

RAPID COMMUNICATION

Ionic conduction in poly(ethylene carbonate)-based rubbery electrolytes including lithium salts

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INTRODUCTION

Ion-conductive polymers are recently developed electrolyte materials that are suitable for electrochemical applications, such as Li-ion secondary batteries,^{1,2} because they are safe (not flammable, no leakage), lightweight, easily processed and flexible. Ionic conduction in poly(ethylene oxide) (PEO)-metal salt complexes was reported in 1973,³ and there have since been many studies of the macromolecular design of PEO-based polymers as electrolyte materials that addressed reducing degrees of crystallinity as well as the exhibition of good conductivity and superior salt solubility.^{4–6} However, these electrolytes suffer from low conductivity in the solid state relative to liquid or gel electrolytes. The maximum conductivity of amorphous polyether-based electrolytes is $\sim 8 \times 10^{-5} \text{ S} \cdot \text{cm}^{-1}$ at 25 °C,⁷ and it is difficult to exceed values on the order of 10^{-5} at room temperature. The migration of ions in PEO arises from the local motion of oxyethylene chains in the amorphous region. The local structure that is crucial to the migration is believed to participate in cation–dipole interactions.⁴ In fact, the interaction sometimes inhibits the fast migration of ions (esp. cations), because the oxyethylene chains coordinate cations with the dipoles and form complex structures, which increases the glass transition temperature, T_g . Novel polymer candidates without oxyethylene units are needed to overcome these problems.

We shall consider polycarbonates that can be obtained by the alternating copolymerization of carbon dioxide with epoxides and comprise novel polymer candidates for electrolytes. Following the first report of the CO₂/epoxide copolymer by the Tsuruta group,^{8,9} there has been considerable development of highly active catalysts for effective polymerization.¹⁰ This copolymer

is a remarkable macromolecule, because it utilizes CO₂ as a raw material and has excellent properties; it is biodegradable, easily processed and colored, and has high transparency and low oxygen permeability. We have focused on the chemical structure of the copolymer, which has one alternating carbonate group (–O–(C=O)–O–) in each repeating unit of the main chain. The carbonate group has a large dipole moment, and it can dissolve many types of salts. Carbonate-based organic solvents, such as dimethyl carbonate, are used as the electrolyte solution in Li-ion batteries because of their high dielectric constant. Therefore, the carbonate group provides a suitable structure for the polymer framework. Polycarbonate-based electrolyte systems, such as poly(vinylene carbonate)¹¹ and poly(trimethylene carbonate),¹² have previously been reported. We recently synthesized glycidyl ether-based polycarbonates and have measured the ionic conductivities of these electrolytes.^{13,14} In our previous studies, it was impossible to determine the ion-conductive properties of these polycarbonates because of poor yields. In the present paper, we used a commercial, readily available polycarbonate, poly(ethylene carbonate) (PEC) for a polymer matrix, and we prepared five types of Li electrolytes with salt concentration varying from 16 to 80 wt%.

EXPERIMENTAL PROCEDURE

PEC was donated by Sumitomo Seika Co. (Osaka, Japan). The as-received chloroform solution of PEC was added into excess methanol, and the precipitated PEC was then dried in a vacuum oven at 60 °C for 24 h. The ¹H and ¹³C NMR spectra of the purified PEC ($M_n = 3.7 \times 10^4$, $M_w/M_n = 5.9$) were measured using a JEOL EX-400. The ratio of the carbonate units to all units (carbonate and ethylene oxide units) in the main chain was determined to be 95.2% from the

¹H NMR measurement (see Supplementary Figure S1 of Supplementary Information). Poly[ethylene oxide-co-2-(2-methoxyethoxy)ethyl glycidyl ether], P(EO/EM2), was donated by the Daiso Co. (Osaka, Japan). The *m/n* ratio was determined to be 83/17 from the ¹H NMR measurement. Figure 1 shows the chemical structures of these polymers. To prepare the electrolyte samples, PEC or P(EO/EM2) was dissolved in acetonitrile with lithium salts, LiX (anion X = N(SO₂CF₃)₂ (TFSI), N(SO₂C₂F₅)₂ (BETI), BF₄, ClO₄ and CF₃SO₃), and the solution was cast onto the plastic dish. The solution was held for several hours in a dry N₂-filled circulation chamber and then dried under vacuum at 60 °C for 24 h. Differential scanning calorimetry (DSC) measurements of all samples were performed using a DSC120 (Seiko Inst., Chiba, Japan) in the temperature range –100 °C to 250 °C at a heating rate of 10 °C·min^{–1} under dry N₂ gas. The ionic conductivities of all electrolytes were measured using the complex impedance method with a potentiostat/galvanostat SP-150 (Bio-Logic, Claix, France) in the frequency range of 100 Hz to 1 MHz in a glove box filled with dry Ar gas.

