

Supporting Information

A Self-Supporting Covalent Organic Framework Separator with Desolvation Effect for High Energy Density Lithium Metal Batteries

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Experimental Procedures

Materials

All the materials and solvents were purchased from commercial sources without further purification. 2,4,6-trihydroxy-1,3,5-benzenetricarboxaldehyde (TP, 95%), 3,3'-dihydroxy-4,4'-diaminobiphenyl [BD(OH)₂, 95%], p-toluenesulfonic acid (PTSA, 98%) were purchased from ShanghaiTengqian Biological Technology Co., Ltd. N, N-dimethylacetamide (DMAc, 99%) and acetone (99.5%) were purchased from Alpha. Ester electrolyte [1M LiPF₆ in EC/EMC (3:7 by wt%)] was purchased from Suzhou Duoduo Chemical Technology Co., Ltd.

Preparation of self-supporting TPB-BD(OH)₂-COF separator

0.6 mmol 2,4,6-trihydroxy-1,3,5-benzenetricarboxaldehyde (TP), 0.9 mmol 3,3'-dihydroxy-4,4'-diaminobiphenyl [BD(OH)₂] and 0.68g p-toluenesulfonic acid (PTSA) were ground in a mortar for 5 minutes. After mixing uniformly, an appropriate amount of deionized water was added to the mixture. By this time, a dough was formed, which was then knife-cast on a clean glass plate. The self-supporting TPB-BD(OH)₂-COF separator was obtained after the glass plates was placed in the oven at 90 °C for 72 hours. The obtained separator was washed three times with DMAc, acetone and deionized water, respectively. Finally, a brown-red self-supporting TPB-BD(OH)₂-COF separator with a continuous surface without cracks was collected¹.

Preparation of self-supporting TPB-BD(OH)₂-COF/PVDF(COF/PVDF) separator

The obtained self-supporting TPB-BD(OH)₂-COF separator was spread on a clean glass plate, and the PVDF solution with a mass fraction of 15% was poured on the surface of the separator. Then the knife coating method was used to distribute the PVDF solution on the self-supporting separator uniformly. Similarly, the COF/PVDF composite separator was obtained after drying the glass plate in a vacuum drying oven at 90 °C for 12 hours. Then the COF/PVDF composite separator was cut into a size suitable for lithium metal batteries.

Electrochemical characterization

To fabricate the LiNi_{0.5}Mn_{1.5}O₄(LNMO) cathode, 0.8 g LNMO, 0.1 g Super-P and

0.1 g polyvinylidene fluoride (PVDF) were physically mixed for 6 hours to get a sticky slurry before evenly coated it onto the surface of Al foil by a scraper. Then coating was place in a vacuum drying oven at 100 °C for 12 hours. After that, LNMO-coated Al foil was cut into circular pieces with a diameter of 12 mm, and the area of LNMO loading was about 2-3 mg cm⁻².

CR2016 coin cells were assembled in an argon-filled glove box (the water and oxygen value were less than 0.1 ppm). For Li-LNMO full batteries assembled with different separators, before testing, different separators were used to assemble a Li-Cu half-cell, and then lithium metal was deposit with a capacity of 5 mAh cm⁻² on the copper foil at a current density of 0.5 mA cm⁻². Then the copper foil with a deposition capacity of 5 mAh cm⁻² lithium metal, 1M LiPF₆ in EC/EMC (3:7 by wt%), LNMO and three kinds of separators (COF/PVDF, PVDF and celgard separator) were assembled to full batteries, respectively. It should be noted that when a COF/PVDF separator is used to assemble a battery, the reverse side of the separator is always in direct contact with lithium metal. Meanwhile, the COF/PVDF separator absorbs the diluted electrolyte in advance, then wiping the electrolyte on the surface of the separator with filter paper. Finally, the separator is placing at 60 °C for vacuum drying for two hours to obtains the desolvated electrolyte, the full cell assembled with the other separators were used diluted electrolyte. In tests in harsh environments, different separators were assembled into Li-LNMO half-cells for testing at 60 °C. For PVDF separator and celgard separator, the amount of diluted electrolyte is only 10 μL, while the processing steps for COF/PVDF separator are the same as the steps for assembling a full battery. Galvanostatic charge/discharge tests were performed in the potential range of 3.5 V and 4.9 V by using a LAND CT2001A multichannel battery testing system at different temperatures. Li-Li and Li-Cu symmetrical cells were also assembled using diluted electrolyte and electrolyte treated with COF/PVDF separator, respectively.

Characterizations

The morphology of TPB-BD(OH)₂-COF and COF/PVDF separators were characterized with scanning electron microscopy (TESCAN, MIRA3). The crystalline nature of TPB-BD(OH)₂-COF and COF/PVDF separator was measured by XRD (Bruke,

D8. $2\theta=2^{\circ}\sim 30^{\circ}$ and $2^{\circ}\sim 90^{\circ}$, voltage=40kV, current=40mA). The composition of the SEI film on the surface of lithium metal is measured by XPS (ThermoFisher, Thermo Scientific K-Alpha+, X-ray source: monochromatic Al Ka source, energy=1486.6eV, voltage=15KV). The coordination of the diluted electrolyte and electrolyte in the COF channel is evaluated by *ex-situ* attenuated total reflection Fourier transform infrared (ATR-FTIR) measurement (Bruker, Vertex 70). Before the ATR-FTIR testing, a certain amount of argon was introduced into the sample chamber of the infrared instrument in advance to remove water vapor and oxygen, and to ensure that the electrolyte is carried out under anhydrous and oxygen-free conditions.

Molecular dynamics (MD) theory calculation details

The simulation calculation was conducted on four structures with an integration time-step of 1 fs. Periodic boundary conditions were applied in the *x*- and *y*-dimensions. The box size of the samples was $6.5 \times 6.5 \times 4.5 \text{ nm}^3$. First, the conjugate gradient algorithm and energy minimization were performed to obtain a stable structure. Condensed-phased Optimized Molecular Potential for Atomistic Simulation Studies force field was also used to optimize these structures in the Materials studio with forcite Module. Each sample was then equilibrated under the NPT ensemble at a constant temperature of 300 K to achieve an equilibrium state with zero pressure for 50 ns. The equilibration molecular systems of the pure separation structure could be obtained after geometrically optimizing structure. One system of O/W separation was composed of 100LiPF₆-300EC-600EMC-TPB-BD(OH)₂-COF. Furthermore, a potential cutoff radius of 2.25 nm was applied in the calculation of the non-bonded interaction. And the PPPM was used to describe the electrostatic. The Andersen feedback thermostat and Berendsen barostat algorithm were applied in the system with temperature and pressure conversion. Finally, the properties of our structures were obtained in the last 3000 ps. The radial distribution functions (RDFs) and $g(r)$ give the probability of molecules occurring at the distance (r) from the atoms.

