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Fast Li-ion conduction in poly(ethylene carbonate)-based electrolytes and composites filled with TiO₂ nanoparticles[†]

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We have found remarkable ion-conductive properties of a novel polymer electrolyte composed of poly(ethylene carbonate) and Li bis-(fluorosulfonyl) imide. The self-diffusion coefficient of Li-ions exceeded 10⁻⁷ cm² s⁻¹ and the Li transference number was estimated at more than 0.8 in composite filled with only 1 wt% of TiO₂ nanoparticle.

Improvement of the ionic conductivity of polymer electrolytes is central to the development of novel energy storage devices such as flexible Li-ion secondary batteries.¹ Since ionic conduction in poly(ethylene oxide) (PEO)-metal salt complexes was first reported in 1973,² there have been many studies of the macromolecular design of polymers,³ improvement in salt solubility,⁴ addition of inorganic fillers,⁵ and organic-inorganic hybrids⁶ with room-temperature conductivity of the order of 10⁻⁴ S cm⁻¹. These PEO-based electrolytes suffer from low conductivity in the solid state composed to liquid, gel-like and ceramic-based electrolytes. Migration of ions in PEO generally arises from the local motion of oxyethylene (OE) chains in the amorphous region, which depends strongly on the cation-dipole interactions.⁷ The interaction inhibits the fast migration of ions, especially cations, because the OE chains trap and coordinate cations with the dipoles, and form stable complexes⁸ which cause the glass transition temperature, T_g , to increase.

In the development of novel polymer candidates as electrolytes without OE units we focus on polycarbonate structures, specifically on alternating copolymer of carbon dioxide with epoxide,⁹ which has a single carbonate group (-O-(C=O)-O-) in each repeating unit of the main chain. Carbonate-based organic solvents are used as the electrolyte solution in Li-ion batteries because of their high dielectric constant. In previous research, some polycarbonates were synthesized and considered for use in ion-conductive polymers,¹⁰ and these show unique ion-conductive properties based on the decoupling structure.¹¹ Below, we report novel polymer electrolytes composed of poly(ethylene carbonate) (PEC) and lithium bis-

(fluorosulfonyl) imide (LiFSI). We also evaluate the effect of TiO₂ nanoparticles on the properties of PEC-LiFSI electrolytes.

The relation between the ionic conductivity and the salt concentration is essential for polymer electrolytes, because the addition of salt usually leads to a drastic increase in T_g for the polymer, which in turn affects ionic migration. Based on the dependence on the salt concentration of the ionic conductivity and T_g for PEO-based electrolytes (Fig. 1 (a)), the conductivity was greatest at a salt concentration of approximately 5 mol% (PEO₂₀LiFSI). This value is almost the same as for other electrolytes which have been reported previously.^{3,7} It is well-known that there are suitable salt concentrations for high ionic conduction in typical polyether system, which are quite low.^{3,7} At high salt concentrations, above 5 mol%, the value of T_g slowly increases and the conductivity decreases with

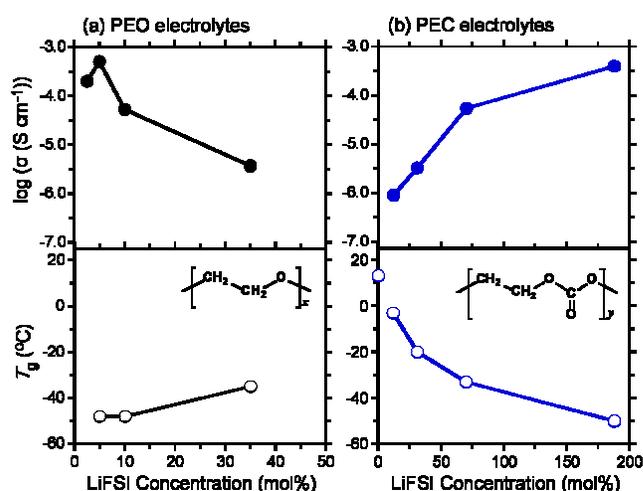


Fig. 1 Dependence on concentration of the ionic conductivity (σ) at 60 °C and the glass transition temperature (T_g) for (a) PEO- and (b) PEC-LiFSI electrolytes. Insets indicate structures of PEO and PEC.

increasing concentration. This is due to the increase in cross-linking (coupling) structures between lithium ions (Li^+) and dipoles of the polyether chains. The coupling structure prevents the segmental motion of local chains in the amorphous regions and gives rise to the increase in T_g . Neat PEO and the 2.5 mol% sample ($\text{PEO}_{40}\text{LiFSI}$) scarcely showed a glass transition, because of their high crystallinity (see Fig. S1 (a) of ESI).

