

Supporting Information

A fluorinated metal-organic framework-based quasi-solid electrolyte for stabilizing Li metal anode

Xiang Wang,^a Mengxi Bai,^a Qiufen Li,^a Jiashuai Li,^a Dongze Li,^a Xiaoyan Lin,^a Siyuan Shao,^a Ziqi Wang*^a

^a: Department of Materials Science and Engineering, College of Chemistry and Materials Science, Jinan University, Guangzhou 511443, P. R. China.

E-mail: wangzq@jnu.edu.cn.

Experimental Section

Synthesis of MIL-125

The preparation of MIL-125 was based on previous reports.¹ In a three-necked flask, 3.53 g of terephthalic acid (TPA) was combined with 56 mL of N,N-dimethylformamide (DMF). The mixture was heated at 105 °C for 1 hour to remove residual moisture, to which 15 mL of MeOH was added. Then a reflux condenser was attached to initiate the reflux process. After boiling for 1 h, 4.85 mL of tetrabutyl titanate (TBOT) was added to the solution. The mixture was continuously stirred and refluxed at 100 °C for 48 hours. After cooling to room temperature, the white solid was collected by centrifugation, washed with ethanol, and heated at 200 °C in nitrogen for 12 hours to remove excess DMF.

Synthesis of NH₂-MIL-125

In brief, 1.81 g of 2-aminoterephthalic acid (2-ATA) was dissolved in 30 mL of DMF and 3.2 mL of MeOH. Subsequently, 0.8 mL of TBOT was added to the solution and stirred for half an hour. The suspension was transferred to a Teflon-lined stainless-steel autoclave and heated at 150 °C for 24 hours. The obtained light yellow solid was

collected by centrifugation, washed three times with ethanol, and heated at 200 °C in a nitrogen atmosphere for 12 hours to remove residual DMF.

Synthesis of MIL-125-NHSO₂CF₃

To prepare the MIL-125-NHSO₂CF₃, a flask was filled with 20 mL of CH₂Cl₂, 260 μL of triethylamine (Et₃N), and 0.276 g of NH₂-MIL-125. The flask was cooled to 0 °C and 252 μL of trifluoromethanesulfonic anhydride was added dropwise. The mixture was stirred at 0 °C for 30 minutes and then reacted at room temperature for 72 h. The MIL-125-NHSO₂CF₃ was collected by centrifuging and washed with CH₂Cl₂. About 14 wt% F is contained in the modified MOF.

Preparation of the QSEs

0.2 g of MIL-125-NHSO₂CF₃ and 22 mg of polytetrafluoroethylene (PTFE) suspension (60 wt% in water) were dispersed in ethanol and stirred for 5 h. Then the mixture was ground to evaporate the ethanol and rolled to form a free-standing membrane of about 200 μm. Then the membrane was heated at 120 °C under vacuum for 12 hours and wetted with 30 μL of PC solution with 1 mol L⁻¹ lithium bis(trifluoromethanesulphonyl)imide (LiTFSI). Additional liquid was wiped out with a tissue to obtain the M-NHSO₂CF₃ QSE. The M-125 QSE was prepared by a similar procedure using the MIL-125 MOF.

Battery assembly

All cells were assembled in an Ar-purified glovebox. The electrochemical performance was investigated by CR2032 coin type cells. The M-NHSO₂CF₃ and M-125 QSEs were cut into 10 mm round pieces for battery assembly. To prepare the cathode, LiFePO₄ (LFP), super-P, and poly(vinylidene fluoride) (PVDF) were mixed in N-methyl pyrrolidone (NMP) with a mass ratio of 7:2:1 to obtain the cathode mixture, and was coated on an aluminum current collector. The prepared electrode films were dried at 60 °C for 24 hours under vacuum and punched into disks with a diameter of 7 mm. The LFP loading in the cathode is about 2.5 mg cm⁻². Coin type LFP LMBs were assembled

with LFP cathodes, lithium anodes, and the QSEs.

