

Supporting Information

Continuous Covalent Organic Framework Membrane as Artificial Solid Electrolyte Interphase for Lithium Metal Anode

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Methods

Materials

Monomers 2,4,6-trihydroxybenzene-1,3,5-tricarbaldehyde (Tp) and 2,5-diaminobenzenesulfonic acid (PaSO₃H) were purchased from Ambeed and Sigma Aldrich, respectively. *n*-Octanoic acid was purchased from TCI America. De-ionized (DI) water was processed using Millipore Milli-Q system for all aqueous solutions. Ethyl alcohol (EtOH) and tetrahydrofuran (THF) were purchased from The Warner-Graham Company and Sigma Aldrich, respectively. Sodium acetate (NaAc) was purchased from Sigma Aldrich.

Electrolyte solvents, 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME), were purchased from Sigma Aldrich. Lithium bis(trifluoromethane)sulfonimide (LiTFSI) and lithium nitrate (LiNO₃) were purchased from TCI and Thermo Scientific, respectively. Coin cells were made using stainless steel 304SS CR2032 coin cell case sets purchased from MSE Supplies. Battery grade lithium chips (12 mm diameter, 0.6 mm thickness) were also purchased from MSE Supplies. Copper foil (25 μm thickness) was purchased from MTI Corporation. Polyvinylidene fluoride (PVDF) membrane (0.22 μm, hydrophilic, 47 mm diameter) was purchased from Millipore.

COF Synthesis

Different Phase Interfacial Synthesis

The membrane was synthesized in a cylindrical 60 mL jar with a base diameter of 5.5 cm. For the organic phase, 0.15 mmol Tp monomer was sonicated until it was fully dissolved in 20 mL *n*-octanoic acid. For the aqueous phase, 0.225 mmol PaSO₃H monomer was sonicated until it was fully dissolved in 30 mL DI water. A PVDF membrane was placed at the bottom of the jar. Then the aqueous solution was poured into the jar, followed by the organic solution, which was added dropwise slowly on top of the aqueous solution. Then, the jar was left in ambient conditions for 72 hours until a thin layer of membrane was formed at the interface.

Different Phase Interfacial Synthesis with Activator

The same procedure was followed as above, except for 0.225 mol NaAc, which was dissolved in DI water together with the PaSO₃H monomer. The jar was left in ambient conditions for 24 hours until a thin layer of membrane was formed at the interface.

Same Phase Interfacial Synthesis with Activator

For same-phase interfacial synthesis, both the Tp (0.15 mmol) and the PaSO₃H (0.225 mmol) monomers were dissolved in 20 mL of *n*-octanoic acid to form the organic phase. Only NaAc was dissolved in 30 mL DI water to form the aqueous phase. The concentration of NaAc varied from 0.113 mmol (0.5 equivalent mole ratio to PaSO₃H), 0.225 mmol (1.0 equivalent), and 0.45 mmol (2.0 equivalent). The jar was left in ambient conditions for 24 hours until a thin layer of membrane was formed at the interface.

When the buffer layer was added, all other conditions were kept the same, except the monomers were dissolved in 15 mL *n*-octanoic acid to form the organic phase. 8 mL of pure *n*-octanoic acid was added as a buffer layer on top of the aqueous phase first, followed by the addition of the organic phase.

Membrane Collection and Washing

The membrane was collected by removing both the organic phase and the aqueous phase. First, the top organic phase was removed using a transfer pipette. Then, the aqueous phase was removed carefully using a transfer pipette until the synthesized membrane was naturally loaded on top of the PVDF membrane present in the jar. The synthesized membrane was washed multiple times with ethanol, THF, and DI water and dried inside a vacuum desiccator overnight before being used for testing and applications.

Coin cell Assembly

All coin cells were made inside an argon-filled glovebox with oxygen content below 1 ppm and water content below 0.1 ppm. Electrolyte was prepared by mixing DOL and DME at 1:1 v/v ratio with 1M LiTFSI and 2 wt% LiNO₃. Both LiTFSI and LiNO₃ were baked at 100 °C under vacuum for 7 days to remove water content before use. All coin cells were made using the same electrolyte unless noted.

Li|Cu half-cells were assembled with Cu foil disk (d = 14.3 mm) and Li chip (d = 12 mm) as the two electrodes. 75 μL of the DOL/DME electrolyte was used with PVDF membrane (d = 16 mm) as the separator. Two pieces of spacers were used for every cell. For coin cells with COF membrane, the COF-coated PVDF membrane (d = 16 mm) was loaded on the Cu foil disk directly, with the COF side facing the Cu foil.

