

In Situ Formed Flexible Three-Dimensional Honeycomb-like Film for LiF/Li₃N-riched Hybrid Organic-Inorganic Interphase on Li Metal Anode

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Experimental Procedures

Calculation details: All DFT calculations are performed with the Gaussian 09 software. All geometry optimizations are optimized to minimum and are carried out by the B3LYP with the 6-311G(d,p) basis set. The single-point energies and solvent effects in a mixed solvent (vDOL: vDME= 1: 1) are computed at the same theory of B3LYP with the 6-311G(d,p) basis set using the gas-phase optimized structures. Solvation energies are evaluated by a self-consistent reaction field (SCRF) using the IEFPCM model with estimated dielectric constant (7.2). For HOMO and LUMO calculations, B3LYP is also used with the 6-311G(d,p) basis set.

Materials: Li foil (China Energy Lithium Co., Ltd.), Copper (Cu) foils (Shenzhen Kejing Star Technology Co., Ltd.), Trifluoroethyl methacrylate (TFEMA, 99%, Aladdin), Dimethyl methylphosphonate (DMMP, 99%, Adamas), 1,3-dioxolane (DOL, 99%, Aladdin), Lithium nitrate(LiNO₃, 99%, Aladdin). The commercial electrolyte (denoted as EC/DEC electrolyte) is composed of 1 M LiPF₆ dissolved in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 v/v) which was purchased from Jiangsu Guotai Co., Ltd. The commercial electrolyte (denoted as DOL/DME electrolyte) is composed of 1 M LiTFSI dissolved in 1,3-dioxolane (DOL)/1,2-dimethoxyethane (DME) (1:1 v/v) which was purchased from Jiangsu Guotai Co., Ltd. Lithium iron phosphate (LiFePO₄) powders were purchased from Shenzhen Kejing Star Technology Co., Ltd. All these materials were used without further purification.

Preparation of PTFEMA-N-protected Cu and Li foils: The TFEMA, DMMP and DOL were mixed with 2:0.5:0.2 by volume, 2 wt.% LiNO₃ was dissolved in the mixed solution at 25°C under stirring 12h, turning to a yellow mixed solution. Then the yellow solution was heated at 65°C for 2h, the viscous yellow solution was acquired. To fabricate a uniform PTFEMA-N layer on Cu foil, the doctor blade technique was used to coat the viscous yellow solution onto Cu foil. Then, the coated Cu foil was dried at 30 °C under vacuum for 6 h.

To prepare PTFEMA-N-protected Li foil, the 20 μL above viscous yellow solution was dropped onto the top surface of polytetrafluoroethylene mold, then PTFEMA-N layer was coated on Li foil with doctor blade technique and dried in glove box (O₂<0.1ppm, H₂O<0.1ppm) at room temperature for 24 h (Figure S2). After drying, the Li foil was covered with uniform PTFEMA-N protection layer and used for coin cell fabrication and tests.

Electrochemical measurements: All coin cells (Li || Cu, Li || Li and Li || LiFePO₄) were assembled to standard 2025 coin-type cells with 50 μL electrolyte in the Ar-filled glove box (O₂<0.1ppm, H₂O<0.1ppm). Li || Cu cells were used to observe Li deposition morphology and to test average coulomb efficiency, the coated Cu foil were punched into 11.0 mm diameter disks as the working electrodes. The Li || Cu cells were firstly discharged for 1.0 h at 1.0 mA cm⁻² and then charged until the voltage reaches 1.0 V. The cells were tested using a LAND multichannel battery cycler (Wuhan LAND electronics Co., Ltd.). The Li || Li symmetric cells were assembled for testing electrochemical stability, the coated or without coated Li foils with 16.0 mm diameter disks were used as the working electrodes. The Li || Li symmetric cells were tested at room temperature under galvanostatic charging/discharging conditions. (Wuhan LAND electronics Co., Ltd.). An ether-based electrolyte with 1M lithium bis (trifluoromethanesulfonyl) imide (LiTFSI) and 1 wt% LiNO₃ in a mixture of 1, 3-dioxolane (DOL) and 1, 2-dimethoxyethane (DME) (1:1 v/v) was employed.