Characterization

XRD patterns of the MIL-125-NH₂ and MIL-125-NHSO₂CF₃ were recorded by a Miniflex 600 X-ray diffractometer with Cu K α radiation. SEM tests of the cycled Li and deposited Li were performed with a Hitachi TM3030 Tabletop Microscope. FTIR data of the MIL-125-NH₂ and MIL-125-NHSO₂CF₃ were collected with a PerkinElmer Spectrum Two spectrometer. NMR data of the MIL-125-NHSO₂CF₃ were obtained by an AVANCE NEO Ascend 400 spectrometer. XPS results of the deposited Li were tested with a Thermo Scientific K-Alpha+ equipment. The ionic conductivity, electrochemical window, Li⁺ transference number, and CV profiles were determined by a IviumStat.h electrochemical workstation. The plating/stripping performance of the symmetric cells and charge/discharge properties of the full cells were tested with a LANHE CT3002A battery tester at room temperature. To following equation was used to calculate the ionic conductivity (σ) of the QSEs,

$$\sigma = \frac{L}{R \cdot A}$$

where R is the total resistance of the SS|QSE|SS. L and A are the thickness and area of the QSE pellet, respectively. The activation energy (E_a) for ionic conduction was determined by the following Arrhenius relationship between σ and temperature (T)

$$\sigma = \sigma_{\infty} \cdot \exp\left(-\frac{E_a}{RT}\right)$$

where σ_{∞} is the conductivity at infinite temperature, and R is the gas constant. The electronic conductivity (σ_e) was determined from

$$\sigma_e = \frac{L}{S} \cdot \frac{I}{E}$$

where σ_e is electronic conductivity. L is the thickness of the QSE. S is the area of the QSE. E is the polarization voltage, and I is the steady-state current. A potentiostatic polarization method was used to obtain the t_{Li^+} of the QSEs as follows

$$t_{Li^+} = \frac{I_s(\Delta V - I_0 R_0)}{I_0(\Delta V - I_s R_s)}$$

where ΔV (10 mV) is the applied voltage. I_0 and R_0 are the initial current and interfacial resistance, respectively. I_s and R_s represent the steady-state current and interfacial resistance, respectively. The average CE of the Li|QSE|Cu cells for the first 20 cycle was calculated by the following equation,

$$ACE = \frac{20Q_c + Q_s}{20Q_c + Q_r}$$

where Q_r is the initial plating capacity. Q_c is the capacity for the 20 plating/stripping cycles. Q_s is the final stripping capacity.

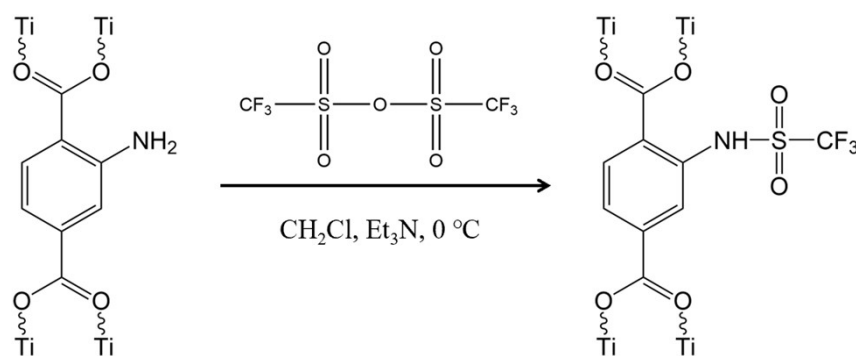


Fig. S1. Schematic illustration of the synthetic procedure of the MIL-125-NHSO₂CF₃.

