

Supplementary Information

High concentration in-situ polymer gel electrolyte for high performance lithium metal batteries

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Experiments

Materials and preparations.

Lithium bis(fluorosulfonyl)imide (LiFSI) powders were purchased from Zhangjiagang Guotai-Huarong New Chemical Materials Corporation. Before used, they were dried at 100 °C for 24 h. The anhydrous 1,3-dioxolane (DOL) solvent was purchased from Guangdong Canrd New Energy Technology Co., Ltd. Lithium nitrate (LiNO_3) was purchased from Aladdin. The 4 M LE, 6 M, 8 M and 10 M GPE were prepared by dissolving quantitative LiFSI powders in DOL solvent using a magnetic stirrer, followed by aging at room temperature for 48 h. In a typical experiment, 4 M LE represents 4 mmol LiFSI powder dissolved in 1 mL DOL solvent. The whole experiments were carried out in an argon-filled glove box, in which the concentrations of oxygen and water were less than 0.01 ppm.

Battery assembly and measurement

Four kinds of batteries were assembled to investigate the electrochemical properties. The electrolytes were added in liquid to assemble cells, which were aged for 48 hours before electrochemical testing. For type I, lithium metal was used as the anode and cathode to assemble 2032-type Li||Li Battery. The lithium plating/stripping behaviors and cycling performances were investigated at the current densities and capacities.

For type II, lithium metal was used as an anode, stainless steel (SS) disc was as a reference electrode to assemble 2032-type Li||SS batteries. The linear sweep voltammetry (3.2 to 5 V) was performed on an electrochemical workstation (CHI760E) at a scan rate of 5 mV s^{-1} to verify the electrochemical stability of this type battery. For type III, lithium metal was used as an anode, copper foil was used as a cathode to assemble 2032-type Li||Cu batteries. In this battery, the coulombic efficiency was studied by plating (charging) quantitative amount of lithium metal onto copper foil, and then the battery was charged to 1 V. The coulombic efficiency was defined as charge capacity/discharge capacity. For type IV, lithium metal was used as an anode, LiFePO_4 electrode was applied as a cathode to assemble 2032-type

LiLiFePO_4 batteries. LFP pole piece purchased from Shenzhen Kejing Zhida Technology Co.

Materials characterization

Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy were performed on Thermo Scientific Nicolet iS20 and Thermo Fisher Evolution instruments, respectively. The microstructure and morphology were detected by a scanning electron microscopy (SEM, NovoNano450). The binding energy information was identified by X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha). Gel-permeation chromatography (GPC) measurements were conducted by first dissolving the synthesized 6 M GPE electrolytes in tetrahydrofuran (THF), then tested using the Agilent PL-GPC220.



Fig. S1 Optical photos of 8 M GPE after 48 h gelation.

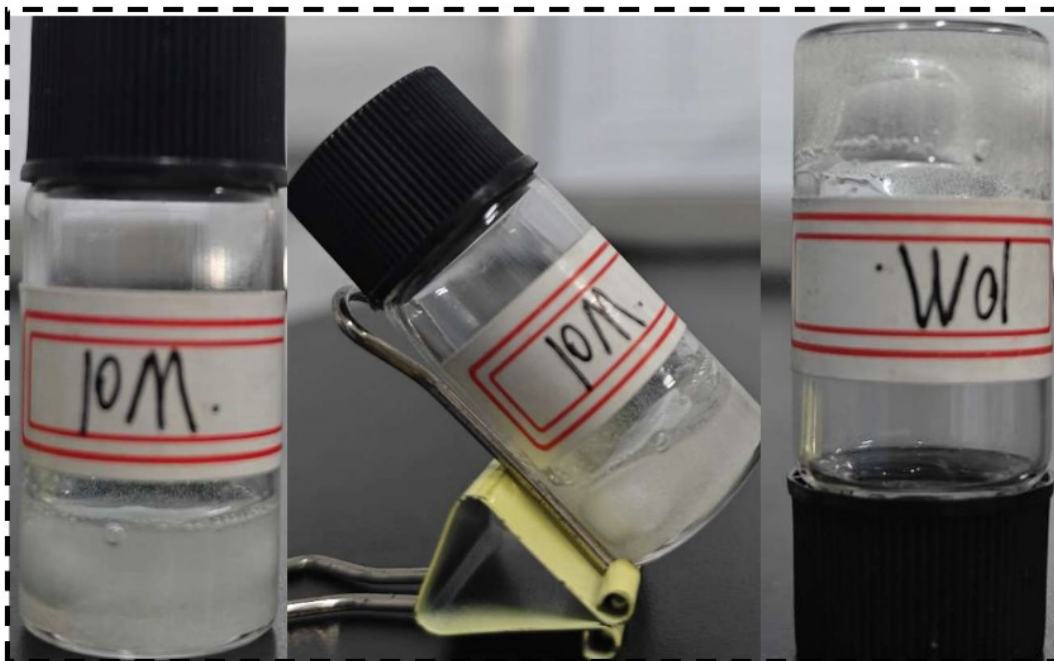


Fig. S2 Optical photos of 10 M GPE after 10 min gelation.