In Li || LiFePO₄ cells, LiFePO₄ cathode was prepared by mixing LiFePO₄, PVDF, and Super P in a weight ratio of 8:1:1 using NMP as the solvent to make a slurry and cast onto an Al foil and dried at 100 °C overnight under vacuum. The Li || LiFePO₄

coin cells were assembled using LiFePO_4 as cathode (the areal loading is about 2.5 mg cm^{-2}), the LiFePO_4 coated on Al foil were punched into 11.0 mm diameter disks as the working electrodes, Celgard 2325 as the separator (19.0 mm diameter disks), and Li foil (400 μm in thickness) with or without the protection as anode. The coin cells were monitored in galvanostatic mode within a voltage range of 2.5 to 3.8 V using a LAND multichannel battery cycler (Wuhan LAND electronics Co., Ltd.). The $\text{Li} \parallel \text{LiFePO}_4$ cells were firstly cycled at 0.1 C for one cycle and then cycled at 1.0 C (170 mA g^{-1}). For the cell tests, 1.0M lithium hexafluorophosphate (LiPF_6) in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 v/v) was used as electrolyte.

The electrochemical impedance spectroscopy (EIS) measurement was performed in a frequency range between 10^5 and 10^{-1} Hz with a voltage amplitude of 10 mV using electrochemical workstation (Shanghai Chenhua, China).

Characterization: Scanning electron microscopy (SEM, JSM 7401F, JEOL Ltd., Japan) images were used to characterize the morphologies of deposited Li. X-ray photoelectron spectroscopy (XPS) analysis was carried out on PHI Quantera SXM (ULVAC-PHI, Inc. Japan). The analyzed area of lithium foil was about 4 mm^2 . The Li foil sample (with a protect layer on the surface) obtained from disassembled cells after 50 cycle and were cleaned by DEC solvent for three times, then dried in the glove box until the solvent was volatilized thoroughly. Fourier transform infrared spectroscopy (FTIR) was performed with a Nicolet 6700 spectrometer instrument. The ^1H and ^{19}F nuclear magnetic resonance (NMR) experiments were carried out on a JNM-ECA600 NMR spectrometer. The deuterated dimethyl sulfoxide (DMSO) was employed as the dispersion to dissolve PTFEMA-N layer. During transferring process before any characterization, all Li foil samples were protected in Ar-filled containers to avoid air.

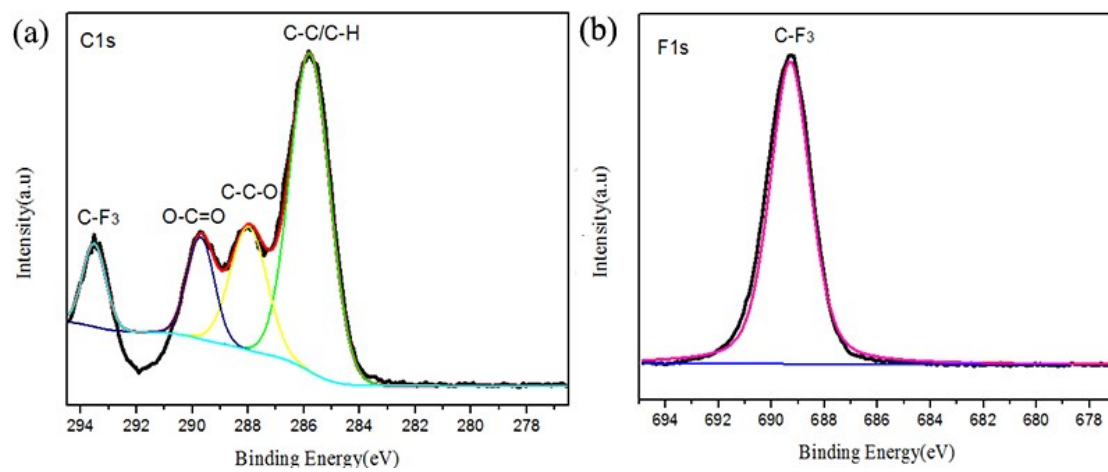


Figure S1 X-ray photoelectron spectroscopy (XPS) of the PTFEMA-N film before cycles. a), b) The C 1s and F 1s spectra before cycling

