through appropriate polymer chemistry and architecture, or through heating and/or the introduction of plasticizers. The polymer segments of the ion-lean domains can be designed such that they contribute to the mechanical rigidity of the polymer electrolyte [69].

The conductivity of heterogeneous polymer electrolytes involves a pre-factor $f\,(\leq 1)$ that accounts for the tortuosity and connectivity of the conducting domains [68]. In the case of block copolymer electrolytes [69] with well-defined nano-scale morphologies [70], an ideal morphology factor, f_{ideal}, can be defined based on perfectly ordered lamellae, cylinders, etc. [68]. Experimentally determined f of heterogeneous polymer electrolytes relevant to Li-ion batteries is typically lower than f_{ideal} [67] indicating the importance of the resistance at grain boundaries, and associated with it, the importance of processing history [71, 72].

The effects of morphology on the ionic conductivities of polymer electrolytes are significant [69]. A polymer electrolyte membrane of a typical 100 μm thickness encompasses several micro-scale grains, each with well-defined nano-scale organization of the polymer, but each with different orientation. For intra-grain ion transport, the continuity and connectivity of the ion-conductive nano-scale domains are important, whereas for inter-grain ion transport, the connectivity of conducting channels across the boundary between adjacent grains is important. The mesoscopic and macroscopic orientation/alignment of nano-structured domains are outstanding issues in the field of microphase-separated polymers, but several methodologies have been found effective, such as thermal or solvent annealing, epitaxy, templating, stretching, shear alignment, application magnetic or electric fields, or combinations thereof [72–83].

While nano-scale polymer organization is driven by thermodynamics, meso-scale grain size and alignment are typically an outcome of processing, either deliberate or unintended consequence of sample preparation and testing [84]. An investigation of thermal history on the ionic conductivity of LiTFSI (lithium bis (trifluoromethanesulfonyl)imide, $LiN(SO_2CF_3)_2$)-doped PEO-PS (polystyrene) block copolymer electrolytes showed the conductivity of low MW samples to decrease after annealing, while the conductivity of high MW samples was unaffected. This was attributed to the development of well-defined nanostructure in the annealed samples [85]. A subsequent study on the dependence of ionic conductivity on the grain size of a lamellar PEO-PS block copolymer electrolyte showed well-formed lamellar grains to be less conducting than poorly defined, small grains [86]. Well-ordered solvent-cast films of polymerized ionic liquid block copolymers (single-ion conductors) exhibited up to an order of magnitude higher conductivity than poorly ordered melt-pressed films [87].

11.3 Composite Polymer Electrolytes

As nanoparticles are incorporated into a PEO + salt electrolyte to form a composite polymer electrolyte (CPE) [24, 25], the concentration of PEO crystalline domains can be reduced without harming the PEO chain flexibility. This is a main reason for the observed ionic conductivity enhancement in CPEs. Moreover, the cation transference number (t^+, fraction of the current carried by lithium ions) and the mechanical strength can be improved simultaneously over a wide temperature range. These effects of nanoparticles on polymer electrolytes are highlighted in this section.

11.3.1 Nanoparticle Effects on Conduction and Transference

The most critical requirement for the application of polymer electrolytes in lithium-ion batteries is the ionic conductivity. This is commonly described by the Vogel–Tamman–Fulcher (VTF) equation [25, 88, 89].

$$\sigma = AT^{-1/2}\exp[-\mathrm{E}_a/(T - T_0)] \tag{11.1}$$

The conductivity variation with inverse temperature for the CPEs PEO (4×10^6 g/mol)–LiTf (lithium trifluoromethanesulfonate or lithium triflate, $LiCF_3SO_3$, EO: $Li^+ = 9$)–x wt% TiO_2 ($x = 0, 5, 10, 15$ and 20) is shown in Fig. 11.4. Only the 5 wt% sample behaves differently compared to the typical VTF behavior of other electrolytes. Specifically, the conductivity increases faster at temperatures $T > 80$ °C due to the increased mobility of ions via Lewis acid–base interaction. The sample with 10 wt% TiO_2 exhibited the optimal ionic conductivity among those studied. Further addition of nanoparticles (20 wt%) led to a drop in conductivity because of nanoparticle agglomeration that hindered ion transport [90].

In addition to their effect on ionic conductivity, nanoparticles also affect the transference number (t^+) of CPEs. t^+ directly describes the charge transport and thus the current of a specific ion [91]. Specifically, t^+ indicates the fraction of the current that is carried by the cation (Li^+) in the electrolytes. It is desirable to achieve a high t^+ value in order to enhance the electrode reaction kinetics and to eliminate the concentration gradients within the battery so that the internal voltage drop could be lowered and the output current increased [92]. t^+ is most commonly calculated by Eq. (11.2) [93, 94].

$$t^+ = \frac{\mu^+}{\mu^+ + \mu^-} = \frac{D^+}{D^+ + D^-} \tag{11.2}$$

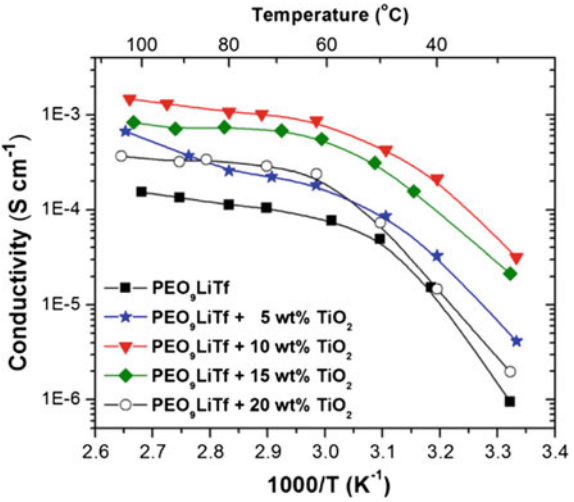

Fig. 11.4 Variation of conductivity with inverse temperature on the heating run for composite polymer electrolytes incorporating TiO_2 ceramic powder; PEO (4×10^6 g/mol)–LiTf (EO: $Li^+ = 9$)–x wt% TiO_2 ($x = 0$, 5, 10, 15 and 20) (Reproduced from Ref. [90] with kind permission of © 2014 Elsevier)

In Eq. (11.2), D^+ and D^- are the cation and anion self-diffusion coefficients; μ^+ and μ^- are the mobility [95, 96] of the cation and anion, respectively.