RESULTS AND DISCUSSION

The PEC electrolytes obtained using Li salt concentrations varying from 16 to 60 wt% were all self-standing films, and those prepared with a Li salt concentration of 80 wt% were rubbery solids. The electrolytes including LiTFSI, LiBETI and LiBF₄ were transparent, but the electrolytes including LiClO₄ (except for the 20 and 40 wt% samples) and LiCF₃SO₃ became opaque films. Figure 2 shows the DSC traces of the neat PEC and the PEC-LiTFSI electrolytes. The neat PEC had an obvious glass transition at 9 °C and was an amorphous polymer, because there were no remarkable transitions between

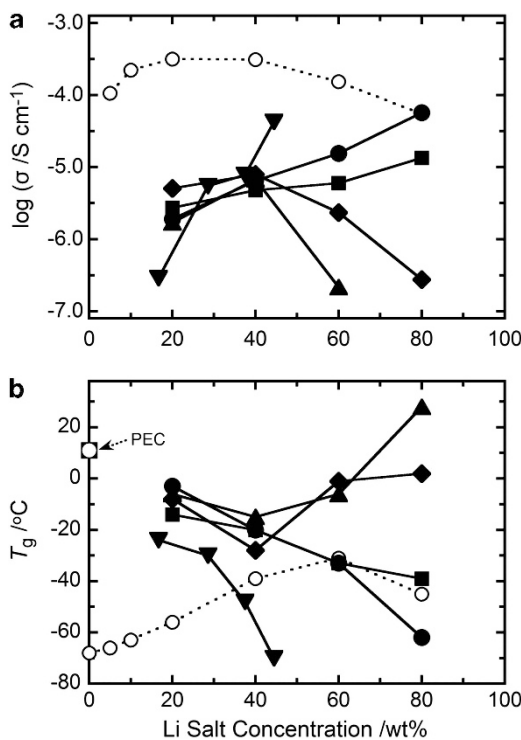


Figure 4 Variation with Li salt concentration of (a) ionic conductivity at 60 °C and (b) T_g of PEC-LiX (anion X = TFSI: ●, BETI: ■, BF₄: ▼, ClO₄: ◆, CF₃SO₃: ▲) and P(EO/EM2)-LiTFSI (○) electrolytes.

conduction in PEC also depends on the segmental motion of the polymer chains. The A and E_a parameters of the PEC electrolytes (20–80 wt%) were estimated to be 6–51 K^{1/2} · S · cm⁻¹ and 11–16 kJ · mol⁻¹, respectively. The values of A for the PEC electrolytes were slightly higher than for the amorphous P(EO/EM2)-LiTFSI electrolytes (5–44 K^{1/2} · S · cm⁻¹). However, there was no great difference in the E_a values between these electrolyte systems. This behavior has been previously observed in the glycidyl ether-based polycarbonate electrolytes,¹³ indicating that the potential energy for ionic transport in PEC and P(EO/EM2) may be almost identical. The carrier ions can migrate, even in the polycarbonate, without ethylene oxide units.

The dependence on salt concentration of the ionic conductivity or T_g for the PEC-LiX and P(EO/EM2)-LiTFSI electrolytes is shown in Figure 4. In Figure 4a, the conductivity of the polyether-based electrolyte was the greatest at a salt concentration of ~20–30 wt% (~5 mol% Li⁺ to the oxyethylene units); this behavior of the polyether system is well known.^{4–7} At high salt concentrations, above 40 wt%, the conductivity slowly decreases with increasing concentration. This behavior arises from the increase in crosslinking structures between the cations and the dipoles of

the polyether chains. The structure prevents the segmental motion of local chains in the amorphous regions and gives rise to the large increase in T_g , as observed in Figure 4b.

