

## Effect of Anions on Lithium Ion Conduction in Poly(ethylene carbonate)-based Polymer Electrolytes

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Poly(ethylene carbonate)-based polymer electrolytes with lithium salts (LiX; X=TFSI, ClO<sub>4</sub>, BF<sub>4</sub> and PF<sub>6</sub>) were prepared and measured their lithium transference numbers ( $t_+$ ) for the comparison between different anion radius and salt concentrations. The LiTFSI electrolytes showed highest  $t_+$  and Li-ion conductivities of all samples at 80 °C, and these values increased with increasing salt concentration. From the results of FT-IR measurements for all concentrated samples, it was revealed that the changes of a band fraction divided at around 1720 cm<sup>-1</sup> for interacted carbonyl groups with Li<sup>+</sup> (C=O --- Li<sup>+</sup>) strongly relate to the mobility of Li<sup>+</sup>.

### Introduction

For more than four decades, polymer electrolytes have attracted much attention as soft ionics materials for novel battery systems such as Li-ion secondary batteries (1-2), because of their safety compared with liquid electrolytes, their flexibility and their lightweight. However, the conductivity of typical polyether-based electrolytes such as poly(ethylene oxide) (PEO)-metal salt mixtures is limited to approximately lower than 10<sup>-4</sup> S/cm at room temperature (3-5). Moreover, it is extremely difficult to enhance the lithium transference number ( $t_+$ ) over 0.5.

On the other hand, we recently consider polycarbonates that can be obtained by the alternating copolymerization of carbon dioxide with epoxides and use as one of novel polymer candidates for electrolytes (6-8). We focused on the chemical structure of the copolymer, which has single carbonate group (-O-(C=O)-O-) in each repeating unit of the main chain. Carbonate-based organic solvents are usually 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. In our previous studies, we have reported that a commercial polycarbonate, poly(ethylene carbonate) (PEC) can be a novel polymer matrix for the electrolyte, and shows extraordinary ion-conductive properties (9). We found that the ionic conductivity of PEC-Li salt electrolytes increases with increasing salt concentration, whereas typical PEO-based electrolytes show maximum conductivities at around 5 mol% and decrease with increasing concentration (9). Moreover, we recently revealed that lithium transference numbers ( $t_+$ ) of PEC-based electrolytes are more than 0.5, and their composites filled with small amount of TiO<sub>2</sub> have extremely high values more than 0.8 (10). In this study, we focused on the effect of anions on Li-ion conduction in PEC and compared  $t_+$  as functions of anion radius and salt concentration. The characterization of interactions between PEC and ions using FT-IR measurement was also carried out for the first time.

## Experimental Procedure

### Preparation of PEC-Li salt electrolytes

Poly(ethylene carbonate) (PEC,  $M_n=3.7 \times 10^4$ ) was donated by Japanese company. As-received PEC was dissolved in chloroform, and the solution was added into excess methanol. The precipitated PEC was dried in a vacuum oven at 60 °C for 24 h. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the purified PEC were measured, and the ratio of the carbonate units to all units (carbonate and ethylene oxide units) in the main chain was determined to be approximately 95% (9). To prepare the electrolyte samples, the PEC was dissolved in acetonitrile with Lithium Battery Grade Li salts ( $\text{LiX}$ ,  $\text{X}=\text{N}(\text{SO}_2\text{CF}_3)_2$  (TFSI),  $\text{ClO}_4$ ,  $\text{BF}_4$  and  $\text{PF}_6$ , purchased from Kishida Chemical Co.). The ratio of the  $\text{Li}^+$  to the EC monomer unit of PEC was set to be 5~80 mol% ( $[\text{Li}^+]/[\text{EC}]=1/20\sim 1/1.25$ ) in all samples. The homogeneous solution was cast onto the plastic dish, and was held for several hours in a dry  $\text{N}_2$ -filled circulation chamber. The sample film was dried under vacuum at 60 °C for 24 h, and then introduced into a glove box filled with dry Ar gas.