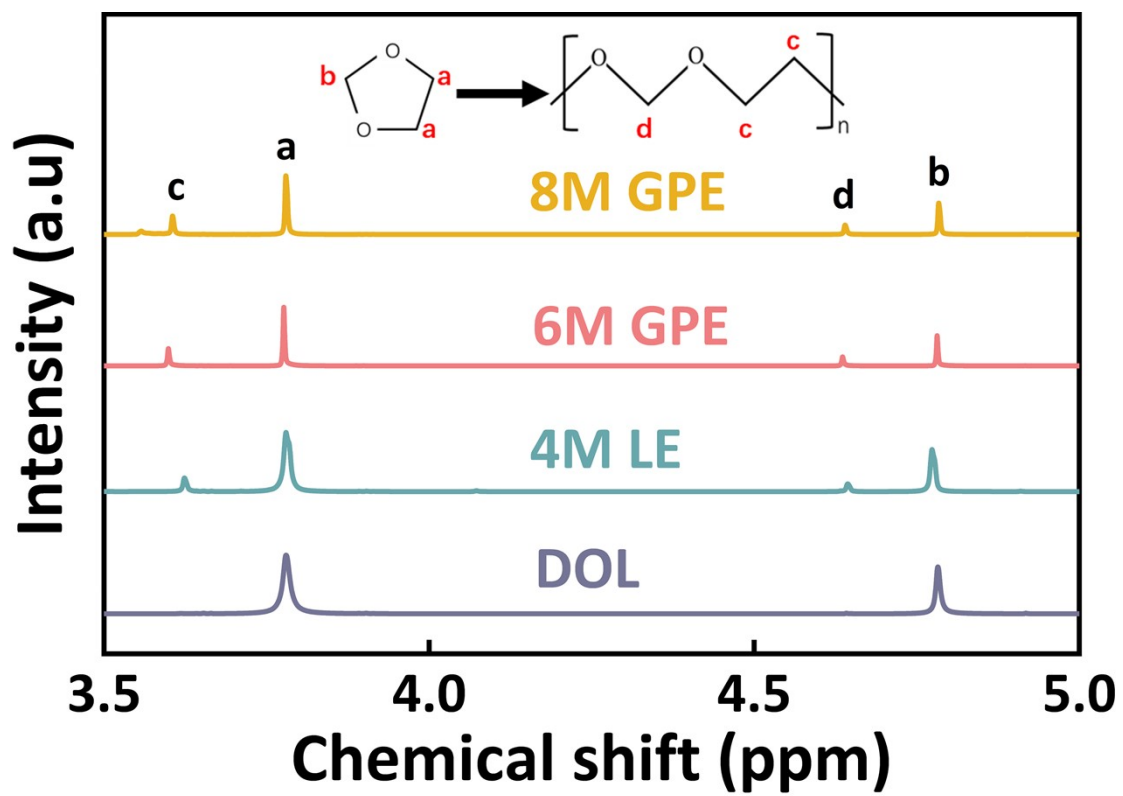


Fig. S3 ¹H NMR of pure DOL, 4 M LE, 6 M and 8 M GPE after 48 h gelation.