High lithium transference number ($t_{Li}{}^+$) at ambient temperature contributes to efficient battery performance [97, 98]. In view of the importance of t^+, the effect of additive surface functional sites on the transference number (t^+) is discussed here. For the system PEO–$LiCF_3SO_3$ (EO:$Li^+ = 20$)–10 wt% Al_2O_3 (basic, neutral, or acidic, $d = 5.8$ nm), the transference number t^+ increased in the sequence of updoped ($t^+ = 0.46$) < basic Al_2O_3 ($t^+ = 0.48$) < neutral Al_2O_3 ($t^+ = 0.54$) < acidic Al_2O_3 ($t^+ = 0.63$) [99]. As for an explanation, the hydrogens of acidic ceramic surfaces (Lewis acid) form hydrogen bonds with the lithium salt anions and the ether oxygens (Lewis base) [99], which promote salt dissociation and also decrease the PEO crystallinity [98, 99]. In this way, t^+ increased. As for the neutral and basic Al_2O_3, the number of Lewis acid sites decreased, leading to a weaker increase in t^+. This discussion would be more interesting if the number of acidic sites on the surface could be quantified in combination with oxygen vacancy analysis. The efficiency of acidic sites on the t^+ increase would thus be revealed.

We discuss above factors affecting the lithium transference number t^+. But how is t^+ related to conductivity? Conductivity and $t_{Li}{}^+$ results have been compared for CPEs, with the additive being ionically active or inert SiO_2 particles (active SiO_2 was mesoporous silica MCM-41 absorbing plasticizers of ethylene carbonate (EC)/propylene carbonate; inert SiO_2 was mesoporous silica MCM-41 without plasticizers). For PEO (300,000 g/mol)–$LiClO_4$ (EO:$Li^+ = 16$)–SiO_2 (1000 $m^2\ g^{-1}$), the conductivity initially increased upon addition of active SiO_2, attained a maximum value of about 2.4×10^{-5} S cm^{-1} at 10 wt% active SBA-15 (even though the free Li ion percentage was optimized at 5 wt%), followed by a mild decline with further loading of active SBA-15 [92]. In parallel, the transference number t^+ increased from 0.42 for the undoped sample, reached a maximum value of 0.54 at 10 wt%

active SBA-15, followed by a drastic decline with further loading of active SBA-15 (Fig. 11.5). As for the reasons, the –OH groups on the surface of SBA-15 compete with Li^+ (both as Lewis acid) to interact with ether oxygens and ClO_4^- (both as Lewis base) to promote Li^+ transport and thus enhance t^+. When the additive content exceeded 10 wt%, nanoparticle aggregation drastically impaired the Li^+ transference number.

In another study, mSBA-15 (silane-functionalized silica of SBA-15, 1000 $m^2\ g^{-1}$) was added into PEO (300,000 g/mol)–$LiClO_4$ (EO:Li^+ = 16). The ionic conductivity (σ) and t^+ presented a similar increasing trend and achieved their peak values simultaneously at a level of 5 wt% doping. This mSBA-15 additive has been proposed to promote lithium salt dissociation and produce more free lithium ion, and to lower the activation for ion transport [100]. Following the peak values, σ decreased gradually and t^+ decreased steeper upon further nanoparticle addition.

11.3.2 Nanoparticle Effects on Mechanical Properties

Polymer electrolytes are promising to avoid drawbacks of the liquid-state electrolytes and help to expand the operating conditions, even in harsh conditions, e.g., high temperature. However, the mechanical strength of neat PEO is not satisfactory, especially at a high working temperature due to its low-melting temperature 66–75 °C. The binary systems of PEO with lithium salt do not exhibit an obvious improvement of mechanical strength despite the transient crosslinks [101] formed between lithium ions and ether oxygens. Thus, the mechanical properties of polymer electrolytes with nano-additives became of interest. In this section, we discuss how nanoparticles can improve CPE mechanical properties such as tensile strength, yield strength, elastic and viscous modulus.

Silane (KH550)-modified silica was added for simultaneous enhancement of the ionic conductivity and mechanical strength of PEO (MW = 300,000 g/mol)–

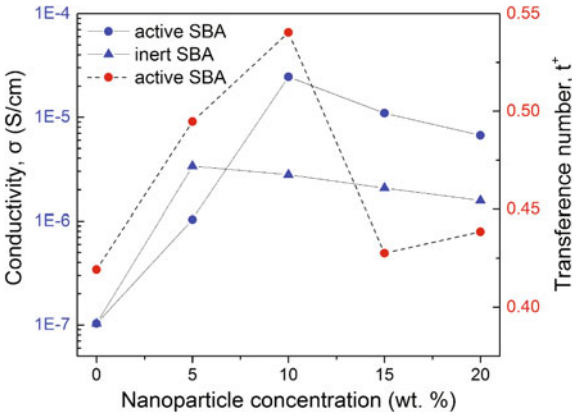

Fig. 11.5 Ionic conductivity σ and lithium transference number t^+ as a function of **a** active SBA-15 and **b** inert SBA-15 content for PEO (300,000 g/mol)–$LiClO_4$–SiO_2 (1000 $m^2\ g^{-1}$) CPE at 25 °C. *Solid lines* correspond to the *Y* axis on the *left*. The *dashed line* corresponds to the *Y* axis on the *right* (Data from Wang et al. Ref. [92])

$LiClO_4$ (EO:Li^+ = 16) [102]. Less than 10 wt% nanoparticles caused the formation of an amorphous interface region around the nanoparticles and an increase in the polymer amorphous fraction [103], which led to an increase of the ionic conductivity as shown in Fig. 11.6. Further addition (>10 wt%) of nanoparticles led to agglomeration that impaired the ionic conductivity. In contrast, the CPE tensile strength kept increasing upon addition of nanoparticles to 15 wt% [102].