### Measurements

Ionic conductivities of all electrolytes were measured at 80 °C using the complex impedance method with a potentiostat/galvanostat SP-150 (BioLogic) in the frequency range of 100 Hz to 1 MHz in the glove box. To determine the lithium-ion transference number ( $t_+$ ) of each sample, we used a conventional electrochemical method combined with DC polarization and AC impedance measurements for  $\text{Li} \mid \text{electrolyte} \mid \text{Li}$  cells at 80 °C. The values of  $t_+$  can be estimated from the following equation (11);

$$t_+ = \frac{I_s(\Delta V - I_0 R_0)}{I_0(\Delta V - I_s R_s)} \quad [1]$$

where  $I$  is the direct current,  $R$  is the electron-transfer resistance between the Li electrode and electrolyte, and  $\Delta V$  is the applied voltage (10 mV). The subscripts  $0$  and  $s$  refer respectively to the initial and steady state (approx. after 24 hours). The current and resistance were measured using an Impedance Analyzer 1280C (Solartron). The sample was sandwiched between two stainless plates, with the 0.2 mm-thick Li foils as non-blocking electrodes. The entire process was carried out in an Ar gas-filled glove box with control of the content of water and oxygen below 1 ppm.

FT-IR spectra of neat PEC and all electrolytes were recorded on a FT-IR spectrometer (FT/IR-4100, JASCO Co.) using an ATR unit (ZnSe lens) in the region from 400 to 4000  $\text{cm}^{-1}$  with a resolution of 1  $\text{cm}^{-1}$  under dry  $\text{N}_2$  gas. The resulting spectra were curve-fitted by a non-linear least-squares method with an original curve resolution program using a straight base line and a Gaussian product function for each band.

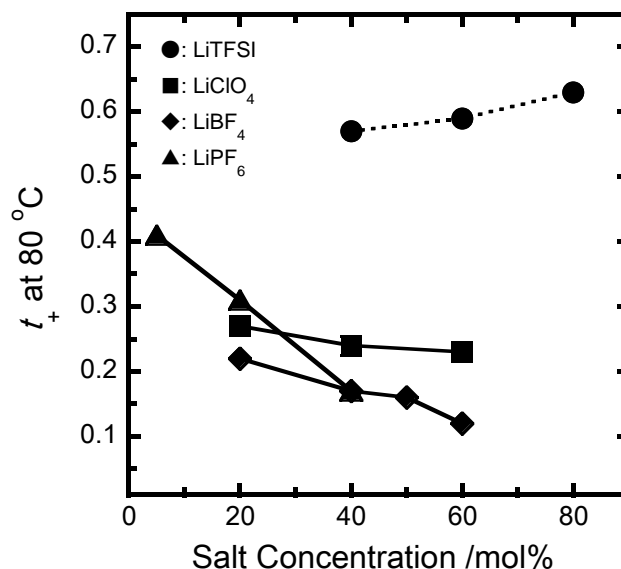
## Results & Discussion

The PEC electrolytes obtained using Li salt concentrations of 5, 20, 40, 50 and 60 mol% were all self-standing films, and those prepared with a Li salt concentration of 80 wt% were rubbery solids. It was impossible to measure  $t_+$  for more than 60 mol% salt

concentrations except for the LiTFSI electrolytes. The LiTFSI, LiClO<sub>4</sub> and LiBF<sub>4</sub> electrolytes were all transparent, and the LiPF<sub>6</sub> electrolytes became slightly opaque films.