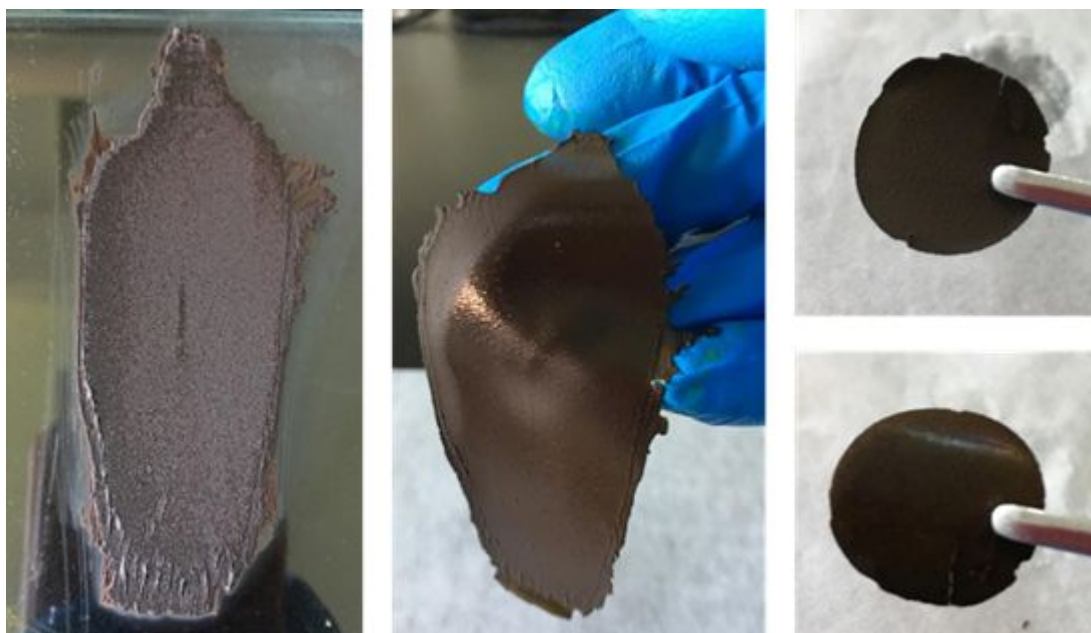


Figure S1. Optical images of the typical self-supported TPB-BD(OH)₂-COF separator.

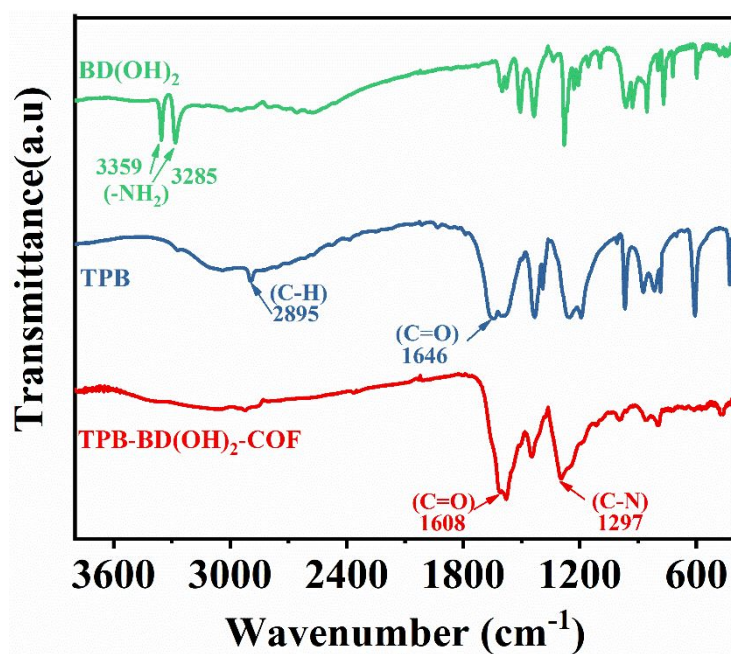


Figure S2. FT-IR spectra of BD(OH)₂, TPB and TPB-BD(OH)₂-COF.

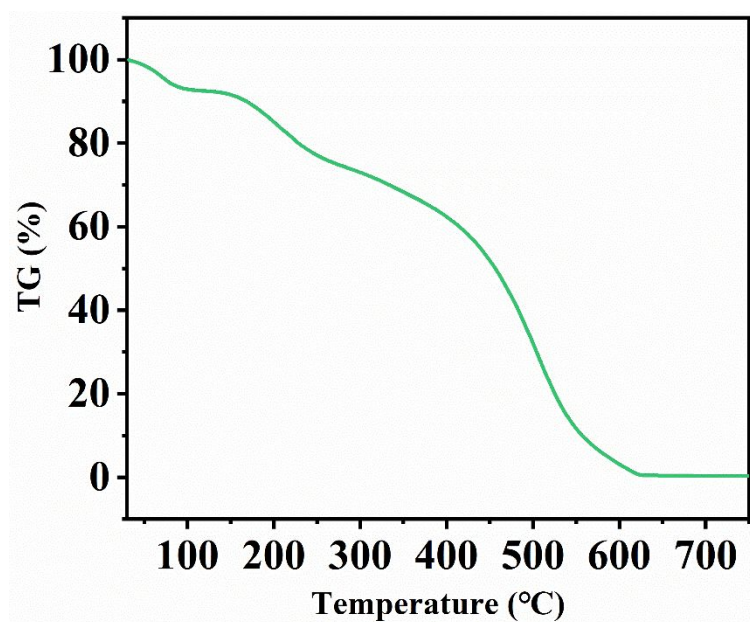


Figure S3. TGA curve of TPB-BD(OH)₂-COF under O₂ atmosphere.

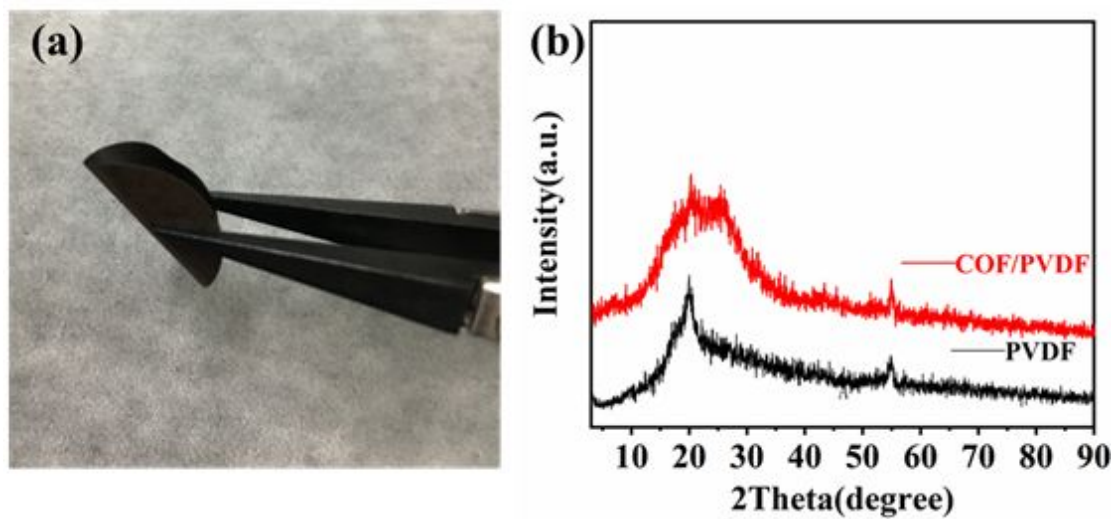


Figure S4. (a) The optical image of the flexibility test of COF/PVDF separator. (b) XRD patterns of COF/PVDF separator (red curve) and PVDF separator (black curve).

