

## FOCUS REVIEW

# Ion-conductive polymer electrolytes based on poly(ethylene carbonate) and its derivatives

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Ion-conductive polymer electrolytes are remarkable materials that have recently been proposed for use as flexible solid electrolytes in next-generation energy storage devices. In particular, the author has proposed the synthesis of novel polymer electrolytes with very high ionic conductivities and the essential properties of polymeric materials. This review describes the synthesis of alternating copolymers of CO<sub>2</sub> with epoxides and their application as novel ion-conductive polymers in the place of typical polyether-based systems. The Li salt electrolytes of poly(ethylene carbonate) (PEC) and of other polycarbonates with different side groups exhibit unique ion-conductive properties, such as increasing conductivity with higher salt concentrations, very high Li transference numbers and good electrochemical stability. The Li-ion conductivity of a PEC-lithium bis(fluorosulfonyl) imide LiFSI electrolyte was estimated to be greater than 10<sup>-4</sup> S cm<sup>-1</sup>, and excellent battery performance of this material was also demonstrated at room temperature.

*Polymer Journal* (2017) 49, 291–299; doi:10.1038/pj.2016.115; published online 21 December 2016

## INTRODUCTION

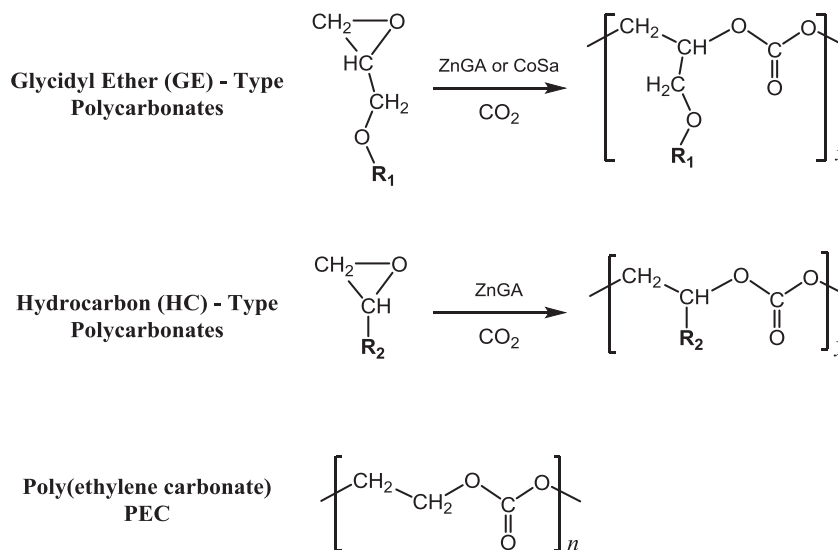
In 1973, Wright *et al.*<sup>1</sup> first reported the ion-conductive properties of 'solvent-free' poly(ethylene oxide) (PEO) systems containing alkali metal salts. In 1978, Armand *et al.*<sup>2</sup> showed that these materials can act as a new class of solid electrolytes for energy storage applications. These new 'polymer electrolytes' have recently attracted significant interest as solid state alternatives to liquid electrolytes in electrochemical devices, ranging from rechargeable batteries<sup>3–5</sup> to solar cells,<sup>6,7</sup> ion sensors and electrochromic displays.<sup>8</sup> Secondary Li-ion batteries based on polymer electrolytes offer outstanding performance by combining easy processability, mechanical stability, reliability and safety.<sup>9</sup> In the past few decades, numerous studies have been focused on the macromolecular design of polyethers as electrolyte materials, mainly with reduced degrees of crystallinity, good electrochemical stability and improved salt solubility.<sup>8</sup> Unfortunately, these materials suffer from low ionic conductivities in the solid state, relative to most liquid or ceramic electrolytes. The maximum conductivity of polyether-based electrolytes is usually on the order of 10<sup>-4</sup> S cm<sup>-1</sup> at room temperature. To facilitate faster migration of ions in these polymers, the local mobility of chains containing cation–anion and cation–dipole interactions should be increased due to the fact that ions are transported via the segmental motion of the ether chains.<sup>10</sup> However, cation–dipole interactions may inhibit the migration of cations because of their strong coordination, which increases the glass transition temperature ( $T_g$ ) of the polymer. Additionally, the coordination structure limits the cation transference values to <0.5 in polyethers,<sup>11,12</sup> affecting the cathodes of electrochemical devices driven under DC polarization.<sup>8</sup> To overcome these problems and to develop

superior polymer electrolytes, novel polymer candidates are needed that are not based on oxyethylene (OE).

Many polymers without OE, such as poly(acrylonitrile),<sup>13,14</sup> poly(vinyl alcohol)<sup>15,16</sup> and poly(phosphazene),<sup>17,18</sup> have been used as polymer electrolytes, and their ion-conductive properties have been determined. However, it is difficult to achieve good conductivity in these polymers in the solid state. In previous studies of polymers without OE, the present author and his group observed that a novel electrolyte system based on poly(trimethylene carbonate)<sup>19,20</sup> has unique properties and an unusual change in  $T_g$  with increasing salt concentration.<sup>21</sup> Over the past few years, the electrochemical performance of polymer electrolytes based on poly(trimethylene carbonate) have also been studied by Brandell *et al.*<sup>22–27</sup> Carbonate-based organic solvents such as ethylene carbonate and diethyl carbonate are still used commercially as electrolyte solutions in Li-ion secondary batteries because of their high dielectric constants.<sup>28</sup> The carbonate group, when used in polymer construction, is therefore capable of providing a polar environment suitable for the dissociation of salts and the solvation of ions. This review focuses on poly(ethylene carbonate) (PEC) and its derivatives as novel candidates for ion-conductive polymer electrolytes.

