

Supporting Information

A Polythiourea Protective Layer for Stable Lithium Metal Anodes

Xiaoya He,^{‡a} Zhu Liu,^{‡a} Yulian Yang,^{‡b} Zhiyong Wang,^a Yuanmao Chen,^a Qicheng Zhang,^a Zhangqin Shi,^a Yihong Tan,^{*a} Xinyang Yue,^{*a} Zheng Liang^{*a}

^aFrontiers Science Center for Transformative Molecules, School of Chemistry and Chemical Engineering Shanghai Jiao Tong University Shanghai 200240 (P. R. China) E-mail: liangzheng06@sjtu.edu.cn

^bState Key Laboratory of Luminescent Materials and Devices, Center for Aggregation-Induced Emission, South China University of Technology, Guangzhou 510640, China

[†] Electronic supplementary information (ESI) available.

[‡] These authors contribute equally to this work.

Synthesis of monomer and PSN



The mixture of 1, 4-benzoylamine (M=136.19 g/mol, m=6.81 g (0.050 mol)), toluene (100 mL) and 98% formic acid (7.5 mL, 0.2 mol) was reflux for 8 h. After cooling, the mixture is evaporated, and the dry residue is treated with new toluene (100 mL) and evaporated again to obtain crude dimethylamide. Afterwards triethylamine (51 mL, 0.36 mol) and methylene chloride (200 mL) were added to the flask containing crude dimethylamide. The resulting crude dimethylamide solution (or suspension) is cooled to 0 °C (ice bath) and phosphorus oxide trichloride (11.3 mL, 0.12 mol) is added by drops within 20-30 minutes. After adding POCl₃, the mixture was stirred at 0 °C (ice water bath) for about 1 hour at room temperature for 2 hours. The reaction mixture was cooled again (0 °C, ice bath) and a solution of about 25 g Na₂CO₃ in 100ml water was added in 15-20 minutes. The final two-phase mixture was stirred for another 1 hour. The organic phase was separated and the aqueous phase was extracted with methylene chloride (3×50 mL). The combined organic matter was washed with brine (4×50 mL), dried with anhydrous Na₂SO₄ and vacuum concentrated to obtain crude isocyanide 1. After purification by silica gel column chromatography, a white solid is obtained, and the yield is 85%. ¹H NMR (500 MHz, DMSO-*d*₆), δ (TMS, ppm): 7.43 (s, 4H), 4.88 (t, 4H).

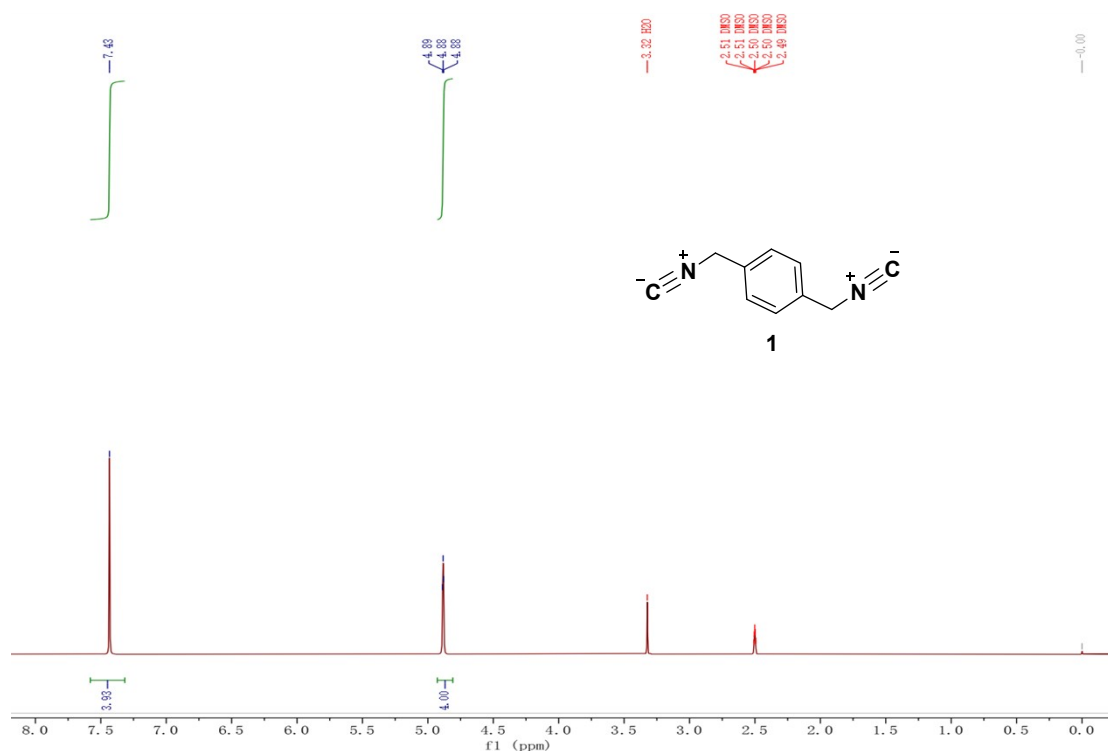


Fig. S1 ¹H NMR spectra (DMSO-*d*₆, room temperature, 500 MHz) of compound 1

PSN was synthesized by room temperature multicomponent polymerization (MCPs)

At room temperature, the elemental sulfur (77 mg, 2.4 mmol), hexamethylene diamine (77 mg, 0.66 mmol), and 1, 4-phenyldimethyl isocyanide (94 mg, 0.6 mmol) were added to 10-mL Schlenker tube with magnetic stirring rods under nitrogen. Then 0.4 mL DMF and 0.4 mL toluene were injected into the Schlenker tube and stirred at room temperature for 4 h. The polymeric solution was then diluted with 4.0 mL DMF, and the mixture was added into 80 mL methanol through a cotton filter. After the precipitate was filtered, it was washed 3 times with methanol (3×50 mL) and dried to a constant weight under vacuum. Polymer **2** was obtained as a white solid with a yield of 90%. Mw = 7392 g/mol, Mw/Mn = 1.36. ¹H NMR (500 MHz, DMSO-*d*₆), δ (TMS, ppm): 7.72 (s, 2H), 7.44 (s, 2H), 7.23 (s, 4H), 4.61 (s, 4H), 3.33 (s, 4H), 1.47 (s, 4H), 1.26 (s, 4H). (See the text for hydrogen spectra) ¹³C NMR (500 MHz, DMSO-*d*₆), δ (TMS, ppm): 182.8 (C=S), 138.0, 127.2, 46.6, 43.6, 28.7, 26.2.