In another study, the tensile modulus and yield strength of PEO (300,000 g/mol)–$LiClO_4$–(mSBA-15: silane-functionalized mesoporous silica) increased with increasing mSBA-15 amount in the 0–15 wt% range [100]. This enhancement is due to the addition of ceramic fillers which acted as crosslinking media inside the polymer matrix by their surface interactions [104]. However, the enhancement was not always monotonic. For PEO (100,000 g/mol)–$LiClO_4$–(montmorillonite–CNT), the optimized tensile strength was achieved upon 5 wt% clay–CNT incorporation into the hybrid. The tensile strength increased by 160% compared to the PEO electrolyte [105]. This reinforcement has been ascribed to the large aspect ratio and surface roughness of the clay–CNT hybrid filler, which lead to strong interactions between nano-fillers and polymer [105]. The different surface roughness may also explain the difference in the optimal nano-additive amount for maximized tensile strength between these two systems. In combination with the knowledge that the maximum conductivity occurred at 10 wt% nano-additive [92, 106, 107], the incorporation of 10 wt% nano-additive appears to offer an optimal combination of improved mechanical properties as well as optimized ion conductivity. Very likely, a CPE composition involving around 10 wt% additive would also correspond to minimized T_g, T_m, and crystallinity. Of course, the surface conditions, e.g., roughness, functionalization, and possible surface defects of the nanoparticle additives may cause the final result to deviate.

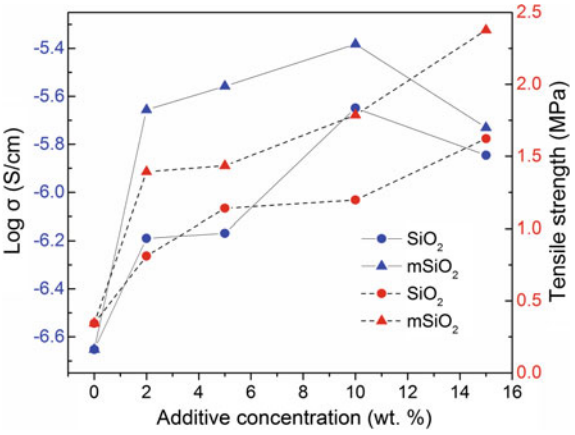

Fig. 11.6 Ionic conductivity and tensile strength for PEO (MW = 300,000 g/mol)–$LiClO_4$ (EO:Li^+ = 16) with various contents of SiO_2 and KH550-modified SiO_2 ($mSiO_2$) at 30 °C. *Solid lines* correspond to the *Y* axis on the *left*. *Dashed lines* correspond to the *Y* axis on the *right* (Data from Fan et al. [102])

11.4 Ternary Polymer Electrolytes

With an aim to further improve the CPE performance, Sect. 11.3 discusses the silica nanoparticle modification by plasticizers treatment or by silane compound to tune the interactions between polymer, nanoparticles, and Li^+ ions (the notion of tuning interactions also applies to the physical modification of CPEs that is discussed in Sect. 11.4). The compatibility of nanoparticles with the polymer matrix can be improved in this way. We discuss here pseudo-ternary systems consisting of polymer, salt, and surface-modified nanoparticles. Typical methods of nanoparticle chemical modification with polymers and ionic liquids are addressed in Sects. 11.4.1 and 11.4.2, respectively.

11.4.1 Polymer-Functionalized Nanoparticles

In order to improve the compatibility of nanoparticles with the polymer matrix for a better performance of CPEs, surface grafting of nanoparticles with oligomers (short chain polymers) that share the same repeating unit as the polymer matrix has been actively investigated. One example involves polyhedral oligomeric silsesquioxane (POSS) nanoparticles functionalized by poly(ethylene glycol) (PEG) [108, 109], and another example concerns silica functionalized by PEO [110]. POSS is an organic–inorganic hybrid compound typically formed by inorganic cubic core (siloxane cage) and outer organic groups (pendant arms), with a general formula of $(RSiO_{1.5})_{n\ =\ 6,\ 8,\ or\ 10}$ [111]. POSS are of interest for their broad applications [73, 83], inlcuding in connection to CPEs [112–115].

Different ways of POSS [116–118] application in combination with ion-conductive polymers (e.g., PEO) for electrolytes in lithium-ion batteries have been reported [73, 108, 109, 111–118]. In the first case, the outer organic groups of POSS are ion-conductive PEO chains, and the organic–inorganic hybrid compound (generally denoted as POSS–PEO) itself acts as an electrolyte with the grafted PEO serving as conducting media. In this case, the POSS–PEO is the matrix. In the second case, POSS–PEO can also be used as an additive for binary PEO + salt polymer electrolytes; with the help of grafted PEO chains, compatibility with the PEO matrix can be improved. A comparison of these two cases is presented next.

For the first case of POSS–R as matrix, POSS–PEO_8 (n = 4, where n denotes the number of PEO-repeating units attached to POSS, while the subscript 8 of PEO denotes octa-functionalization on POSS) and PEO 600 K were compared as ion conduction medium upon addition of $LiClO_4$ at a fixed amount of EO:Li^+ = 12. As shown in Fig. 11.7a, the POSS–PEO_8 (n = 4)-based electrolyte exhibited higher conductivity than that of PEO (600 K)-based electrolyte over the whole temperature range. In contrast, in Fig. 11.7b, PEO (600 K)–$LiClO_4$ (O/Li = 12:1) exhibited an abrupt conductivity change [108] at the PEO-melting temperature of around 327 K. At low temperatures ($T < T_m$), neat POSS–PEO_8 (n = 4, O/Li = 12:1) presented a