## SYNTHESIS OF POLYCARBONATES HAVING DIFFERENT SIDE GROUPS

Alternating copolymerization of CO<sub>2</sub> with epoxides was first carried out by the Tsuruta group at the University of Tokyo in 1968.<sup>29,30</sup> This group has published many studies, especially on the development of highly active copolymerization catalysts.<sup>31–33</sup> The resulting



**Figure 1** Synthesis of polycarbonates with glycidyl ether (GE) or hydrocarbon (HC)-based side groups. The structure of poly(ethylene carbonate) (PEC) is also shown.

polycarbonates, which are  $\text{CO}_2$ /epoxide copolymers, have excellent properties compared with other polymers, including a lack of crystallinity, lightness, high transparency and ease of processing as well as are colored.<sup>34</sup> The synthetic method is promising not only for the implementation of a novel polymerization reaction but also for the environmental and sustainability potential of carbon sources. Polycarbonates have recently been used as novel functional materials, including as biodegradable polymers,<sup>35,36</sup> nanocomposites,<sup>37</sup> liquid-crystalline hybrids<sup>38</sup> and ion-conductive polymers.<sup>39–50</sup>

In previous studies,<sup>39,40,42,48</sup> Tominaga *et al.* synthesized eleven polycarbonates having different side groups as electrolyte materials. The synthetic procedures for two types of polycarbonates, with glycidyl ether (GE) and hydrocarbon (HC) side groups, are shown in Figure 1. These polymers were synthesized by alternating copolymerization of  $\text{CO}_2$  with epoxides having  $\text{R}_1$  or  $\text{R}_2$  groups in the presence of copolymerization catalysts, zinc glutarate ( $\text{ZnGA}$ )<sup>51,52</sup> or cobalt salen complex ( $(R,R)$ -SalcyCoOCOBzF<sub>5</sub>, CoSa).<sup>31</sup> Polycarbonates synthesized in previous studies<sup>39,40,42,48</sup> were obtained as high molecular weight polymers, as summarized in Table 1. The nature of the substituents (denoted by  $\text{R}_1$  and  $\text{R}_2$  in Figure 1) of the polycarbonates determines their  $T_g$ , which varies from  $-33$  to  $45$  °C, color and stiffness. GE-type polycarbonates obtained from differential scanning calorimeter (DSC) were transparent and amorphous; only P(GE-*t*Bu) was obtained as a white fibrous solid, as indicated by an endothermic transition at  $141$  °C. P(GE-*n*Bu), P(GE-Et) and P(GE-*i*Pr) were jellylike rubbers. P(GE-OE1) and P(GE-OE2) were sticky paste-like solids, much softer than the others at room temperature. All of the HC-type polycarbonates and PECs were transparent solids. Commercial PEC and poly(propylene carbonate) (PPC) were obtained as rubbery films. HC-type polycarbonates with alkyl side chains became softer with increasing chain length. In both cases, polycarbonates possessing a phenyl end group, P(GE-Phe) and P(HC-Bn), were glassy polymers. Table 1 also summarizes the thermal properties of these polycarbonates. P(GE-Phe) and P(HC-Bn) were unable to form films because their  $T_g$  values were greater than room temperature. Polycarbonates having longer alkyl or ether side groups had lower  $T_g$  values.<sup>53</sup> P(GE-OE1) and P(GE-OE2) have flexible ether side groups and very low  $T_g$  values. The introduction of side groups increased weight-loss temperatures by 5% ( $T_{d5}$ , in dry  $\text{N}_2$ ); these temperatures



are more than  $10$  °C higher than that of PEC. The steric hindrance of side groups may prevent the backbiting reaction,<sup>54</sup> which involves terminal groups on the main chain.

#### TEMPERATURE DEPENDENCE OF THE IONIC CONDUCTIVITY OF POLYCARBONATE-LI SALT ELECTROLYTES

Tominaga *et al.* have revealed that PEC, PPC and polycarbonates synthesized in their work can dissolve many different types of Li salts over wide concentrations, giving rise to transparent films without any salt precipitation. Figure 2 summarizes the temperature dependence of the ionic conductivity for these polycarbonate-Li salt electrolytes. The polycarbonates gave characteristic amorphous-type Arrhenius plots, similar to previous polyether-based electrolytes, which are convex in shape throughout the temperature range measured. This characteristic implies that ionic conduction in the polycarbonates occurs via segmental motion of the main chain. As Figure 2a shows, the conductivity values of the GE-type polycarbonates strongly depend on the structure of the side groups. The conductivity of the P(GE-Phe) electrolyte was the lowest of the GE-type polycarbonate electrolytes, at  $\sim 10^{-8}$   $\text{S cm}^{-1}$  at  $80$  °C, whereas the addition of 10 mol% lithium bis(trifluoromethane sulfonyl)imide (LiTFSI) reduced the  $T_g$  slightly from  $45$  to  $41$  °C.<sup>39</sup> This result occurred because P(GE-Phe) is a glassy polymer with the highest  $T_g$  of all polycarbonates, as shown in Table 1. The P(GE-*t*Bu) electrolyte also had very low conductivity, on the order of  $10^{-9}$   $\text{S cm}^{-1}$  at  $40$  °C, but the P(GE-*n*Bu) electrolyte had good conductivity relative to P(GE-Phe) and P(GE-*t*Bu) because of its low  $T_g$  value. This improved conductivity stems from the large difference in  $T_g$  between polymers and their electrolytes, as a result of steric hindrance involving the side groups.