Materials Characterization

Scanning electron microscopy (SEM) images were taken using a Thermo Fisher Helios G4 UC FIBSEM. All COF samples were sputter-coated with platinum (thickness = 10 nm) using a Leica EM ACE600 Sputter-Coater to increase the conductivity of the material. For *ex-situ* lithium deposition observations, cycled coin cells were transferred back to the glovebox, where they were de-crimped. Cu foil with deposited lithium was removed from the coin cell, gently washed with DME solvent, and dried in the glove box. Once dried, the samples were sealed and transferred to SEM for characterization.

Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) was conducted on a ThermoNicolet Nexus 670 FTIR spectrometer. Powder X-ray diffraction (PXRD) was measured on a Malvern Panalytical Aeries powder X-ray diffractometer.

Electrochemical Measurements

All cyclic voltammetry measurements were conducted on a BioLogic SP-150 Potentiostat with a scan rate of 1 mV s^{-1} . All galvanostatic charge/discharge testing was done on LANDT CT3002AU Battery Testing System.

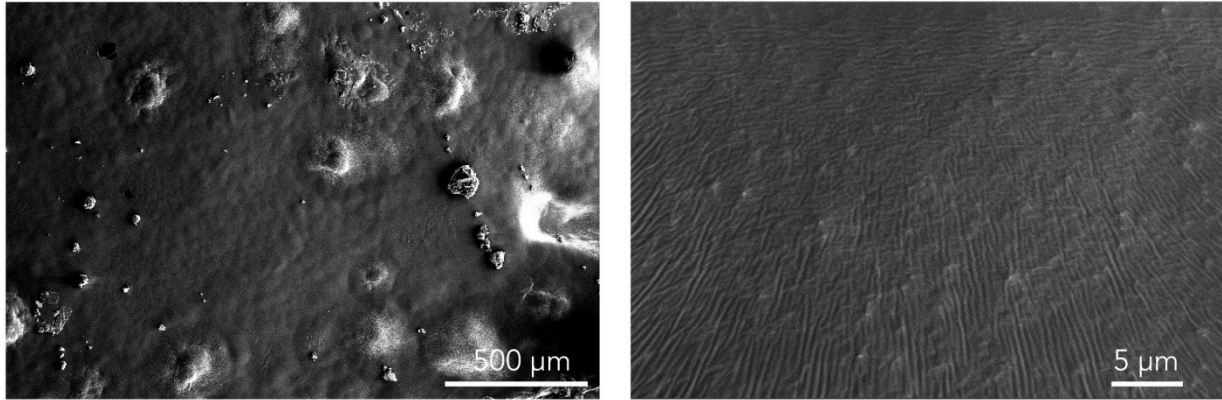


Figure S1. SEM images of Tp-PaSO₃H COF obtained via different-phase synthesis and transferred to a PVDF membrane. Although the membrane has a smooth morphology, it is mechanically fragile and cannot be transferred to foreign substrates in a defect-free manner.