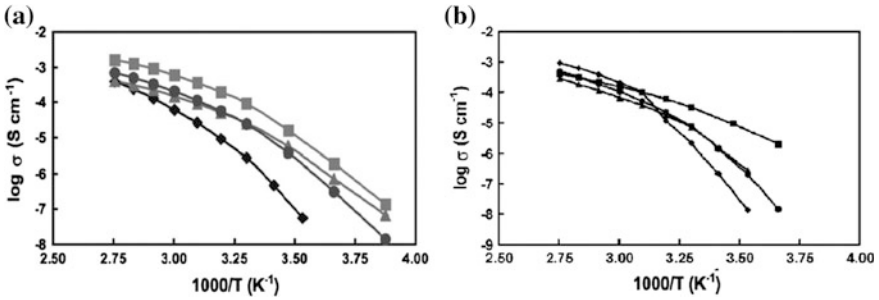

Fig. 11.7 **a** Conductivities of (i) POSS–PEO (n = 3)$_8$ (*filled triangle*); (ii) POSS–PEO (n = <8>)$_8$ (*filled circle*); (iii) PEGDME (MW = 500 g/mol) (*filled square*); and PEO (MW = 600 K) (*filled diamond*). All samples are prepared using $LiClO_4$ with O/Li = 8:1. Reproduced from Ref. [109] with kind permission of © 2006 The Electrochemical Society; **b** conductivity plots of (i) POSS–PEO_8 (n = 4) (*filled square*); (ii) PEO (MW = 600 K) (*filled diamond*); (iii) blend of 50 wt% POSS–PEO_8 (n = 4) with 50% PEO (600 K) (*filled triangle*); and (iv) blend of 60 wt% POSS–PEO(n = 4)$_8$ with 40 wt% PEO (600 K) (*filled circle*); all samples are prepared using $LiClO_4$ with O/Li = 12:1 (Reproduced from Ref. [108] with kind permission of © 2007 American Chemical Society)

higher conductivity than that of PEO (600 K)–$LiClO_4$ (O/Li = 12:1) because of the low viscosity of POSS–PEO_8 and the crystallization of PEO. At high temperatures ($T > T_m$), it is the opposite case because of the inert $SiO_{1.5}$ core of POSS–PEO.

For the second case of POSS–R as additive, at low temperatures, the mixture of POSS–PEO_8 (n = 4) /PEO (600 K) exhibited a conductivity between that of POSS–PEO_8 (n = 4)- and PEO (600 K)-based electrolytes. This was attributed to the crystallinity decrease by addition of POSS–PEO_8 into PEO (600 K); at high temperatures, the mixture of POSS–PEO_8 (n = 4) /PEO (600 K) exhibited lower conductivity than PEO (600 K)–$LiClO_4$ (O/Li = 12:1) because of the presence of the inert $SiO_{1.5}$ core [108].

Fumed silica (FS) (d = 12 nm, surface area = 200 m^2/g) functionalized by non-polar alkyl moieties (FS-C_8) or by polar PEO oligomers with MW = 200 g/mol (FS-C3EG3ME) has been used in oligomer-based electrolytes with two different lithium salts, respectively: polyethylene glycol dimethyl ether (PEGDME, Mw = 250 g/mol)–$LiN(CF_3SO_3)_2$/$LiCF_3SO_3$ (Li:O = 1:20) [110]. The conductivity was not improved but rather dropped marginally with the addition of fumed silica at a doping amount of 10 and 20 wt%. FS-C3EG3ME even brought down the conductivity to a larger extent compared to FC-C8. High conductivities of over 10^{-3} S/cm at the 295–400 K temperature range were reported [110]. This high conductivity was attributed to the low molecular weight matrix of PEGDME with MW = 250 g/mol. In this case of low molecular weight oligomer electrolyte, the conductivity benefited from the liquid state of the matrix, while the addition of nanoparticles increased the viscosity to impair the ionic conductivity to some degree. This is opposite to the nanoparticle effect in SPEs to improve ion conduction. However, when it comes to a solid polymer matrix, it is possible that

FC-C3EG3ME would act more effectively to facilitate ion transport for its lithium ion coordination sites of EO units [114, 117]. Therefore, the incorporation of these differently grafted fumed silica into solid polymer electrolytes awaits to be investigated for comparison.

Other studies of polymer-functionalized nanoparticles include silica grafted with: [119] (1) homopolymer of poly(ethylene glycol) methyl ether methacrylate (PEGMA) of different molecular weight, or (2) poly(ethylene glycol) methyl ether methacrylate (PEGMA) copolymer, as additive for matrix of poly(ethylene glycol) dimethyl ether (PEGDME, Mw = 500 g/mol)–LiI/I_2 (EO:Li = 10:1). This system was reported to achieve room temperature conductivity 10^{-4} S/cm, but this result was around a threefold decrease from the undoped binary samples [119]. Thus, it can be concluded that the effectiveness of modified nanoparticle on properties of CPEs differs depending on the liquid or solid state of the polymer matrix, and it is not always the case that chemically functionalized nanoparticles can help improve the performance of the electrolytes. Similar work has been published, e.g., PEO-grafted silica was used in the matrix of PEO/sulfoisophthalate ionomers to improve the room temperature ionic conductivity by an order of magnitude [120].

11.4.2 Ionic Liquid-Modified Nanoparticles

In addition to PEO oligomer grafting on POSS surfaces, ionic liquids have also been introduced for nanoparticle chemical functionalization. The application of ionic liquids in polymer electrolytes has been motivated by their good chemical and electrochemical stability, low flammability, and negligible vapor pressure [18, 121–126]. Researchers then considered nanoparticles and ionic liquids chemically combined together as additives for CPEs. For example, studies have been reported on 1-methyl-3-[(triethoxysilyl)propyl]imidazolium chloride (TMICl) tethered to TiO_2 nanoparticles (20 nm in size) used in electrolytes for dye-sensitized solar cells (DSSC) [127], and on 1-undecyltrimethoxysilane-3-butyl imidazolium bis (trifluoromethylsulfonyl) imide tethered to ZrO_2 (average particle size 86 ± 2 nm) as hybrid electrolytes for lithium-ion batteries [128].

In a recent study, 1-methyl-3-propyl-imidazolium bromide ionic liquid attached on silica (MPIm-AS or AS-IL, size not given) was reported to improve the ionic conductivity of PEO (MW = 10^6 g/mol)/poly(ethylene imine) (PEI, MW = 1.2×10^5 g/mol)–$LiClO_4$ [129]. (PEO:PEI = 10:1, lithium salt, and nanoparticle amount not specified.) The novelties included: (1) physical mixing of PEI with PEO as polymer matrix, PEI itself providing alternative coordination sites to complex with lithium ions by its nitrogens on polymer chains; (2) blending with PEI makes the electrolyte formation easier due to its lower viscosity, and thus unnecessary to use plasticizers.

