# Supporting Information

### Ternary-Salt Solid Polymer Electrolyte for High-Rate and Long-Life Lithium Metal

## Batteries

Zhi Kang Liu, Jun Guan, Hai Xia Yang, Peng Xiao Sun, Nian Wu Li\*, and Le Yu\*

\*Corresponding authors

State Key Lab of Organic-Inorganic Composites, Beijing University of Chemical Technology, Beijing 100029, P. R. China.

E-mail: yule@mail.buct.edu.cn; linianwu@mail.buct.edu.cn

#### **Experimental section**

**Chemicals:** Lithium (Li) foil (0.55 mm thick) was purchased from China Energy Lithium Co., Ltd. Lithium bis-trifluoromethanesulfonimide (LiTFSI), lithium bis(fluorosulfonyl)imide (LiFSI), 1,3-dioxolane (DOL) were purchased from Alfa Aesar Co., Ltd. Lithium iron phosphate (LiFePO<sub>4</sub>, LFP) cathode materials, conductive carbon black, and poly(vinylidene fluoride) (PVDF) were purchased from MTI Kejing Group. Lithium hexafluoro phosphate (LiPF<sub>6</sub>), 1-methyl-2-pyrrolidinone (NMP) were purchased from Macklin.

**Electrolyte preparation:** Electrolyte preparation and cell assembly were conducted in an Arfilled glove box, in which both the  $O_2$  and  $H_2O$  content were maintained below 0.5 ppm. The raw materials, including LiTFSI, LiFSI and LiPF<sub>6</sub>, were stored in the glove box and used without further purification. First, a certain mass of LiTFSI (0.5 M) and LiFSI (0.5 M) were added to DOL (1 mL), and stirred by magnetic force for 2 h. After the Li salts were completely dissolved, the dual-salt liquid electrolyte (DS-LE) was configured. Next, a certain amount of LiPF<sub>6</sub> (0.01 M) was added to the DS-LE with the above configuration, and stirred by magnetic force for 1h. After the LiPF<sub>6</sub> was completely dissolved, the ternary-salt liquid precursor solution was obtained. 60  $\mu$ L of liquid precursor was injected into both sides of separator. After assembling the battery for two days, the DOL was polymerized to obtain ternary-salt solid-state polymer electrolyte (TS-SPE). In the same way, dual-salt solid-state polymer electrolytes with LiTFSI (1 M) and LiPF<sub>6</sub> (0.01 M) in DOL, LiFSI (1 M) and LiPF<sub>6</sub> (0.01 M) in DOL were obtained.

Cathode preparation: The LFP cathode was prepared by mixing the LFP, super P carbon

black, and PVDF (8:1:1 by weight) in NMP solvent under vigorous stirring. The obtained slurry was cast onto an Al foil with an active-material loading of  $5 \sim 6 \text{ mg cm}^{-2}$ . After drying under vacuum, the cathode material was sliced into circular sheets with a diameter of 10 mm for subsequent coin cell assembly or  $5 \text{ cm} \times 6$  cm rectangle for pouch cell assembly. The full cell was cycled at  $4 \sim 2.5$  V. The amounts of liquid precursor used in coin cells were 60 µL and 3 mL in pouch cell.

**Material characterizations:** TS-SPE was dissolved in chloroform-d (CDCl<sub>3</sub>) for <sup>1</sup>H Nuclear magnetic resonance (NMR) and <sup>13</sup>C NMR analysis on Advance HD/600MHz (Bruker BioSpin) Fourier-transform infrared (FTIR) spectrum of the prepared SPE was recorded using Nicolet 6700 (Thermo Fisher Scientific) in the range of 600 to 4000 cm<sup>-1</sup> to investigate the functional groups of SPE. The thermogravimetric analysis (TGA) of SPE was measured by an apparatus Q50 (Waters Corporation) under an N<sub>2</sub> atmosphere at a temperature increase of 5 °C min<sup>-1</sup> from 60 to 600 °C. The surface chemical states of the samples were examined by an ESCALAB 250 X-ray photoelectron spectroscopy (XPS) system (Thermo Fisher Scientific). The morphology of Li metals after cycling was investigated by field-emission scanning electron microscope (JEOL JSM-7800F; TESCAN Clara).

Electrochemical measurements: To evaluate the electrochemical performance of Li plating/stripping, CR2032 coin cells were assembled in an Ar-filled glovebox. Celgard2325 membrane was used as the separator. Li||Cu battery, symmetric battery and full battery tests were carried out under constant charging-discharging conditions through LAND multichannel battery test system at the temperature of 25 °C. The electrochemical impedance spectroscopy

(EIS) measurements were carried out on Autolab electrochemical workstation over the frequency from 0.1 Hz to 100 kHz with an amplitude of 10 mV. The liquid ternary-salt electrolyte precursor was injected between two stainless sheets. After the polymerization was complete, the ionic conductivity was recorded via the electrochemical workstation and calculated by the following equation:

$$\sigma = \frac{d}{R_{\rm b}S}$$

where *d* is the distance between two stainless steel sheets,  $R_b$  is the resistance value, and *S* is the effective area below the liquid surface. The calculation of reaction activation energy (*E*a) follows the formula:

$$Ea = RT \ln \frac{A}{a}$$

where the  $E^{a}$  represents the activation energy that needed for Li<sup>+</sup> conduction, *R* is the molar gas constant and *T* is the measurement temperature, *A* is the pre-exponential factor and  $\sigma$  represents Li<sup>+</sup> conductivity. Linear sweep voltammetry (LSV) curves of TS-SPE and DS-LE were obtained by placing the TS-SPE/DS-LE between a stainless and Li foil at a sweep speed of 1 mV s<sup>-1</sup>. Li<sup>+</sup> ion transference number  $\binom{t_{\text{Li}^+}}{\text{Li}^+}$  was determined by the following equation:

$$t_{\mathrm{Li}^{+}} = \frac{I_{\mathrm{S}}(\Delta U - I_{0}R_{0})}{I_{0}(\Delta U - I_{\mathrm{S}}R_{\mathrm{S}})}$$

where  $\Delta U$  is the constant polarization voltage applied (10 mV),  $I_0$  and  $R_0$  are the initial current and resistance, respectively, and  $I_S$  and  $R_S$  are the steady-state current and resistance.