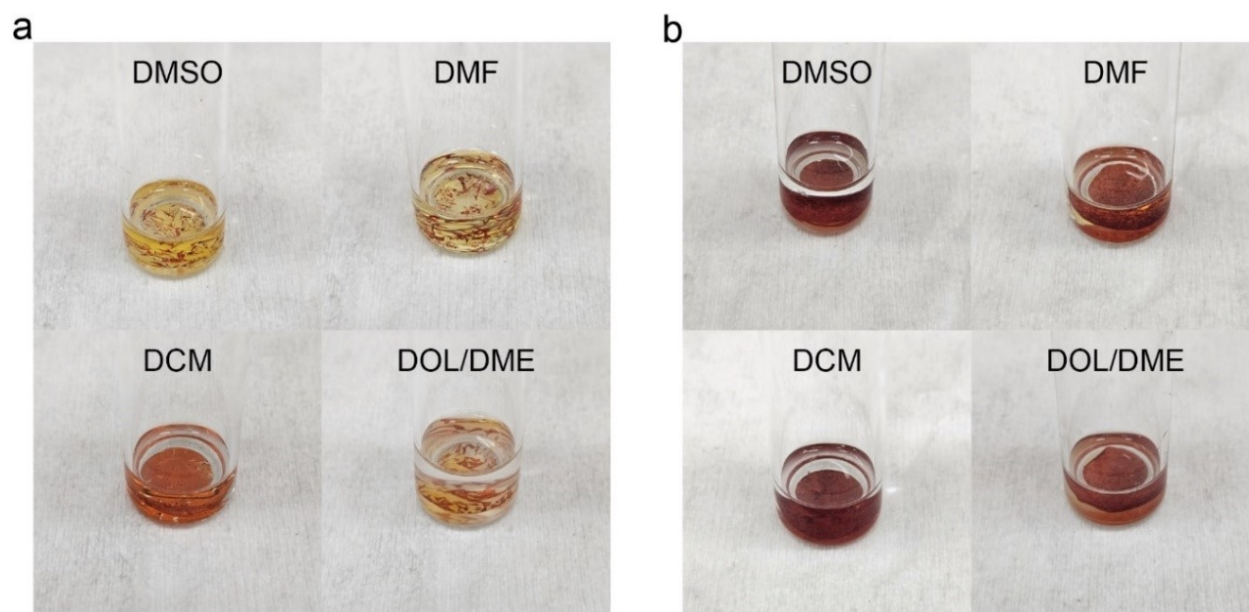


Figure S2. Tp-PaSO₃H COF obtained via **a**, different-phase synthesis with activator and **b**, same-phase synthesis with activator in different organic solvents.

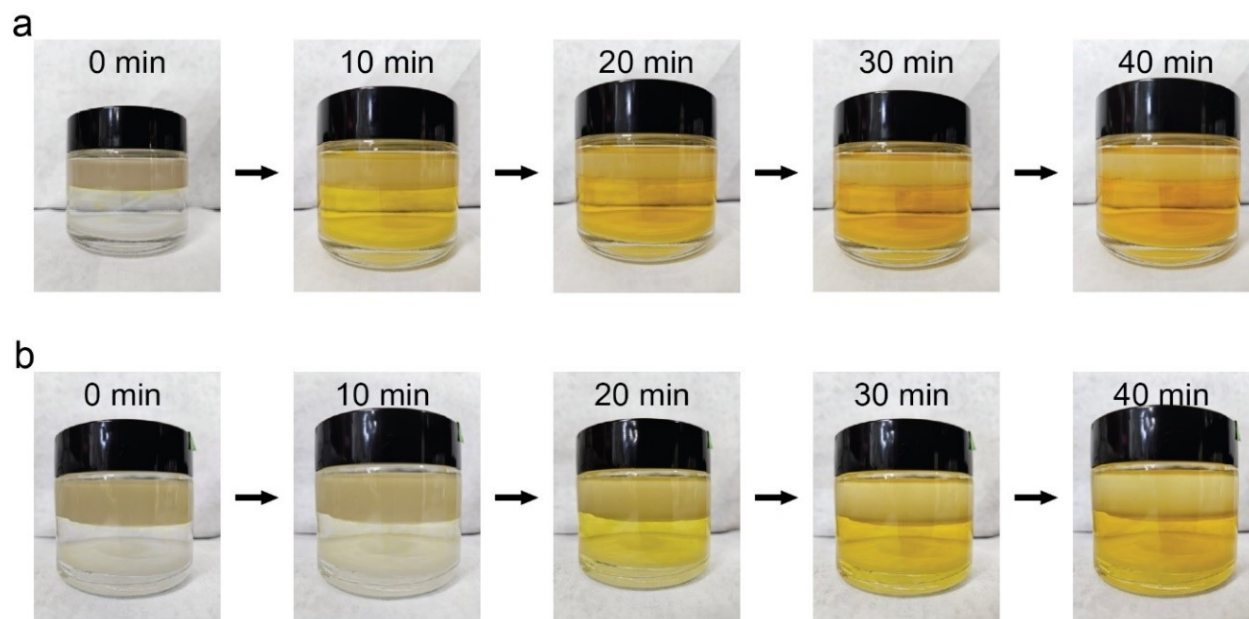


Figure S3. Digital images of same-phase interfacial synthesis in the first 40 minutes of reaction **a**, without buffer layer and **b**, with buffer layer. Based on the degree of color change, the addition of the buffer layer slowed the diffusion of monomers to the interface, preventing abrupt reactions between the monomers and the activators to afford a smoother and more uniform COF membrane.