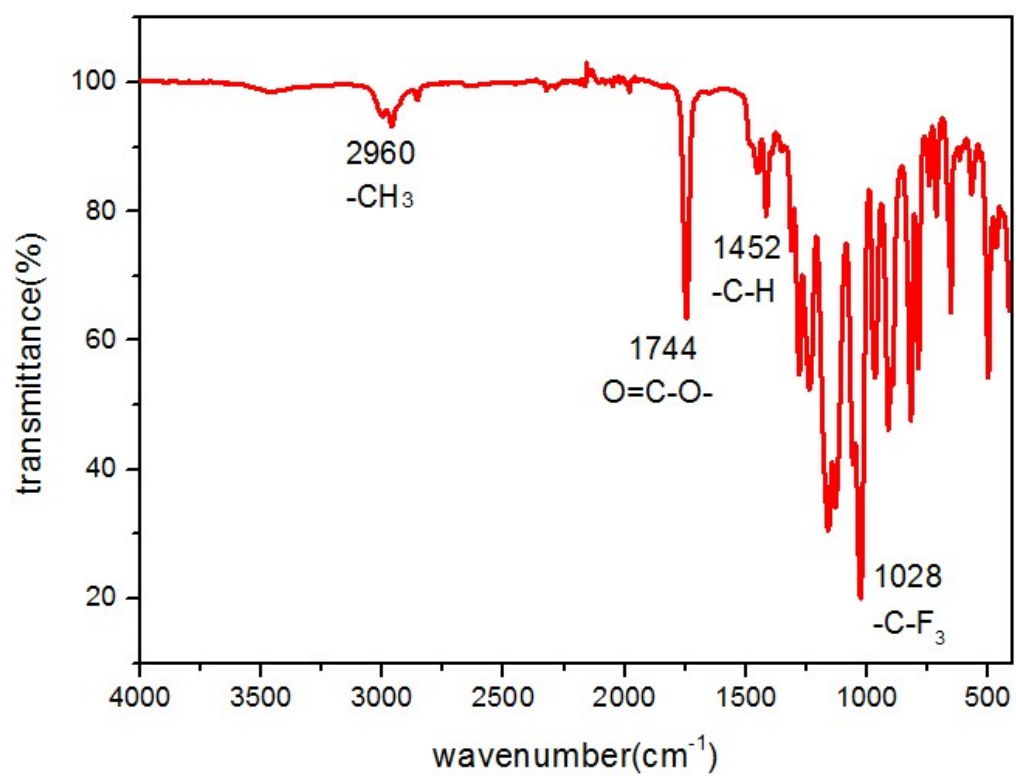


Figure S2 The FTIR spectra of the PTFEMA-N film

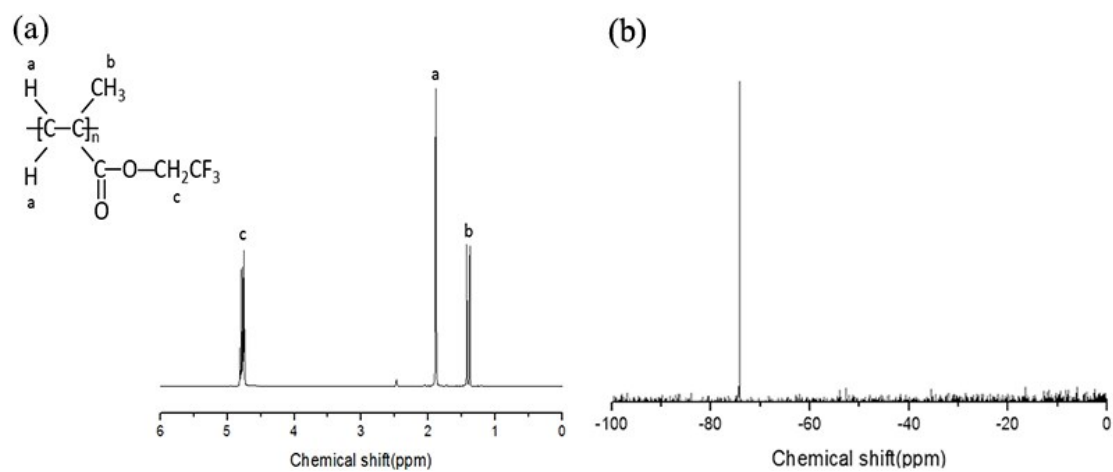


Figure S3 The NMR spectra of the PTFEMA-N film. a) ¹H NMR and b) ¹⁹F NMR

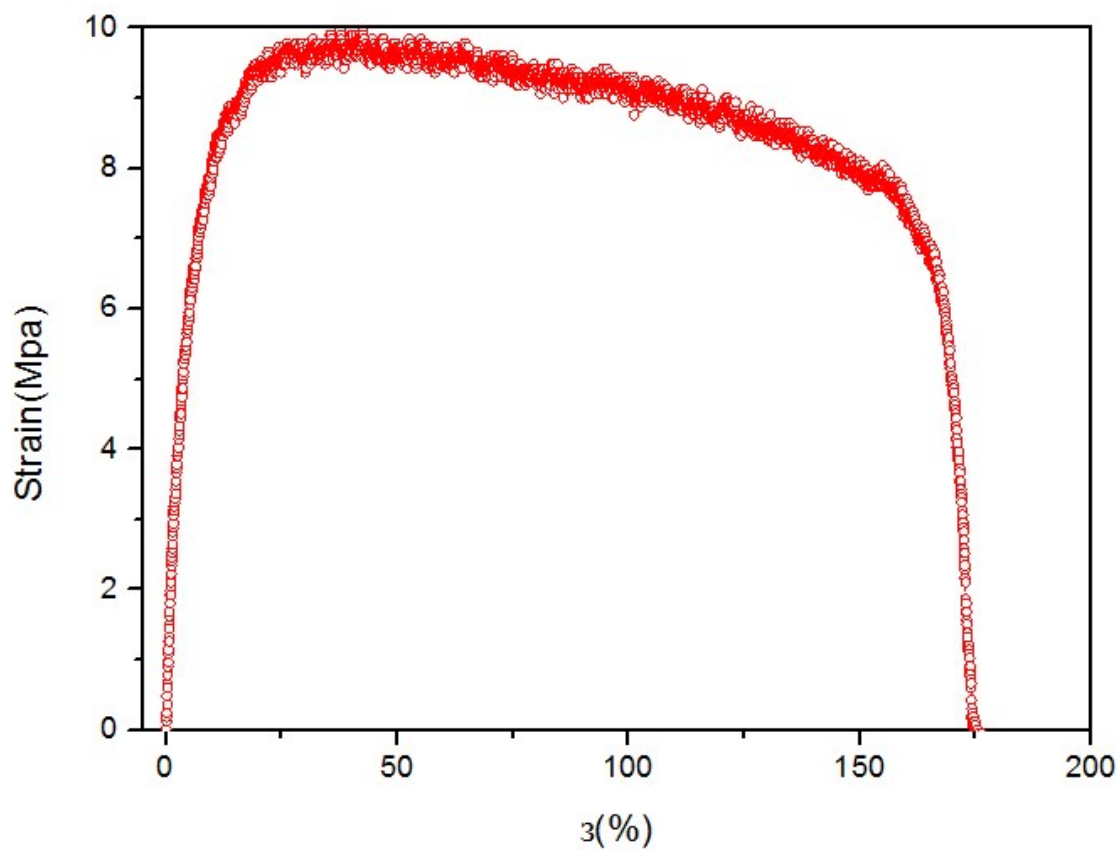


