Electronic Supplementary Information

Fast Li$^+$ conduction in poly(ethylene carbonate)-based rubbery electrolytes and composites filled with TiO$_2$ nanoparticles

Yoichi Tominaga* and Kenta Yamazaki

Tokyo University of Agriculture and Technology
Koganei, Tokyo 184-8588, JAPAN
ytominag@cc.tuat.ac.jp

I. Experimental detail

II. Additional figures

Figure S1: DSC curves of (a) PEO and (b) PEC-based electrolytes.

Figure S2: VTF plots of PEC-based electrolytes and composite.

Figure S3: Dependence on TiO$_2$ content of the ionic conductivity at 40 °C for PEC$_x$LiFSI composite electrolytes.

Figure S4: (a) ^{7}Li and (b) ^{19}F NMR spectra of PEO and PEC-based electrolytes.

Figure S5: FT-IR spectra of (a) neat PEC, (b) PEC$_{0.53}$LiFSI and (c) TiO$_2$ composite in the region from 1700 to 1800 cm^{-1}.

References

I. Experimental detail

1. Sample preparation

Poly(ethylene oxide) (PEO, $M_v=1.0\times10^5$) was purchased from Aldrich Co. and used as received. Poly(ethylene carbonate) (PEC, $M_w=2.2\times10^5$, $M_w/M_n=5.9$ from GPC) was donated by the company and dissolved in chloroform. The solution was mixed into excess methanol, and the PEC precipitated was then dried in a vacuum oven at 60 °C for 24 h. The ratio of the carbonate units to all units (carbonate and ethylene oxide units) in the main chain of PEC was 95.2% according to ^{1}H NMR measurement.[1] To prepare the electrolyte samples, PEO or PEC was dissolved in acetonitrile with lithium bis-(fluorosulfonyl) imide ($LiN(SO_2F)_2$ (LiFSI), > 99%), and the solution was cast onto a plastic dish. The compositions of the PEO- and PEC-LiFSI systems are specified as monomer : Li^+ (x), which is the ratio of the number of monomer units to the number of lithium ions. The solution was stored for several hours in a dry N_2-filled circulation chamber and then dried under vacuum at 60 °C for 24 h. For preparation of the composites, 1~10 wt% of TiO_2 nanoparticles (NanoTek® by Kanto Chemical Co., particle size: 20~100 nm) was added to the PEC_xLiFSI electrolytes in acetonitrile, and the resulting slurry was dried in the same way as the TiO_2-free samples. These electrolytes, obtained with concentrations (x) varying from 8.33 (20 wt% of LiFSI) to 1.43 (60 wt%), were all self-standing films, whereas those with x=0.53 (80 wt%) and the TiO_2 (1 wt%) composite were rubbery solids.

2. Measurements

Differential scanning calorimetry (DSC) measurements of all samples were performed using a DSC120 (Seiko Inst.), in the temperature range –100°C to 250 °C at a heating rate of 10 °C·min^{-1} under dry N_2 gas. The ionic conductivities of all electrolytes and the TiO_2 composites were measured using the complex impedance method, with a potentiostat/galvanostat SP-150 (BioLogic) in the frequency range from 100 Hz to 1 MHz in a glove box filled with dry Ar gas. We undertook lithium-7 and fluoride-19 NMR spectroscopic and pulsed field gradient (pfg) diffusion measurements on the PEO and PEC electrolytes using a JNM-ECA500 II spectrometer (JEOL Co.) with a GR probe (JEOL Co.) at 60 °C. A quartz tube (5 mm) was used, and the sample was introduced into the tube in the

glove box. The self-diffusion coefficients of Li cation (D_{Li}) and FSI anion (D_F) can be determined from the attenuation of the echo amplitude at time 2τ which is given by

$$M(2\tau,G) = M(0) \cdot exp\left(-\frac{2\tau}{T_2} - (\gamma G\delta)^2 D\left(\Delta - \frac{\delta}{3}\right)\right)$$

where $M(0)$ is the signal amplitude immediately after the pulse, γ is the nuclear gyromagnetic ratio, G is the amplitude, δ is the duration, $\Delta\,(=\tau)$ is the diffusion (relaxation) time, D is the self-diffusion coefficient, and T_2 is the transverse relaxation time.[2] Fitting of this equation to the echo amplitudes for a series of G values allows D to be estimated.