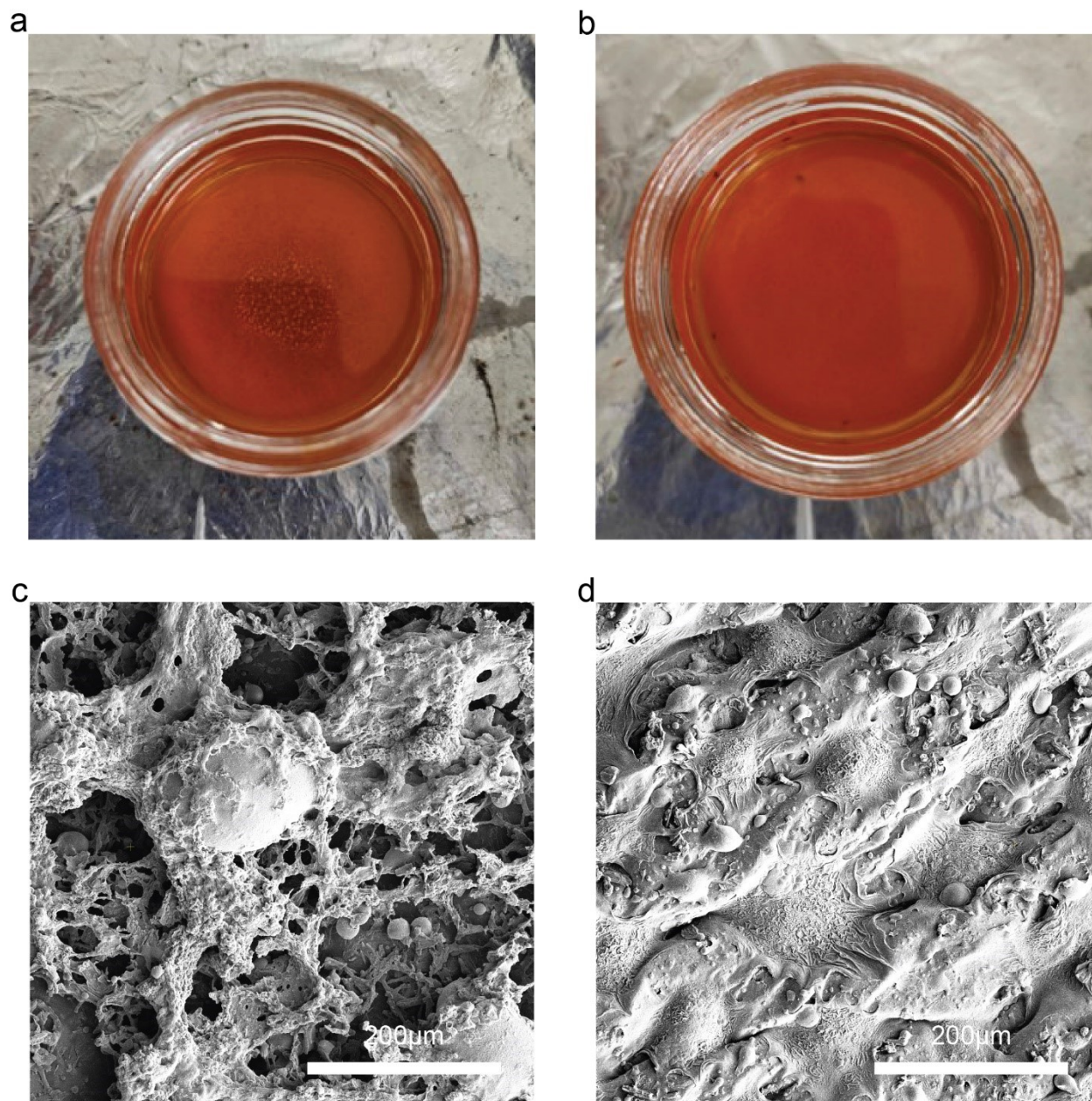


Figure S4. Digital images of the Tp-PaSO₃H COF membrane after 24 hours of synthesis **a**, without buffer layer and **b**, with buffer layer. SEM Images of Tp-PaSO₃H membrane synthesized **c**, without buffer layer and **d**, with buffer layer.

