

Electronic supplementary information (ESI):

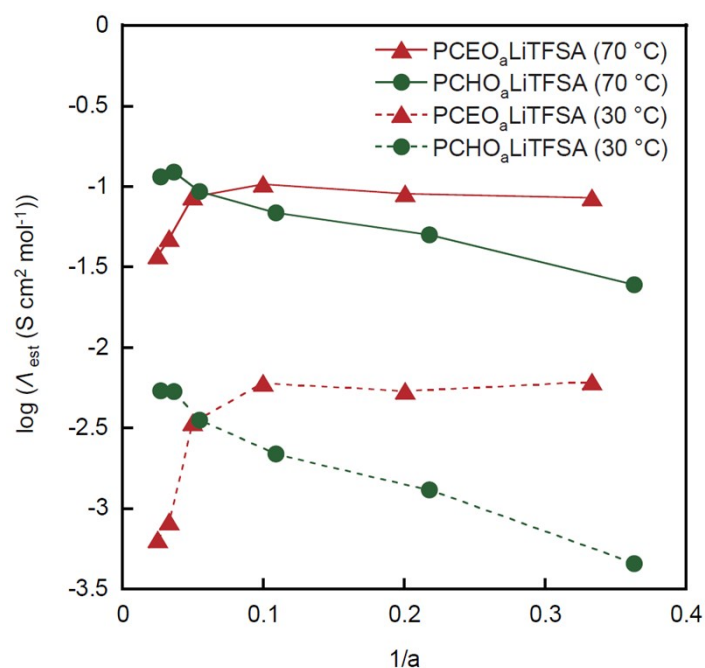
# **Steric effect on Li<sup>+</sup> coordination and transport properties in polyoxetane-based polymer electrolytes bearing nitrile groups**

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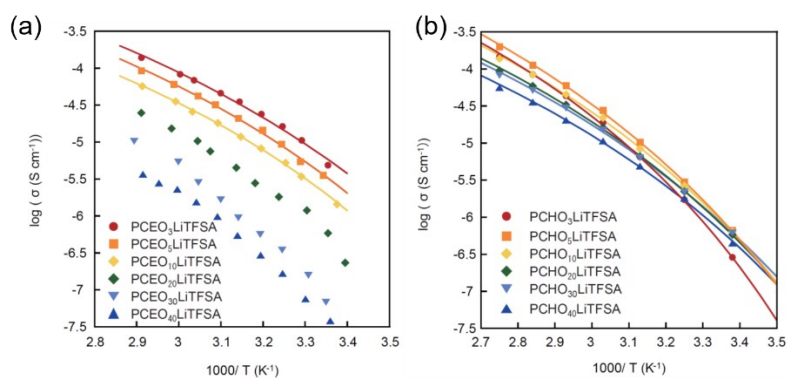
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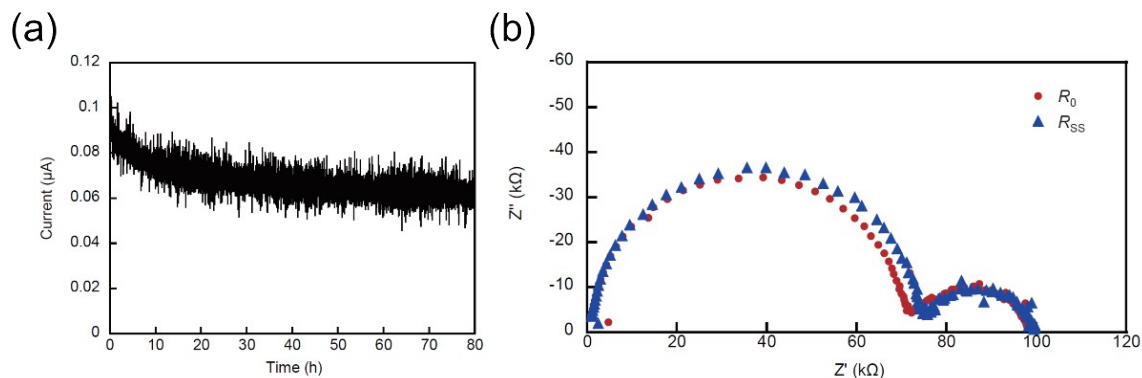
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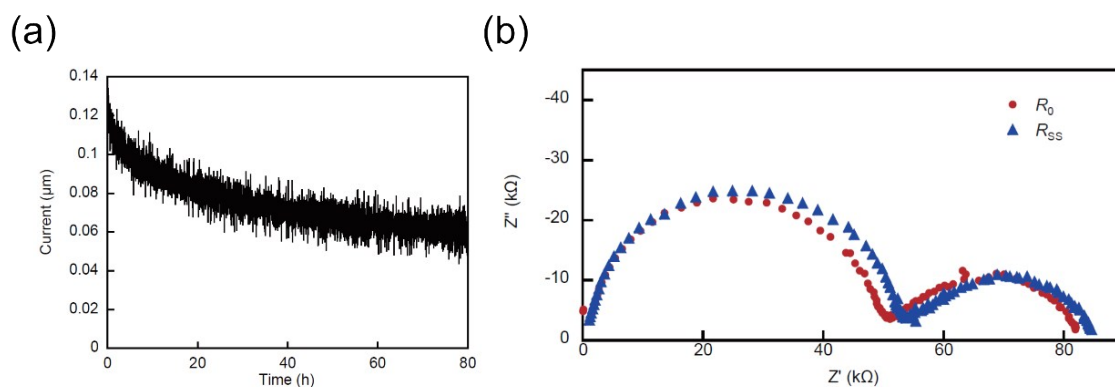
**Figure S1.** Estimated molar conductivity ( $\Lambda_{\text{est}}$ ) of the PEs as a function of LiTFSA content ( $1/a = [\text{Li salt}]/[\text{monomer unit}]$ ) at 30 °C and 70 °C. The  $\Lambda_{\text{est}}$  values were calculated by dividing the conductivity at each temperature by  $c_{\text{Li}}$  at room temperature.