The conduction and glass transition behavior of the PEC-based electrolytes was quite different from the PEO system (Fig. 1 (b)). The conductivities of PEC-LiFSI electrolytes increase linearly with increasing concentration; the electrolyte with 188 mol% of LiFSI ($\text{PEC}_{0.53}\text{LiFSI}$) had the highest conductivity of all PEC samples ($4.0 \times 10^{-4} \text{ S cm}^{-1}$). The glass transition behavior is completely different from the typical PEO system. The values of T_g for the PEC electrolytes decreased with increasing concentration, and the electrolyte with 188 mol% of LiFSI had lowest T_g , which was approximately 60°C lower than the T_g of neat PEC. This behavior can also be seen in our previous PEC electrolytes.¹² The addition of salts to polyether usually leads to an increase in T_g as a result of the strong interactions of the dissociated Li^+ with the ether oxygen and coordination with the polymer chains. The PEO-based electrolyte is therefore called a coupling system; ionic migration is coupled to the segmental motion.⁷ For PEC-based electrolytes the migration may be decoupled from the segmental dynamics, so that this can be termed a “decoupling” system. The dipole moment of the carbonate group in the main chain of PEC is strong enough to dissociate salts and interact with Li^+ , but tight coordination or solvation as seen in the PEO-salt complexes is probably negligible.

Comparison of the temperature dependence of the ionic conductivity for these two LiFSI electrolytes shows the difference in ion-conductive behavior between the PEO and PEC systems. PEO-based electrolytes have low conductivities of the order of 10^{-7} - $10^{-8} \text{ S cm}^{-1}$ at room temperature (Fig. 2 (a)), because of a transition at approximately 60°C corresponding to the melting temperature of crystalline PEO domains (see Fig. S1 (a) of ESI). Above the transition point, the conductivity increases linearly with temperature and the temperature dependence essentially follows an Arrhenius-type equation. The conductivity of the $\text{PEO}_{20}\text{LiFSI}$ (5 mol%) was higher than that of the $\text{PEO}_{10}\text{LiFSI}$ (10 mol%), since T_g increases

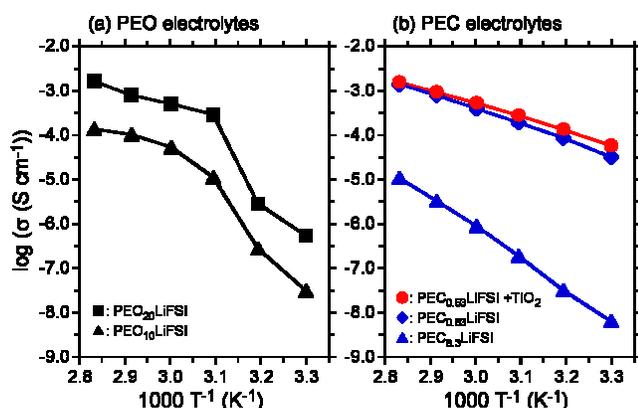


Fig. 2 Arrhenius plots of ionic conductivity for (a) PEO- and (b) PEC-LiFSI electrolytes.