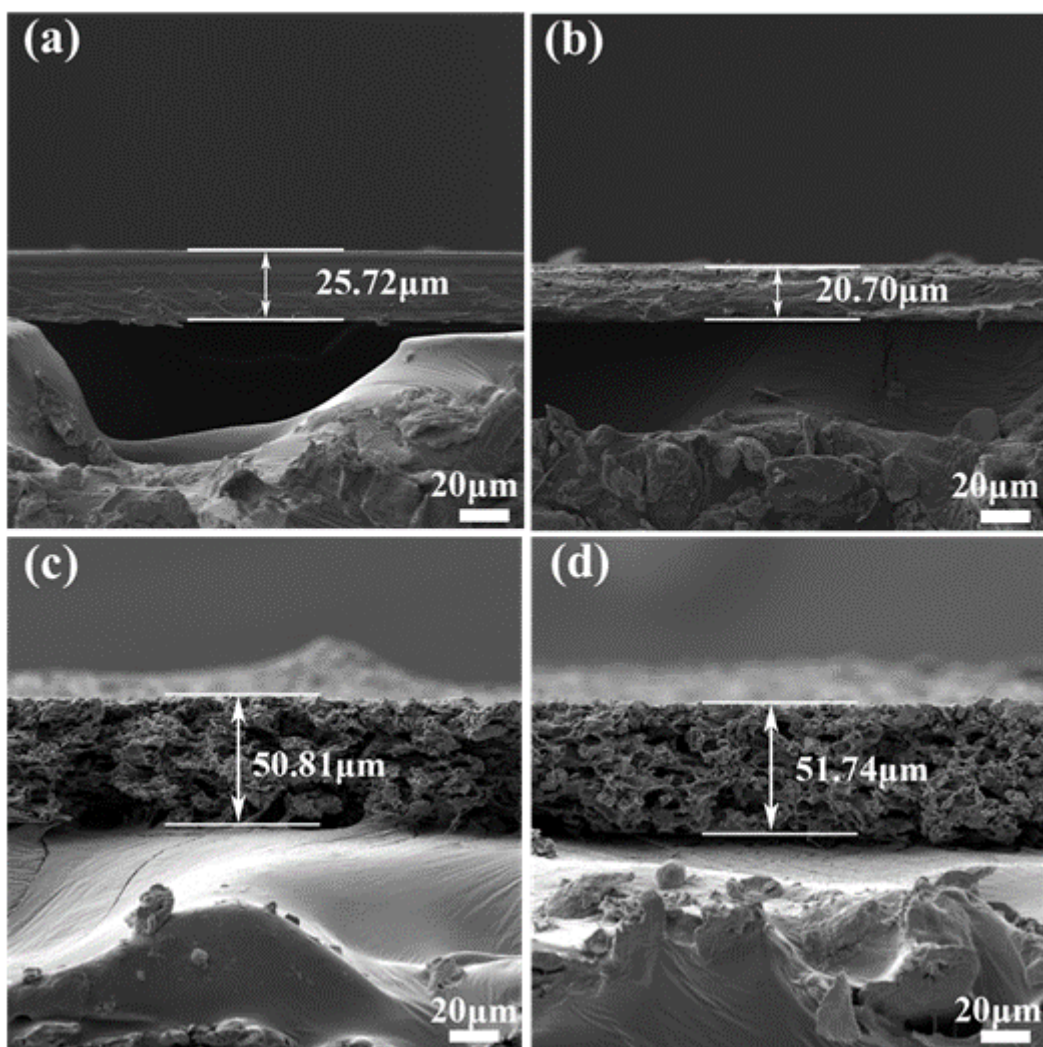


Figure S5. The cross-section SEM images of different kinds of separators: (a) PP separator, (b) PVDF separator, (c) TPB-BD(OH)₂-COF separator and (d) COF/PVDF separator.

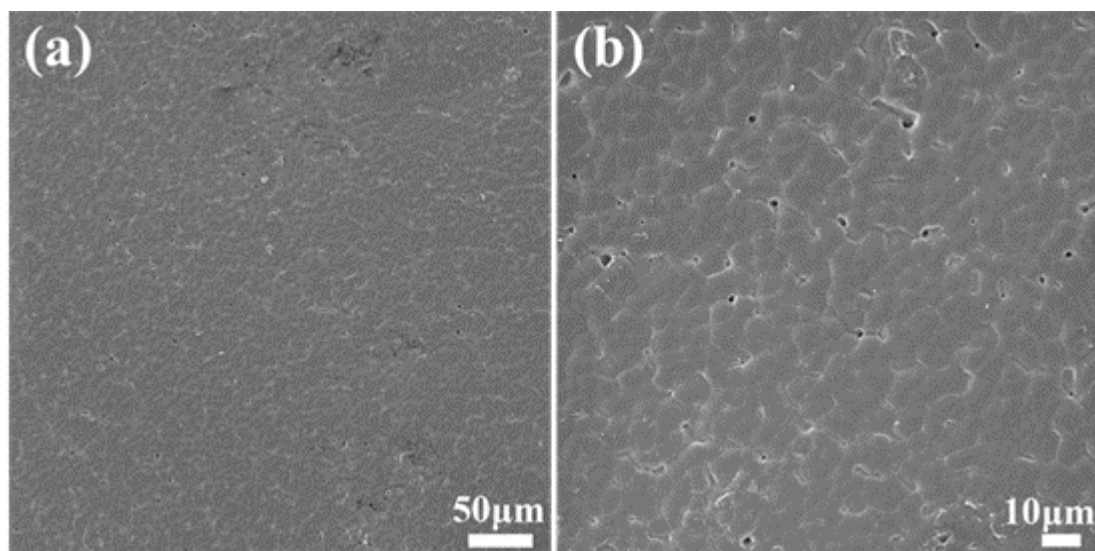


Figure S6. Different-magnification SEM images of PVDF separator.

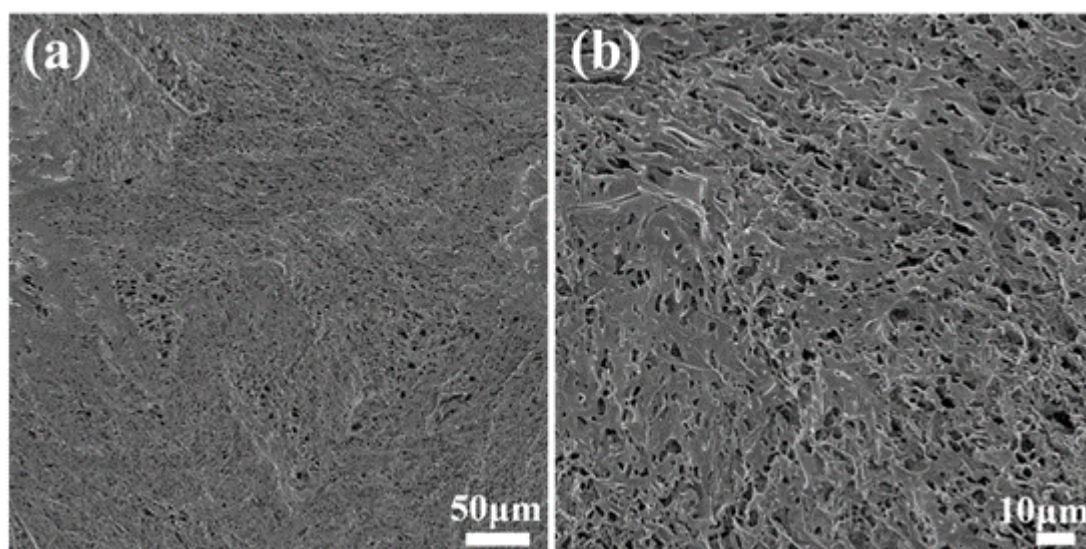


Figure S7. Different-magnification SEM images of the front side of TPB-BD(OH)₂-COF separator.