Figure S4 The stress–strain curve of PTFEMA-N film

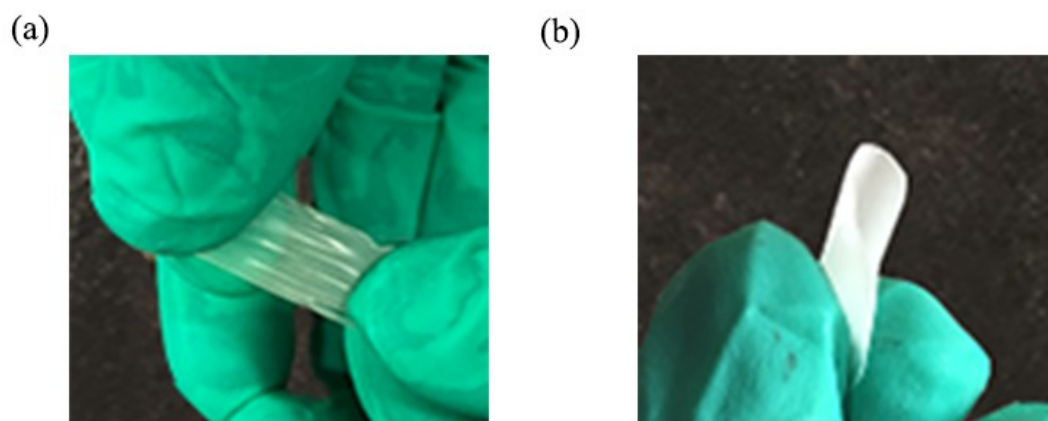


Figure S5 The flexible performance of PTFEMA-N film a) stretching property and b) bending property.

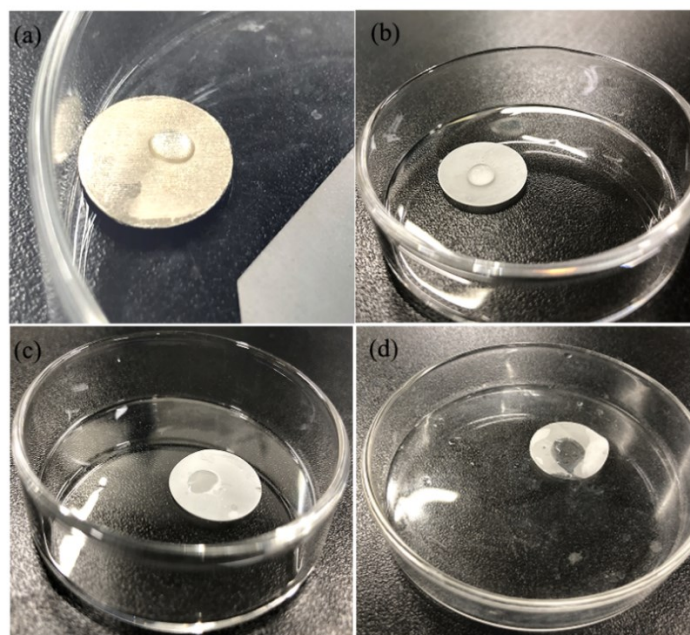


Figure S6 a) The image of moisture stability test of Li foil with PTFEMA-N layer; b) The hydrophobicity of PTFEMA-N membrane; The wettability of PTFEMA-N membrane in c) EC/DEC electrolyte and d) DOL/DME electrolyte