The conduction and glass transition behavior was different for the PEC-based electrolytes. As shown in Figure 4a, the LiCF₃SO₃ and LiClO₄ electrolytes exhibited the typical polyether-like conduction behavior, but with the maximum values shifted to the higher concentration region, from 20–30 to 40 wt%. In addition, the conductivities of the LiBETI, LiBF₄ and LiTFSI electrolytes increased linearly with increasing concentration, and the electrolyte with 80 wt% LiTFSI had the highest conductivity of all of the PEC systems. The glass transition behavior of the PEC system is unique. As shown in Figure 4b, the T_g value of PEC falls by more than 10 °C with the addition of salts to at least 16 wt% of LiBF₄, whereas the T_g for P(EO/EM2) increases with increasing salt concentration. At high salt concentrations (above 40 wt%), the T_g for the LiCF₃SO₃ and LiClO₄ electrolytes increased with increasing concentration. In contrast, for the LiBETI, LiBF₄ and LiTFSI electrolytes, the value of T_g decreased with increasing concentration, and the electrolyte with 44.4 wt% of LiBF₄ presented the lowest T_g , which was ~80 °C lower than the T_g of the pure PEC. For salt concentrations from

20 to 80 wt%, the behavior of the PEC-based electrolytes is opposite to that of typical polyether systems. 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.⁴ For the PEC system, the dipole moment of the carbonate group in the main chain is strong enough to dissociate salts and interact with cations, but tight coordinations or solvations, such as PEO-salt complexes, are negligible. We believe that there are many mobile ions (esp. Li⁺) in PEC, which can migrate faster than coordinated cations, ion pairs and aggregated ions; the existence of these free ions may be involved in the large decrease in T_g . This behavior of the salt-rich PEC electrolytes and the partial P(EO/EM2) electrolytes (more than 60 wt% LiTFSI) leads to the title of ‘polymer-in-salt’ system. Angell *et al.* have reported that polymer-in-salt electrolytes, such as superionic glasses that have a small amount of a low M_w poly(propylene oxide) included, have greater conductivities than the salt-in-polymer electrolyte and that there is a decrease in T_g .^{16,17} A ⁷Li nuclear spin relaxation measurement was also performed on the polymer-in-salt electrolytes. The results of these studies found that there are serial decoupling structures with different relaxation modes in the liquids and that the conductivity of the polymer-in-salt electrolytes is dominated by the migration of free Li⁺.¹⁷ We attempted to measure the Li⁺ transference number, t_+ , of the PEC-LiBF₄ (44.4 wt%) electrolyte, and the value was estimated to be 0.49 at 100 °C (see Supplementary Figure S3 of Supplementary Information). This value is very high relative to the typical polyether-based electrolytes, for example, $t_+ \sim 0.1$ for PEO₂LiBF₄ (~51.6 wt%) at 100 °C.¹⁸ According to a previous report, the t_+ drastically decreases with increasing salt concentration in PEO.¹⁸ Those authors suggested that the decreases in t_+ are caused by the decrease in the number of free PEO segments and that the motion of Li⁺ is hindered by the subsequent formation of ion-pairs. However, the PEC electrolyte has a very high t_+ value, in spite of the high salt concentration. We believe that there may be many mobile Li⁺ ions and free PEC segments that are not related to the tight coordination structure as observed in the PEO-based electrolytes.

CONCLUSIONS

The ion-conductive behavior of PEC-Li salt rubbery electrolytes was studied. The

dependencies of ionic conductivity and T_g on the salt concentration revealed that the LiCF_3SO_3 and LiClO_4 electrolytes exhibit typical polyether-like behavior. However, the LiBETI , LiBF_4 and LiTFSI electrolytes were found to be much different such that the conductivity increases and T_g decreases with increasing salt concentration. The Li^+ transference number (t_+) of the PEC-LiBF_4 (44.4 wt%) electrolyte was very high, compared with the values of PEO-based electrolytes; it was estimated to be ~ 0.5 at 100°C . PEC may have many mobile ions, which can migrate faster than coordinated cations, ion-pairs and aggregated ions. Moreover, the existence of free PEC segments, which do not form strong coordinations with cations, most likely relates to the prevention of a large increase in T_g and consequently, the conductivity increases. We believe that the salt-rich PEC electrolytes incorporate decoupling structures, as observed in the salt-in-polymer system.

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Supplementary Information accompanies the paper on Polymer Journal website (<http://www.nature.com/pj>)