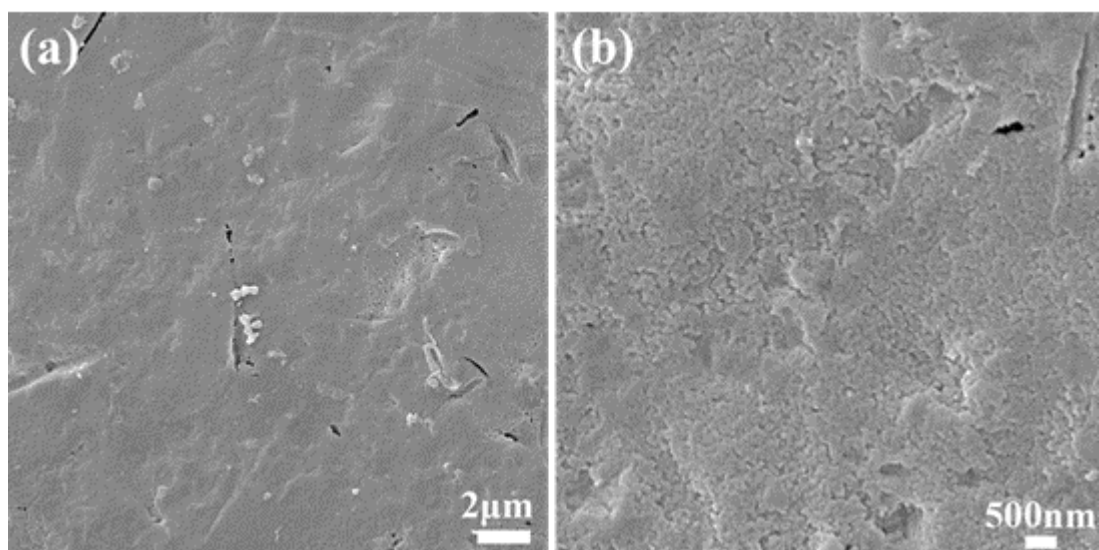


Figure S8. SEM images of the back of COF/PVDF separator under high magnification.

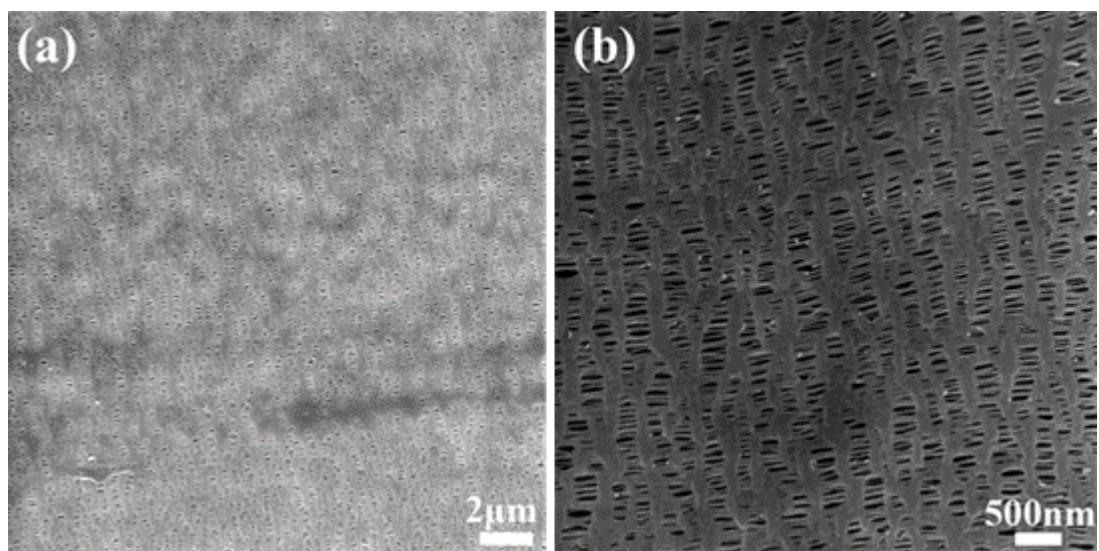


Figure S9. SEM images of the commercial celgard separator at high magnification.

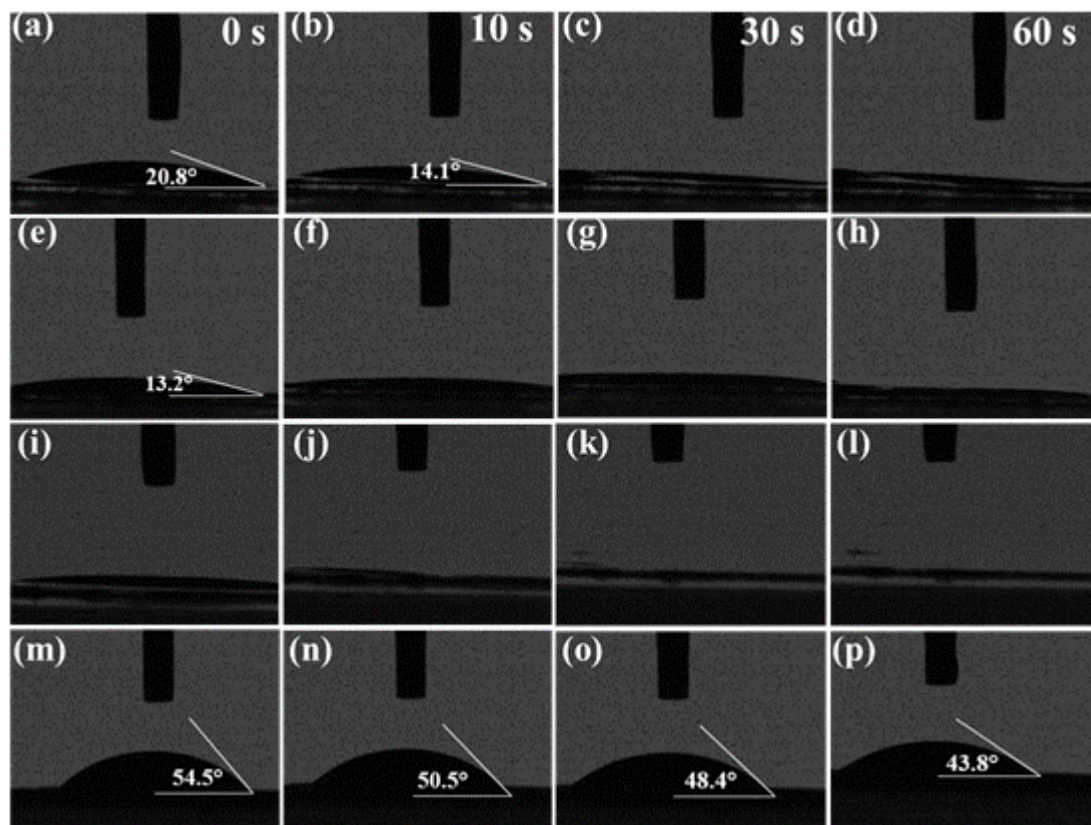


Figure S10. The photographs of contact angles of COF/PVDF separator, PVDF separator and commercial celgard separator with diluted electrolyte: (a-d) the back of COF/PVDF separator, (e-h) the front face of COF/PVDF separator, (i-l) PVDF separator, (m-p) commercial celgard separator.