Figure S1. Reaction illustration of DOL polymerization induced by LiPF<sub>6</sub>.



**Figure S2.**  ${}^{t}_{Li^{+}}$  test for the Li symmetric cell using DS-LE. Insert: Nyquist plots of initial (black color) and steady (red color) polarization.



Figure S3. TGA and derivative thermogravimetry (DTG) curves of TS-SPE.



Figure S4. F1s XPS spectra of lithium anode in TS-SPE (a) and DS-LE (b) at initial state and

after 2 cycles and 50 cycles.



**Figure S5.** The F, S, N, and P atomic composition of the interphase on Li metal anode using (a) TS-SPE and (b) DS-LE.



Figure S6. CE profiles of Li plating/stripping with DS-LE and TS-SPE on Cu foil.



Figure S7. Voltage profiles during initial Li plating for DS-LE and TS-SPE at the current density of 0.5 mA cm<sup>-2</sup>.



Figure S8. The charge/discharge curves of Li||Cu cell for DS-LE and TS-SPE at the current

density of 0.5 mA cm<sup>-2</sup>.



Figure S9. Polarization of different cycle numbers for DS-LE and TS-SPE in Li||Cu cell.



Figure S10. Symmetric battery cycling performances of TS-SPE and DS-LE at the current density of 2 mA cm<sup>-2</sup> with a capacity of 1 mAh cm<sup>-2</sup>.



Figure S11. Symmetric battery cycling performances of TS-SPE and DS-LE at the current density of 3 mA cm<sup>-2</sup> with a capacity of 1 mAh cm<sup>-2</sup>.



Figure S12. Rate capability of DS-LE and TS-SPE at different current density.



**Figure S13.** Symmetric battery cycling performances of DS-LE, TS-SPE, Poly DOL (PDOL) with LiTFSI and LiPF<sub>6</sub>, PDOL with LiFSI and LiPF<sub>6</sub> at the current density of 1 mA cm<sup>-2</sup> with a capacity of 4 mAh cm<sup>-2</sup>.



Figure S14.Charging-discharging curves for (a) TS-SPE and (b) DS-LE in Li||LFP batteries at

2.5-4 V at 0.5 C.



Figure S15. Charging-discharging curves for (a) TS-SPE and (b) DS-LE in Li||LFP batteries at

0.5 *C*.



Figure S16. The Charging-discharging curves in Li||LFP battery of (a) TS-SPE and (b) DS-

LE at different rates.



**Figure S17.** Cycling stability of TS-SPE in Li||LFP battery at 5 *C*.



Figure S18. Digital picture of the pouch cell being tested.

Table S1.	Comparative summar	y of cycling	g performance	e of symme	tric cells	using different
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Strategy	Electrolyte	Current (mA cm <sup>-2</sup> )	Capacity (mAh cm <sup>-2</sup> )	Time (h)	Polarization (mV)	Ref.	
SPE	2 M LiTFSI and 0.5 mM Al(OTf) <sub>3</sub> in DOL	1	1	200	30	<b>S</b> 1	
Gel polymer	2 M LiPF <sub>6</sub> and 1 M LiTFSI in DOL/	0.5	1	750	25	<b>C</b> 2	
electrolyte (GPE)	1,2-dimethoxyethane	1	1	450	50	52	
SPE	1 M LiTFSI and 0.1 mM SnF <sub>2</sub> in DOL	0.5	1.25	300	50	S3	
GPE	1 M LiTFSI and 0.6 M LiPF <sub>6</sub> in DOL:methyl propionate:fluoroethylene carbonate (FEC)=4:5:1 (vol%)	0.1	0.1	2000	40	S4	
CDE	2 M LiTFSI and 0.4 mM Al(OTf) <sub>3</sub>	0.5	0.25	800	15	S5	
GPE	in DOL	1	0.5	250	25		
GPE	2 M LiTFSI and 0.3 M lithium diuoro(oxalato)borate (LiDFOB) + 30 wt% SN in DOL	0.5	0.5	750	100	S6	
SPE	2 M LiTFSI and 0.2 wt% Al(OTf) <sub>3</sub> + 1 wt% diallyl disulfide (DADS) in DOL	0.5	0.5	200	100	S7	
CDE	1 M LiTFSI and 1 wt% LiPF <sub>6</sub>	0.5	1	500	15	- 58	
SPE	in DOL + 1 wt% DADS	1	1	500	20		
SPE	2 M LiTFSI and 2 mM Sn(OTf) <sub>2</sub> in DOL	1	1	200	30	S9	
	2 M LiTFSI and 0.2 M LiDFOB +	0.2	0.4	1000	15	- S10	
GPE	25 wt% succinonitrile (SN), 5 wt% FEC in DOL	0.5	0.5	200	20		
SPE	1 M LiTFSI and 0.5 mM Al(CF <sub>3</sub> SO <sub>3</sub> ) <sub>3</sub> in DOL	0.2	0.4	1600	25	S11	
		0.5	1	1600	12	this work	
SPE	0.5 M LiFSI, 0.5 M LiTFSI and	1	1	700	15		
	0.01 WI LIFF <sub>6</sub> III DOL	2	1	250	20		

polymer electrolytes in LMAs.

#### **Supplementary References**

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