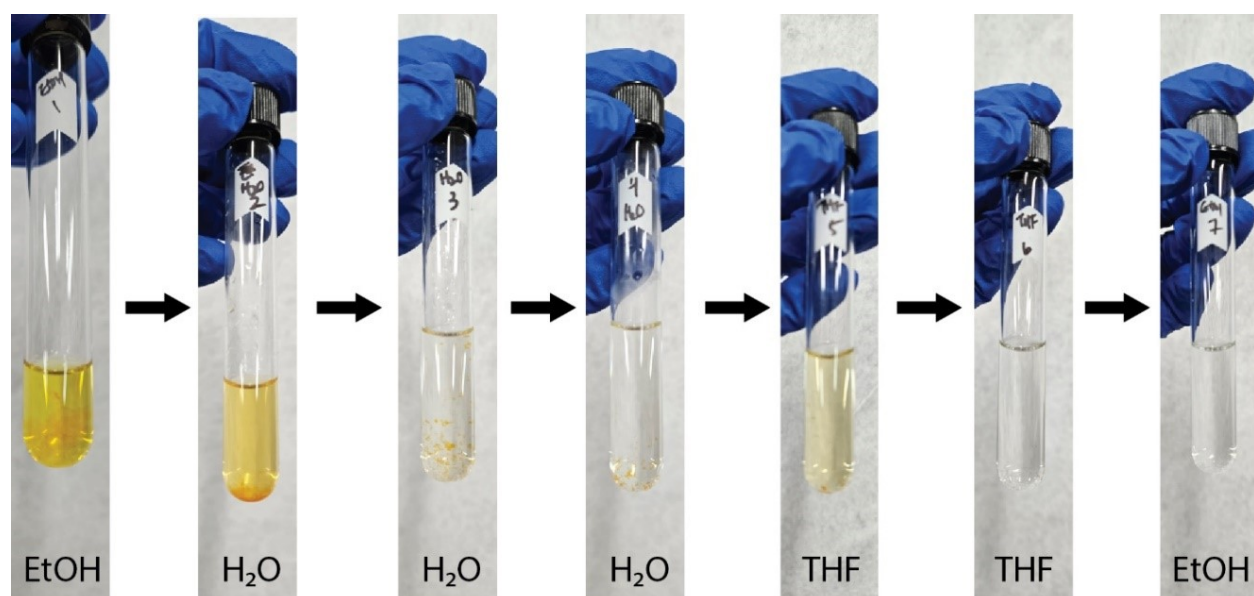


Figure S5. Digital images of solvents (EtOH, water, and THF) extracted after washing the membrane.

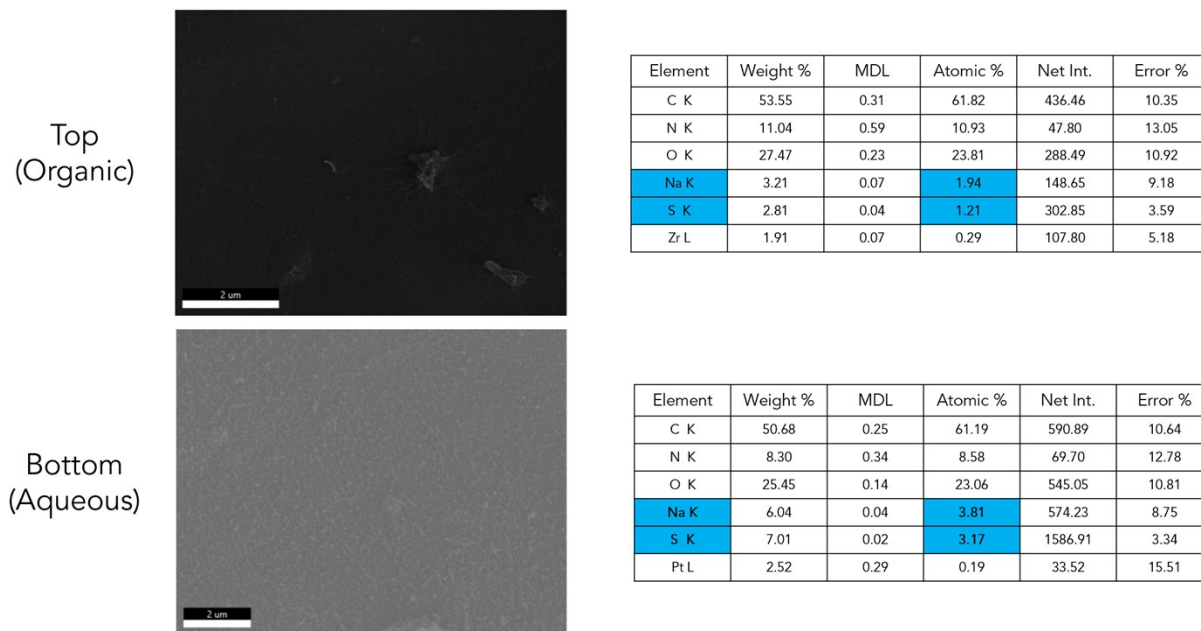


Figure S6. Energy-dispersive X-ray elemental analysis of the COF film after the washing protocol.