with increasing salt concentration. On the other hand, PEC-based electrolytes exhibited typical amorphous-type Arrhenius behavior with convex curves throughout the entire range of measurement temperatures (Fig. 2 (b)). From the DSC measurement, neat PEC and all electrolytes were amorphous because of the absence of further transitions above the glass transition (see Fig. S1 (b) of ESI), so these electrolytes follow a VTF-type equation (see Fig. S2 of ESI). The conductivity of $\text{PEC}_{8.3}\text{LiFSI}$ (12 mol%) was low, but the addition of a small amount (only 1 wt%) of TiO_2 nanoparticle approximately doubled the conductivity of $\text{PEC}_{0.53}\text{LiFSI}$ (188 mol%), to $1.4 \times 10^{-4} \text{ S cm}^{-1}$ at 40°C . Previous studies of PEO-based composite electrolytes showed that the addition of inorganic fillers can lead to a significant increase in the conductivity, and also inhibits re-crystallization of the polymer, lowers the T_g and increases the lithium transport number, t_+ .⁵ The enhanced cationic conduction is believed to be due to the active interface between the polymer and the filler surface, according to the Lewis acid-base characterization.⁵ Fillers having high acidity, such as TiO_2 , are therefore suitable for increasing the conductivity.

To confirm the effect of TiO_2 on the migration of Li^+ in PEO and PEC-based electrolytes, we tried to estimate t_+ values using two methods. The first method is a typical electrochemical measurement that is combined with DC polarization and AC impedance techniques, and the second is estimation from values of the self-diffusion coefficients of ions measured by solid state NMR and the pulsed field gradient (pfg) technique^{13,14} (see experimental details of ESI). The electrochemical measurements revealed significant differences between PEO and PEC-based electrolytes in the current changes and impedance responses (Fig. 3 and Table 1). As seen in Fig. 3 (a), the direct current value for $\text{PEO}_{20}\text{LiFSI}$ dropped sharply

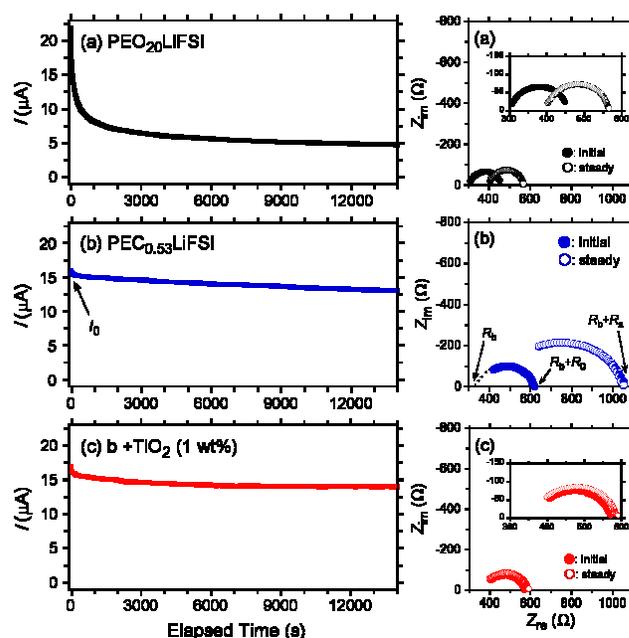


Fig. 3 Results of DC polarization and AC impedance measurements for (a) $\text{PEO}_{20}\text{LiFSI}$ (80°C), (b) $\text{PEC}_{0.53}\text{LiFSI}$ (60°C) and (c) $\text{PEC}_{0.53}\text{LiFSI}$ - TiO_2 composite (60°C). The insets are expanded impedance plots of (a) and (c).

within a few minutes, and then decreased gradually with time. The sharp fall is due to polarization at the Li cathode, which arises mainly from the migration of FSI anions. The impedance response was obvious, but the bulk resistance (R_b) increased after 24 h. In contrast, the current changes for PEC-based electrolytes were clearly improved (Fig. 3 (b)), and there was no significant drop of the current values, as seen in Fig. 3 (a). In particular, the PEC composite filled with 1 wt% of TiO₂ nanoparticle had very stable values of the current and impedance response (Fig. 3 (c)). This implies that there are many mobile ions, especially Li⁺ in PEC, which can migrate faster than coordinated, paired and aggregated ions; these free ions may be involved in the large decrease in T_g . Table 1 shows the values of t_+ EIS for three electrolytes. Typical PEO electrolyte (sample (a)) had a very low t_+ EIS, as has been reported by many researchers.^{12,15} The PEC-based electrolyte (sample (b)) gave a relatively high value, more than 0.5, whereas with PEO this is a bi-ion conductive system with very high salt concentration. The other samples, with different concentrations, also had high values of t_+ EIS, e.g. 0.38 for PEC_{3.23}LiFSI (31 mol%) and 0.71 for PEC_{1.43}LiFSI (70 mol%). For polyether systems such as PEO, t_+ EIS falls sharply with increasing salt concentration.¹⁵ The TiO₂ composite (sample (c)) had a surprisingly high t_+ EIS, greater than 0.8, and this value is as high as for single-ion conductive polymers.¹⁶