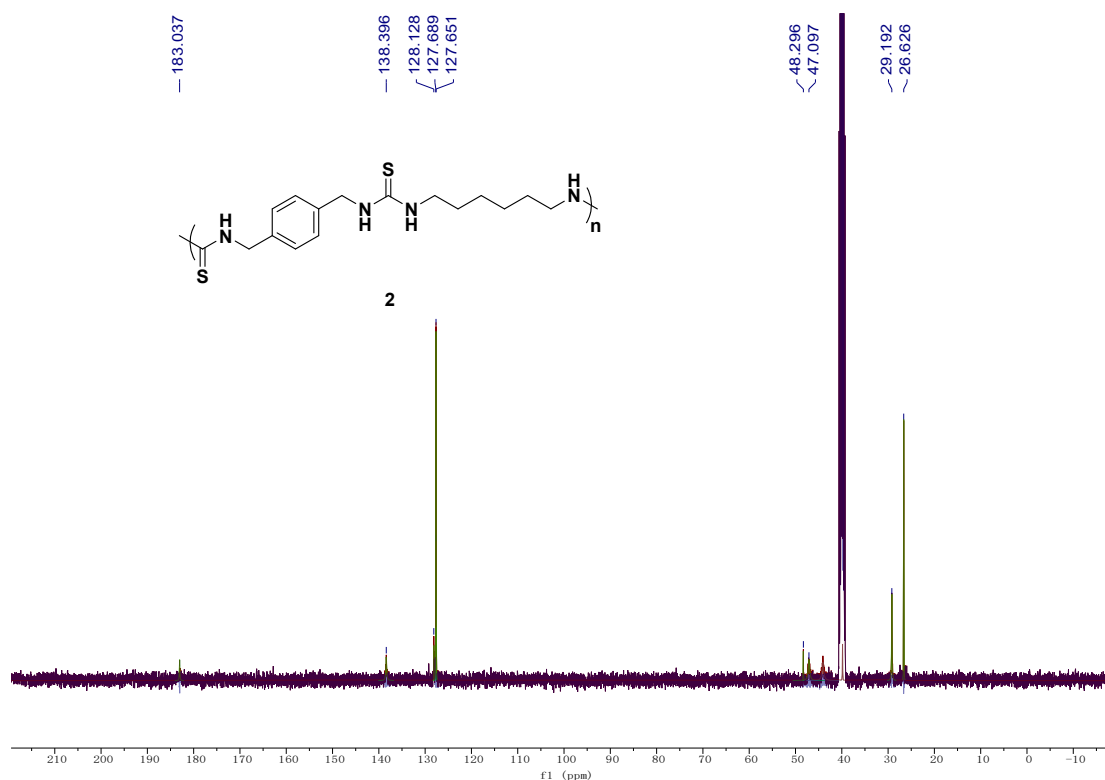


Fig. S2 ¹³C NMR spectra (DMSO-*d*₆, room temperature, 500 MHz) of Polymer **2**.