Electrolytes of polycarbonates having smaller side groups, such as Et and *i*Pr, had higher relative conductivities,<sup>40</sup> and the conductivity of the P(GE-OE1) electrolyte was the highest of all the GE-type polycarbonates tested ( $2.2 \times 10^{-6}$   $\text{S cm}^{-1}$  at  $30$  °C).<sup>39</sup> These materials still have lower conductivities than typical polyether electrolytes at the same concentration, however, and the value for the P(GE-OE1) electrolyte is ten times less than that of the PEO<sub>10</sub>LiTFSI electrolyte. The conductivities of HC-type polycarbonate electrolytes are very low, below  $10^{-8}$   $\text{S cm}^{-1}$ , at room temperature. To analyze the effect of the side group structure, the author and his group have compared the

Table 1 Results of GPC, DSC and TG/DTA measurements for commercial PEC, PPC and all polycarbonates synthesized

Polycarbonate Type	Side Group ( $R_1, R_2$ )	$M_n$ ( $\times 10^4$ )	$M_w/M_n$	$T_g$ / $^\circ\text{C}$	$T_{d5}$ / $^\circ\text{C}$
GE	Et $-\text{CH}_2\text{CH}_3$	2.8	6.2	10	238
	$i\text{Pr}$ $-\text{CHCH}_3$ $\quad  $ $\quad \text{CH}_3$	4.6	2.0	-9	-
	$n\text{Bu}$ $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	19	2.3	-24	-
	$t\text{Bu}$ $-\text{C}(\text{CH}_3)_3$	4.4	1.5	13	-
	Phe 	1.5	4.5	45	-
	OE1 $-(\text{CH}_2\text{CH}_2\text{O})_1\text{CH}_3$	1.7	1.5	-22	241
	OE2 $-(\text{CH}_2\text{CH}_2\text{O})_2\text{CH}_3$	1.8	1.3	-33	-
HC	Me $-\text{CH}_3$ (PPC)	5.0	3.0	34	248
	Et $-\text{CH}_2\text{CH}_3$	2.6	1.8	11	235
	$n\text{Pr}$ $-\text{CH}_2\text{CH}_2\text{CH}_3$	1.2	2.3	3	249
	Bn $-\text{CH}_2$ 	1.2	11	45	-
PEC	-	3.1	3.9	13	225

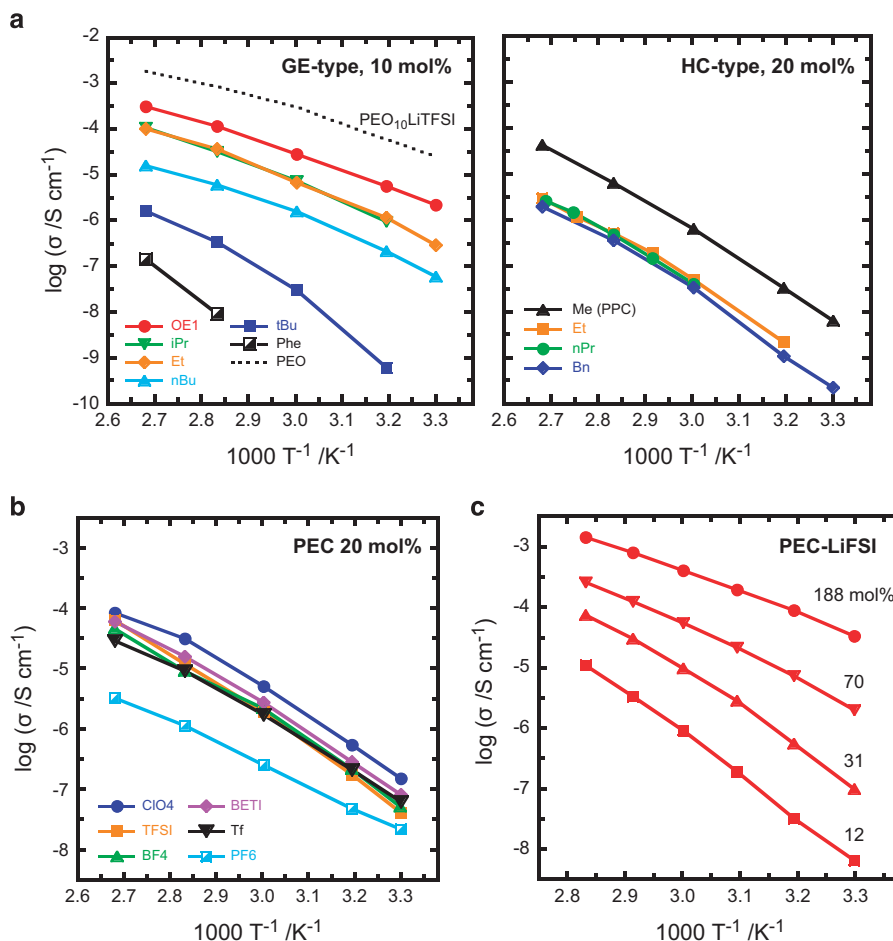
Abbreviations: GE, glycidyl ether; HC, hydrocarbon; OE, oxyethylene; PEC, poly(ethylene carbonate); PPC, poly(propylene carbonate).

effect of the presence of ether linkages in the side groups on the ion-conductive properties of P(GE-Et) and P(HC-Et). The difference in the conductivity between these electrolytes was quite large, and the conductivity of the P(GE-Et) electrolyte was >100 times greater than that of P(HC-Et).<sup>40</sup> This conductivity difference is due to the large difference in the  $T_g$  of the LiTFSI electrolytes (10 mol%) between P(GE-Et) (-32  $^\circ\text{C}$ ) and P(HC-Et) (-4  $^\circ\text{C}$ ).<sup>40</sup> The presence of an ether side group in the polycarbonate increases the ionic conduction because the ether group has low rotational energy and undergoes fast relaxation. In FT-IR ATR measurements of these electrolytes, the spectrum of P(GE-Et) in the region from 1700 to 1800  $\text{cm}^{-1}$  had a single peak, representing the stretching vibration mode for the free carbonyl group in the main chain, whereas P(HC-Et) showed two peaks, which were due to the existence of free and interacting ( $\text{C}=\text{O}\dots\text{Li}^+$ ) carbonyl groups.<sup>21</sup> This difference suggests that the increase in conductivity for the P(GE-Et) electrolyte is due to the interaction of Li ions with the flexible ether side groups.

