# **Supplementary Information**

# Tetra-arm poly(ethylene glycol) gels with highly concentrated sulfolane-based electrolytes exhibiting high Li-ion transference numbers

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## **Experimental**

### Materials

Battery-grade sulfolane (SL) was purchased from Kishida Chemical (Japan) and used as received. Battery-grade LiN(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub> (LiTFSA) was supplied from Solvay Japan and used without further purification. Tetra-arm poly(ethylene glycol) (TPEG) prepolymers (10 kDa, with each arm having a molecular weight of 2.5 kDa) with thiol and maleimide terminals (TPEG-SH and TPEG-MA, respectively) were purchased from Yuka Sangyo Co., Ltd. (Japan). The TPEGs were stored in a freezer (below -15 °C) and used as received. Li metal foil was purchased from Honjo Metal and used as received. All other reagents were purchased from Wako Pure Chemical Corporation (Japan).

SL and LiTFSA were mixed to prepare an electrolyte solution with a [LiTFSA]/[SL] molar ratio of 1:2 and stirred at 60 °C for 24 h in an Ar-filled glovebox (dew point, <-80 °C).

Pre-doping of the TPEG prepolymer with LiTFSA was carried out as follows.<sup>1</sup> TPEG prepolymer and LiTFSA were dissolved in acetonitrile at a [LiTFSA]/[EO] molar ratio of 1:5, where EO is the ether oxygen of TPEG, and the solvent was completely removed by vacuum drying at 60 °C for 48 h (hereafter denoted as LPD-TPEG).

## Measurements

UV-vis spectroscopy was performed using a UV-2700 spectrophotometer (Shimadzu, Japan).

The thermal stability of the electrolytes was evaluated by thermogravimetry (STA7200, Hitachi High-Tech Science) under a  $N_2$  atmosphere.

Tensile tests were performed using a Shimadzu EZ-LX tensile tester at a tensile speed of 6 mm min<sup>-1</sup>. The gel electrolyte was cut into dumbbell-shaped pieces (JIS K 6251; thickness: 0.5 mm).

Dynamic viscoelastic measurements were performed using a Physica MCR102 rotary rheometer (Anton Paar) equipped with a parallel plate (diameter: 12.5 mm) and temperature controller (H-PTD200).

Raman spectra were recorded using a Raman spectrometer (RMP-330, JASCO) with 532 nm laser excitation at room temperature and calibrated using a polypropylene standard. The samples were sealed in capillary tubes in an Ar-filled glove box.

The ionic conductivities of the electrolytes were determined via the complex impedance method using a Hewlett-Packard 4192 LF impedance analyser in the frequency range of 13 MHz– 5 Hz with a sinusoidal alternating voltage amplitude of 10 mV. The ionic conductivity of the [LiTFSA]/[SL] = 1:2 solution was measured using a conductivity cell equipped with a pair of platinised Pt electrodes. The ionic conductivity of the gel membrane was measured using a cell

equipped with two stainless-steel electrodes. Here, the gel membrane was punched into a circular shape (diameter: 12 mm; thickness: 0.5 mm) and encapsulated into the cell.

The electrochemical properties of the electrolytes were characterised using an electrochemical measurement system (Biologic Science Instruments, VMP2). Linear scan voltammetry of the gel electrolyte was performed using a [Li | gel electrolyte | Pt] cell at a scan rate of 1 mV s<sup>-1</sup> at 30 °C. A two-electrode cell with Li foil (diameter: 13 mm; thickness: 0.2 mm), gel electrolyte (diameter: 13 mm; thickness: 0.5 mm), and Pt plate (diameter: 13 mm) was assembled in an Ar-filled glove box. Cyclic voltammetry of the gel electrolyte was performed using a [Li | gel electrolyte | Cu] cell at a scan rate of 1.0 mV s<sup>-1</sup> at 30 °C. Li foil (diameter: 16 mm), the gel electrolyte (diameter: 17 mm; thickness: 0.5 mm), and Cu foil (diameter: 16 mm) were encapsulated in a 2032-type coin cell in an Ar-filled glove box.