### Lithium ion conduction in PEC-LiX electrolytes

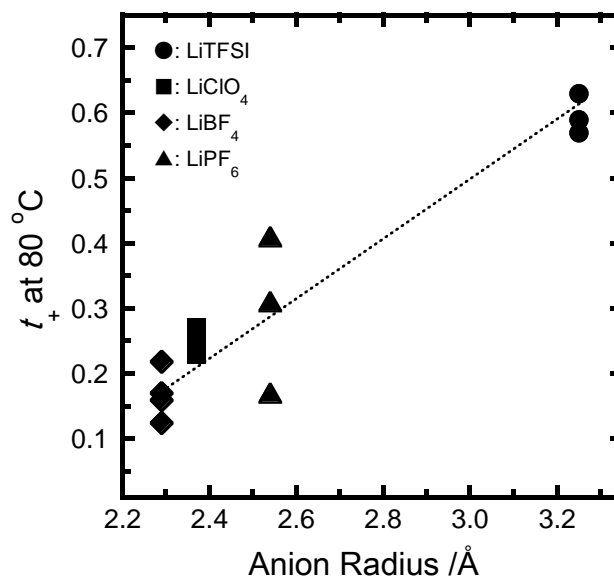
The values of  $t_+$  for all electrolyte samples were successfully estimated from eq. 1 and were summarized as a function of salt concentration in Figure 1. In case of the LiPF<sub>6</sub> electrolytes, the value of  $t_+$  at a concentration of 5 mol% was relatively high to be more than 0.4, however the value drastically decreased with increasing concentration. The decrease was also seen in the LiClO<sub>4</sub> and LiBF<sub>4</sub> systems, and the values gradually decreased with increasing concentration to be lower than 0.3. These behaviors and values were good agreement with the polyether-based electrolytes with some Li salts (12). In case of the PEO-LiPF<sub>6</sub> electrolyte (12), the transference number was more than 0.5 at low salt concentration, but the value decreased with increasing concentration and was 0.15 at concentrations higher than 30 mol%. This means that the Li<sup>+</sup> conduction strongly depends on the segmental motion of PEO chains and the decrease in  $t_+$  gives rise to the decrease in the number of free PEO segments, resulting in a decrease in the mobility of Li<sup>+</sup>. The PEC-LiClO<sub>4</sub>, LiBF<sub>4</sub> and LiPF<sub>6</sub> electrolytes are also considered to have the same conduction mechanism with the PEO system. On the other hand, as seen in Figure 1, the LiTFSI system showed completely opposite behavior. The values of  $t_+$  were greater than 0.5 and increased with increasing concentration to be 0.63 in a concentration of 80 mol%. There are previously no reports on such high  $t_+$  values of polyether-based electrolytes, and the values are usually lower than 0.5 in PEO-salt mixtures. Watanabe *et al.* have shown that amorphous polyether-based LiTFSI electrolytes have very low  $t_+$  values lower than 0.1 (5). In the polyether electrolyte, it is well known that dissociated Li<sup>+</sup> stable interact with dipoles of ether oxygens in the polymer chains where the transference number is lowered.



**Figure 1** Dependence on salt concentration of  $t_+$  for PEC-Li salt electrolytes.

Figure 2 shows relation between transference numbers and radius of anions dissociated into PEC electrolytes. The values of anion radius were quoted from data previously reported by Ue (13). From this figure, we can confirm that average  $t_+$  value in