The impedance became much smaller upon the introduction of MPIm-AS, with the optimal content observed at 6 wt% and the corresponding conductivity at 9.1×10^{-5} S/cm as shown in Fig. 11.8 [129]. In contrast to the Sect. 11.3

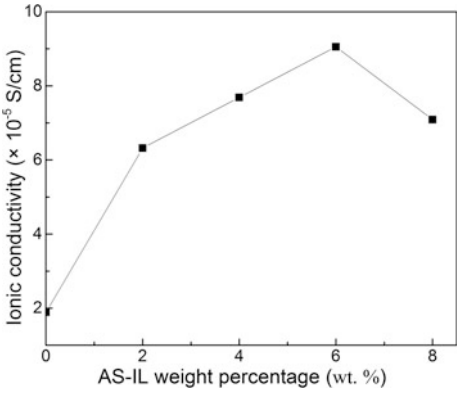

Fig. 11.8 Ionic conductivity of poly(ethylene oxide) ($M_W = 10^6$ g/mol)/poly (ethylene imine) ($M_W = 1.2 \times 10^5$ g/mol)–$LiClO_4$ (PEO:PEI = 10:1) containing 0, 2, 4, 6, and 8 wt % of AS-IL at room temperature (Data from Kim et al. [129])

discussion of optimal doping at 10 wt%, [92, 106, 107], the optimal doping concentration of AS-IL is decreased in this case to 6 wt%. The difference may be due to the different composition of the polymer matrix. The different electron-donating ability of oxygen and nitrogen led to a different solvating ability for the lithium ions and interactions with AS-IL [129]. When the amount of AS-IL exceeded 6 wt%, particle aggregation hindered the ion transport and decreased the ionic conductivity.

Decreasing melting temperature T_m and heat of fusion ΔH_m values are reported in Table 11.1. It is worth noting that the optimal conductivity point, at 6 wt% MPIm-AS, is not the point of lowest PEO crystallinity. This was explained by a greater amount of additive that aggregated and impaired the ion transport within the matrix [129].

Another report of this type concerns 1-methylimidazole chloride (ImCl) ionic liquid-tethered TiO_2 (size not provided) as additives for plasticized polymer electrolytes: PEO ($Mw = 10^6$ g/mol) /PMMA ($Mw = 1.2 \times 10^5$ g/mol)–$LiClO_4$–propylene carbonate–(3–12 wt%) IL-TiO_2 [130]. This study also followed the idea of "tuning the recipe" for CPEs by blending polymers as co-matrix, and also by the addition of plasticizer. The maximum conductivity was 1.05×10^{-4} S/cm at 9 wt% IL-TiO_2 [130]. Further addition of IL-TiO_2 led to conductivity drop due to immiscibility or aggregation of IL-TiO_2. For this type of IL-tethered nanoparticles, the topic of how the two counterparts, i.e., ionic liquid and nanoparticle, work in tandem with the CPEs remains of interest to this field.

To sum up Sect. 11.4, chemical modification of ternary CPEs is seeking to improve the compatibility of nanoparticles with the polymer matrix or to improve the "solubility" of the nano-additives in the polymer matrix. One common method is to graft functional groups onto the nanoparticle surface to interact with ether oxygens of the PEO matrix. Following the chemical modification of the nanoparticles, pre-existing Lewis acid–base interactions have been disturbed. The optimum doping (for optimal ionic conductivity) is no longer the typical 10 wt% for untreated nanoparticles [92, 106, 107]. For different studies, either the polymer matrix can accommodate more nanoparticles [108, 109] for a higher performance, or a smaller amount of nanoparticle doping [129] can function as well as the

Table 11.1 Melting point (T_m), melting enthalpy (ΔH) and crystallinity (χ_c) of for poly (ethylene oxide) (MW = 10^6 g/mol)/poly(ethylene imine) (MW = 1.2×10^5 g/mol)–$LiClO_4$ (PEO: PEI = 10:1) CPEs containing 0, 2, 4, 6 and 8 wt% AS-IL [129]

Content of AS-IL	T_m (°C)	ΔH_m (J/g)	χ_c (%)
a (0 wt%)	60.67	32.1	46.5
b (2 wt%)	55.23	31.7	45.8
c (4 wt%)	53.66	28.7	41.5
d (6 wt%)	51.89	27.8	40.2
e (8 wt%)	46.29	27.2	39.6

unmodified ternary CPEs. Moreover, in CPE studies with modified nanoparticles, the observation that "the sample with nanoparticle doping amount for lowest crystallinity point did not exhibit highest conductivity" [129] has not been thoroughly explained, even though the ion transport is believed to be facilitated in the amorphous state of the polymer matrix.

11.5 Quaternary Polymer Electrolytes

After the discussion in Sect. 11.4 concerning chemically modified nanoparticles in CPEs, we discuss here an alternative for CPE formulation, which is the physical addition of a fourth component in order to improve the performance. The advantages of this approach are the vast choice of co-additives and its ease of implementation (blending as opposed to organic/inorganic chemistry). We discuss here pseudo-quaternary systems consisting of polymer, salt, nanoparticles, and solvent. Two typical classes of the fourth CPE component are organic solvents as plasticizers and ionic liquids. These are highlighted in Sects. 11.5.1 and 11.5.2, respectively.

11.5.1 Organic Solvent Additives

Organic solvent-based electrolytes have been traditionally employed to obtain a high ionic conductivity such as 10^{-2} S/cm [16, 131, 132]. Organic solvents have also been added to polymer electrolytes to produce gel polymer electrolytes (GPE) [133–135]. Given the organic solvent contribution to a high conductivity, organic solvents have been employed as co-additives together with nanoparticles in CPEs. This is a popular approach due to a wide range of additive choices. Selected examples of such quaternary CPEs are discussed in this section.