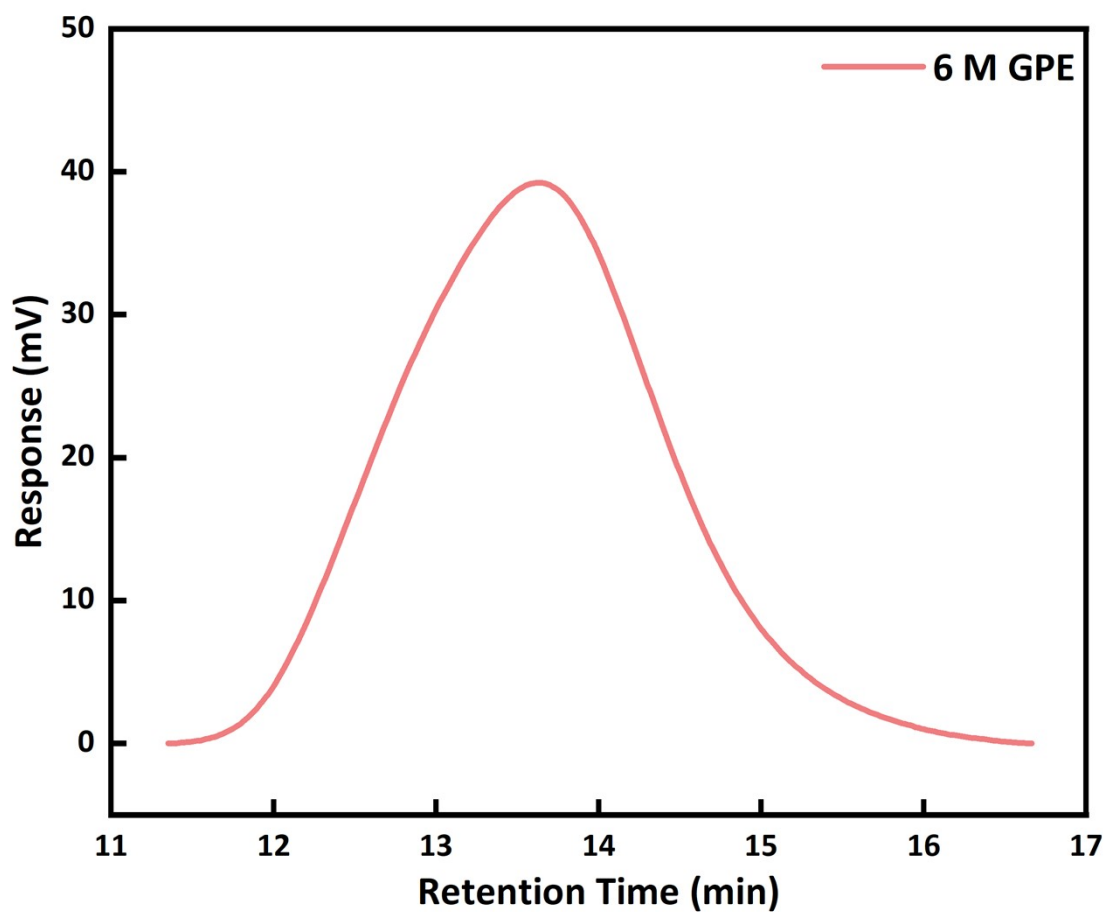


Fig. S4 GPC profile of 6 M GPE; the THF was used as the eluent.

From GPC spectra, the weight-average molecular weight (M_w) and the number-average molecular weight (M_n) of PDOL with 6 M GPE were 162884 and 57828. The value of polydispersity (PDI) is 2.82. The average degree of polymerization (DP) of DOL (6 M GPE) was 781 calculated based on GPC results.

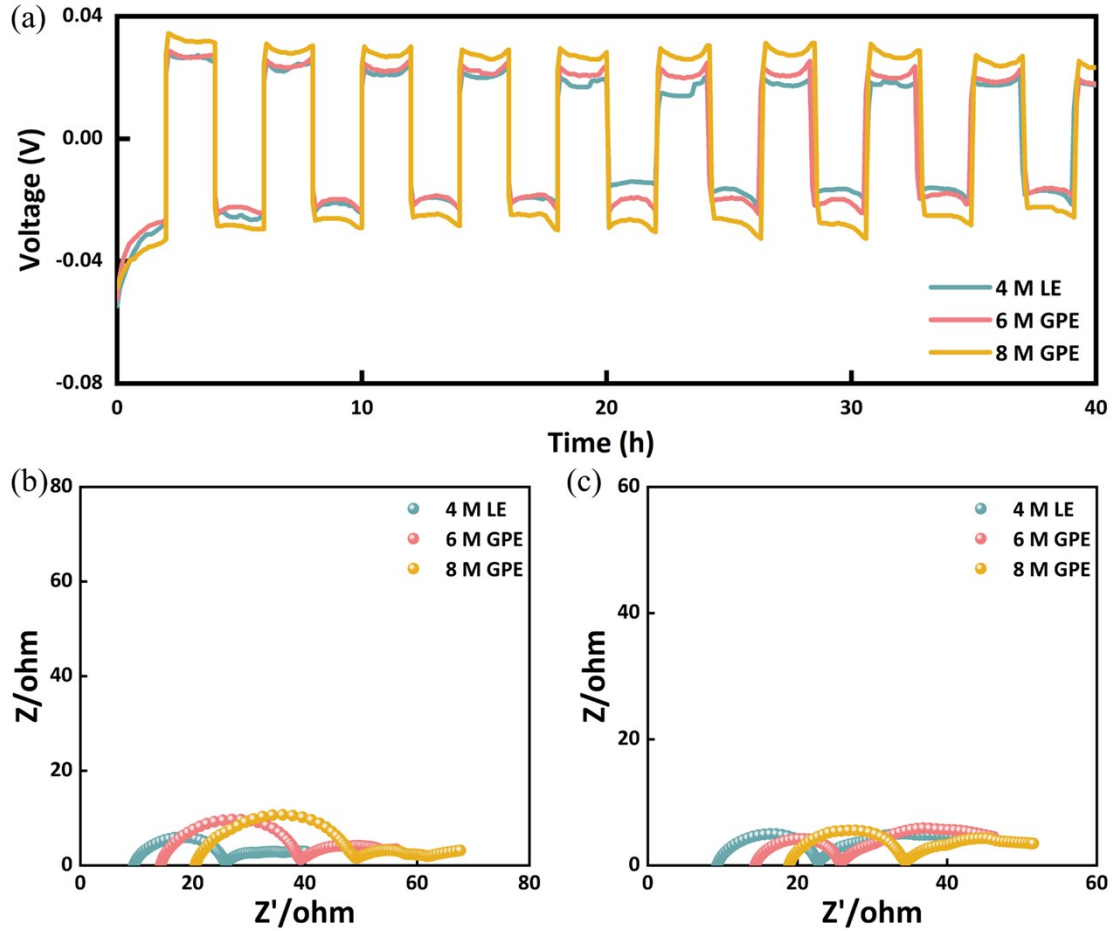


Fig. S5 (a) Cycle performance of Li||Li symmetric cells with different electrolytes.