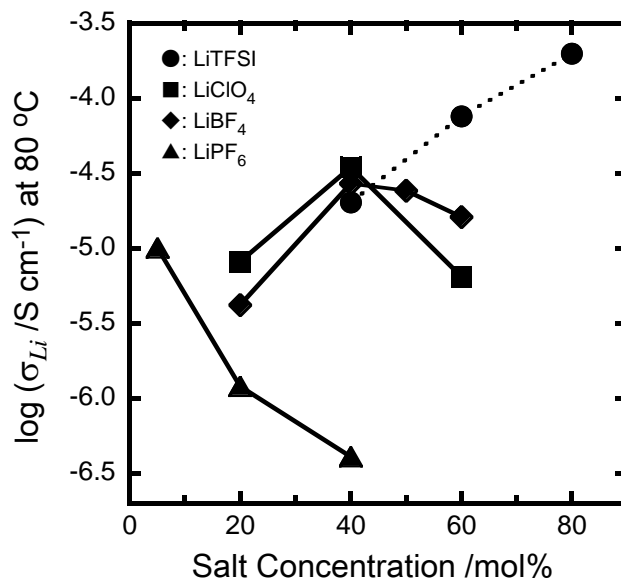
each electrolyte sample increase with increasing anion radius. This indicates that the large anions such as TFSI promote the migration of  $\text{Li}^+$  in PEC. In case of the lithium bis-(fluorosulfonyl) imide (LiFSI) in PEC, we can estimate the  $t_+$  to be approximately 0.40~0.45 from Figure 2, when we use the radius of a FSI anion calculated to be approximately 2.83 Å from the van der Waals volume (14). These estimated values are in relatively good agreement with our previous results (0.4~0.5 at low salt concentrations, unpublished work) and published reports (0.54 at 188 mol%) (10). Comparing with two LiTFSI electrolyte systems, we can clearly confirm that there are large differences in the transference numbers more than 0.5 between PEO and PEC. In the PEO system, low  $t_+$  values are due to the formation of strong coordination structures which depend on the interactions between  $\text{Li}^+$  and ether chains. On the other hand, significant high values of  $t_+$  for the PEC electrolytes were observed because of the structure of the polymer chain. The PEC has single carbonate group in a monomer unit, and probably interactions exist between  $\text{Li}^+$  and dipoles such as carbonyl groups of the main chain. However, strong and stable coordination structures such as PEO system are negligible in PEC (9,10).



**Figure 2** Relation between dissolved anion radius and  $t_+$  for PEC-Li salt electrolytes with different salt concentrations in each electrolyte system.

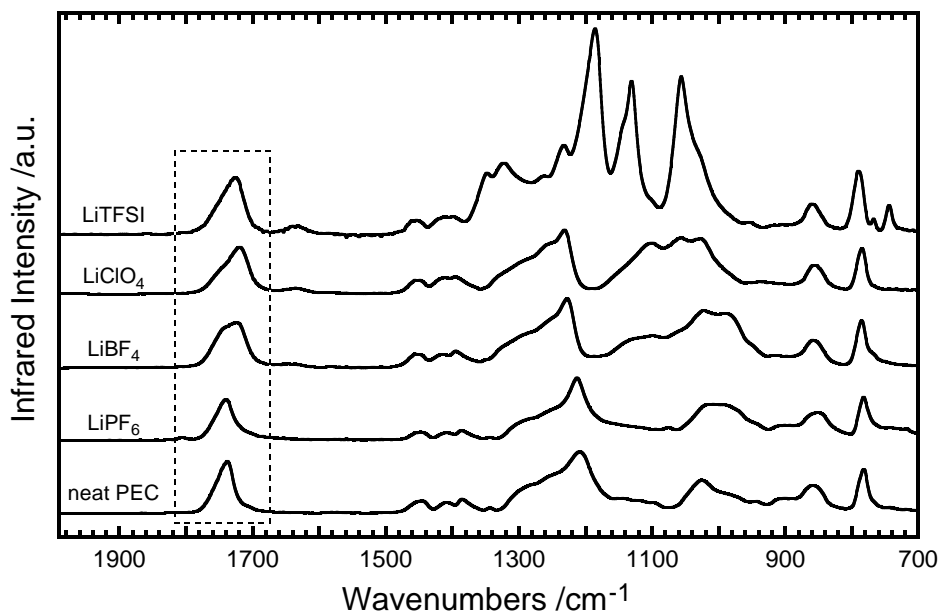
According to the estimation of  $t_+$  for PEC-based electrolytes with a variety of anions, we can also compare Li-ion conductivities  $\sigma_{\text{Li}}$  ( $= t_+ \times$  ionic conductivity ( $\sigma$ ) at 80 °C) of these electrolytes as a function of salt concentration (Figure 3). The dependence on salt concentration of  $\sigma$  for PEC-LiX electrolytes has already been reported (9), and the dependences for LiClO<sub>4</sub> and LiTFSI electrolytes are very similar with those as seen in Figure 3. In case of the LiPF<sub>6</sub> electrolyte,  $\sigma_{\text{Li}}$  drastically decreased with increasing concentration. The LiClO<sub>4</sub> and LiBF<sub>4</sub> electrolytes had greatest  $\sigma_{\text{Li}}$  at a concentration of 40 mol%, which are extremely high compared with the typical polyether system (approx. 5 mol%) (3-5). The  $\sigma_{\text{Li}}$  of LiTFSI electrolytes linearly increased with increasing concentration, and the value at 80 mol% exceeded the order of  $10^{-4}$  S cm<sup>-1</sup>. This was also observed in the LiFSI electrolyte system (10), and the increase in the conductivity at very high salt concentrations is due to the decrease in glass transition temperature,  $T_g$  of PEC (9,10). Especially for the LiTFSI electrolytes, the plasticizing effect of TFSI anions may