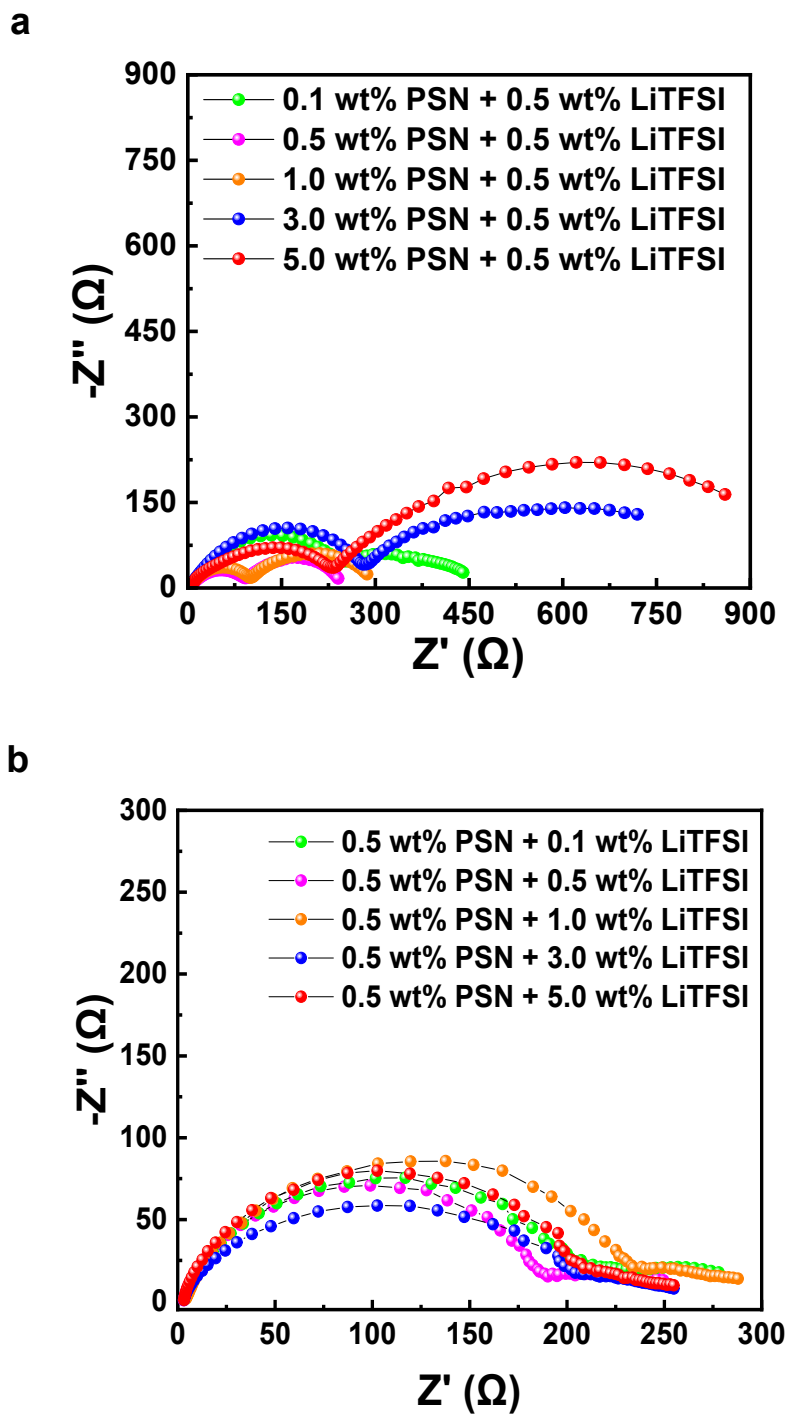


Fig. S3 Electrochemical impedance spectra of symmetric cells coated with different concentrations and ratios of PSN@LiTFSI. (a) The concentration of PSN was varied at a certain concentration of LiTFSI. (b) The concentration of LiTFSI was varied at a certain concentration of PSN.

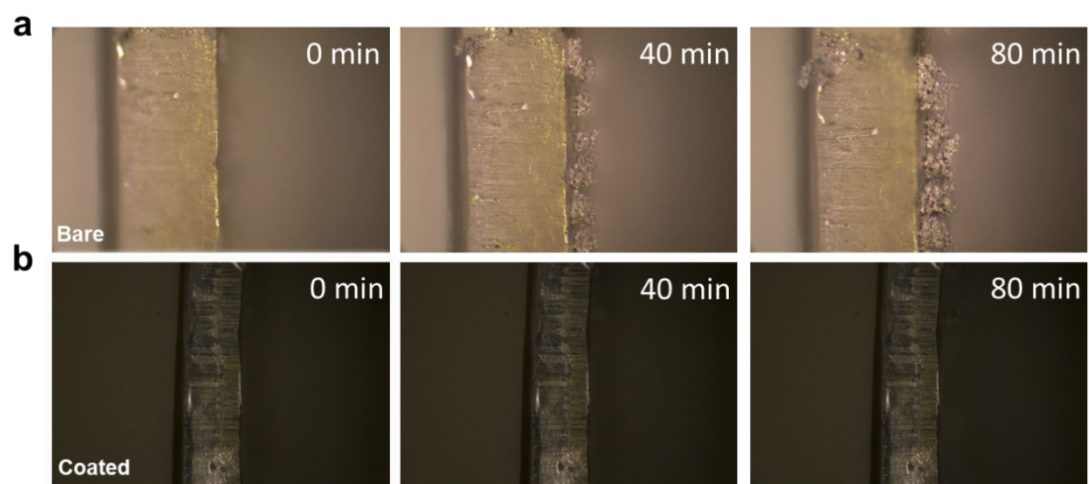


Fig. S4 In-situ digital microscope observation of lithium metal deposition on bare Li (a) and Li-PSN@LiTFSI (b).

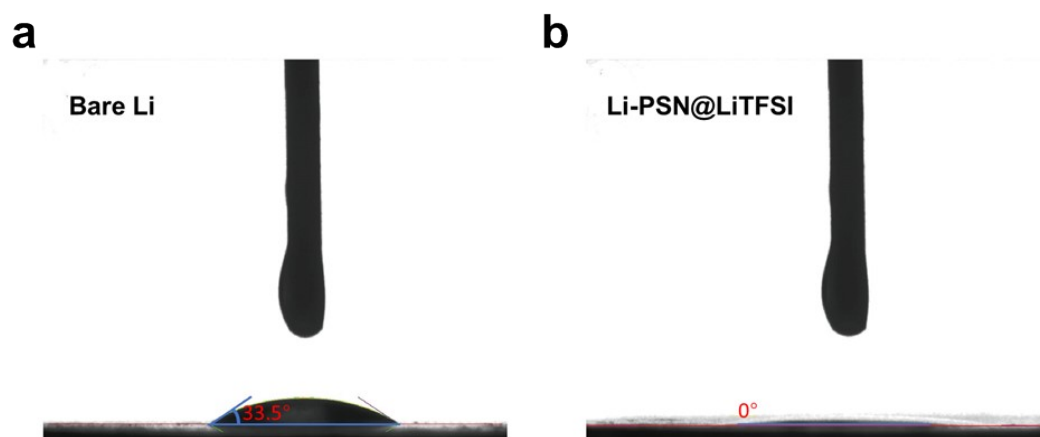


Fig. S5 Contact angles of carbonate electrolytes on bare Li (a) or Li-PSN@LiTFSI (b).