The Li-ion transference numbers ( $t_{Li}^{abc}$ ) of the gel electrolytes were determined via a series of electrochemical impedance measurements and chronoamperometry using a Li/Li symmetric cell at 30 °C. Li foil was punched into a circular shape (diameter: 16 mm; thickness: 0.2 mm). The gel membrane was also punched into a circular shape (diameter: 17 mm; thickness: 0.5 mm). A 2032-type coin cell with a [Li | gel electrolyte | Li] configuration was assembled in an Ar-filled glove box and left to stand overnight at 30 °C to stabilise the interface. Electrochemical measurements were performed using an electrochemical measurement system (VMP2, Biologic).

The battery test of the gel electrolyte was performed using a cell with a Li metal anode and LiCoO<sub>2</sub> composite cathode. The LiCoO<sub>2</sub> composite cathode was composed of LiCoO<sub>2</sub> powder (AGC Seimi Chemical, Japan), acetylene black (AB, DENKA, Japan), and PVDF (#1100, Kishida Chemical). LiCoO<sub>2</sub> (80 wt%), AB (10 wt%), and PVDF (10 wt%) were mixed and dispersed in *N*-methyl-2-pyrrolidone (NMP, Kanto Chemical) to prepare a slurry. The slurry was spread uniformly on Al foil using a print applicator (K Control Coater, RK Print Coat Instruments Ltd.) and dried at 80 °C for 24 h. The prepared LiCoO<sub>2</sub> composite sheet was punched into a circular shape (diameter: 13.8 mm, thickness: 0.02 mm) and dried under vacuum at 80 °C for 24 h. The mass loading of LiCoO<sub>2</sub> on the Al foil was 2.1 mg cm<sup>-2</sup>. The LiCoO<sub>2</sub> cathode, gel electrolyte (diameter: 17 mm; thickness: 0.5 mm), and Li foil (diameter: 16 mm; thickness: 0.2 mm) were assembled in a 2032-type coin cell in an Ar-filled glove box. The cell was left to stand overnight at 30 °C prior to the electrochemical measurements; during this period, the [LiTFSA]/[SL] = 1:2 electrolyte permeated from the gel to the LiCoO<sub>2</sub> cathode. The galvanostatic charge–discharge measurements of the [Li | gel electrolyte | LiCoO<sub>2</sub>] cell were performed using an automatic charge–discharge instrument (Hokuto Denko HJ1010mSM8A) in the voltage range of 3.0–4.2 V at 30 °C.

Sample	[Li]/[[SL]
[LiTFSA]/[SL] = 1/2	1/2
5 wt% LPD-TPEG gel	1/1.76
10 wt% LPD-TPEG gel	1/1.53

Table S1. Molar ratios of [LiTFSA]/[SL] = 1/2 electrolyte solution and pre-doped TPEG gels.

### **UV-Vis spectroscopy**

Two solutions, 5 wt% LPD-TPEG-SH/([LiTFSA]/[SL] = 1:2) and 5 wt% LPD-TPEG-MA/([LiTFSA]/[SL] = 1:2), were mixed at a volume ratio of 1:1. This mixture was placed in a quartz cell (thickness: 1 mm) in an Ar-filled glove box and tightly sealed. The time variation of the UV-vis spectra during the gelation reaction was observed at 80 °C to evaluate the reaction efficiency between TPEG-SH and TPEG-MA (**Fig. S1**). Although the [LiTFSA]/[SL] = 1:2 solution exhibited significant absorption below 240 nm, the maleimide group exhibited clear UV absorption at ~300 nm, while the reacted maleimide group exhibited absorption at ~265 nm. The absorbance at 300 nm decreased with increasing reaction time and became nearly constant after 168 h. Based on the absorbance of the unreacted maleimide group at 300 nm, the reaction efficiency after 168 h was estimated to be 91% (**Fig. S2**).