influence on the decrease in  $T_g$  of PEC, but it is impossible to explain such large decrease only this effect. In fact, LiTFSI has the same effect for polyethers such as PEO, but the  $T_g$  of PEO increases with increasing LiTFSI concentration (5).



**Figure 3** Dependence on salt concentration of  $\sigma_{Li}$  for PEC-Li salt electrolytes.

#### FT-IR spectra of PEC-LiX electrolytes



**Figure 4** FT-IR spectra ( $2000\sim 700\text{ cm}^{-1}$ ) of neat PEC and the electrolytes at a salt concentration of 40 mol%.

To analyze the dissociation state of  $Li^+$  in PEC, we carried out measuring FT-IR spectra of neat PEC and the Li salt electrolytes. These spectra of electrolytes with a salt concentration of 40 mol% were summarized in Figure 4. It has already been reported that dissolved  $Li^+$  usually make strong interactions with dipoles of carbonyl oxygens (C=O)

and ether oxygens (O-C-O) in electrolyte solutions such as propylene carbonate (PC) and dimethyl carbonate (DMC) (15,16). The O-C-O asymmetric stretching mode at around  $1300\text{ cm}^{-1}$  in DMC is known to be very sensitive to the interaction with  $\text{Li}^+$  (16), but the band sometimes overlaps with other bands such as TFSI anion ( $1300\sim 1200\text{ cm}^{-1}$  in Figure 4) and it is difficult to characterize interactions. On the other hand, the band of C=O stretching vibration ( $\nu_{\text{C=O}}$ ) mode at around  $1750\text{ cm}^{-1}$  usually appears without overlaps and is suitable for the characterization in detail, therefore we focused on this region (highlighted by dot-line square in Figure 4). In case of DMC, it is known that the interacted  $\nu_{\text{C=O}}$  band newly appears at the lower wavenumber by the addition of Li salt (15). As seen in Figure 4, interacted band (C=O ---  $\text{Li}^+$ ) at around  $1720\text{ cm}^{-1}$  shifted from the free C=O band (in neat PEC at  $1740\text{ cm}^{-1}$ ) clearly appears in the LiTFSI, LiClO<sub>4</sub> and LiBF<sub>4</sub> electrolytes. The LiPF<sub>6</sub> electrolyte seems to have no interacted band, but very small shoulder-like band is included with the free C=O band.

**TABLE I.** Fractions of free and interacted carbonyl groups in PEC-Li salt electrolytes determined by the curve-fitting analysis of FT-IR spectra for the C=O stretching vibrational ( $\nu_{\text{C=O}}$ ) mode.