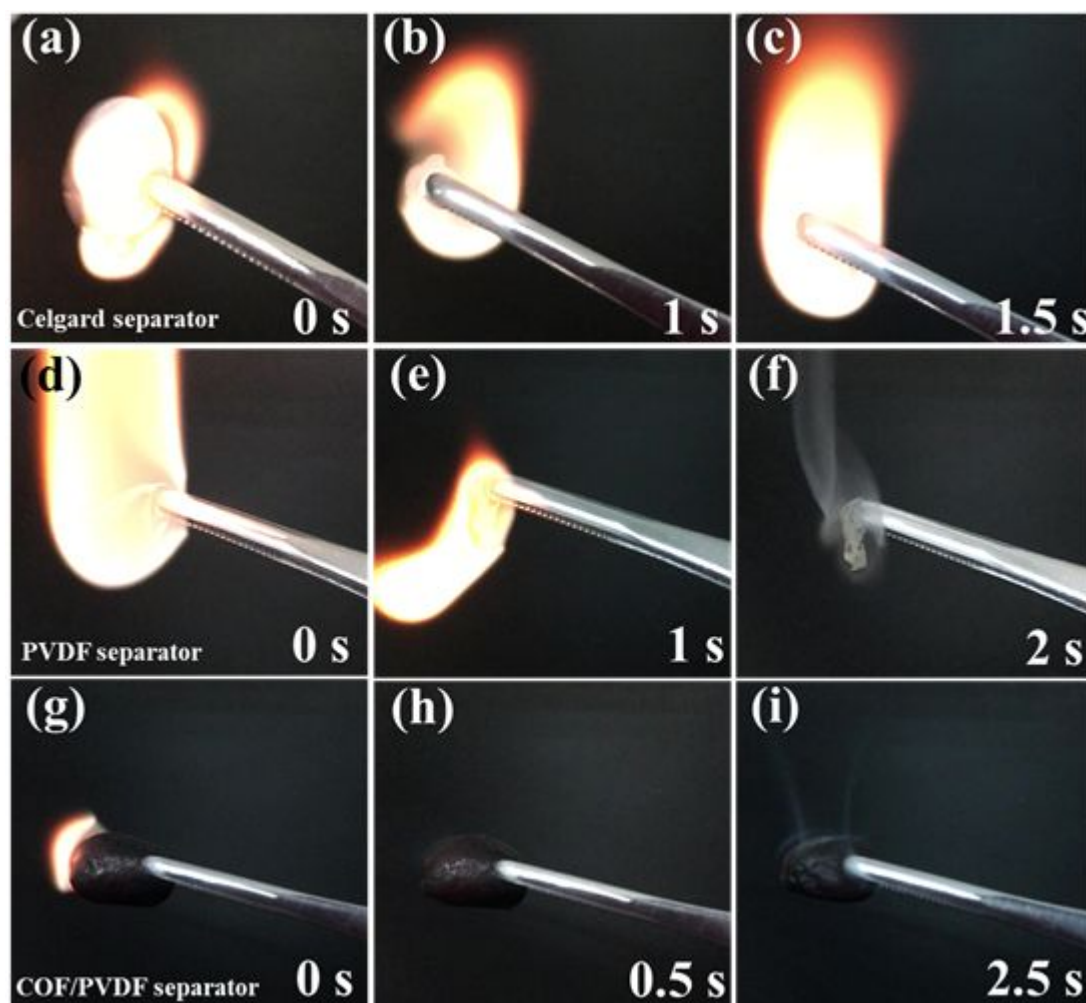


Figure S11. The combustion experiment of different separators with diluted electrolyte: (a-c) commercial celgard separator, (d-f) PVDF separator and (g-h) COF/PVDF separator.

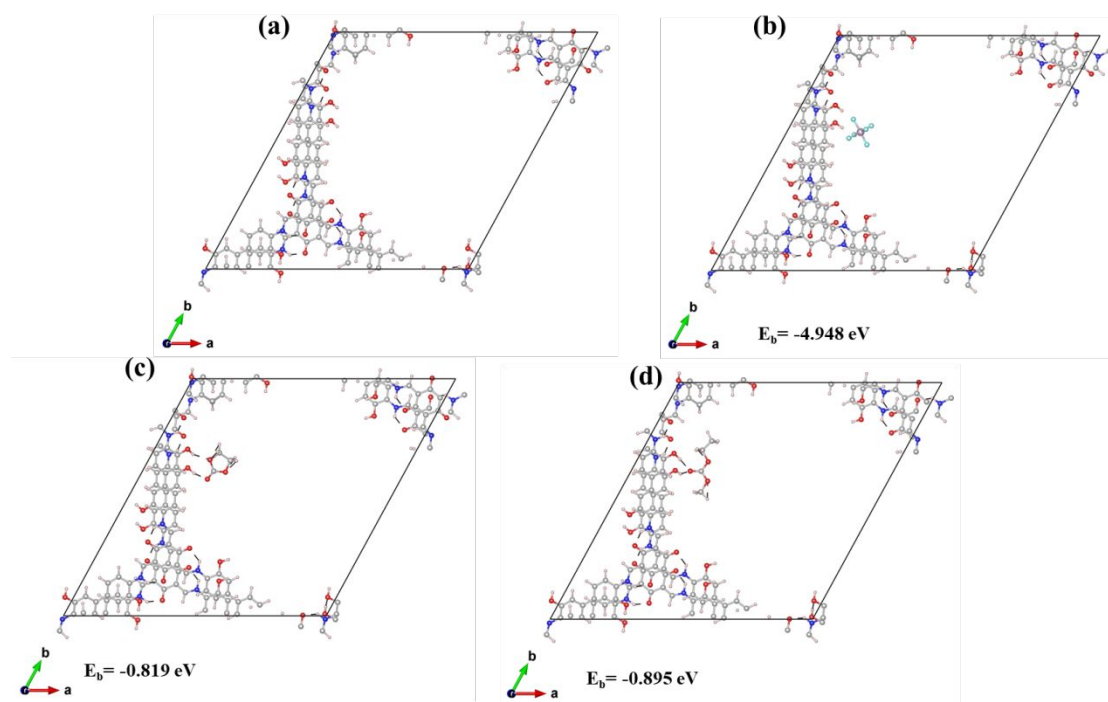


Figure S12 (a) The segment of TPB-BD(OH)₂-COF for modelling. (b-d) The interaction fragment between TPB-BD(OH)₂-COF and PF₆⁻ anion (b), EC (c), and EMC (d).

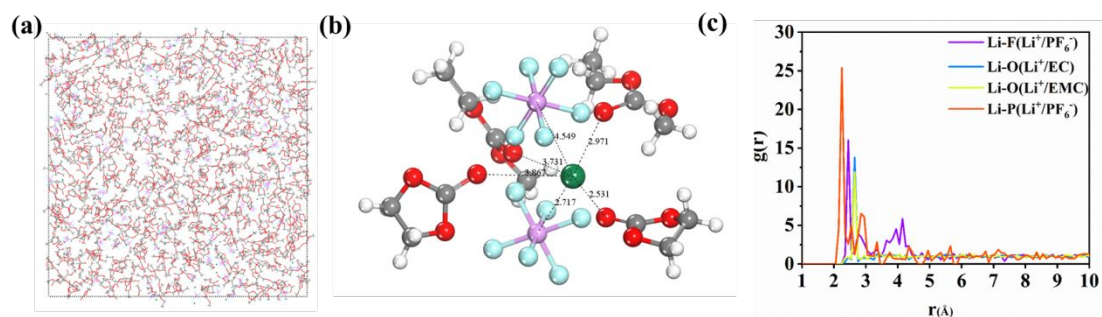


Figure S13. (a) The initial MD models of diluted electrolyte. (b) The MD snapshot of Li ion solvated shell within a 5 Å radius at 4 ns. (c) The RDFs between the Li⁺ ion and electrolyte.