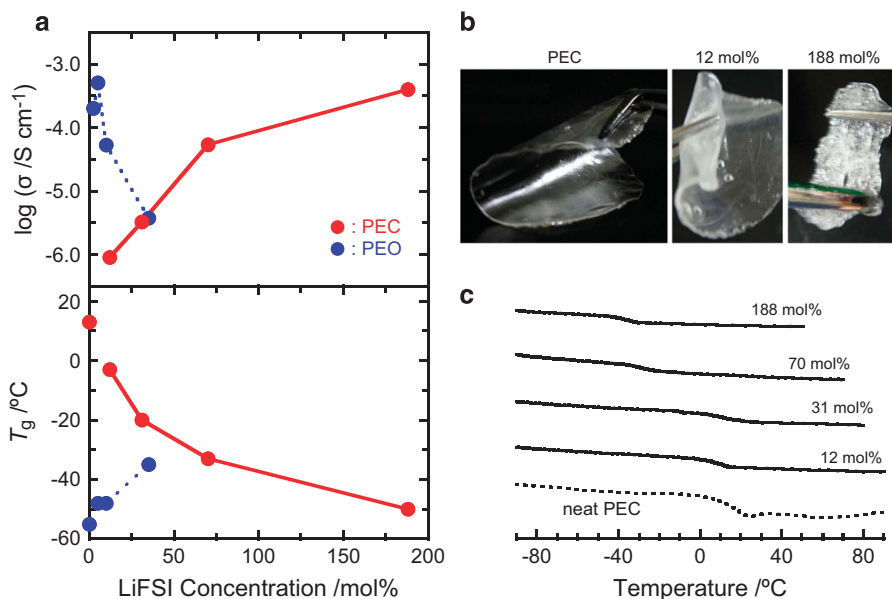
The addition of salt species to the polymer matrix caused clear changes in the  $T_g$  and ion-conductive properties of the electrolytes because of their solubility. The addition of Li salts with low lattice energies and large anion radii, as calculated from the van der Waals volume, to polyether is an effective method of increasing conductivity; the conductivities of LiPF<sub>6</sub> and LiClO<sub>4</sub> electrolytes should therefore be

higher than that of LiBF<sub>4</sub>.<sup>55</sup> Imide-type Li salts with larger anionic radii, such as LiTFSI and lithium bis(fluorosulfonyl)imide (LiFSI), have a plasticizing effect and the potential to have a high conductivity with a low  $T_g$  in PEO polymers.<sup>56–58</sup> As shown in Figure 2b, LiClO<sub>4</sub> gave rise to the highest conductivity of all electrolytes in PEC at a salt concentration of 20 mol%. The conductivity of LiPF<sub>6</sub> in particular was lower than that for other systems, and LiPF<sub>6</sub> has a larger anionic radius than LiClO<sub>4</sub>. The local structure of PEC in the presence of ions is different from that of the PEO system; this difference suggests that the PEC does not form the solvated structures observed in PEO, in which a stable ion-dipole interaction is formed.

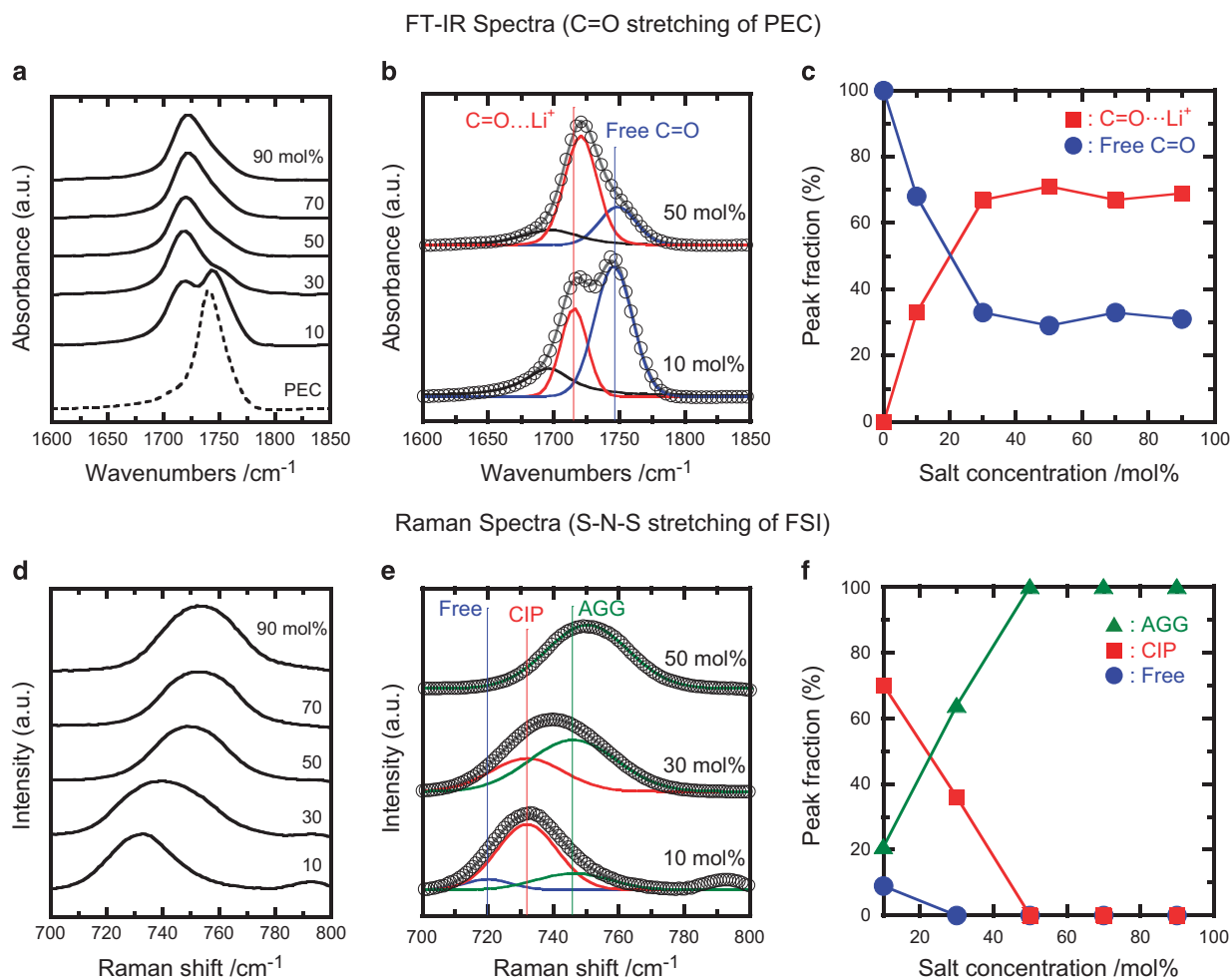
An increase in the salt concentration of PEC electrolytes induced a significant change in the ion-conductive behavior, as shown in Figure 2c. The conductivity increased, and the slope of the plots decreased, with increasing LiFSI concentration. The greatest conductivity resulted from a very high concentration of electrolyte; the ratio of Li ions to the monomer unit of PEC was 1.88 (that is, 188 mol% Li).<sup>43</sup> The smaller slope of the plot indicates that the activation energy for the ionic conduction in PEC becomes smaller with increasing salt concentration. This remarkable behavior can also be observed in the LiTFSI system<sup>41,42</sup> and has not been observed in polyether-based electrolytes. It is possible that the ion-conduction mechanism in PEC is quite different from that in the typical polyether system.