Li salt	Concentration to PEC /mol%	Free C=O groups		Interacted C=O groups	
		Fraction /%	Wavenumber / $\text{cm}^{-1}$	Fraction /%	Wavenumber / $\text{cm}^{-1}$
LiTFSI	20	45	1755	55	1721
	40	42	1748	58	1724
	60	43	1746	57	1720
	80	43	1749	57	1723
LiClO <sub>4</sub>	20	58	1746	42	1716
	40	30	1750	70	1720
	60	34	1747	66	1721
LiBF <sub>4</sub>	20	61	1750	38	1718
	40	34	1751	66	1723
	50	43	1750	57	1724
	60	48	1748	52	1721
LiPF <sub>6</sub>	20	61	1750	39	1720
	40	60	1742	40	1720

The  $\nu_{\text{C=O}}$  region of all PEC-based electrolytes were divided into two bands at around  $1750$  and  $1720\text{ cm}^{-1}$ , and each fraction and wavenumber at the peak-top were summarized in Table 1. If the fraction of interacted C=O groups is larger than that of the free ones, this means that dissociated  $\text{Li}^+$  (carrier ions) are more than undissociated and aggregated ions in PEC. Average fraction of interacted C=O groups in LiPF<sub>6</sub> electrolytes was smallest of all samples, and this probably indicates that LiPF<sub>6</sub> has low dissociation degree in PEC. Both LiClO<sub>4</sub> and LiBF<sub>4</sub> electrolytes showed the largest fractions of interacted C=O groups at a concentration of 40 mol%, and these results correlate with the highest values of  $\sigma_{\text{Li}}$  in Figure 3. On the other hand, the LiTFSI electrolytes showed continuously high fractions of interacted C=O groups approximately 60 % at any salt concentrations. The transference numbers and conductivities of the LiTFSI electrolytes are therefore higher as seen in Figures 1, 2 and 3 because of its better dissociation state of  $\text{Li}^+$ . Interacted C=O groups in PEC are considered to be able to migrate  $\text{Li}^+$  faster than that coordinated with ether chains in PEO. The size of TFSI anion is much larger than that of  $\text{Li}^+$  (approx.  $0.76\text{ \AA}$ ), and the increases in the transference numbers in PEC may be simply caused by the difference in the molecular mass between these ions.

## Conclusions

In this study, we focused on the effect of anions on Li-ion conduction in PEC and compared with lithium transference number ( $t_+$ ) as functions of anion radius and salt concentration. The values of  $t_+$  for PEC-LiTFSI electrolytes were greater than 0.5 and increased with increasing concentration to be 0.63 at a concentration of 80 mol%. From the dependence on anion radius of  $t_+$ , it was revealed that the large anions such as TFSI promote the migration of  $\text{Li}^+$  in PEC. The Li-ion conductivity  $\sigma_{\text{Li}}$  of LiTFSI electrolytes linearly increased with increasing concentration, and the value at 80 mol% was the highest of all electrolytes and exceeded the order of  $10^{-4} \text{ S cm}^{-1}$ .

On the other hand, we carried out FT-IR measurements for neat PEC and all concentrated electrolytes to characterize the dissociation state of carrier ions in PEC. The stretching vibration mode of carbonyl (C=O) groups for all PEC-based electrolytes was divided into two bands at around 1750 and 1720  $\text{cm}^{-1}$ , which are due to the free and interacted C=O groups. It was revealed that the changes of a band fraction divided at around 1720  $\text{cm}^{-1}$  for interacted C=O groups with  $\text{Li}^+$  (C=O ---  $\text{Li}^+$ ) strongly relate to the mobility of  $\text{Li}^+$  in PEC. The PEC may form no strong and stable coordination structures with  $\text{Li}^+$  as seen in the typical polyether system.

## Acknowledgments

This work was financially supported by a Grant for Advanced Industrial Technology Development (Project ID: 11B01015c) from NEDO, Japan.

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