(b) EIS profiles after 20 h of cycling for Li||Li symmetric cells using different electrolytes. (c) EIS profiles after 40 h of cycling for Li||Li symmetric cells using different electrolytes.

As illustrated in Fig. S5a, following repeated charge/discharge cycles, the 4 M LE displays reduced overpotentials, while the overpotentials of the 6 M GPE increasingly converge with those of the 4 M GPE as the number of cycles grows. This trend aligns with the findings depicted in Fig. S5b and Fig. S5c, which show that the impedance of the 6 M GPE progressively nears that of the 4 M LE.

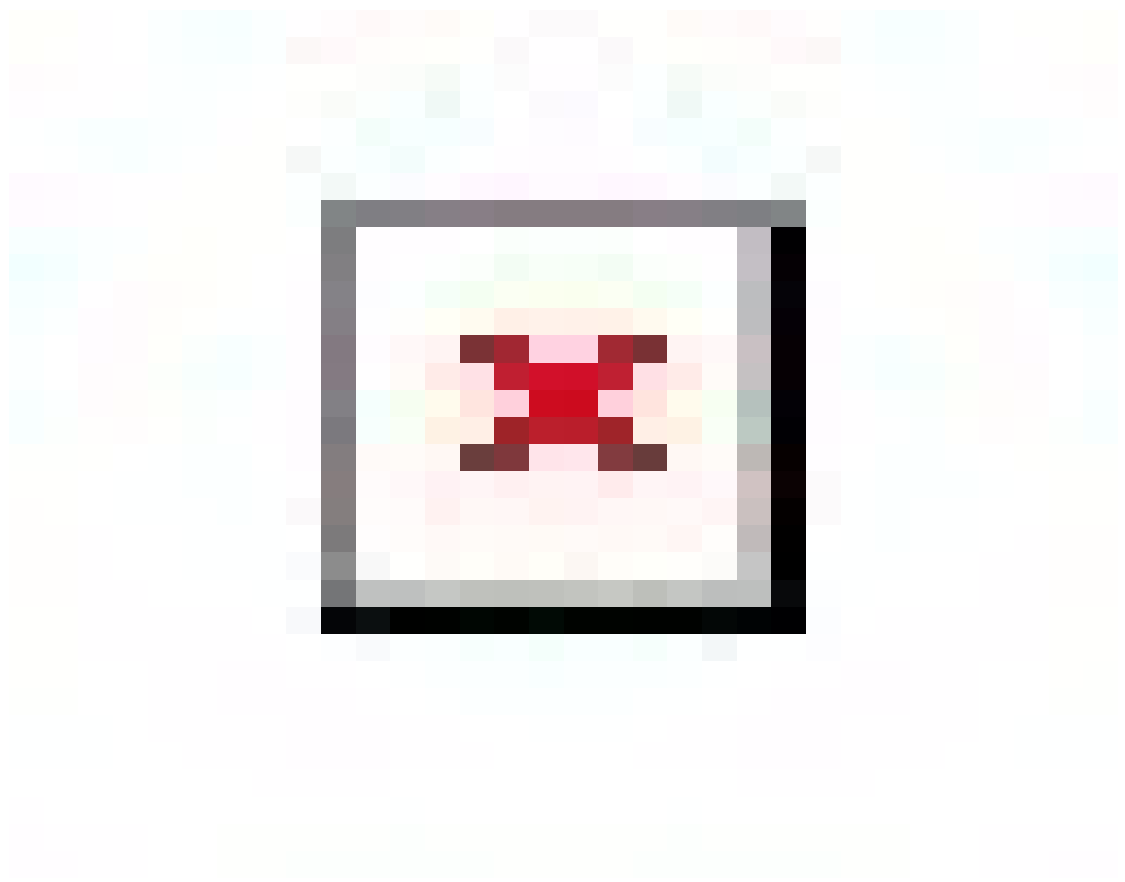


Fig. S6 First charge/discharge curves of Li|Cu cells at different concentrations.