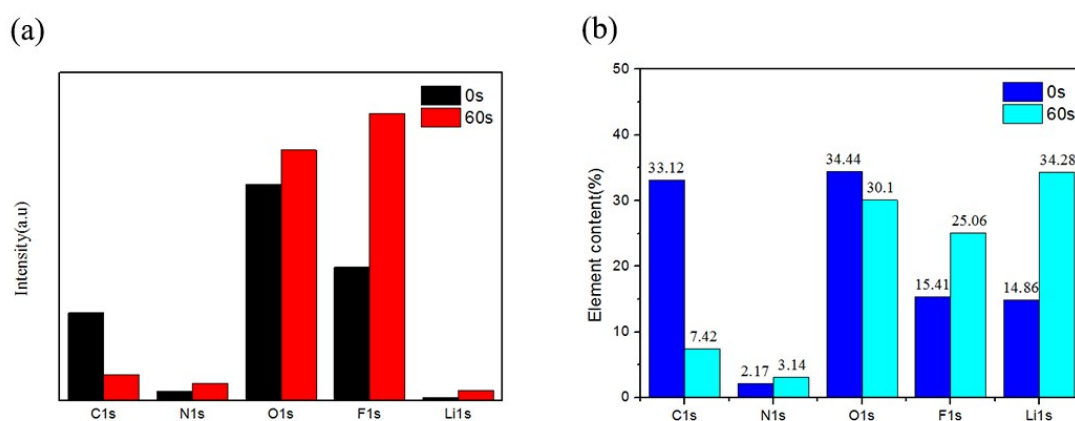


Figure S7 a) The relative element intensities and b) element contents along the sputter time with PTFEMA-N layer protected Li after 100 cycles.