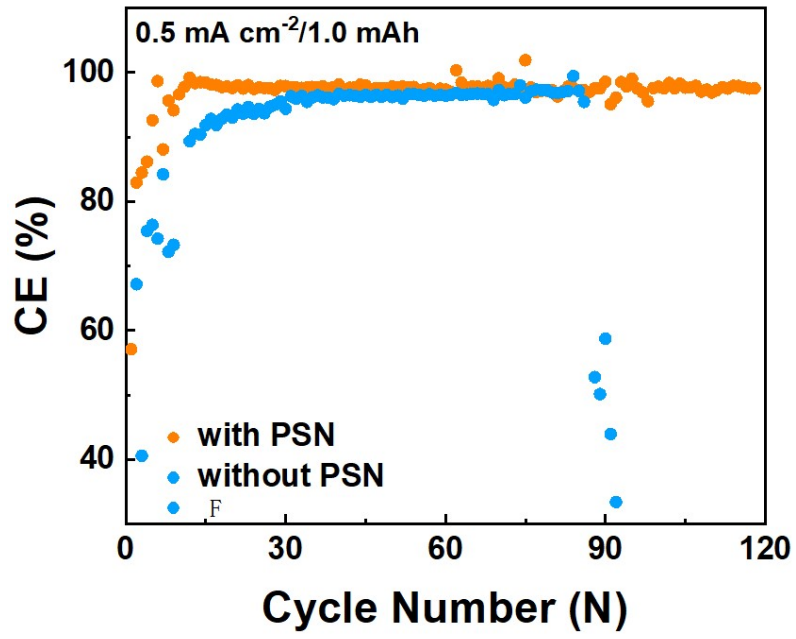


Fig. S6 CEs of Li || Cu cells with or without PSN@LiTFSI coating at 0.5 mA cm⁻² and 1.0 mA h cm⁻².

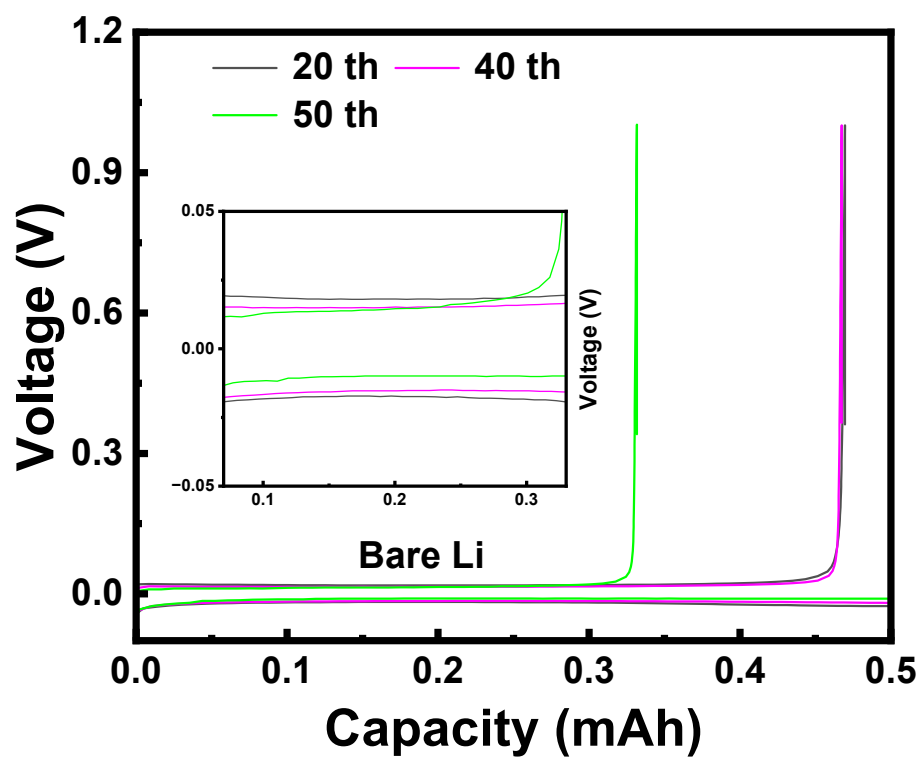


Fig. S7 Voltage profiles of bare Li at 0.5 mA cm^{-2} and 0.5 mA h cm^{-2} at different cycles.

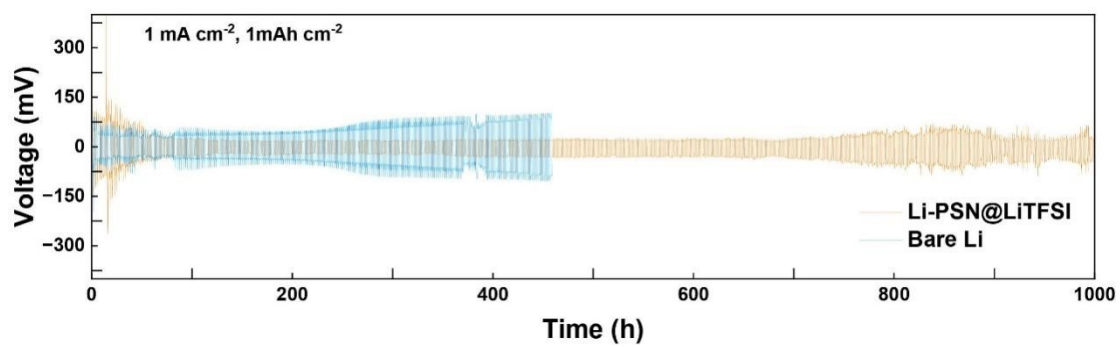


Fig. S8 Li || Li symmetric cells at $1 \text{ mA cm}^{-2} / 1 \text{ mA h cm}^{-2}$ using Li-PSN@LiTFSI and bare Li electrodes.