**Figure 2** Temperature dependence of the ionic conductivities of (a) glycidyl ether (GE)-type or hydrocarbon (HC)-type polycarbonate electrolytes with LiTFSI (lithium bis(trifluoromethane sulfonyl)imide); (b) PEC-LiX electrolytes (X: anion) with a salt concentration of 20 mol%; and (c) PEC-LiFSI (lithium bis(fluorosulfonyl)imide) electrolytes with differing salt concentrations. PEC, poly(ethylene carbonate).



**Figure 3** (a) Dependence of the conductivities for PEC (poly(ethylene carbonate)) and poly(ethylene oxide) (PEO)-based electrolytes at 60 °C on the LiFSI (lithium bis(fluorosulfonyl)imide) concentration; (b) photographs of neat PEC and electrolytes with 12 and 188 mol% LiFSI; and (c) DSC curves of neat PEC and electrolytes with different concentrations of LiFSI.



**Figure 4** Spectroscopic analysis of PEC-LiFSI electrolytes using FT-IR (a, b, c) and Raman (d, e, f) techniques: (a, d) original spectra; (b, e) examples of peak separation analysis; and (c, f) dependence on LiFSI concentration on peak fractions in the stretching vibrational modes. The unassigned peak (black line) at  $\sim 1700\text{ cm}^{-1}$  in b was ignored in the estimation of the peak fraction, as shown in c. LiFSI, lithium bis(fluorosulfonyl)imide; PEC, poly(ethylene carbonate).

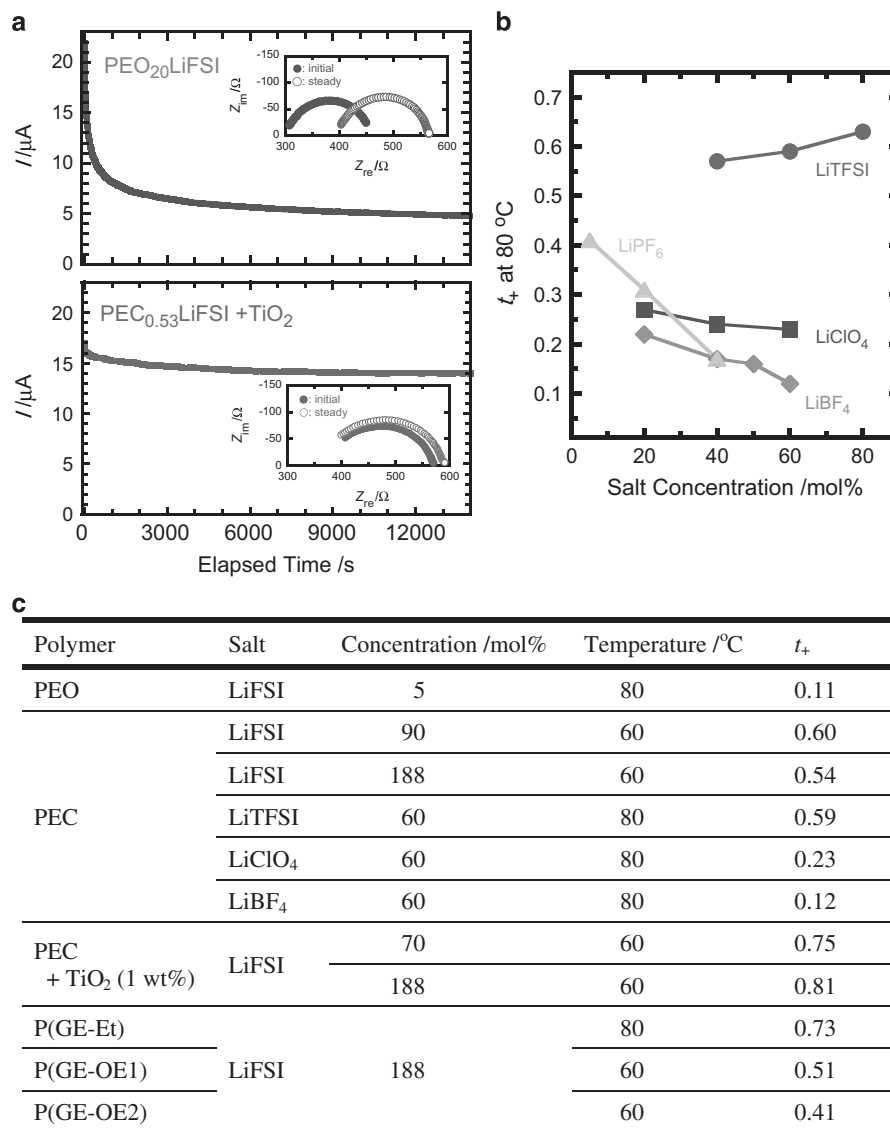
#### DEPENDENCE ON THE SALT CONCENTRATION OF THE IONIC CONDUCTIVITY AND THE GLASS TRANSITION TEMPERATURE