Conductivity results of plasticized PEO–16 wt% $LiCF_3SO_3$–20 wt% EC incorporating 3–18 wt% of Al_2O_3 (d = 11.8 nm) [136] are shown in Fig. 11.9.

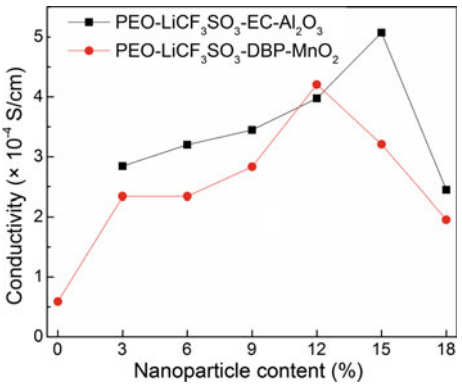

Fig. 11.9 Conductivity for PEO–$LiCF_3SO_3$–EC CPEs at different wt% Al_2O_3, and for PEO–$LiCF_3SO_3$–DBP CPEs as a function of MnO_2 content at room temperature (Data from Johan et al. [136, 137])

The addition of 15 wt% Al_2O_3 fillers maximized the ionic conductivity to 5.07×10^{-4} S/cm. For plasticized PEO (600,000 g/mol)–$LiCF_3SO_3$ (LiTf, Lithium triflate)–dibutyl phthalate (DBP) (20 wt%) incorporating MnO_2 (d = 12–15 nm), a maximum conductivity of 4.3×10^{-4} S/cm was achieved at 12 wt% MnO_2 [137]. Noticeably, the organic solvent-plasticized CPEs tend to accommodate more nanoparticles for optimized ionic conductivity.

The ionic conductivity of systems comprising PEO (4×10^6 g/mol)–$LiCF_3SO_3$ (EO:Li^+ = 9)–EC–Al_2O_3 (5.8 nm pore size, 150 mesh, neutral) is shown in Fig. 11.10 [138]. The observed conductivity enhancement originated from the structural modifications caused by the plasticizer and the nanoparticles. A sample consisting of PEO (4×10^6 g/mol)–$LiCF_3SO_3$ (EO:Li^+ = 9)–50 wt% EC–15 wt% Al_2O_3 (5.8 nm pore size, 150 mesh, neutral) exhibited the lowest T_g and T_m values together with the highest conductivity. However, in the case where EC was not added, the conductivity versus nanoparticle amount revealed that the highest conductivity occurred at 13 wt% Al_2O_3, which is lower than that at 15 wt% observed in the presence of EC. Compared to results from other ternary systems which usually present optimal conductivity at 10 wt% nanoparticle doping [92, 106, 107], the plasticized polymer electrolytes can accommodate higher amounts of nano-additives, with the assistance of organic solvent.

In parallel with the conductivity results, the thermal properties of polymer electrolytes incorporating co-additives reflect the conductivity trend to some extent, and thus can be employed to explain the conductivity changes. The T_g and T_m values for the binary PEO (4×10^6 g/mol)–$LiCF_3SO_3$ (Lithium triflate, LiTf, EO:Li^+ = 9) electrolytes were −44 and 58 °C, respectively [138]. Both T_g and T_m decreased with the addition of either Al_2O_3 filler or EC plasticizer. A quaternary system containing both nanoparticle and plasticizer further brought down both T_m and T_g as shown by samples 1–6 in Table 11.2 [138]. Follow-up work with TiO_2 (particle size not provided [90]) together with EC plasticizer added to the same binary system of PEO (4×10^6 g/mol)–Lithium triflate (LiTf) (EO:Li^+ = 9) exhibited a similar trend of T_m and T_g drop [90]. For samples 7–9 in Table 11.2, the activation energy (E_a) decreased from 120.6 to 78.8 kJ/mol with the addition of 10

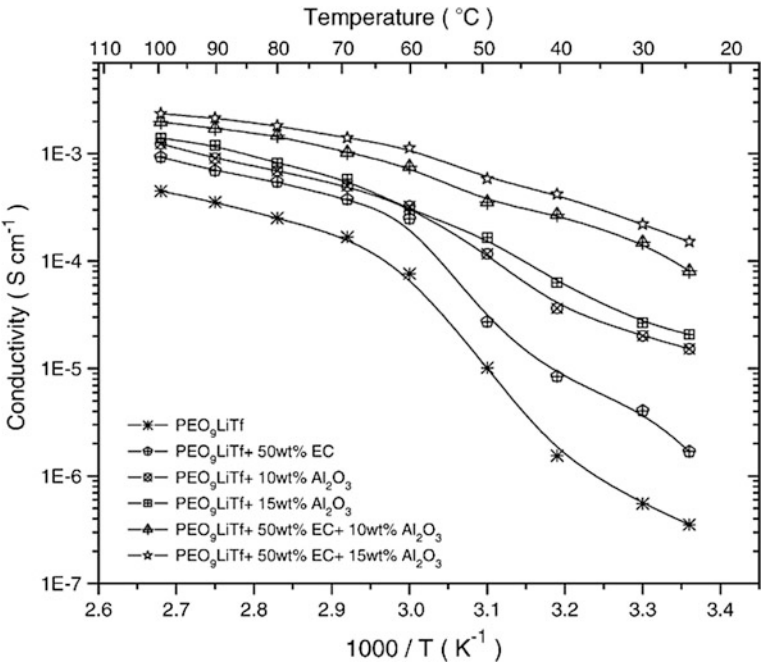

Fig. 11.10 Variation of the ionic conductivity with inverse temperature for the composite polymer electrolyte systems: PEO–LiTf, PEO–LiTf–50 wt% EC, PEO–LiTf–10 wt% Al_2O_3, PEO–LiTf–15 wt% Al_2O_3, PEO–LiTf–50 wt% EC–10 wt% Al_2O_3, PEO–LiTf–50 wt% EC–15 wt % Al_2O_3. EO:Li^+ = 9 for all samples (Reproduced from Ref. [138] with kind permission of © 2007 Elsevier)