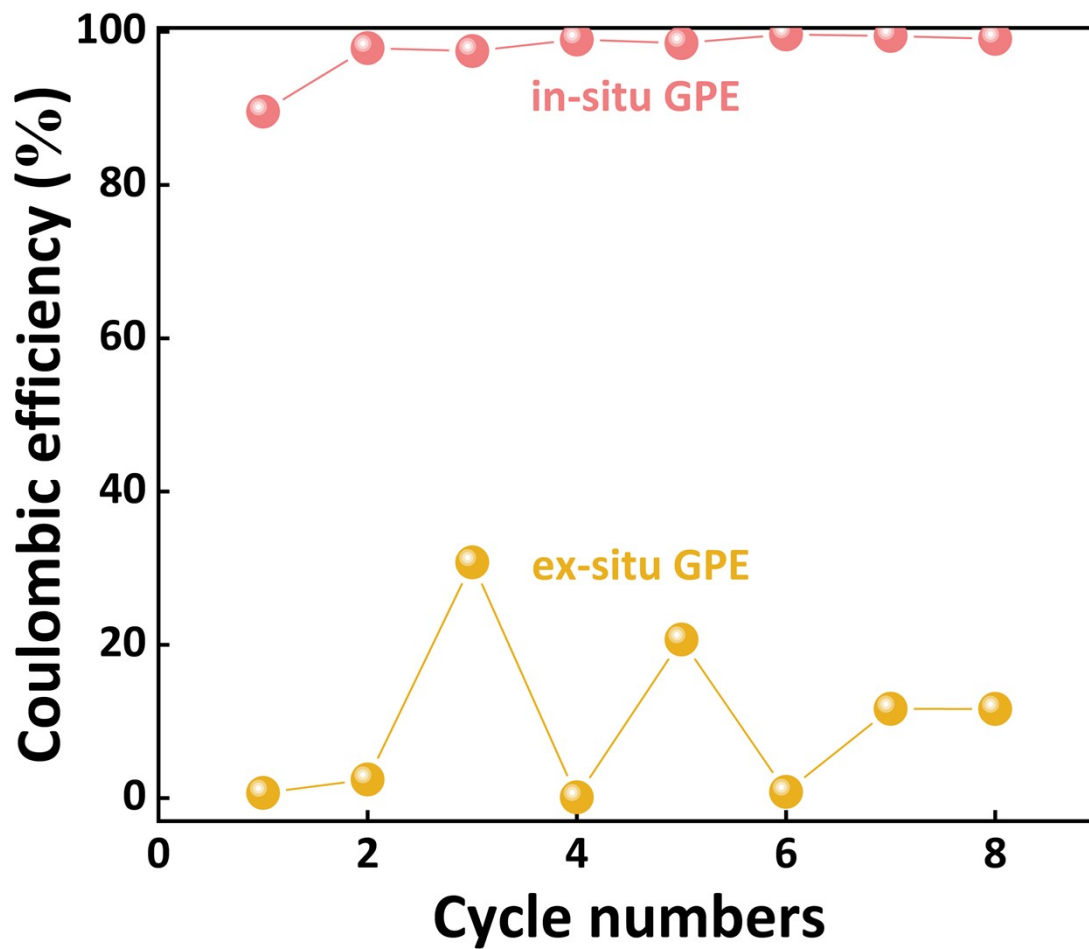


Fig. S7 Coulombic efficiency of LilCu cells with in situ and ex-situ polymerized GPE.

For the ex-situ approach, the electrolyte is polymerized on the separator before assembling the cell for testing. The GPE synthesized via the ex-situ method tested with an efficiency of less than 40% and exhibited significant instability.

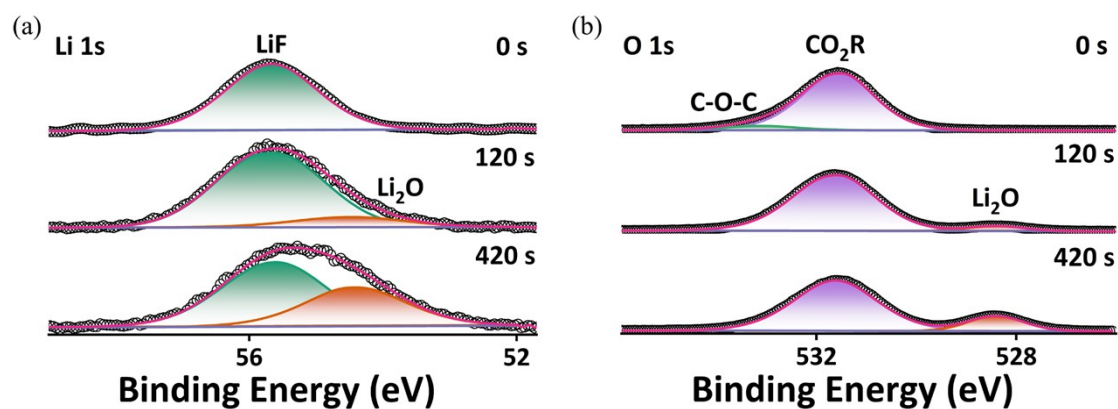


Fig. S8 XPS spectra of (a) Li 1s, (b) O 1s in the Li||Cu cell with 6 M GPE after the first discharge at 0.5 mA cm^{-2} .