**Fig. S1.** (a) Time variation of the UV absorbance (ABS) of a mixture composed of 5 wt% LPD-TPEG-SH/([LiTFSA]/[SL] = 1:2) and 5 wt% LPD-TPEG-MA/([LiTFSA]/[SL] = 1:2) and (b) UV absorbance (ABS) of the [LiTFSA]/[SL] = 1:2 solution (without polymer) at 80 °C.



Fig. S2. Fitting results of the UV spectra recorded at 0 h and 7 days at 80 °C.

# Thermogravimetry



**Fig. S3.** Thermogravimetric curves of the [LiTFSA]/[SL] = 1:2 solution and gels measured at a heating rate of 10 °C min<sup>-1</sup>.

# Viscoelasticity



**Fig. S4.** Strain-dependent variation of the dynamic moduli (storage elastic modulus *G*' and loss elastic modulus *G*'') and tan  $\delta$  of the 5 wt% LPD-TPEG gel measured at a frequency of 1 Hz at 25 °C.

#### Li-ion transference numbers

 $t_{\text{Li}^{abc}}$  was estimated using symmetric Li/Li cells under anion-blocking conditions.<sup>2,3</sup> A constant voltage ( $\Delta V = 10 \text{ mV}$ ) was applied to the symmetric Li/Li cell for 6 h and a chronoamperogram was recorded. Electrochemical impedance measurements were performed on the same cell before and after chronoamperometry in the frequency range of 500 kHz–100 mHz with a sinusoidal alternating voltage amplitude of 10 mV.  $t_{\text{Li}}^{abc}$  was calculated using the following equation:<sup>3</sup>

$$t_{\rm Li}^{\rm abc} = \frac{I_{\rm ss}(\Delta V - I_{\Omega}R_{\rm i,0})}{I_{\Omega}(\Delta V - I_{\rm ss}R_{\rm i,ss})}$$

where *I*ss is the steady-state current observed by chronoamperometry;  $R_{i,0}$  and  $R_{i,ss}$  are the interfacial resistances at the Li metal electrodes measured by AC impedance before and after chronoamperometry, respectively; and  $I_{\Omega}$  is the current calculated using Ohm's law,  $I_{\Omega} = \Delta V/(R_b + R_{i,0})$ , where  $R_b$  is the bulk resistance of the Li/Li cell.



**Fig. S5.** (a) Chronoamperogram and (b) Nyquist plots measured before and after the polarization for the [Li | 5 wt% LPD-TPEG gel | Li] cell measured at 30 °C. Inset: Equivalent circuit model used to estimate  $R_b$ ,  $R_{i,0}$ , and  $R_{i,ss}$ .

## Linear scan voltammetry and cyclic voltammetry



**Fig. S6.** Linear sweep voltammograms of the [LiTFSA]/[SL] = 1:2 electrolyte solution and 5 wt% LPD-TPEG gel electrolyte at a scan rate of 1 mV s<sup>-1</sup> at 30 °C.



**Fig. S7.** Cyclic voltammograms of (a) the [LiTFSA]/[SL] = 1:2 electrolyte solution and (b) 5 wt% LPD-TPEG gel electrolyte at a scan rate of 1 mV s<sup>-1</sup> at 30 °C. The current densities for Li deposition and stripping in the 5 wt% LPD-TPEG gel electrolyte were lower than that in [LiTFSA]/[SL] = 1/2 solution. This can be attributed to the lower ionic conductivity of the 5 wt% LPD-TPEG gel electrolyte (0.26 mS cm<sup>-1</sup>) compared to that of the [LiTFSA]/[SL] = 1:2 electrolyte solution (0.42 mS cm<sup>-1</sup>).

# Charge-discharge tests



**Fig. S8.** (a) Charge–discharge curves and (b) charge–discharge capacities and Coulombic efficiency of the [Li | 5 wt% LPD-TPEG gel electrolyte | LiCoO<sub>2</sub>] cell measured at a current density of 29  $\mu$ A cm<sup>-2</sup> at 30 °C.

## **References for Supplementary Information**

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