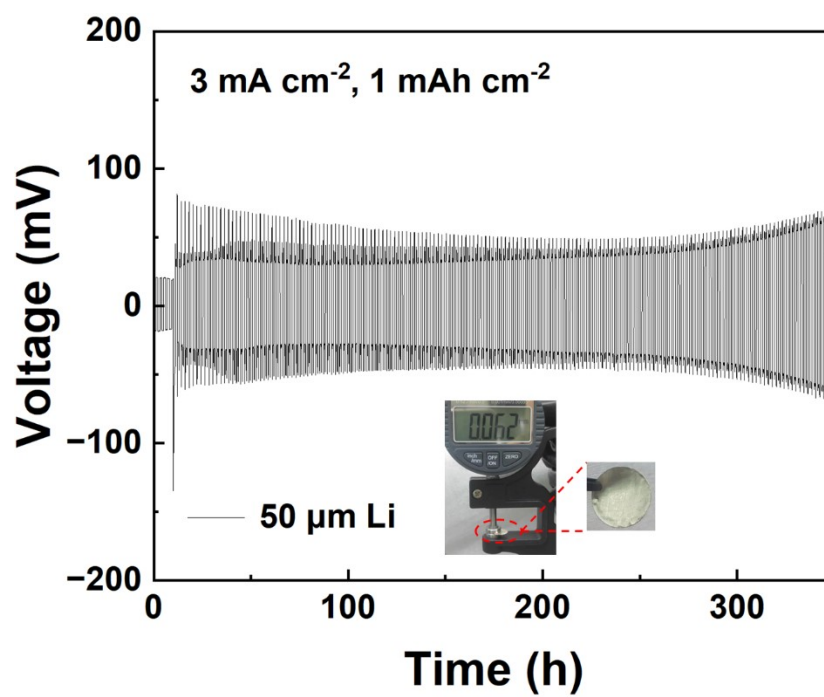


Fig. S9 Li || Li symmetric cells at 3 mA cm⁻² / 1 mA h cm⁻² using thin Li (50 μm) Li-PSN@LiTFSI (The lithium is on the copper foil, which is 11-12 μm thick).

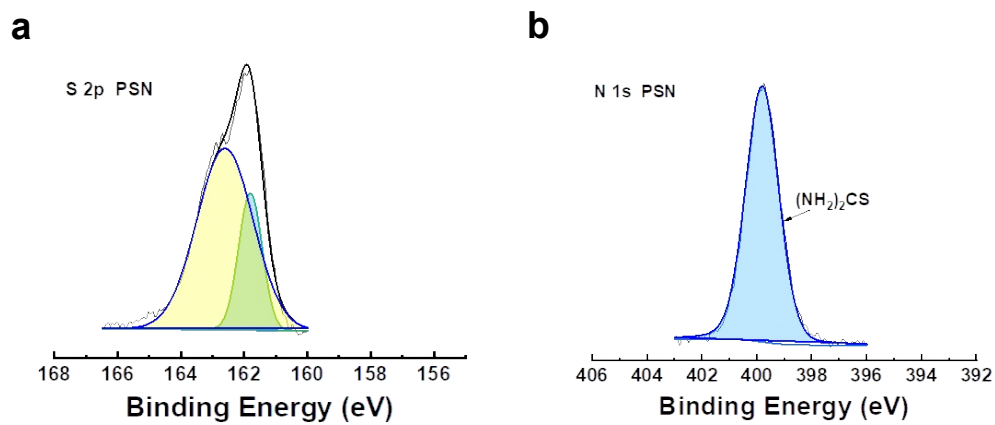


Fig. S10 XPS spectra of polythiourea coated Cu foil, (a) S 2p. (b) N 1s.

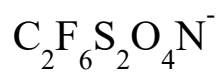
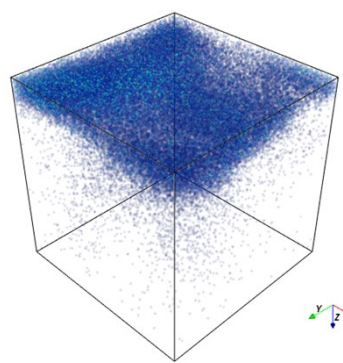
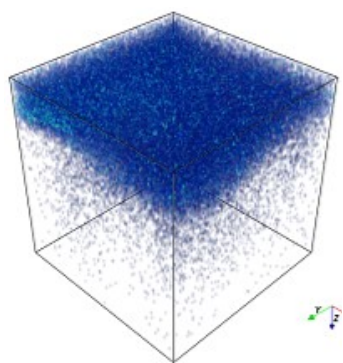


Fig. S11 3D views of depth profiles respectively showing spatial localization of LiN^- and $\text{C}_2\text{F}_6\text{S}_2\text{O}_4\text{N}^-$ after cycling.

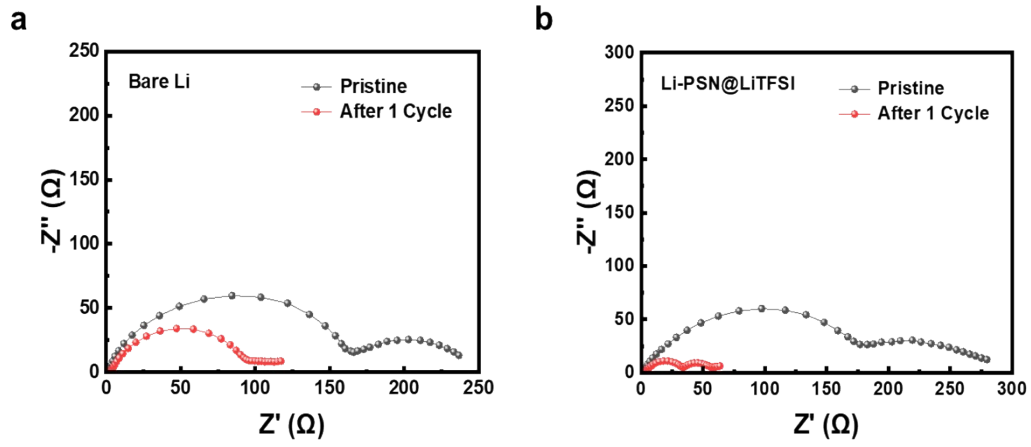


Fig. S12 Electrochemical impedance spectra of bare Li (a) and Li-PSN@LiTFSI (b) of symmetric cells at pristine state and after 1st cycle, respectively.