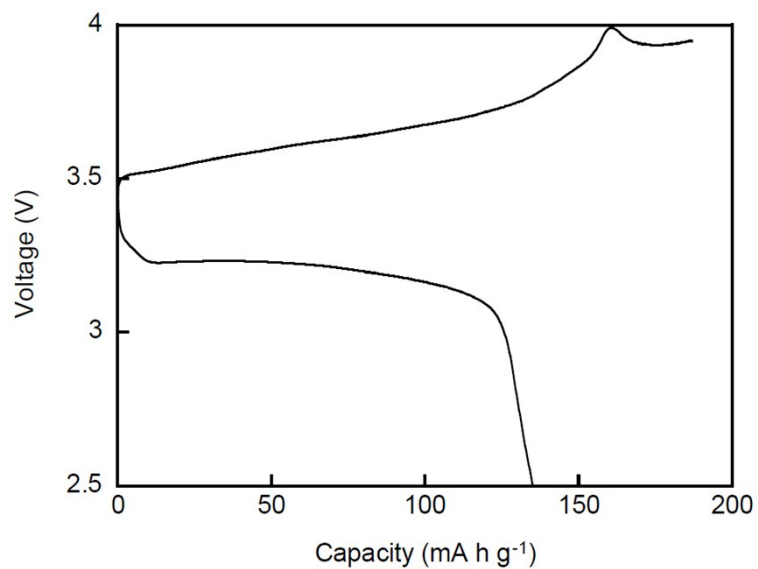
**Figure S2.** Temperature dependencies of the ionic conductivity for (a) PCHO<sub>a</sub>LiTFSA and (b) PCEO<sub>a</sub>LiTFSA. The solid lines represent the Vogel-Tammann-Fulcher fit results.



**Figure S3.** Data for various electrochemical measurements used to calculate the transference number of PCEO<sub>5</sub>LiTFSA at 50 °C. (a) Current with respect to time and (b) Nyquist plots of the initial ( $R_0$ ) and steady state ( $R_{SS}$ ).



**Figure S4.** Data for various electrochemical measurements used to calculate the transference number of PCHO<sub>5</sub>LiTFSA at 50 °C. (a) Current with respect to time and (b) Nyquist plots of the initial ( $R_0$ ) and steady state ( $R_{SS}$ ).



**Figure S5.** Charge/discharge curves of a Li/PCEO<sub>5</sub>LiTFSA/LiFePO<sub>4</sub> cell at a 0.05 C rate and 70 °C. The measurements were carried out in a range of 2.5–4.0 V (1 C = 117 μA, 149 μA cm<sup>-2</sup>).