To determine the lithium-ion transference number (t_+) of all samples, we used two methods. One is the electrochemical combination method of DC polarization and AC impedance measurements for Li │ electrolyte │ Li cells at 60 °C (for PEO electrolytes, the measurement temperature was 80 °C because of crystallization). The values of t_+EIS (where EIS means electrochemical impedance spectroscopy) can be estimated from the following equation[3]

$$t_+ EIS = \frac{I_s(\Delta V - I_0 R_0)}{I_0(\Delta V - I_s R_s)} \qquad (1)$$

where I is the direct current, R is the electron-transfer resistance between the Li electrode and electrolyte, and ΔV is the applied voltage (10 mV). The subscripts 0 and s refer respectively to the initial and steady state (applox. 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.

The second method is the use of D values obtained from the pfg-NMR measurements. The values of t_+NMR can be estimated from the following equation[4]

$$t_+ NMR = \frac{D_+}{D_+ + D_-} \qquad (2)$$

where D_+ and D_- are the self-diffusion coefficients of the cation and anion in the electrolyte.
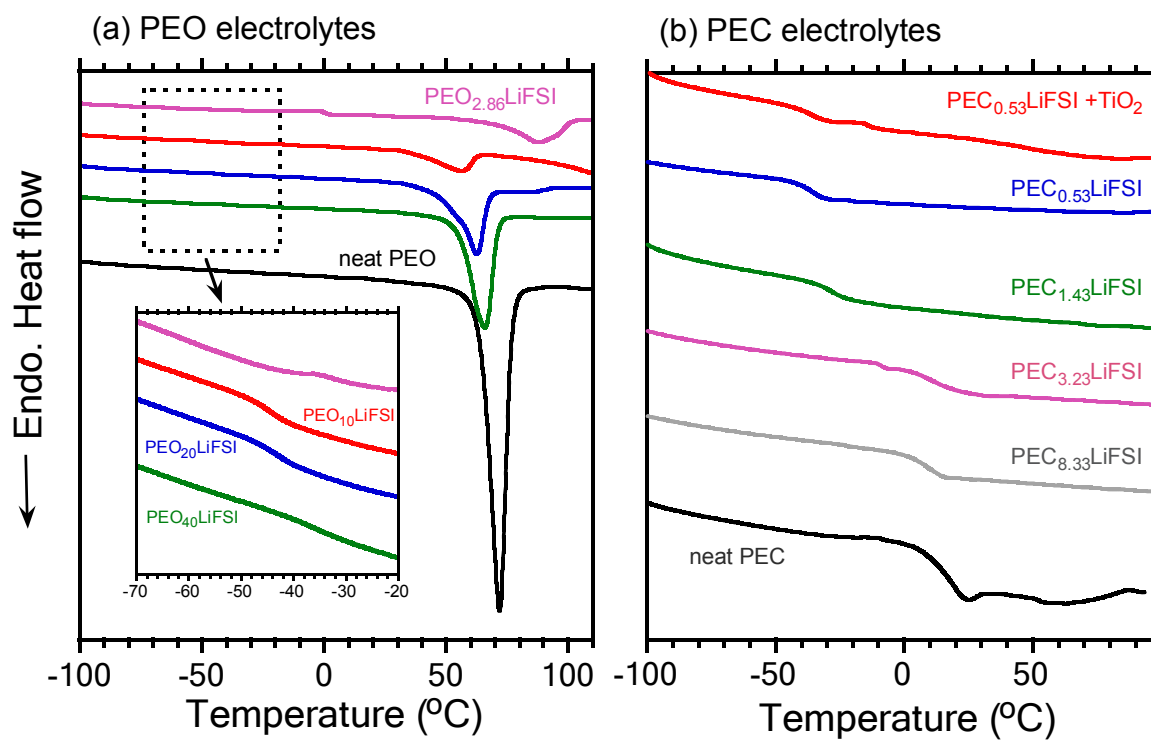
II. Additional figures