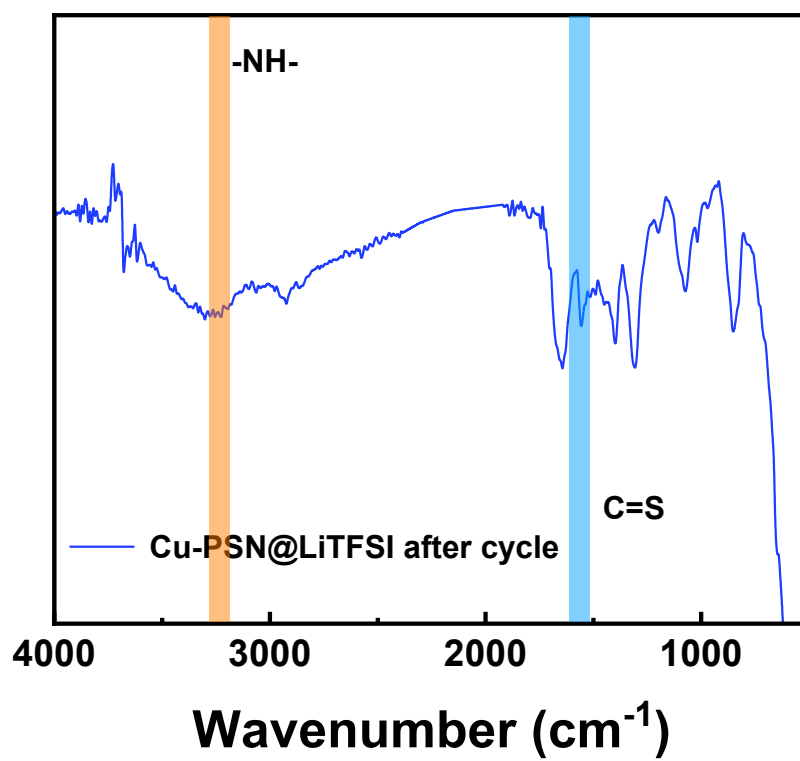


Fig. S13 ATR-FTIR spectra of Cu-PSN@LiTFSI after 20 cycles.

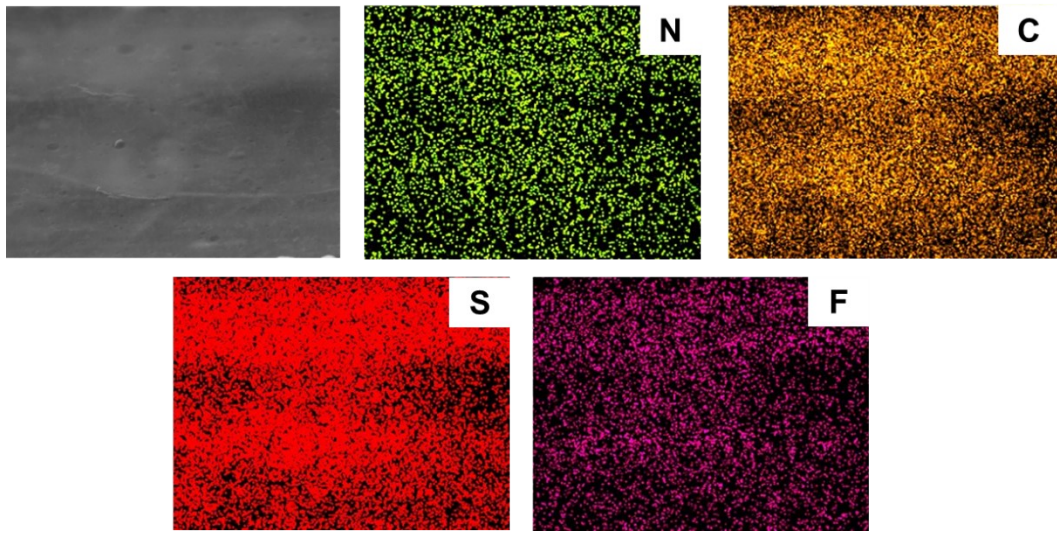


Fig. S14 SEM image and its N, C, S, F elemental mapping of coated Li after 20 cycles.

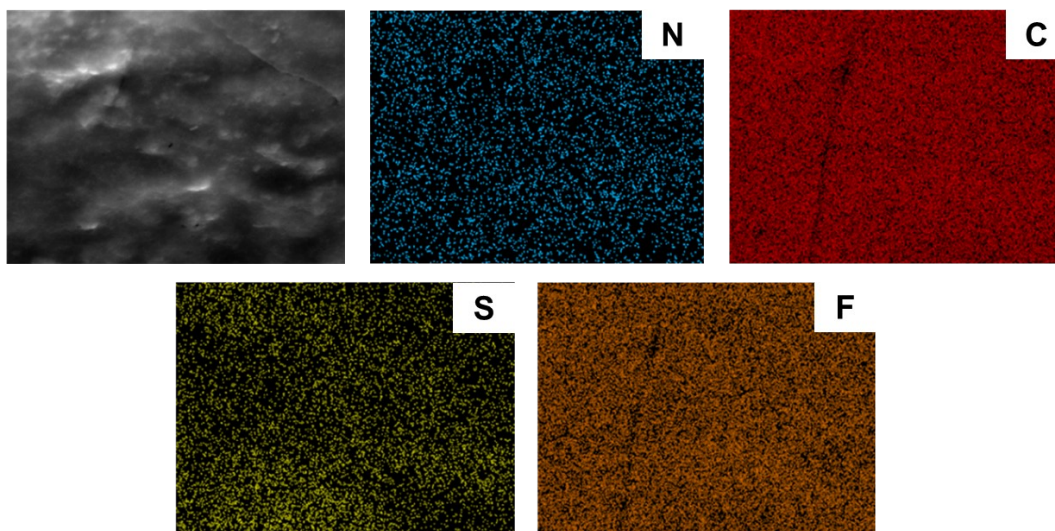


Fig. S15 SEM image and its N, C, S, F elemental mapping of coated Li after 100 cycles.