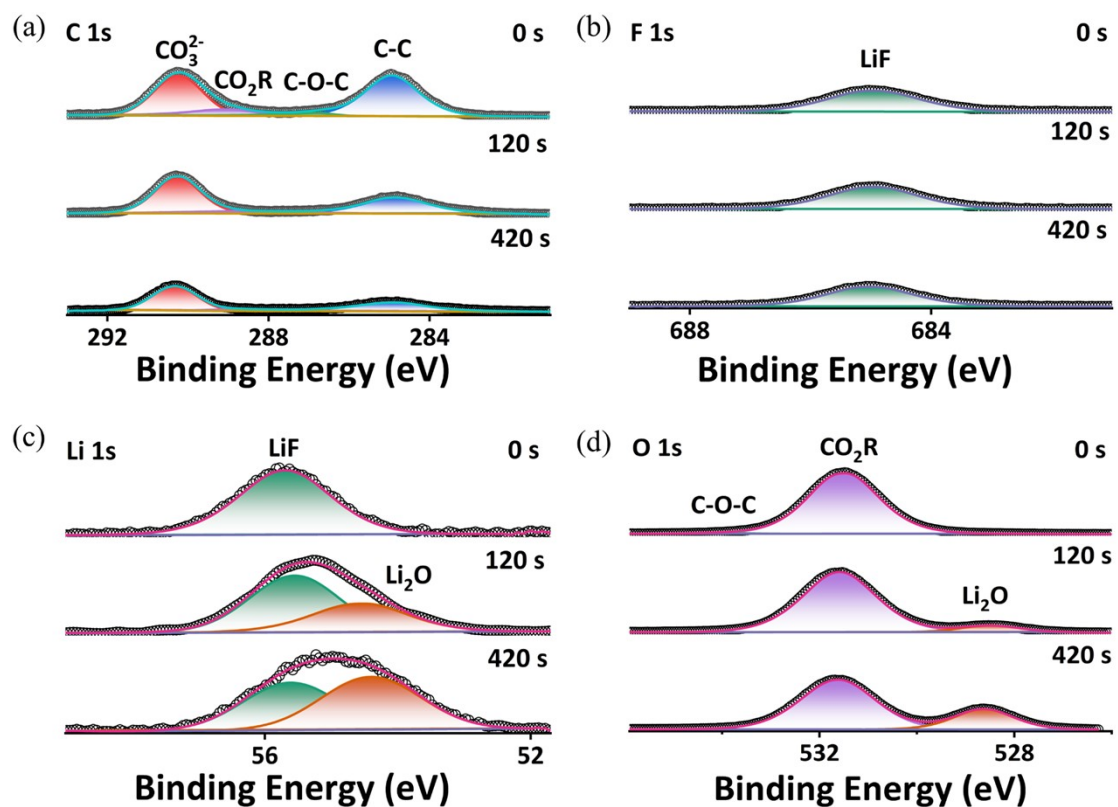


Fig. S9 XPS spectra of (a) C 1s, (b) F 1s, (c) Li 1s, (d) O 1s in the Li||Cu cell with 6 M GPE after the 50th discharge at 0.5 mA cm^{-2} .

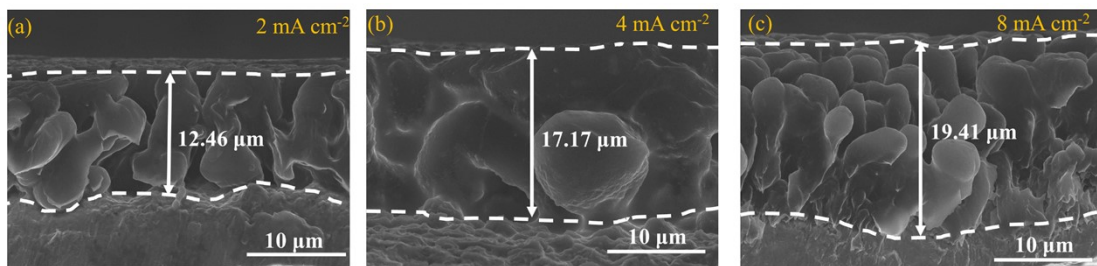


Fig. S10 Cross-sectional SEM images of lithium deposition in the cells with 6 M GPE at (a) 2 mA cm^{-2} , (b) 4 mA cm^{-2} , (c) 8 mA cm^{-2} .