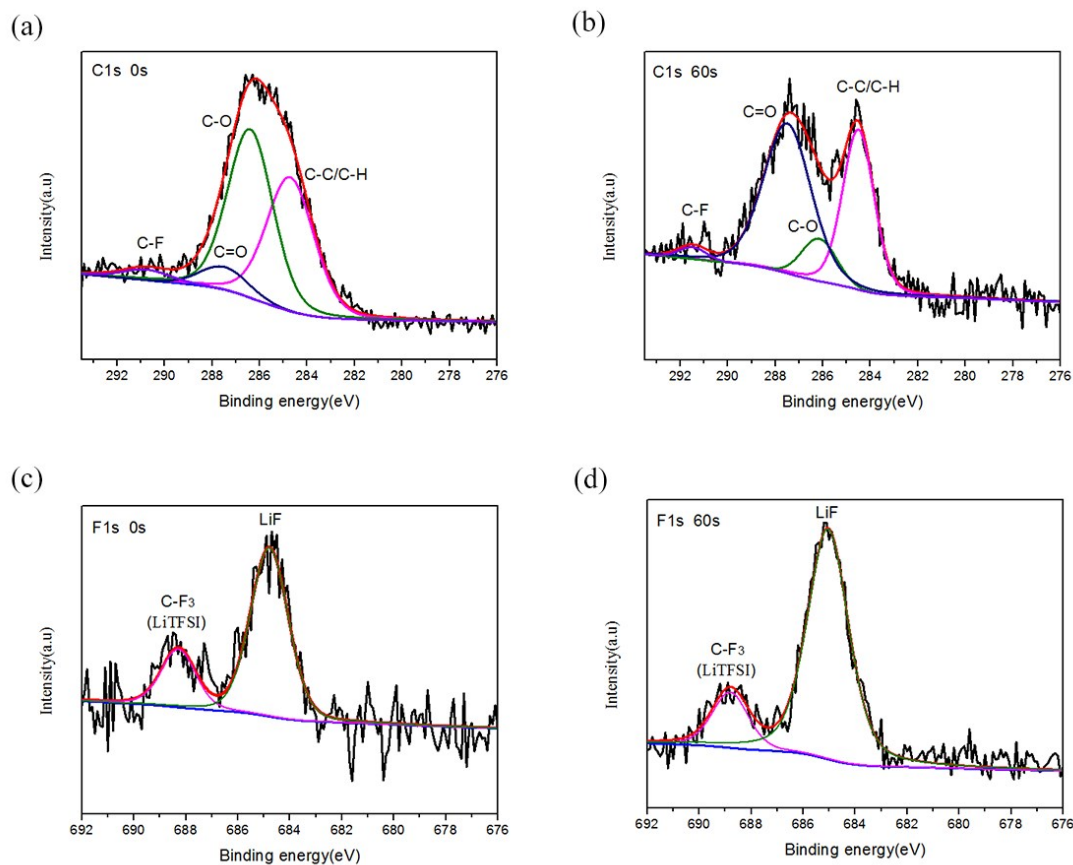


Figure S8 The XPS characterization of the SEI with pristine Li in ether electrolyte after 200 cycles: The C1s spectra of Li surface a) without sputter and b) with sputter for 60s; F1s spectra of Li surface c) without sputter and d) with sputter for 60s

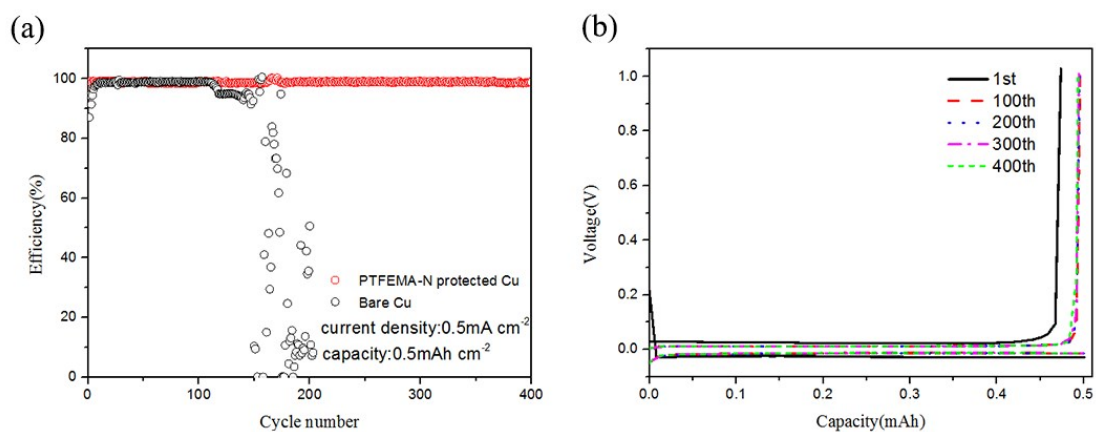


Figure S9 a) Cycling performance of Li||Cu cells at 0.5 mA cm^{-2} ; b) Voltage profiles of Li||Cu cells using PTFEMA-N protected Cu foil cycled at different cycle number at 0.5 mA cm^{-2} with 0.5 mAh cm^{-2}

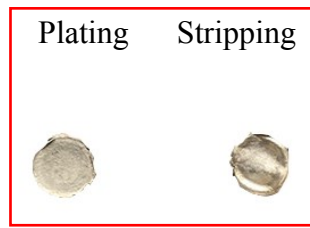


Figure S10 The image of surface morphology of Li foil in Li||Li symmetric cells after 500 cycles