a



b

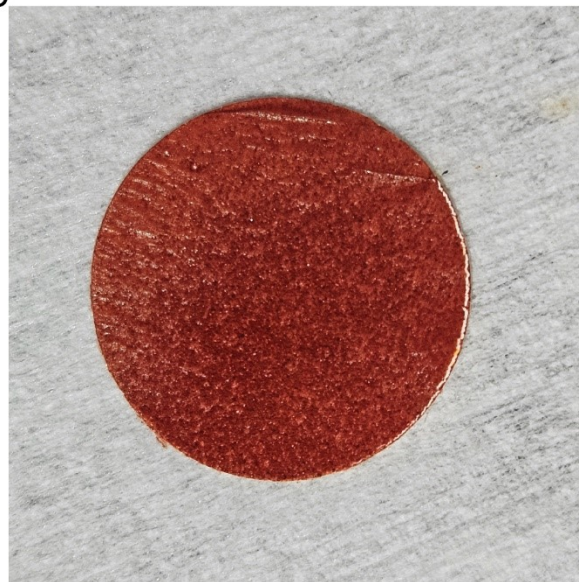


Figure S7. Digital images of Tp-PaSO₃H COF membrane synthesized with **a**, 0.5 equivalent NaAc and **b**, 2.0 equivalent NaAc.

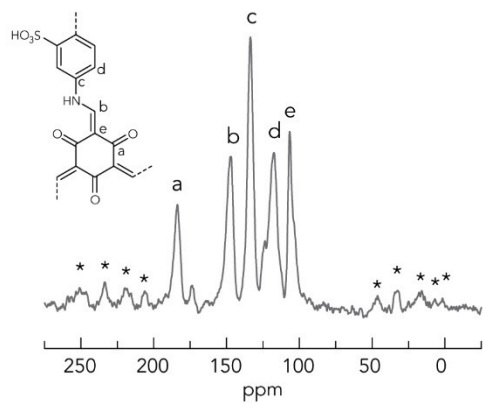


Figure S8. Solid-state ^{13}C NMR of Tp-PaSO₃H COF (asterisks are spinning sidebands).

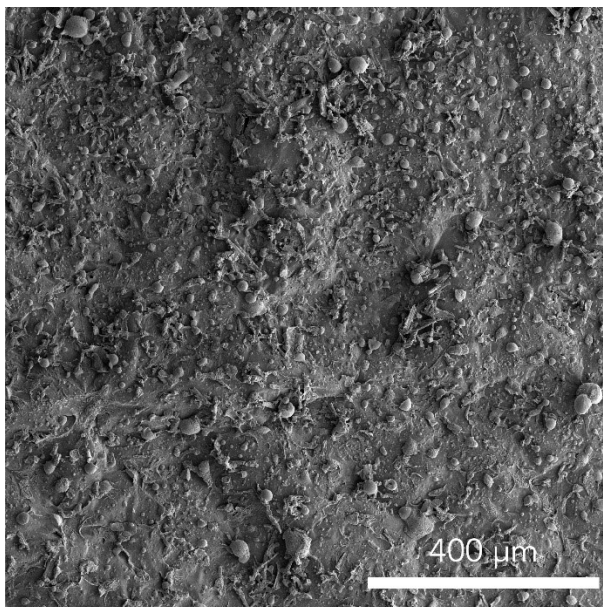


Figure S9. Low-magnification SEM image of Tp-PaSO₃H COF membrane obtained using the same-phase synthesis method.

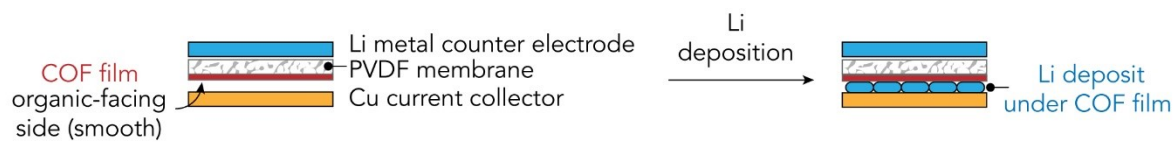


Figure S10. Schematic showing the layout of the COF thin film with respect to Cu current collector in the battery configuration for electrochemical measurements.