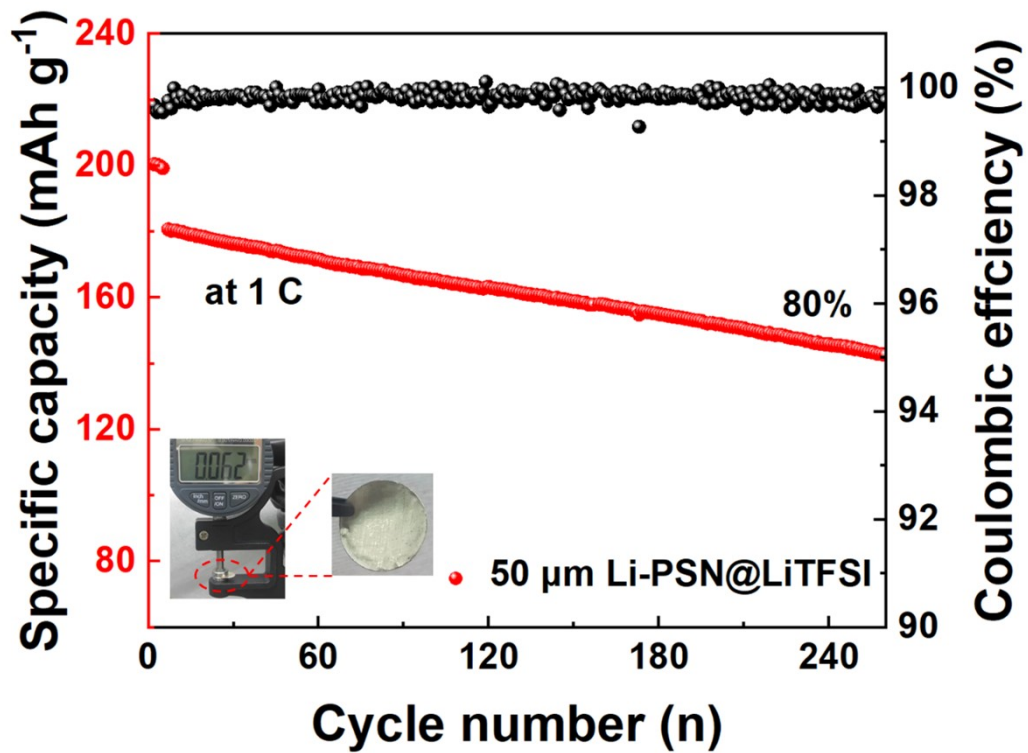


Fig. S16 Discharge capacity and Coulombic efficiency of thin Li (50 μm) Li-PSN@LiTFSI || NCM88 (The lithium is on the copper foil, which is 11-12um thick)

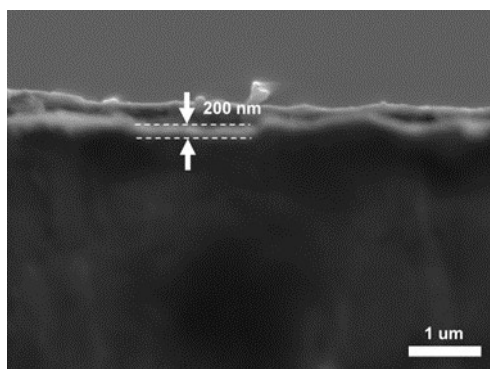
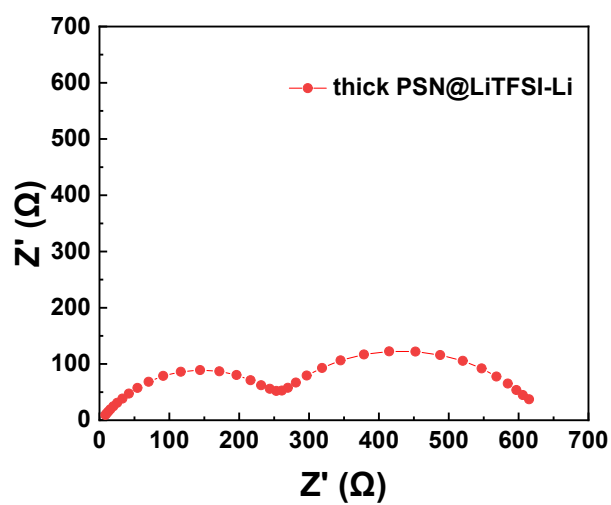
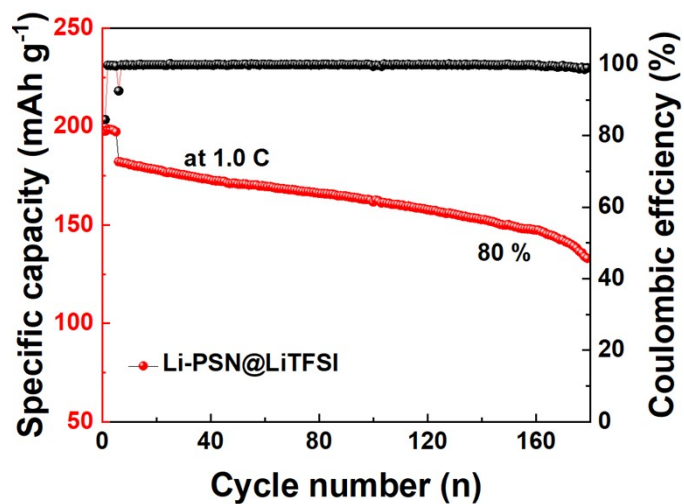
a**b****c**

Fig. S17 (a) The SEM images of cross section. (b) Electrochemical impedance spectra of thick PSN@LiTFSI-Li. (c) Discharge capacity and Coulombic efficiency of thick PSN@LiTFSI-Li @LiTFSI || NCM88 performance at 1 C.