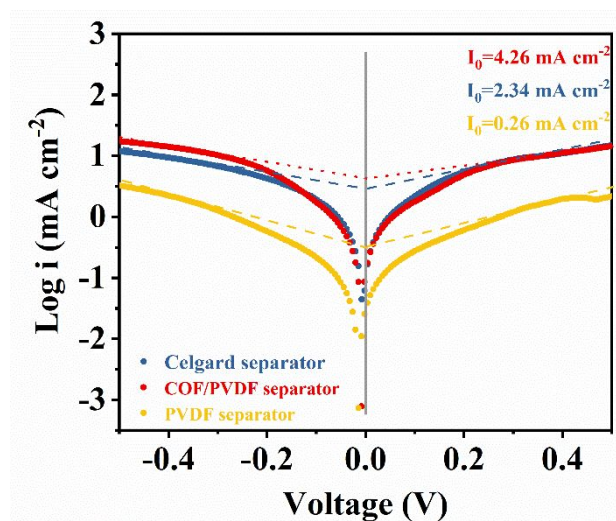
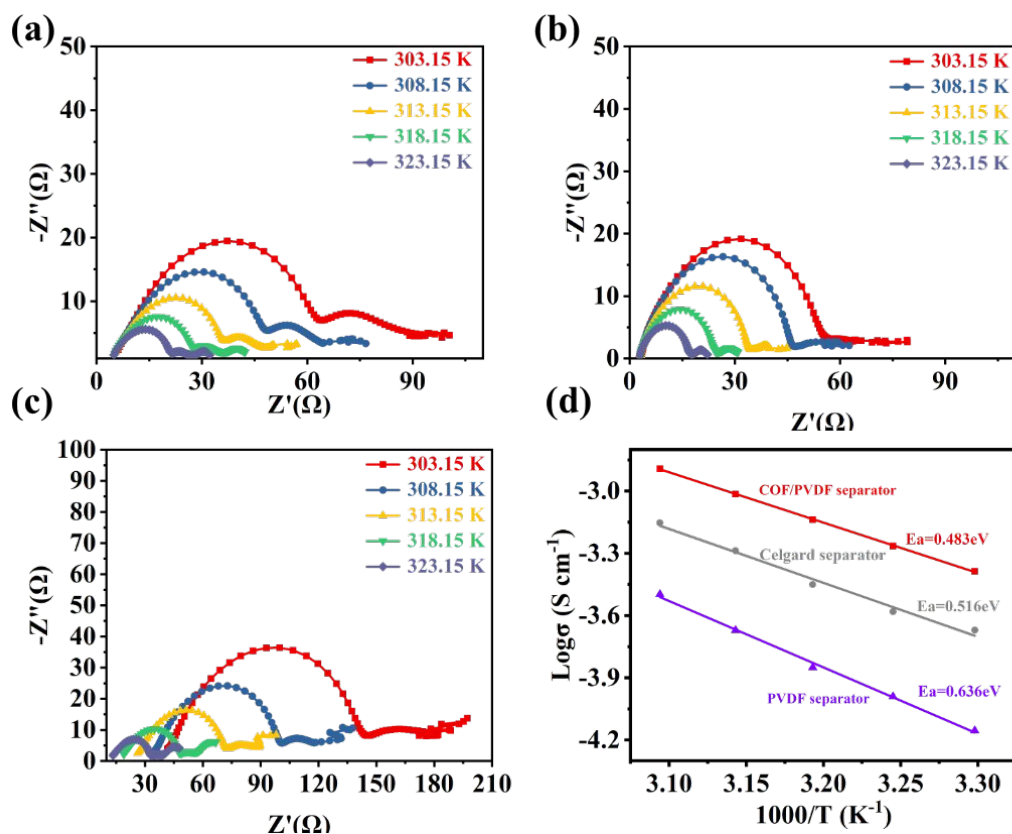


Figure S14. Tafel plots obtained from the linear sweep voltammetry at 1mV/s.



• **Figure S15.** (a-c) EIS spectra of Li-Li symmetric batteries with different separators in the temperature range of 30 to 50 °C: (a) COF/PVDF separator, (b) PVDF separator and (c) commercial celgard separator. (d) The Arrhenius curves of these three separators.

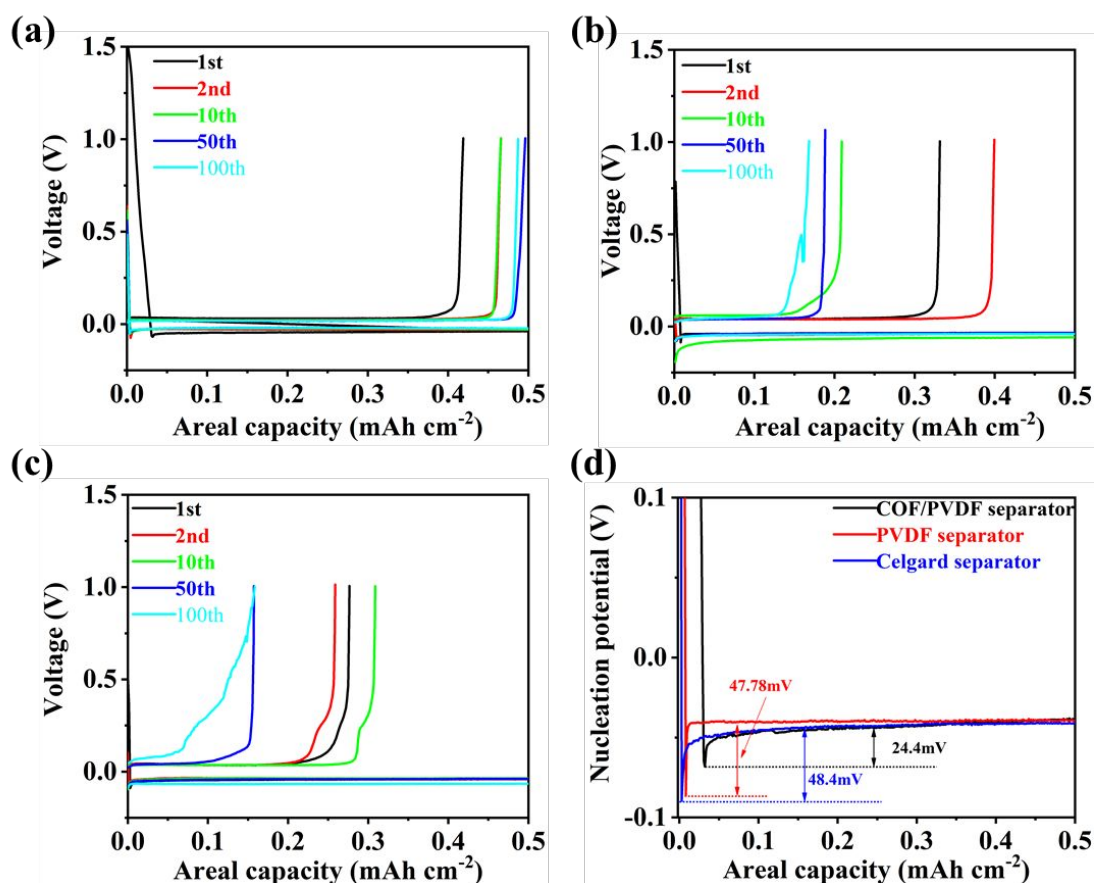


Figure S16. The charge and discharge curves of lithium-copper half-cells assembled with different separators: (a) COF/PVDF separator, (b) PVDF separator and (c) PP separator. (d) The nucleation overpotential using different separators.

