Supplementary Information for

An elastic and Li-ion-percolating hybrid membrane stabilizes Li metal plating

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Materials and Methods

Electrochemical measurements

Measurement of the Cu|Li cells for Coulombic efficiency (CE) were conducted by assembling the cells with Cu foil and polished Li (Ø11 mm, 200 µm thick) as the working and counter electrode, respectively. The CE of each cycle over the first 100 cycles were used to calculate the average CE and the standard deviation, which determined the error bar (Figure 4C). The Li|Li symmetric cells for impedance and plating/stripping studies were assembled with polished Li foil as both electrodes in 2032 coin cells fabricated with an in-glove box argon automatic hydraulic press. The electrolyte used for the CE measurement and symmetric cell cycling was 1 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in a mixed solvent of 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) with 2 wt% of LiNO₃ (BASF, 40 µl in each cell). The electrolyte for the cyclic voltammetry measurement was 1M LiPF₆ in ethylene carbonate/dimethyl carbonate (EC/DMC, BASF). The LTO electrodes were prepared by casting a slurry of Li₄Ti₅O₁₂ (200 nm, Sigma-Aldrich), Super P and PVDF at a weight ratio of 8:1:1 in dimethylformamide (DMF) onto carbon-coated Al foil. Electrodes (Ø11 mm) with an areal LTO loading of ~2.5 mg cm⁻² were dried at 120 °C before use. The LTO|Li full cells using Li or LPS-PMDS protected Li foil (Ø11 mm) as the anode were cycled at 5 C (1C = 175 mA g⁻¹) in the voltage window 1-2.5 V, using 1M LiTFSI in DOL/DME as the electrolyte. The Li metal foil was 200 µm thick, representing about a 20 fold excess capacity relative to the LTO electrodes. All cells were cycled using a BT2000 battery cycler (Arbin Instruments). For characterization of the Li electrode morphology/composition after cycling, the cells were dissembled and the Li electrodes were retrieved after thorough washing with DME three times followed by drying in vacuo at room temperature.

Electrochemical impedance spectroscopy measurements were carried out on a VMP3 potentiostat/galvanostat station with EIS/Z capabilities (Bio-Logic Science Instruments). The DC voltage was maintained at open-circuit voltage and an AC voltage of 5 mV in amplitude was applied with a frequency of 200 kHz–20 mHz. Cyclic voltammetry experiments were conducted using protected copper foil as the working electrode and Li foil as the working counter and reference electrodes. A scan rate of 2 mV/s in the voltage window of -0.5 to 2V was used.
The Li$^+$ transference number was measured by DC polarization. Typically, 80 mg of the $\beta$-Li$_3$PS$_4$ powder was placed between two stainless steel rods and pressed into a 10 mm diameter pellet by a hydraulic press at 2 tons for 3 min in an Ar-filled glovebox. The pellet was then soaked in a PDMS solution (PDMS: curing agent = 10:1, w/w, 20 wt% in toluene) overnight and dried in vacuo at 100 °C for 10 hours to cross-link the PDMS and remove the remaining toluene. The $\beta$-Li$_3$PS$_4$/PDMS hybrid pellet was then placed between two stainless steel electrodes and pressed at 2 tons, and a small dc bias 0.25 V was applied. The DC polarization time was 30 min in order to obtain steady-state current. Details of the calculation are shown in Figure S5.

In stripping/plating studies, the Coulombic efficiency of each cycle was calculated by the standard convention: namely, the amount of stripped Li divided by the amount of plated Li. The average CE over the first 100 cycles was then calculated based on the CE of each cycle. The standard deviation was calculated based on the average CE and a sample size of 100. In comparing cycling data shown in Figure 4 for bare Cu and LPS-PDMS coated Cu, if we assume the CE loss can represent the amount of the electrolyte decomposed, then the protective film results in a decrease in electrolyte degradation of about 83% (i.e. 1-((100-95.8)/(100-75.30))).

**Material Characterization**

X-ray diffraction patterns were collected on a Bruker D8-Advance X-ray diffractometer, operating at 40 kV/30 mA with Cu-Kα radiation. A LEO 1530 field emission SEM (Zeiss) was used for SEM imaging. The cross-section of Li was carefully cut with a ceramic knife. XPS analysis was performed on a Thermo ESCALAB 250 instrument, using a monochromatic Al Kα source. The cross-section of Li was prepared by cutting with a ceramic knife. The samples for SEM and XPS measurements were transported to the instrument in an air-tight vial and anaerobically transferred into the chamber. All XPS spectra were fitted with Gaussian-Lorentzian functions and a Shirley-type background. The binding energy values were all calibrated using the C 1s peak at 284.8 eV. Fourier transform infrared spectroscopy was carried out on a Bruker Tensor 37 spectrometer to characterize the successful cross-linking of PDMS by the curing agent. Samples were prepared by dip coating of the PDMS or the blended solutions onto a pressed KBr pellet. The electrolyte swelling experiment was performed by soaking a cross-linked PDMS film in the electrolyte for 48 hours. The weight of the film after and before treatment ($M_t, M_o$, respectively) was used to calculate the change: $(M_t - M_o)/M_o \times 100\%$. 
Figure S1. Conductivity measurement and the X-ray diffraction pattern of the nanoporous β-Li$_3$PS$_4$ phase. (a) Nyquist plot of the EIS measurement on a pressed nanoporous β-Li$_3$PS$_4$ pellet (Φ 10 mm, 3 ton) with a thickness of 0.7 mm. The semi-circle in the inset represents the bulk resistance of the pressed pellet; the value of ionic conductivity is calculated based on the intercept of the straight line with the x-axis (Re Z). The conductivity is calculated to be 1.54 ×10$^{-4}$ S cm$^{-1}$. (b) XRD pattern of the as-synthesized β-Li$_3$PS$_4$. 
Figure S2. Morphological characterization of the precursors and membrane. (A) The surface SEM image of the pressed Li$_3$PS$_4$ before PDMS infiltration. (B) The cross-section SEM images of the LPS-PDMS membrane and (C,D) the surface SEM images of the hybrid membrane fabricated by infiltrating PDMS solution diluted at a (C)1:15 and (d)1:4 ratio.