wt% TiO_2, and further decreased to 57.5 kJ/mol with addition of both 10 wt% TiO_2 and 50 wt% EC at temperatures below 60 °C. This activation energy decrease suggested an improved mobility of ions within the polymer matrix, and hence increased conductivity. Whereas at temperatures above 60 °C, nearly equal E_a values were obtained for binary, ternary, and quaternary samples [138]. The conductivity increase could be explained by the improved ion mobility in the melted matrix above T_m, which overwhelmed the effect from added nanoparticles or plasticizer. For the plasticized CPE of PEO–LiTf (EO:Li^+ = 9)–50 wt% EC, addition of 15 wt% Al_2O_3 exhibited the lowest T_g and T_m (T_g decreased to −56 °C and T_m to 49 °C, respectively). The doping amount of 15 wt% differs from that reported to give optimal thermal property in ternary CPEs (without EC) at 10 wt% nanoparticles [92, 106, 107]. The difference originated from the plasticizing effect to accommodate more nanoparticles before aggregation would take place. As a result, the optimal content of nanoparticle doping increased from 10 to 15 wt%.

A similar trend was obtained for a system of the same components but with different formulation for optimal properties [136]. PEO (MW not provided)–16 wt % $LiCF_3SO_3$–20 wt% EC–15 wt% Al_2O_3 (d = 11.8 nm) gave the lowest T_g and T_m

Table 11.2 Crystallite melting temperatures (T_m), glass transition temperatures (T_g), and conductivity of different PEO (4×10^6 g/mol)–$LiCF_3SO_3$ (LiTf: Lithium triflate, EO:Li^+ = 9)–Al_2O_3/TiO_2 samples from [138] and [90]

Sample number	Polymer electrolyte	T_m (°C)	T_g (°C)	σ at 25 °C (Scm^{-1})
1	[a](PEO)$_9$LiTf	58	−44	3.5×10^{-7}
2	[a](PEO)$_9$LiTf–50 wt% EC[a]	57	−48	1.6×10^{-6}
3	[a](PEO)$_9$LiTf–10 wt% Al_2O_3	54	−49	1.5×10^{-5}
4	[a](PEO)$_9$LiTf–15 wt% Al_2O_3	51	−50	2.1×10^{-5}
5	[a](PEO)$_9$LiTf–50 wt% EC–10 wt% Al_2O_3	50	−53	8.2×10^{-5}
6	[a](PEO)$_9$LiTf–50 wt% EC–15 wt% Al_2O_3	49	−56	1.5×10^{-4}
7	[b](PEO)$_9$LiTf	64	−39	[c]1.4×10^{-6}
8	[b](PEO)$_9$LiTf–10 wt% TiO_2	60	−46	[c]4.9×10^{-5}
9	[b](PEO)$_9$LiTf–10 wt% TiO_2–50 wt % EC	50	−50	[c]1.6×10^{-4}

[a]Results from Pitawala's work [138]
[b]Results from Vignarooban's work [90]
[c]: σ at 30 °C

values, resulting from increased amorphous percentage and segmental flexibility caused by the EC plasticizer and the nano-filler [139–141]. However, the PEO (600,000 g/mol)–$LiCF_3SO_3$–dibutyl phthalate (DBP)–MnO_2 (12–15 nm) CPE exhibited a different change of T_g. As related to the polymer chain segmental movement, T_g increased marginally to −70 °C when MnO_2 was added to the plasticized system (T_g = −74 °C) and to the binary system (T_g = −71 °C).

From a comparison of these quaternary CPE systems with binary polymer + salt electrolytes and ternary CPE systems, we can see that for binary systems, T_g increased from neat PEO to binary PEO–Li^+ mixtures due to the transient crosslink formation between Li^+ and ether oxygens [98, 142, 143]. In ternary CPEs, nanoparticles tended to further decrease T_g, by different extent as different types of nanoparticles were used, while this is not always the case for quaternary systems. Organic solvent and nanoparticle co-additives make it more complicated to draw a general rule to predict property change upon additive incorporation. Further knowledge [144] on this promising direction would be desirable.

11.5.2 Ionic Liquid Additives

Ionic liquids have been extensively studied as additives for polymer electrolytes due to the unique properties of low-melting temperature and low vapor pressure [122, 145–147]. Reviews and research papers on ionic liquids as additives for polymer electrolytes have been published [148–151]. Here, we focus on physical co-doping of ionic liquids together with nanoparticles in CPEs.

Ternary systems of PEO–lithium bis (trifluoromethanesulfonyl) imide (LiTFSI, EO:Li^+ = 18)–10 wt%–nano-sized SiO_2 [152] and PEO–LiTFSI (EO:Li^+ = 18)–*N*-methyl-*N*-propylpiperidinium bis(trifluoromethanesulfonyl) imide (1.44 PP_{13}TFSI) have been reported [153]. In the discussion of quaternary systems of this subsection, nanoparticles and ionic liquids are doped together for the system of PEO (6×10^5 g/mol)–LiTFSI (EO:Li^+ = 18)–10 wt% SiO_2 (d = 50 nm)–PP_{13}TFSI (Li^+/PP_{13}^+ = 1:1.44) [154]. The conductivity exhibited an Arrhenius behavior as shown in Fig. 11.11. Conductivity enhancement in the melt state ($T > T_m$) by co-doping is not obvious, but at temperatures below the melting point ($T < T_m$), the enhancement is significant as explained by the activation energy decrease. From the Arrhenius plots of conductivity, with the addition to PEO_{18}LiTFSI of (1) nano-SiO_2, (2) PP_{13}TFSI, or (3) both nano-SiO_2 and PP_{13}TFSI, the activation energy (E_a) decreased from 115.3 kJ/mol for the binary PEO_{18}LiTFSI to (1) 105.0 kJ/mol, (2) 97.6 kJ/mol, and (3) 82.9 kJ/mol, respectively. The lower E_a value implies a higher mobility of the lithium cations within the polymer matrix; the lowest E_a and highest σ values were achieved by the co-doped sample at the low-temperature region. In contrast, in the high-temperature region, E_a remained almost constant for all samples (35.1–37.2 kJ/mol) [154].