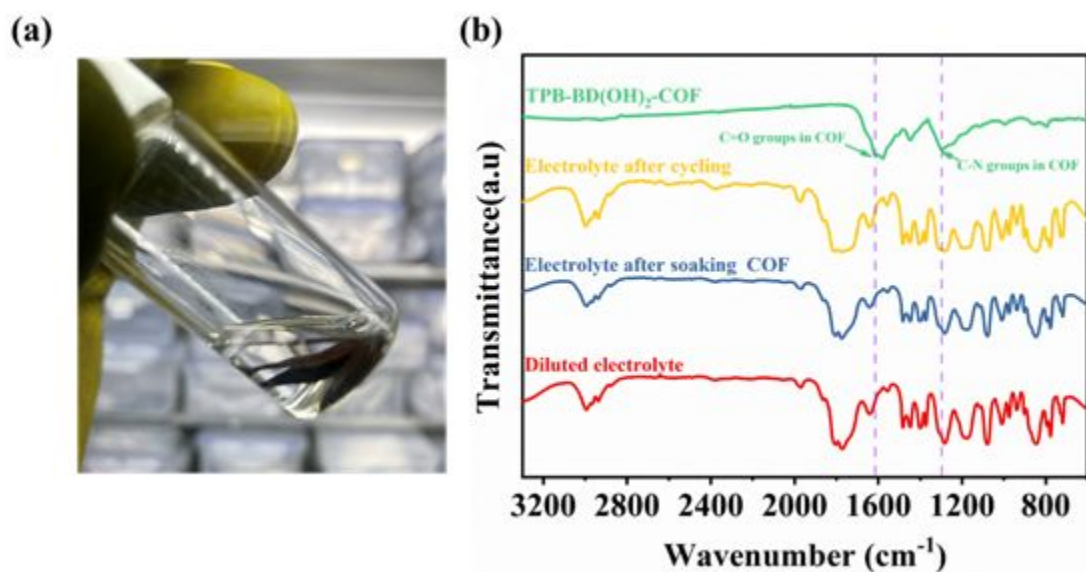


Figure S17. (a) The dissolution experiment of COF/PVDF separator in electrolyte. (b) FT-IR spectra of TPB-BD(OH)₂-COF and different electrolytes.

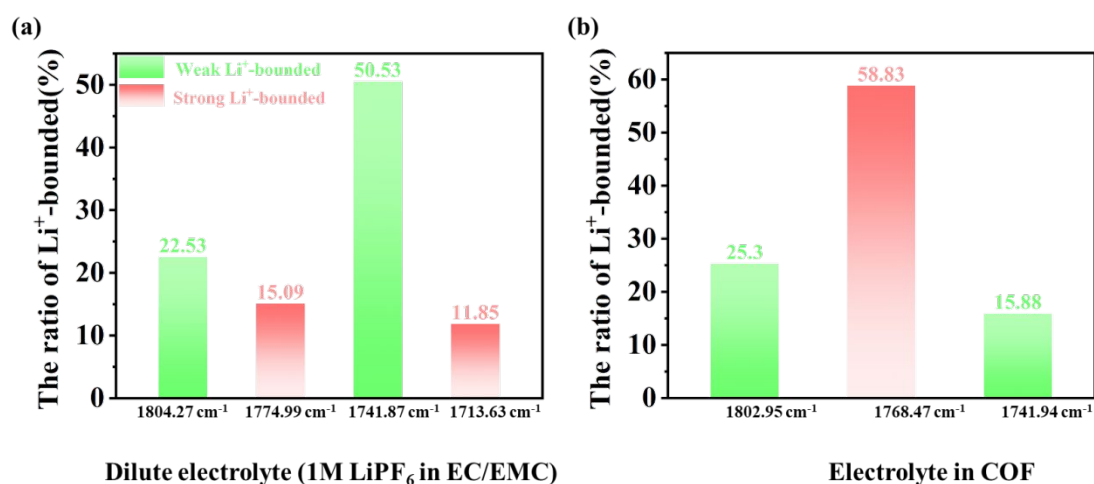


Figure S18. The ratio of weak Li⁺-bounded and strong Li⁺-bounded areas of the two electrolytes in the *ex-situ* attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra: (a) diluted electrolyte, (b) electrolyte in the COF channel.

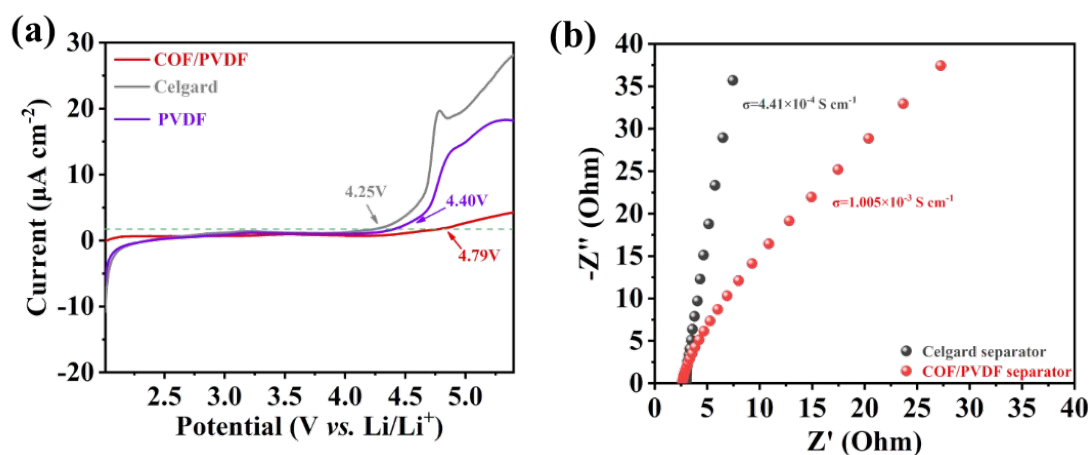


Figure S19. (a) Linear sweep voltammetry curves of COF/PVDF, PVDF and commercial celgard separators. (b) The lithium-ion conductivities of COF/PVDF separator and commercial celgard separator.

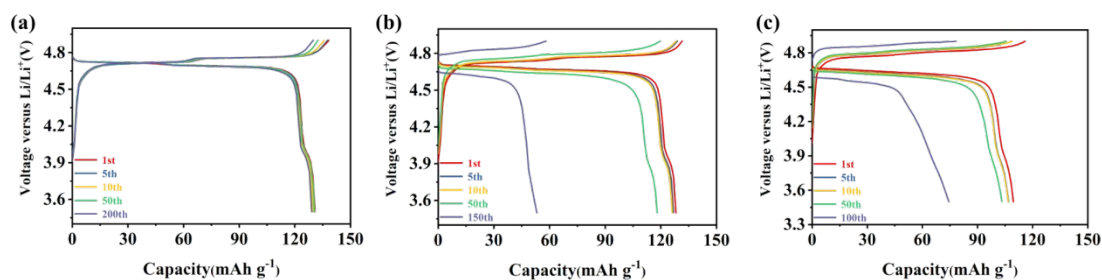


Figure S20. The charge and discharge curves of Li-LNMO full batteries at 0.5C: (a) COF/PVDF separator; (b) PVDF separator; (c) commercial celgard separator.