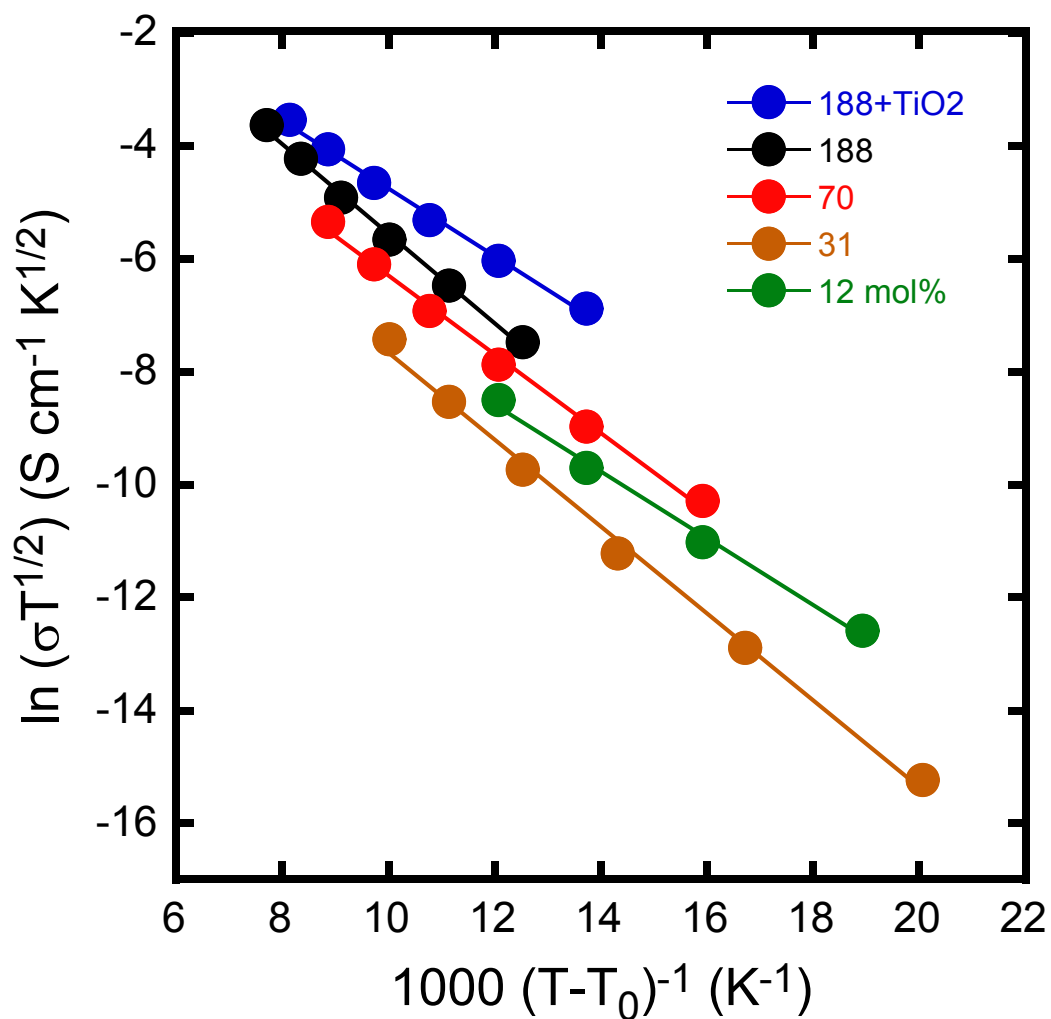Figure S1: DSC curves of (a) PEO and (b) PEC-based electrolytes.

Figure S2: VTF plots of PEC-based electrolytes and composite.