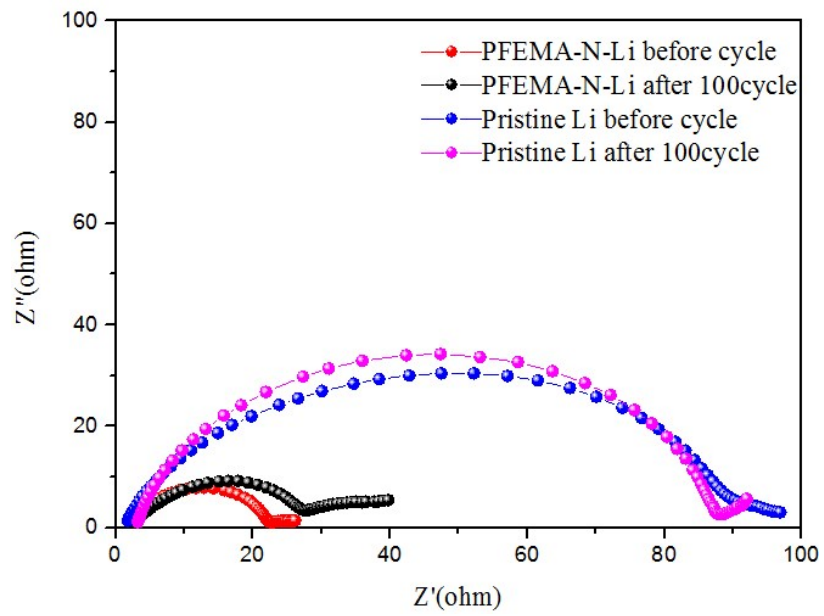


Figure S11 EIS of Li||Li symmetric cells before and after 100 cycle

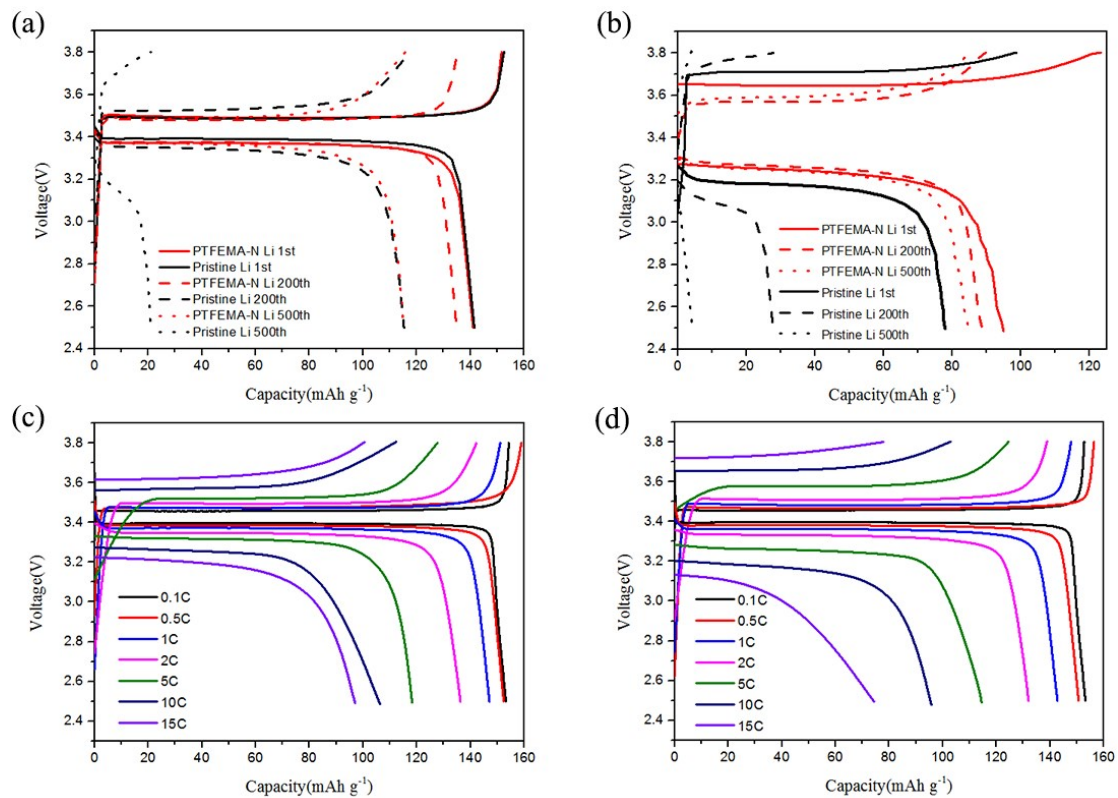


Figure S12 Voltage profiles of Li||LFP cells at a) 1C, b) 10C; Voltage profiles of Li||LFP cells at various rates between 0.1 C and 15 C with c) PTFEMA-N protected Li metal anode and d) pristine Li metal anode