The relationship between ionic conductivity and salt concentration is essential in explaining the behavior of polymer electrolytes because the addition of salt usually leads to a drastic increase in the  $T_g$  value of polymers, especially in the case of polyethers. Figure 3a shows the dependence of salt concentration on the conductivity at  $60^\circ\text{C}$ , as well as on the  $T_g$  values, for PEO and PEC-LiFSI electrolytes. In the PEO electrolyte, the conductivity was greatest at a salt concentration of  $\sim 5\text{ mol}\%$ . This value is almost the same as that previously reported for other electrolytes.<sup>8,55</sup> At salt concentrations above  $5\text{ mol}\%$ , the  $T_g$  value of the PEO electrolyte gradually increases, and the conductivity decreases, with increasing concentration. This effect is most likely due to the increase in cross-linking structures between Li ions and the dipoles of the polyether chains, so that the coupling structure prevents the segmental motion of local chains in the amorphous regions, resulting in an increase in  $T_g$ .<sup>10</sup> However, the conduction and glass transition behavior of the PEC-based electrolytes are very different from those of the PEO system. The conductivity of PEC-LiFSI electrolytes increases linearly with increasing concentration, and the electrolyte with  $188\text{ mol}\%$  LiFSI has the highest conductivity,  $4.0 \times 10^{-4}\text{ S cm}^{-1}$  at  $60^\circ\text{C}$ .<sup>43</sup> The glass transition behavior is very different from the typical PEO system; the  $T_g$  value of the PEC

electrolytes decreased with increasing concentration, and the lowest value was for electrolytes with  $188\text{ mol}\%$  LiFSI, which is  $\sim 60^\circ\text{C}$  lower than that of neat PEC. Figure 3b shows that samples of neat PEC as a film become softer upon addition of LiFSI, becoming a gel-like solid. As Figure 3c shows, neat PEC and the electrolytes are amorphous, without any further transitions above the glass transition, and  $T_g$  decreases with increasing salt concentration. The addition of salts to PEO induces a large increase in  $T_g$  as a result of the strong interactions between ether oxygen atoms and dissociated Li ions, as well as coordination with the polymer chains.<sup>8,10</sup> For PEC-based electrolytes, the dipole moment of the carbonate group in the main chain is strong enough to dissociate salts and interact with Li ions. Tight coordination or solvation, as observed in polyether-based electrolytes, is likely negligible.

#### SPECTROSCOPIC ANALYSIS OF THE SALT SOLVATION STRUCTURE IN PEC

The dissociation of salt added to ionic polymers can be confirmed using spectroscopic analysis techniques, such as FT-IR and Raman spectroscopy. Many studies of ionic association in polyethers, including amorphous poly(propylene oxide)<sup>59,60</sup> and crystalline PEO,<sup>61,62</sup> have been published. FT-IR measurements on the PEC system revealed a stretching vibration mode of C=O in the main chain that



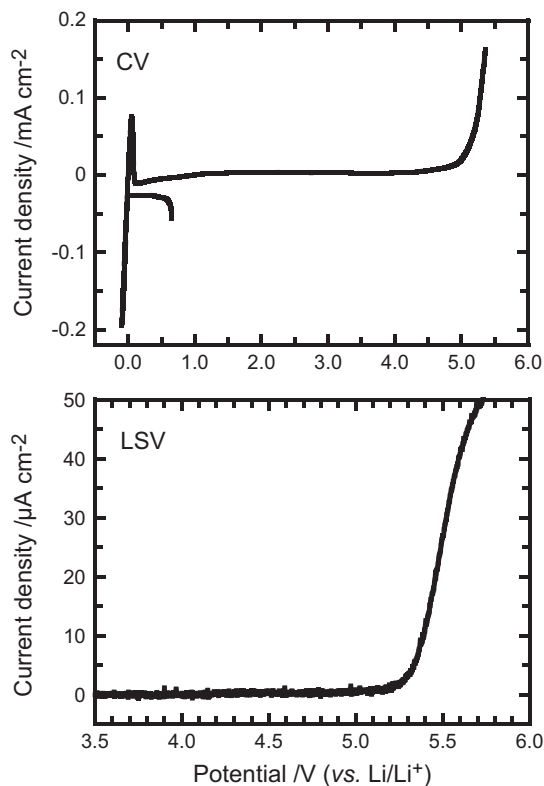
**Figure 5** (a) d.c. polarization and a.c. impedance measurements for PEO- and PEC-based electrolytes; (b) dependence of  $t_+$  on salt concentration for PEC-LiX electrolytes; and (c) summary of  $t_+$  values for PEO and polycarbonate-based electrolytes. PEC, poly(ethylene carbonate); PEO, poly(ethylene oxide). A full color version of this figure is available at *Polymer Journal* online.

appeared clearly at  $\sim 1700\text{--}1800\text{ cm}^{-1}$  (Figure 4a). The C=O band can be divided into two peaks (Figure 4b); one appears at  $1740\text{ cm}^{-1}$  and is indicative of the free PEC chains, and the other appears at  $1720\text{ cm}^{-1}$  and is indicative of chains interacting with cations (C=O...Li<sup>+</sup>).<sup>63,64</sup> As Figure 4a shows, the C=O...Li<sup>+</sup> peak at  $1720\text{ cm}^{-1}$  gradually becomes larger with increasing salt concentration, whereas the free peak at  $1740\text{ cm}^{-1}$  becomes smaller. The proportion corresponding to the C=O...Li<sup>+</sup> peak fraction was nearly saturated at  $\sim 70\%$ , above salt concentrations of 50 mol% (Figure 4c); this phenomenon is due to the drastic increase in the conductivity that occurs at higher concentrations.