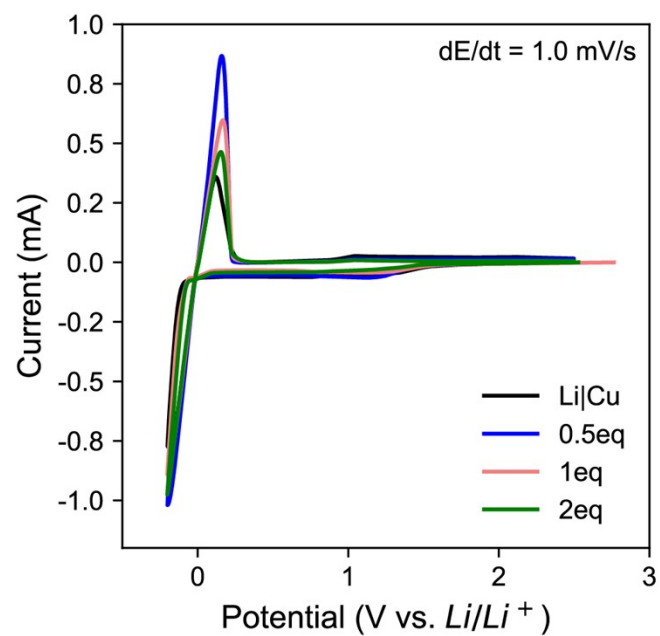


Figure S11. Cyclic voltammograms of Li|Cu control cell and Li|Cu-COF cell with Tp-PaSO₃H aSEI layer obtained at varying sodium acetate concentrations.

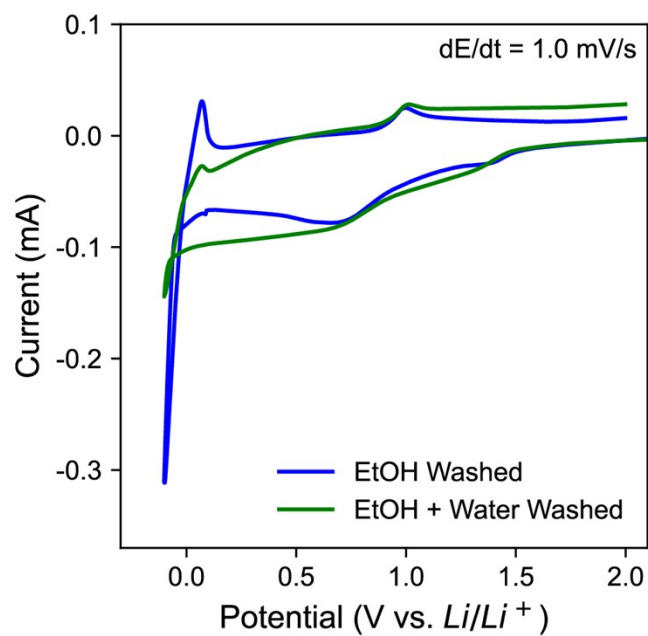


Figure S12. Cyclic voltammograms of Li|Cu-COF cell with Tp-PaSO₃H aSEI layer washed only using ethanol and washed only using ethanol and water.

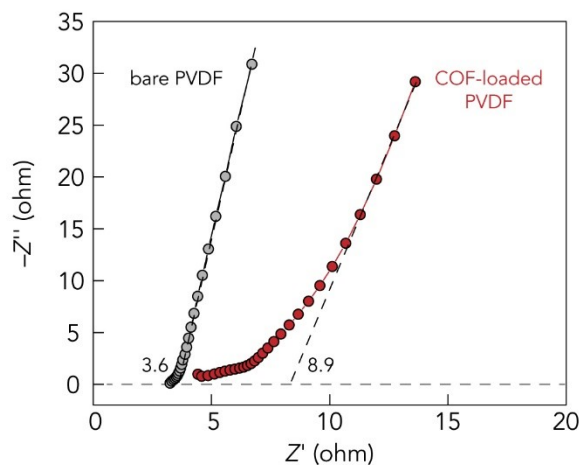


Figure S13. Electrochemical impedance spectroscopy of bare PVDF membrane and COF-loaded PVDF membrane. Both membranes were 1 cm² and soaked in 1 M LiTFSI DOL/DME electrolyte. The ionic conductivity of bare PVDF + electrolyte is ~3.6 ohm cm², while that of COF-loaded PVDF + electrolyte is ~8.9 ohm cm². Therefore, the impedance of the COF thin film is ~5.3 ohm cm².