The VTF parameters (activation energy E_a, constant A) for PEC-based electrolytes with LiFSI concentration (mol%) of 12, 31, 70, 188 and 188 + TiO$_2$ (1 wt%) were estimated to be 4.92, 6.40, 5.80, 6.59 and 4.97 kJ mol^{-1} and 0.23, 1.04, 1.97, 7.22 and 3.44 K$^{1/2}$ S cm^{-1}, respectively.
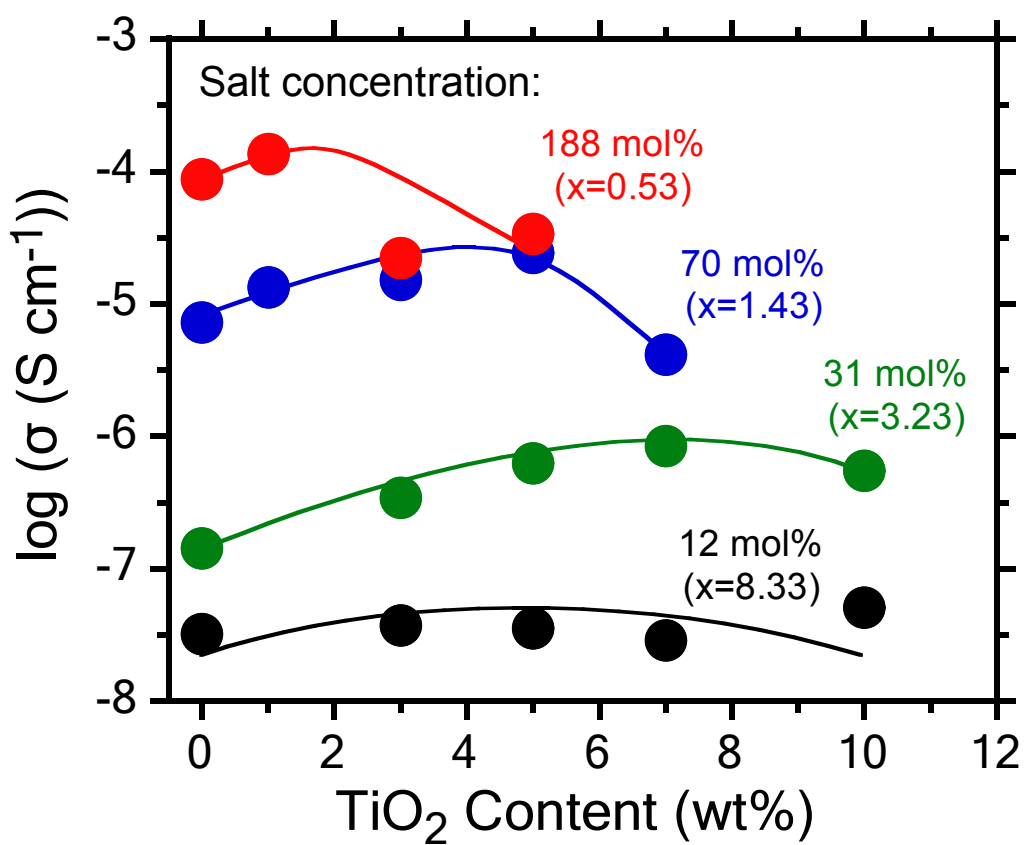
Figure S3: Dependence on TiO$_2$ content of the ionic conductivity at 40 °C for PEC$_x$LiFSI composite electrolytes.
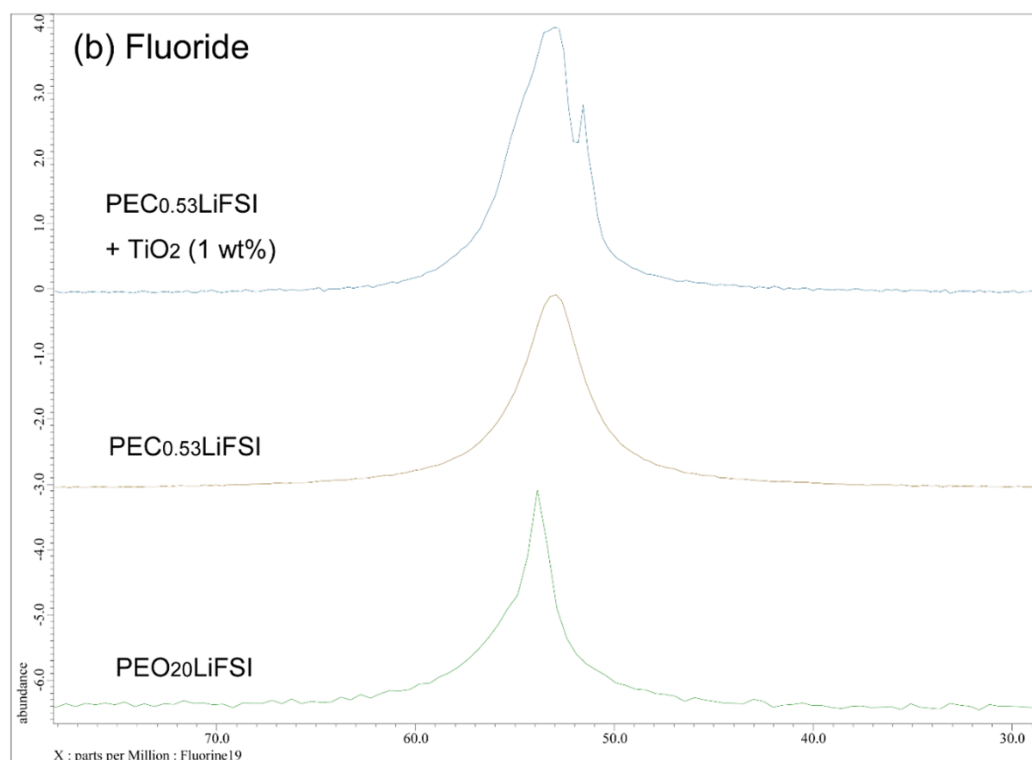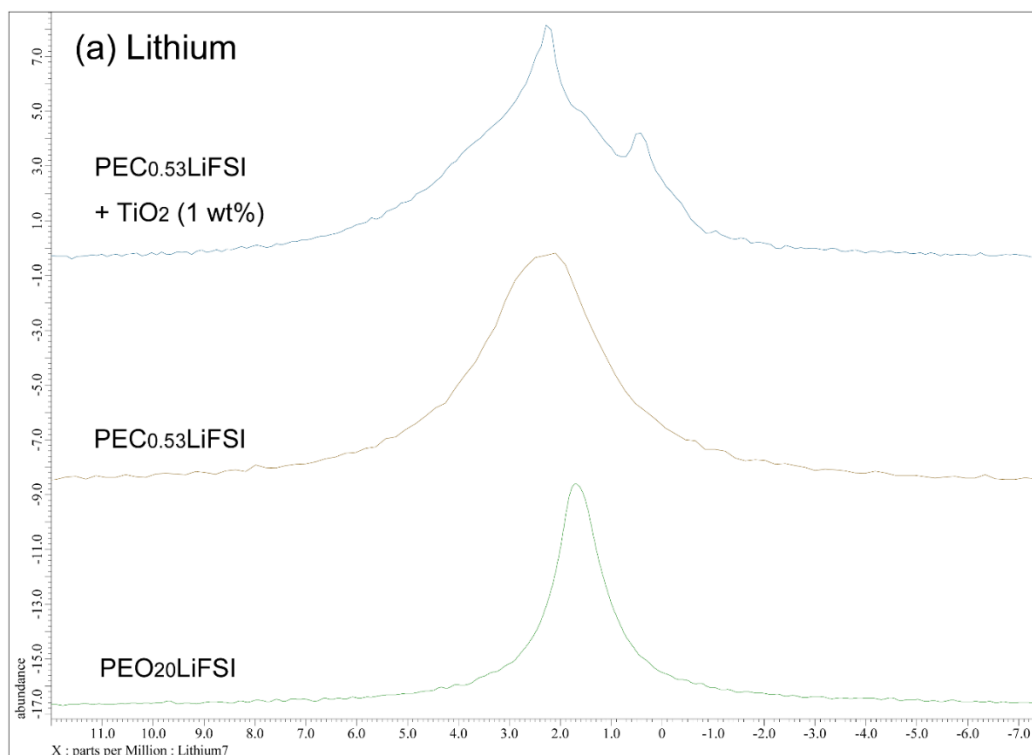
Figure S4: (a) ^{7}Li and (b) ^{19}F NMR spectra of PEO and PEC-based electrolytes.