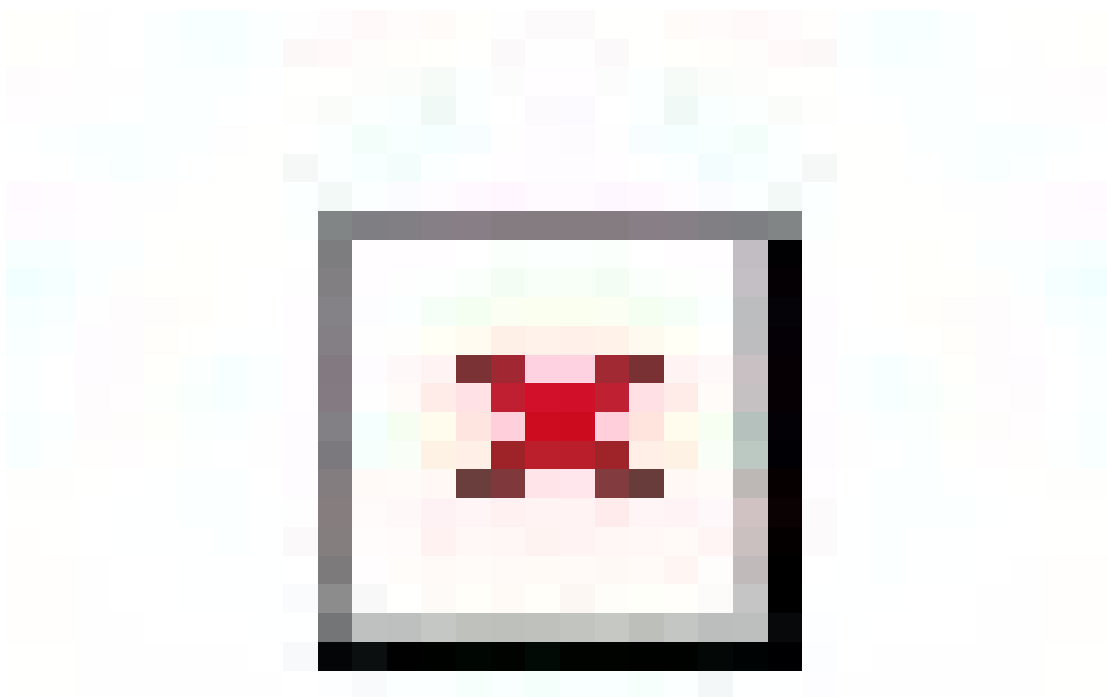


Fig. S11 The electrochemical performance of the Li||LFP cell. Discharge/charge curves of different N/P: ~ 0.6 .

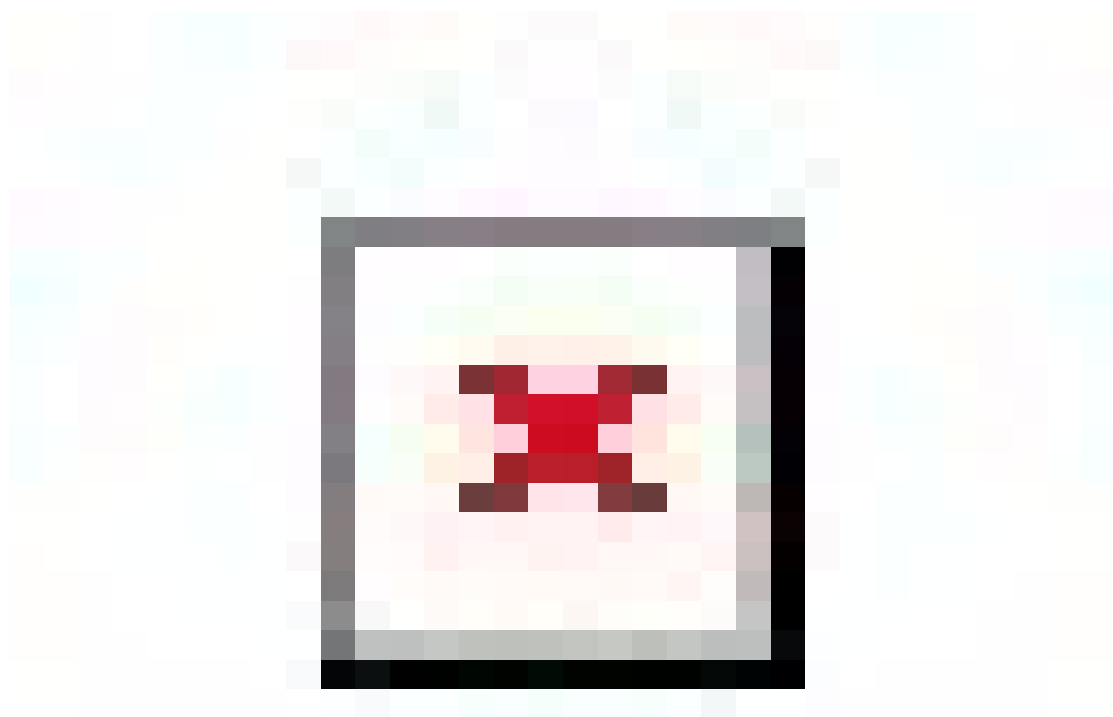


Fig. S12 The electrochemical performance of the Li/LFP cell. Discharge/charge curves of different N/P: ~ 0.2 .