Figure S3. Fourier-transform infrared spectroscopy study of the PDMS oligomer, physical blend and the cross-linked PDMS. The peaks at 1600 cm$^{-1}$ (C=C bond) and 2170 cm$^{-1}$ (-Si-H) are significantly weakened in the cross-linked polymer, indicating successful cross-linking of PDMS.
Figure S4. SEM-EDX mapping of the semi-cross section of the LPS-PDMS film. (A) The element overlapped SEM image (the dotted line outlines the cross-section area, above which is the surface) and (B-D) the corresponding mapping of S, Si and Cu. The Cu map region indicates where the underlying Cu substrate lies. We observe that the S (in Li$_3$PS$_4$) and Si (in PDMS) maps overlap with each other, indicating effective infiltration of PDMS.

Figure S5. Current response during the DC polarization relaxation for transference number measurement. The initial current obtained from DC polarization is $i_i = 0.0633$ mA which is the total current from Li$^+$/e$^-$/ diffusion inside the pellet. The steady-state current after 30 min polarization is $i_{ss} = 9.42 \times 10^{-6}$ mA which corresponds to the current from electronic conductivity.

The transference number $t_{Li} = (i_i - i_{ss})/i_i = (0.0633 - 1.04 \times 10^{-5})/0.0633 = 0.9998$. 
Figure S6. Elemental mapping of the Li plated electrode with both bare and protected areas. (A) The back-scattered SEM image and (B) the phosphorus EDX mapping of the junction area of a Cu electrode surface after Li plating, where the left side is bare Cu and the right side is coated with LPS-PDMS. The dendritic Li shows a darker contrast than the LPS-PDMS membrane, which is correlated to the phosphorus mapping in (B).

Figure S7. Cyclic voltammetry of Li plating/stripping showing the stability of hybrid membrane. First cycle CV curve of the cell using protected Cu foil as the working electrode, a Li foil as the counter and reference electrode in a 1 M LiPF₆ EC/DMC electrolyte, at a scanning speed of 2 mV s⁻¹. No redox peaks are observed that can be ascribed to the membrane, showing the stability of the membrane.
Figure S8. X-ray photoelectron spectroscopy of the pristine and Li plated membrane surface. High-resolution Si 2p XPS spectra of the pristine LPS-PDMS coated electrode, and after 4 mA h cm$^{-2}$ Li plating. One 2p component consists of the 2$p_{1/2}$ and 2$p_{3/2}$ doublets, whose relative area and energy spacing was constrained according to practice. By convention, the energy of the 2$p_{3/2}$ component is quoted.
Figure S9. The Li plating/stripping coulombic efficiency of different Cu electrodes. (A) The Coulombic efficiency (CE) evolution of the Li plating/stripping on bare Cu, Cu coated with PDMS only (Cu-PDMS), β-Li$_3$PS$_4$ only (Cu-LPS) and LPS-PDMS (Cu-LPS-PDMS) on cycling at 1 mA cm$^{-2}$ and 1 mA h cm$^{-2}$ capacity per cycle. (B) The CE evolution of Li plating/stripping on a Cu electrode coated with a physical mixture of LPS and PDMS, compared to that coated using the two-step method (pressing-infiltration). (C) The 2$^{nd}$ cycle voltage profile of the cell using the mixed-LPS/PDMS - coated Cu electrode.
Figure S10. The Li plating/stripping coulombic efficiency at an intermediate capacity. Evolution of Li plating/stripping with cycling on bare Cu and Cu-LPS-PDMS at 1 mA cm\(^{-2}\) and 2 mA h cm\(^{-2}\) capacity per cycle.

Figure S11. The Li plating/stripping coulombic efficiency at high current and capacity. Evolution of Li plating/stripping with cycling on bare Cu and Cu-LPS-PDMS at 4 mA cm\(^{-2}\) and 2 mA h cm\(^{-2}\) capacity per cycle.
Figure S12. Electrochemical performance of the protected Li electrode coupled with LTO electrodes.  
(A) The 2nd and (B) 100th cycle voltage profiles of the LTO|Li cells using unprotected Li and LPS-PDMS protected Li (Li-LPS-PDMS), with the voltage polarization labelled. (c) The evolution of energy efficiency (EE) of LTO|Li cells over 2000 cycles at 5C.