Raman spectroscopy can also provide information on the dissociation of LiFSI in PEC using the S–N–S stretching vibrational mode of the FSI anions, which appears at  $\sim 700\text{--}800\text{ cm}^{-1}$  (Figure 4d). The S–N–S band can be divided into the following three different dissociation states (Figure 4e): free FSI anions at  $720\text{ cm}^{-1}$ , contact ion pairs at  $732\text{ cm}^{-1}$  (FSI ions interacting with a single Li-ion), and

aggregates at  $746\text{ cm}^{-1}$  (FSI ions interacting with two or more Li ions).<sup>65</sup> As shown in Figure 4d, the peak at  $\sim 730\text{ cm}^{-1}$  shifts gradually to higher frequencies  $\sim 750\text{ cm}^{-1}$  with increasing salt concentration. This shift implies that there is a small amount of free FSI anions in PEC electrolytes with low salt concentrations and that the number of contact ion pairs increases with increasing salt concentration. The aggregates gradually predominate, and all anions exist as aggregates above 50 mol% (Figure 4f). A previous study found that a less stable coordination structure between poly(trimethylene carbonate) chains and Li ions causes significant ion-pairing, which leads to a high value of the Li transference number ( $t_+$ ).<sup>27</sup> PEC-based electrolytes also do not have a tight coordination structure between the PEC chains and Li ions, which induces an increase in  $T_g$ , in contrast to the polyethers. Salt-rich PEC electrolytes above a salt concentration of 50 mol% can be referred to as a ‘polymer-in-salt’ system.<sup>66,67</sup> Polymer-in-salt electrolytes invoke a decoupling ion-conductive mechanism, in which the mobility of ions is less correlated with segmental motion of the



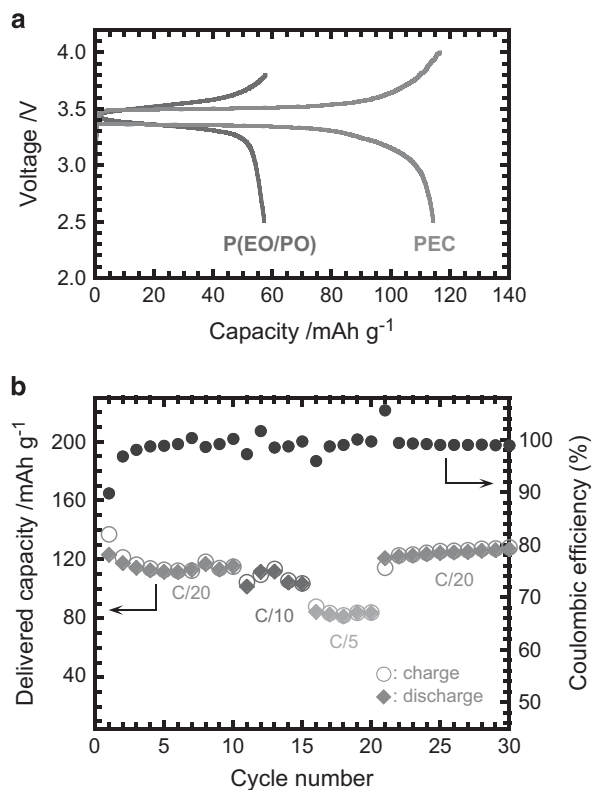


**Figure 6** Cyclic voltammogram of a PEC-LiTFSI electrolyte (scan rate:  $0.1 \text{ mV s}^{-1}$ ) at  $80^\circ\text{C}$  and linear sweep voltammogram of a PEC-LiTFSI electrolyte (scan rate:  $0.1 \text{ mV s}^{-1}$ ) at  $30^\circ\text{C}$  (working electrode: stainless steel, counter/reference electrode: Li). LiTFSI, lithium bis(fluorosulfonyl)imide; LiTFSI, lithium bis(trifluoromethane sulfonyl)imide; PEC, poly(ethylene carbonate).

polymers because the salts quantitatively dominate the system.<sup>66–68</sup> Tominaga *et al.* reported that the aggregated ions may migrate in the salt-rich electrolyte phase such as an ionic liquid, as has been proposed in a poly(acrylonitrile)-based polymer-in-salt system,<sup>13,14</sup> in which there is moderate interaction with C=O groups via the segmental motion of PEC chains.<sup>49</sup>

### LI TRANSFERENCE NUMBER MEASUREMENTS OF PEC ELECTROLYTES

The value of  $t_+$  can be estimated using the method of Bruce *et al.*<sup>69</sup> This method is based on electrochemical measurements in combination with d.c. polarization and a.c. impedance techniques. As shown in Figure 5a, the direct current of the PEO electrolyte drops sharply within a few minutes and then gradually decreases over time. This fall is due to polarization at the Li cathode, arising mainly from the migration of anions. In contrast,  $t_+$  was higher for the PEC electrolyte. In a composite with only 1 wt%  $\text{TiO}_2$ , the current and impedance response were highly stable. This behavior implies that there are many mobile ions, especially Li ions in PEC, that can migrate faster than coordinated, paired, and aggregated ions; these free ions may be responsible for the large decrease in  $T_g$ .<sup>43</sup> Figure 5b shows the values of  $t_+$  for PEC-Li salt electrolytes as a function of salt concentration. The LiTFSI electrolytes behaved in an opposite manner than electrolytes in other systems; the values of  $t_+$  increased with increasing concentration, up to 0.63 at a concentration of 80 mol%.<sup>46</sup> The values of  $t_+$  in PEC and polycarbonates possessing side groups are summarized in the table in Figure 5c. Surprisingly, the  $\text{TiO}_2$  composite had a



**Figure 7** (a) Charge–discharge curves of the third cycles for P(EO/PO)-LiTFSI (5 mol%) and PEC-LiTFSI (188 mol%) electrolytes at C/20 rate; and (b) charge–discharge cycling behavior of the PEC-LiTFSI electrolytes at different C-rates. The operating temperature was fixed at  $30^\circ\text{C}$ . LiTFSI, lithium bis(fluorosulfonyl)imide; PEC, poly(ethylene carbonate). A full color version of this figure is available at *Polymer Journal* online.