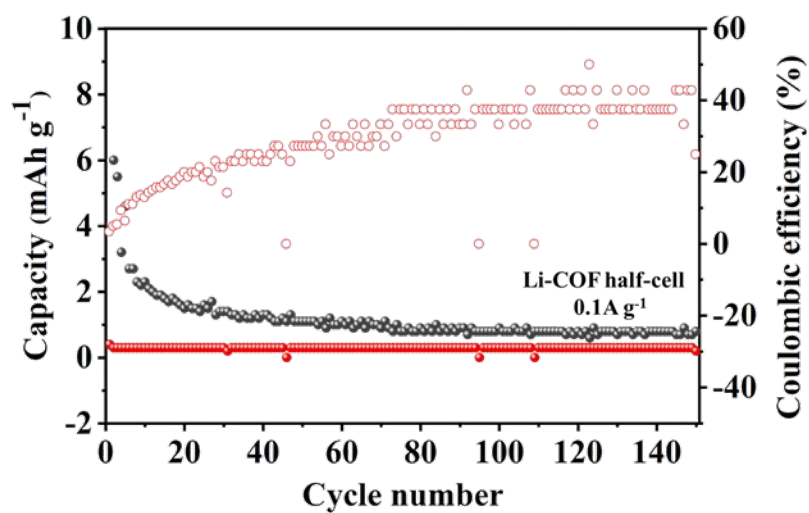


Figure S21. The cycling performance of Li-COF half-cell assembled with commercial celgard separators at 0.1 A g^{-1} .

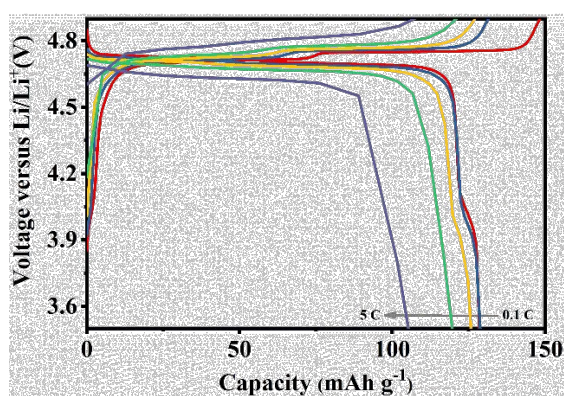


Figure S22. The charge-discharge curves of the full cell with COF/PVDF separator at different current densities.

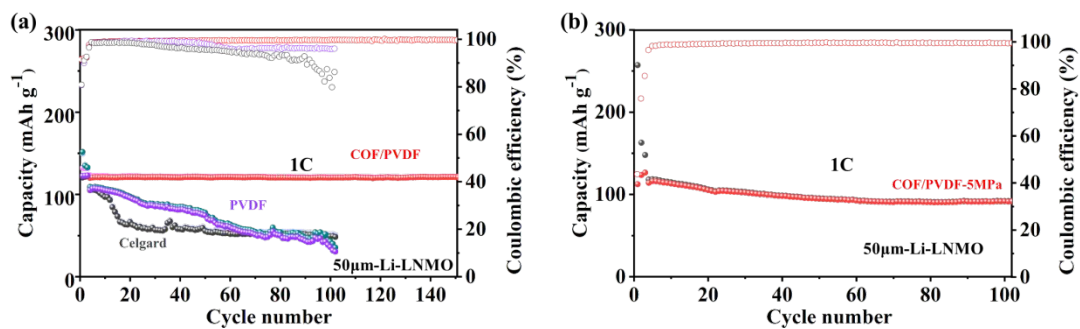


Figure S23. The performance of 50 μm Li-LNMO half-cells at 1C with different separators.

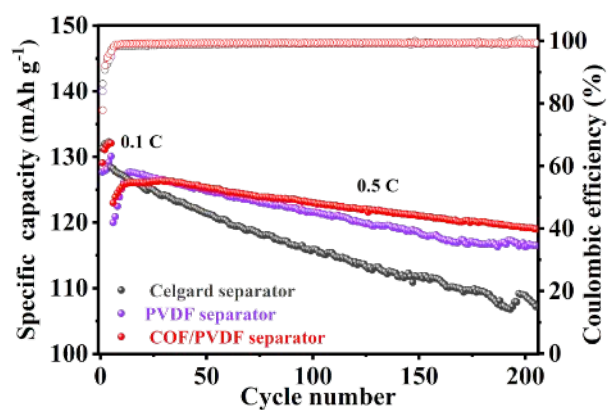


Figure S24. The cycle performance of Li-LNMO half-cells at 0.5C with different separators.

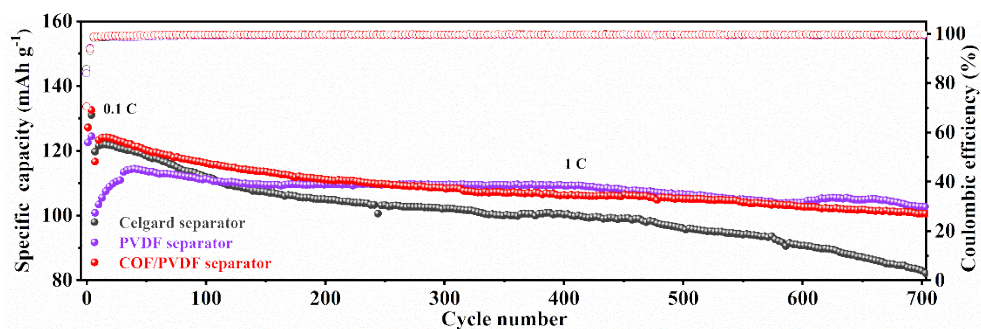


Figure S25. The cycle performance of Li-LNMO half-cells at 1C with different separators.

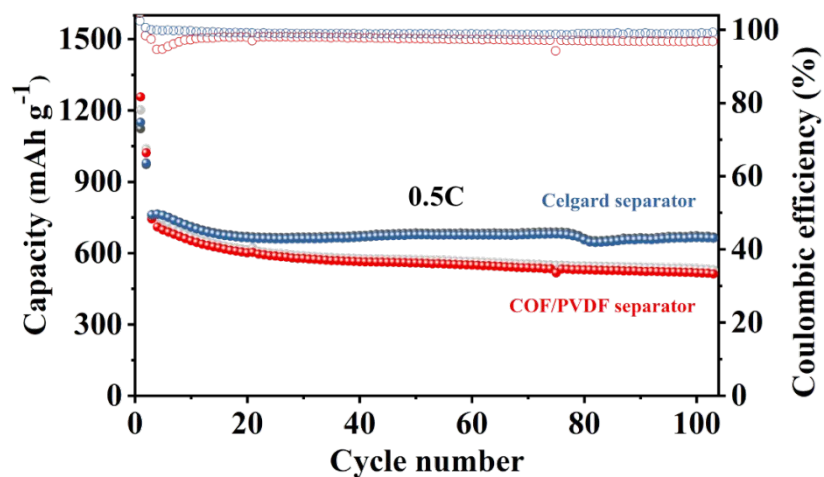


Figure S26. The cycling performance of Li-S batteries at 0.5C (837.5 mA/g) with different separators.

References

- (1) Kandambeth, S.; Biswal, B. P.; Chaudhari, H. D.; Rout, K. C.; Kunjattu H, S.; Mitra, S.; Karak, S.; Das, A.; Mukherjee, R.; Kharul, U. K.; Banerjee, R., Selective Molecular Sieving in Self-Standing Porous Covalent-Organic-Framework Membranes. *Adv. Mater.* **2017**, 29 (2), 1603945.