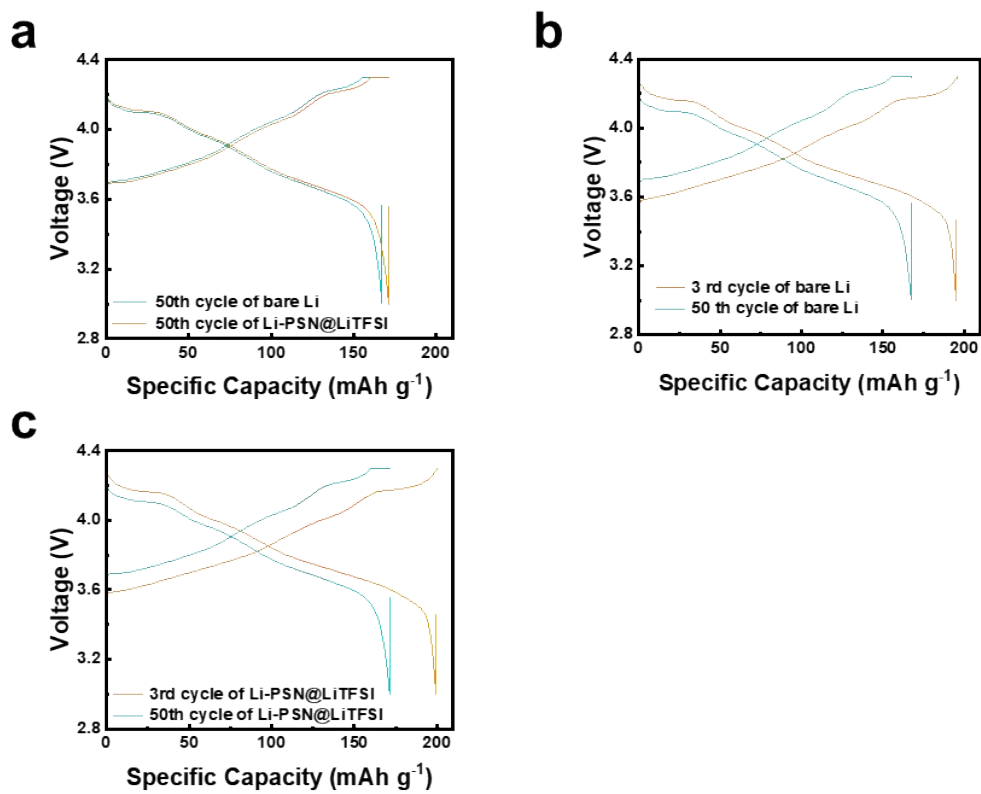


Fig. S18 (a) Voltage profiles of bare Li and Li-PSN@LiTFSI in the 50th circle. (b) Voltage profiles of Li-PSN@LiTFSI in the third and 50th circle. (c) Voltage profiles of bare Li in the third and 50th circle.

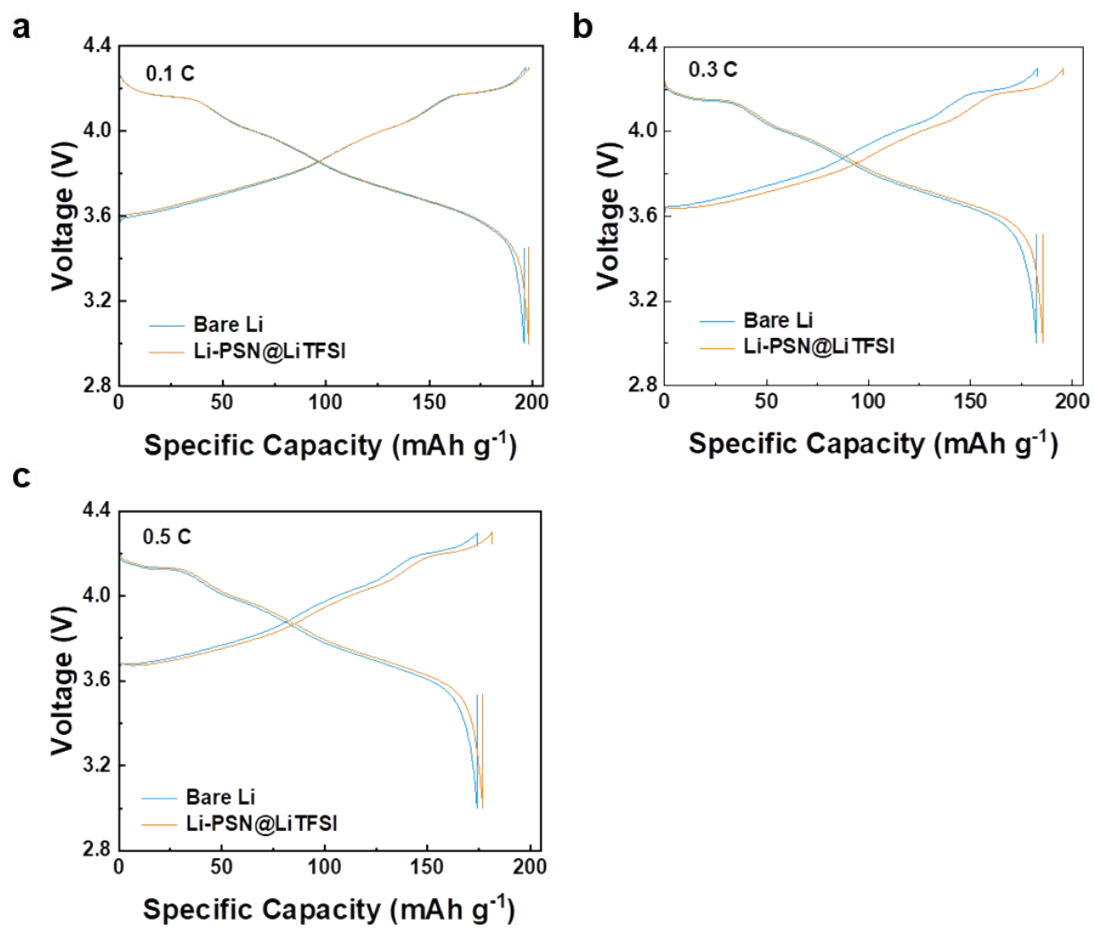


Fig. S19 The overvoltage difference at (a) 0.1 C, (b) 0.3 C, (c) 0.5 C.