Table 1 Direct currents (I_0 , I_s), charge transfer resistances (R_0 , R_s) and lithium transference numbers (t_+ EIS) estimated by equation (1) (see ESI) for Li|electrolyte|Li cells.

Sample	I_0 (μ A)	I_s (μ A)	R_0 (Ω)	R_s (Ω)	t_+ EIS
(a) PEO ₂₀ LiFSI	22.0	3.4	155	167	0.11
(b) PEC _{0.53} LiFSI	15.9	8.2	263	531	0.54
(c) b +TiO ₂ (1 wt%)	16.8	14.0	198	224	0.81

Table 2 Self-diffusion coefficients of Li cation (D_{Li}) and FSI anion (D_F) at 60 °C and lithium transference numbers (t_+ NMR) estimated by equation (2) (see ESI) for PEO and PEC-based electrolytes.

Sample	D_{Li} (cm ² s ⁻¹)	D_F (cm ² s ⁻¹)	t_+ NMR
(a) PEO ₂₀ LiFSI	1.8×10^{-8}	1.1×10^{-7}	0.14
(b) PEC _{0.53} LiFSI	1.1×10^{-8}	3.5×10^{-8}	0.24
(c) b +TiO ₂ (1 wt%)	1.4×10^{-7}	4.4×10^{-8}	0.76

The results of NMR measurements are summarized in Table 2. For D_{Li} and D_F , there are large differences between PEO and PEC systems. In PEO electrolytes, values of D_{Li} and D_F have been reported of the order of 10^{-8} and 10^{-7} cm² s⁻¹, e.g. D_{Li} : 6.6×10^{-8} and D_F : 1.9×10^{-7} cm² s⁻¹ in an amorphous P(EO/EM-2/AGE)-LiTFSI (6 mol%) electrolyte at 80 °C;¹⁴ these values are consistent with our data. This observation indicates that the PEO acts as an anionic conductor in the electrolyte. The value of t_+ NMR for sample (a) was therefore very low, in good agreement with the estimated value as shown in Table 1. Values of t_+ NMR for PEC electrolytes were much higher than in the PEO system. The value for sample (b) was

normal, but t_+ NMR was 0.1 more than for sample (a). Sample (c) had a large value of t_+ NMR as well as of t_+ EIS (Table 1). The value of D_{Li} for sample (c) was approximately one-order of magnitude greater than for the other samples, so we believe that there are many mobile Li⁺ and PEC segments, where tight complex structures as seen in the PEO-based electrolytes are negligible.

In summary, we have found fast Li⁺ conduction in PEC-based electrolytes and TiO₂ composites using impedance and NMR techniques. The values of D_{Li} and t_+ NMR for PEC-LiFSI-TiO₂ are more than 10^{-7} cm² s⁻¹ and 0.8 at 60 °C. The Li-ion conductivities (σ at 60 °C $\times t_+$ EIS) of samples (a) PEO₂₀LiFSI, (b) PEC_{0.53}LiFSI and (c) PEC_{0.53}LiFSI-TiO₂ (1 wt%) were calculated to be 5.6×10^{-5} , 2.2×10^{-4} and 4.3×10^{-4} S cm⁻¹ respectively. We conclude that the polycarbonate is superior as a structure to polyether as an electrolyte for flexible batteries.

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† Electronic Supplementary Information (ESI) available: Experimental details and additional figures (Figs. S1-S5). See DOI: 10.1039/c000000x/

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