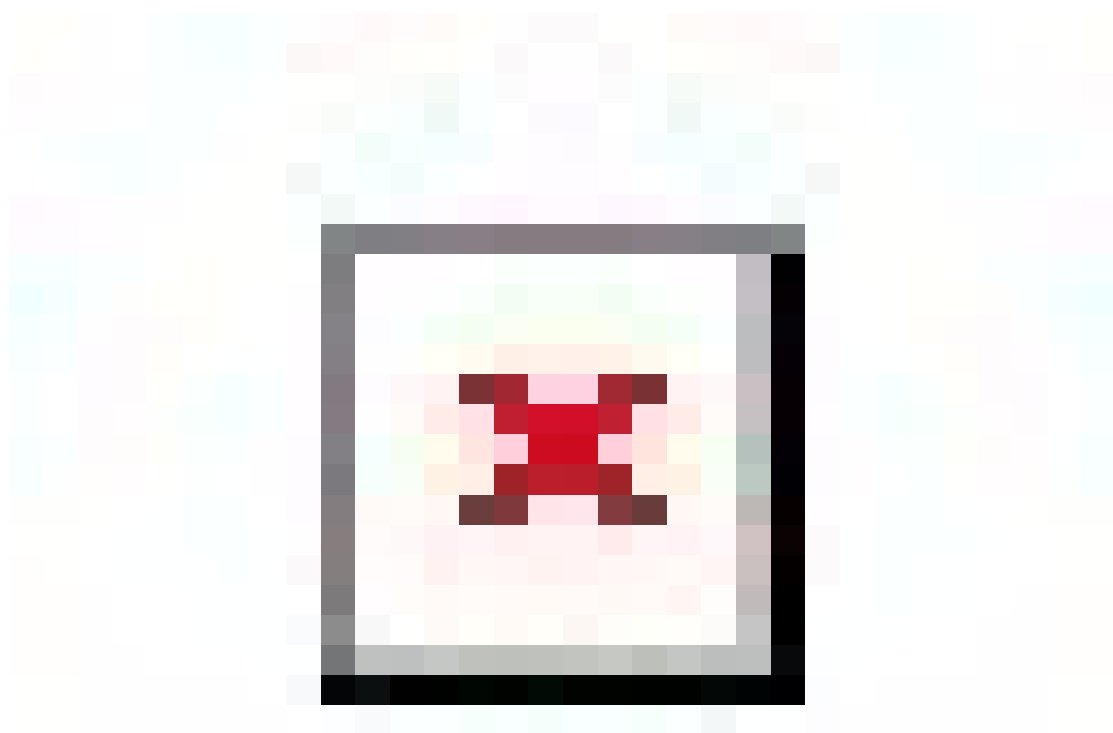


Fig. S13 The electrochemical performance of the Li/LFP cell. Discharge/charge curves of different N/P: 0.

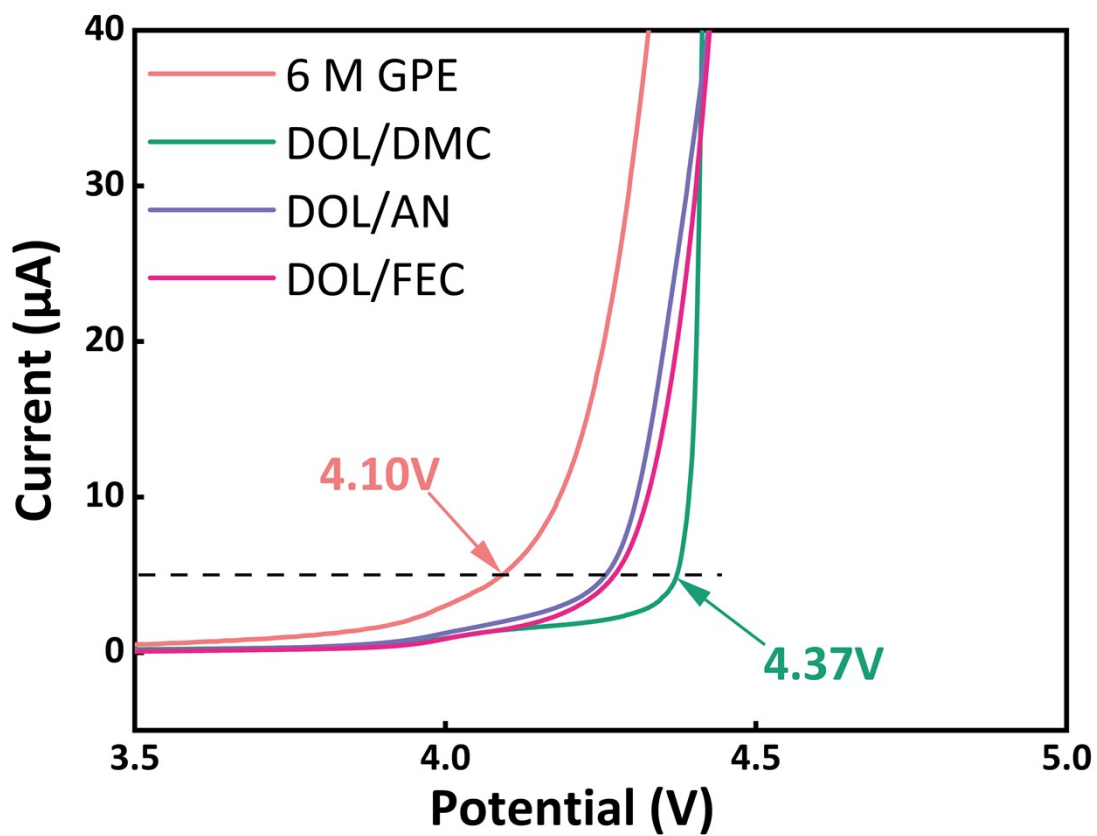


Fig. S14 LSV tests of 6 M LiFSI in different solvent combinations.