The PEC-LiFSI-TiO$_2$ composite showed different spectra for both ^{7}Li and ^{19}F. These include two components with different chemical shifts, which are due to the sharp and broad signals. Self-diffusion coefficients of both Li and F based on these two signals were calculated to be almost the same.
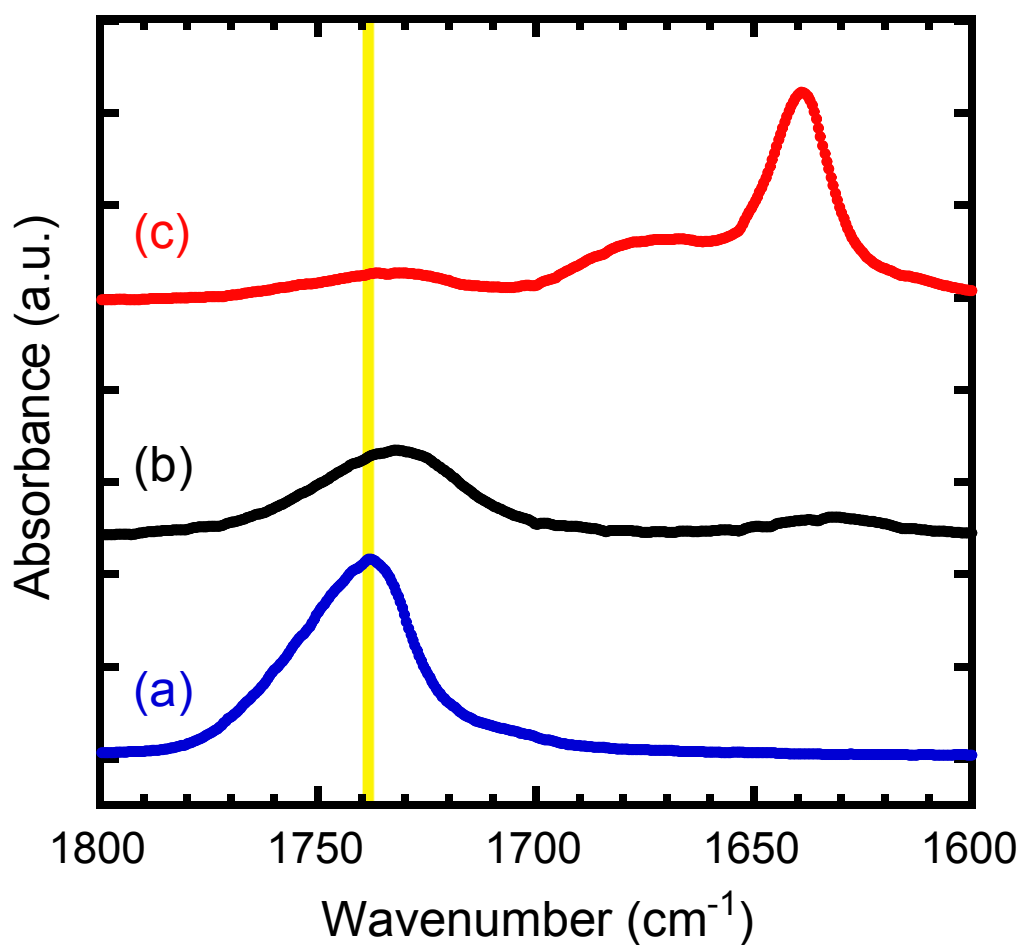
Figure S5: FT-IR spectra of (a) neat PEC, (b) $PEC_{0.53}LiFSI$ and (c) TiO_2 composite in the region from 1700 to 1800 cm^{-1}.

Samples were measured using an ATR unit (ZnSe lens) in dry N_2. A peak at approximately 1740 cm^{-1} of (a) can be identified as stretching vibration mode of the carbonyl (C=O) groups on the PEC main chain. In our previous study, we have revealed that a shoulder-like small peak at lower wavenumber newly appears by the addition of Li salt.[5] In the spectra (b) and (c), the C=O peaks were shifted to lower wavenumber by the addition of LiFSI and was observed at approximately 1730 cm^{-1}.

References

1. Y. Tominaga, V. Nanthana and D. Tohyama, *Polym. J.*, 2012, **44**, 1155.

2. E. O. Stejskal and J. E. Tanner, *J. Chem. Phys.*, 1965, **42**, 288.

3. J. Evans, C. A. Vincent and P. G. Bruce, *Polymer*, 1987, **28**, 2324.

4. A. Ferry, G. Orädd and P. Jacobsson, *Electrochim. Acta*, 1998, **43**, 1471.

5. M. Nakamura and Y. Tominaga, *Electrochim. Acta*, 2011, **57**, 36.