In closing Sect. 11.5, the physical modification of ternary CPEs can be summarized as "tuning the recipe" of binary polymer electrolytes (polymer + Li^+) by adding more ingredients to modulate interactions among nanoparticles, PEO (ether oxygens), and lithium ions within the system, and to affect properties such as crystallinity, glass transition temperature, and dielectric. The property changes favor an improvement of the ionic conductivity performance.

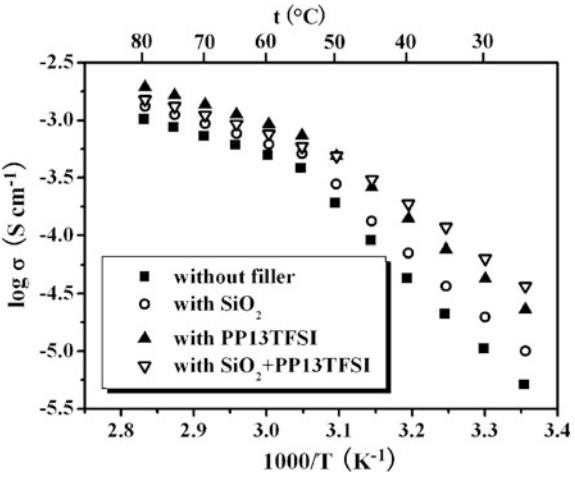

Fig. 11.11 Temperature dependence of the conductivity for PEO–LiTFSI, PEO–LiTFSI–SiO_2, PEO–LiTFSI–PP_{13}TFSI and PEO–LiTFSI–SiO_2–PP_{13}TFSI (EO:Li^+ = 18 for all samples) (Reproduced from Ref. [154] with kind permission of © 2011 Elsevier)

11.6 Summary and Outlook

Polymer electrolytes typically based on poly(ethylene oxide) and a lithium salt are being considered to improve the mechanical strength, thermal stability, and safety over traditional organic solvent-based electrolytes. The development of polymer electrolytes involves the simultaneous improvement of desirable properties for lithium-ion batteries.

For binary systems (polymer + lithium salt) [21], given the knowledge of Li^+ motion mechanism in PEO-based polymer electrolytes, controlling the polymer architecture and morphology are effective methods to improve the polymer electrolyte performance. However, it is difficult in binary polymer + salt systems to meet the performance required in practical applications. A breakthrough occurred when nano-additives were incorporated into binary systems for conductivity improvement [24–27]. This conductivity improvement can be explained by functions affected by nanoparticle: creating more amorphous domains, promoting lithium salt dissolution. Generally, samples with 5–12 wt% nanoparticle (depending on the type of additive and its surface, typically at 10 wt%) and molar ratio EO:Li^+ = 6–20 (typically at 8–10) yield the optimal ionic conductivity together with lowest degree of polymer crystallinity (χ_c), decreased glass transition temperature (T_g) and melting temperature (T_m), and improved mechanical strength [92, 103, 106, 155].

However, CPEs also suffer from possible nanoparticle agglomeration within the polymer matrix. This can limit the performance enhancement due to nanoparticles. The room temperature ionic conductivity, a critical performance indicator of ternary CPEs, remains below the desired level of 10^{-3} S/cm. In order to further improve the CPE performance, modified CPEs (PEO + salt +-modified nanoparticle and PEO + salt + nanoparticle + solvent) are being considered aiming to tune pre-existing interactions within polymer matrix.

Section 11.4 discusses nanoparticles that are chemically modified for an improved compatibility within CPEs. POSS–PEO_8 can be accommodated up to 30 wt% in high molecular weight polymer matrix due to the improved compatibility conferred by the PEO end groups. The conductivity improvement ranged from a few times in temperatures above T_m to almost two orders of magnitude in the low-temperature range. However, the conductivity dropped marginally when adding 10 and 20 wt% [110]. PEO–silica into PEGDME (200 g/mol) matrix due to the increased viscosity. Incorporation of PEO–silica in high molecular weight polymer electrolyte has not been reported yet; as for non-polymer modification of silica, the best conductivity that can be achieved in this case is a little higher than 10^{-5} S/cm at room temperature, which is less effective than that reported for the quaternary (polymer + salt + nanoparticle + solvent) polymer electrolytes discussed in Sect. 11.5.

Section 11.5 discusses the doping of CPEs with a fourth component in order to further modulate interactions. In the case of nanoparticle doping with an ionic liquid, the optimal room temperature conductivity can be in the range $10^{-4.5}$–10^{-4} S/cm. This approach did not always increase the conductivity over the whole temperature

range studied when compared to ternary systems of polymer + Li^+ + ionic liquid. In comparison, co-doping with nanoparticles and organic solvents for CPEs led to an obvious degree of crystallinity drop and marginal T_g and T_m decreases compared to ternary plasticized system (polymer + Li^+ + organic plasticizer). The conductivity enhancement is less than one order of magnitude (about 2–8 times) and presented an optimal conductivity a little lower than 10^{-4} S/cm at room temperature. It becomes apparent from the above that for quaternary polymer electrolytes, a level of 10^{-4} S/cm room temperature ionic conductivity is still difficult to achieve, and co-doping has shown limited contribution toward conductivity enhancement.

The research in CPEs is experiencing a bottleneck in that the highest ionic conductivity reported for solid-state CPEs just got close to 10^{-3} S/cm at room temperature [156–158], still not high enough to compete effectively with traditional organic solvent-based electrolytes. Future research in this field could fall into two broad directions. The first direction encompasses three-dimensional nano-scale ordered structure fabrication [105], such as ion tunnels [159] or ion paths [160], to facilitate ion conduction. Grafting side chains [161, 162] or a block of different chemistry [163–165] on the PEO polymer backbone can also be viewed as a nano-scale fabrication if further ordered structure can be obtained. The second direction is to adjust the CPE composition, with addition of certain other additives conferring special functions [90, 92, 137, 138, 166]. Sections 11.4 and 11.5 exemplify the current status of these two directions. The discussion in this chapter of various formulation strategies for electrolyte performance enhancement is intended to further stimulate the design of novel CPEs.

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