$t_+$  value greater than 0.8; this value is as high as that of single-ion-conductive polymers.<sup>70,71</sup> These higher  $t_+$  values for the PEC system have been confirmed via estimation from the self-diffusion coefficients of ions measured by solid state NMR with the pulsed field gradient technique.<sup>43</sup> There are no previous reports of such high  $t_+$  values for bis-ion systems, and these values are usually lower than 0.5 in PEO-salt mixtures. Munshi *et al.*<sup>11</sup> reported that crystalline PEO-based electrolytes also have low  $t_+$  values,  $<0.2$ , at Li salt concentrations greater than 30 mol%. It is well known that dissociated Li ions interact with dipoles of ether oxygens in polymer chains where the transference number is lower. A previous study showed that the Li-ion conductivity  $\sigma_{\text{Li}}$  ( $=t_+ \times$  ionic conductivity ( $\sigma$ ) at  $80^\circ\text{C}$ ) of a PEC-LiTFSI electrolyte (80 mol%) was estimated to be  $\sim 2.0 \times 10^{-4} \text{ S cm}^{-1}$ .<sup>43</sup>

### ELECTROCHEMICAL PERFORMANCE OF PEC ELECTROLYTES

The redox reactions of  $\text{Li/Li}^+$ , and the electrochemical stability of polymer electrolytes, have been evaluated by standard electrochemical techniques such as cyclic voltammetry (CV) and linear sweep voltammetry (LSV). The measurement cells for PEC-based electrolytes were made of two electrodes comprising a stainless steel plate as a working electrode and a Li foil on a Cu plate as a reference/counter electrode. From the CV data in Figure 6, a deposition and a stripping process of  $\text{Li/Li}^+$  in a PEC-LiTFSI electrolyte is clearly observed at 0 V, and the anodic limit was irreversible oxidation at  $\sim 4.5 \text{ V}$ . The LSV measurement in Figure 6 shows that the PEC-LiTFSI electrolyte has an

oxidation stability above 5 V at 30 °C. This stability may enable its use as a 5 V-class cathode material in Li batteries.<sup>47</sup>

An all-solid-state LiISPE/LiFePO<sub>4</sub> cell, based on a PEC-LiFSI electrolyte, has been assembled successfully with a 3DOM separator by the direct casting of the electrolyte solution onto the cathode.<sup>47</sup> In a galvanostatic battery test at 30 °C, the third charge–discharge profile of the PEC electrolyte exhibited flat plateaus centered at 3.45 V, indicating a good electrochemical reaction at the LiFePO<sub>4</sub> cathode (Figure 7a). This coin cell exhibited a reversible capacity close to 120 mAh g<sup>-1</sup> at the C/20 rate, a performance comparable to that of the copolymer-based systems reported by Brandell *et al.*<sup>24</sup>

The same coin cell, assembled with a typical electrolyte based on an ethylene oxide/propylene oxide random copolymer (P(EO/PO), [EO]:[PO]=89:11), had a discharge capacity lower than 60 mAh g<sup>-1</sup>. Battery tests on cells using polyether-based electrolytes are usually performed at higher temperatures of least 40 °C because of the low conductivity and also the crystalline nature of the PEO domain.<sup>72</sup> The difference in conductivity at 30 °C between PEC-LiFSI (188 mol%,  $2.5 \times 10^{-5}$  S cm<sup>-1</sup>) and P(EO/PO)-LiFSI (5 mol%,  $3.4 \times 10^{-5}$  S cm<sup>-1</sup>) is very small. The good cell performance of the PEC system is due probably to the following factors as an electrolyte: (1) a higher  $t_+$ ; (2) a higher salt concentration; and (3) better adhesiveness at the electrodes.<sup>47</sup> The charge/discharge cycling behavior of the coin cell of the PEC-LiFSI electrolyte is shown in Figure 7b. The efficiency after the second cycle was close to 100% and fairly constant. Capacities ranging from 80 to 120 mAh g<sup>-1</sup> were delivered at different C-rates, C/5, C/10 and C/20, at an operating temperature of 30 °C. The high  $t_+$  values of the PEC system and good contact between the electrode and electrolyte promote stable battery performance at 30 °C, due to attenuated polarization at the cathode and, probably, the formation of a better solid electrolyte interface.

## CONCLUSIONS

Recent studies on the ion-conductive properties and electrochemical performance of electrolytes based on PEC and its derivatives possessing GE and HC side groups have been reviewed. The author and his group determined the physicochemical properties of PEC and synthesized polycarbonate-based Li electrolytes and found the following deviations from the typical polyether system: (1) the ionic conductivity increases and the  $T_g$  value decreases with increasing salt concentration when imide-type salts are used; (2) Li transference numbers are higher than 0.5; (3) the oxidative stability is greater than 5 V vs Li; and (4) the resulting battery can operate at room temperature. This unique combination of desirable properties is due essentially to the unique solvation structure that is based on a very high salt concentration of greater than 50 mol%, where the polycarbonate chain does not form a strong coordination with Li ions, which is observed in polyether-based electrolytes. An interesting feature of this work is that it demonstrates that polycarbonate is a uniquely good candidate for polymer electrolytes because of its flexible, hydrophobic, transparent and ion-conductive properties. In view of increasing environmental concerns regarding the rising global concentration of CO<sub>2</sub> gas in the atmosphere, the results summarized here offer a way of mitigating CO<sub>2</sub> by fixing it on polymers.

## CONFLICT OF INTEREST

The author declares no conflict of interest.

## ACKNOWLEDGEMENTS

The author thanks the following entities for financial support: the Sumitomo Foundation in 2008, the Ogasawara Foundation in 2009, and the Inamori

Foundation in 2011. This work was supported financially by a Grant for Advanced Industrial Technology Development (Project ID: 11B01015c) of NEDO, the Specially Promoted Research for Innovative Next Generation Batteries of the Advanced Low Carbon Technology Research and Development Program (ALCA-SPRING) of JST, and JSPS KAKENHI Grant Numbers 25288095 and 16H04199. The 3DOM polyimide separator was kindly donated from Professor Kiyoshi Kanamura and Dr Hirokazu Munakata of Tokyo Metropolitan University.

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