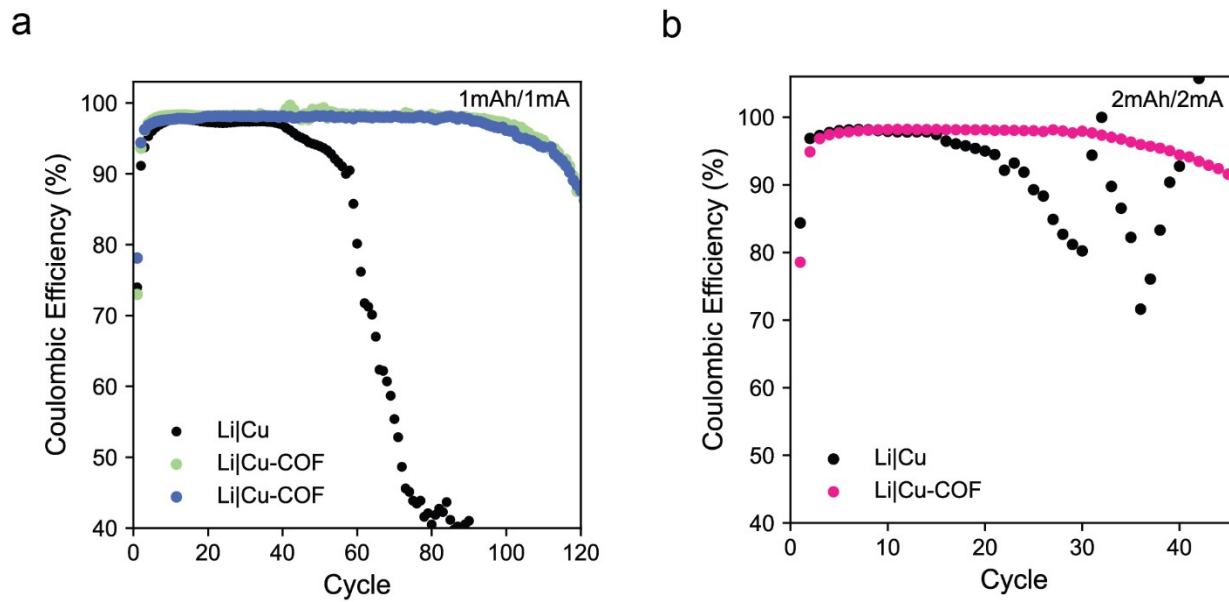


Figure S14. a, Repeated measurement of the CE of Li|Cu control cell and Li|Cu-COF cell with a cycling current of 1 mA cm⁻² (1 mAh cm⁻² capacity). **b**, Repeated measurement of the CE of Li|Cu control cell and Li|Cu-COF cell with a cycling current of 2 mA cm⁻² (2 mAh cm⁻² capacity).

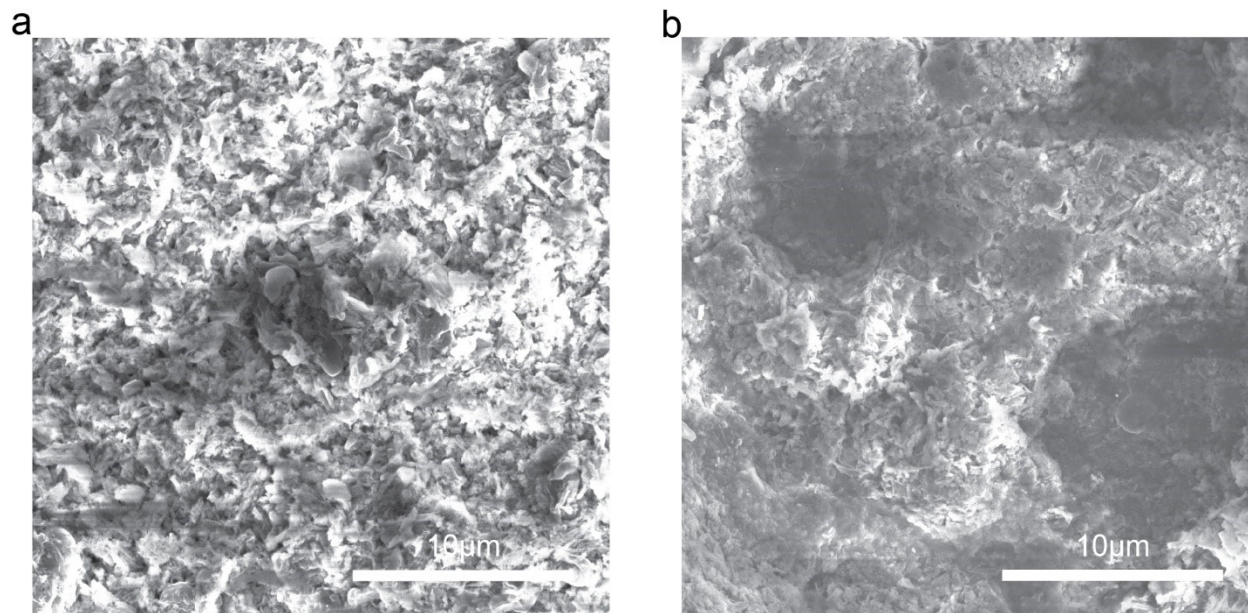


Figure S15. SEM images of Li deposited onto **a**, bare Cu current collector and **b**, Cu current collector protected by Tp-PaSO₃H aSEI at a current of 1 mA cm⁻² and capacity of 1 mAh cm⁻² after 20 plating/stripping cycles.