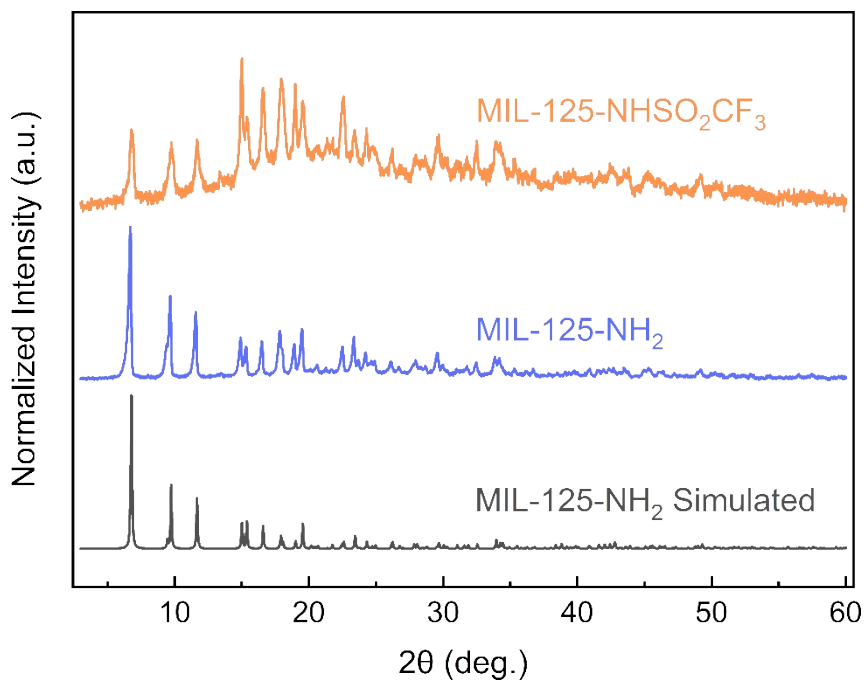


Fig. S2. XRD patterns of the simulated and synthesized MIL-125-NH₂ and MIL-125-NHSO₂CF₃.

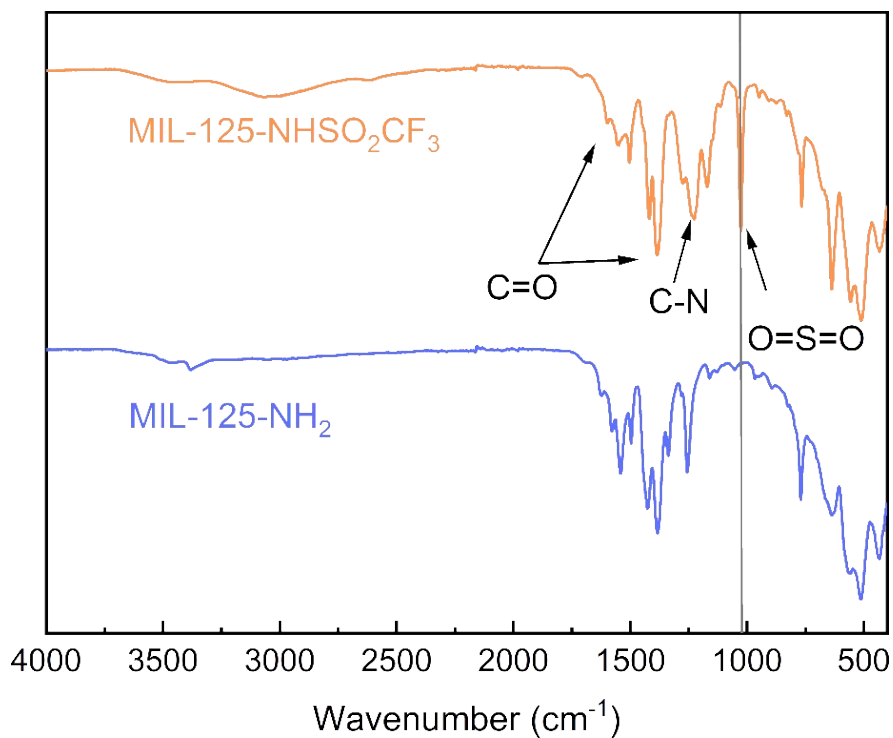


Fig. S3. FTIR of the MIL-125-NH₂ and MIL-125-NHSO₂CF₃.

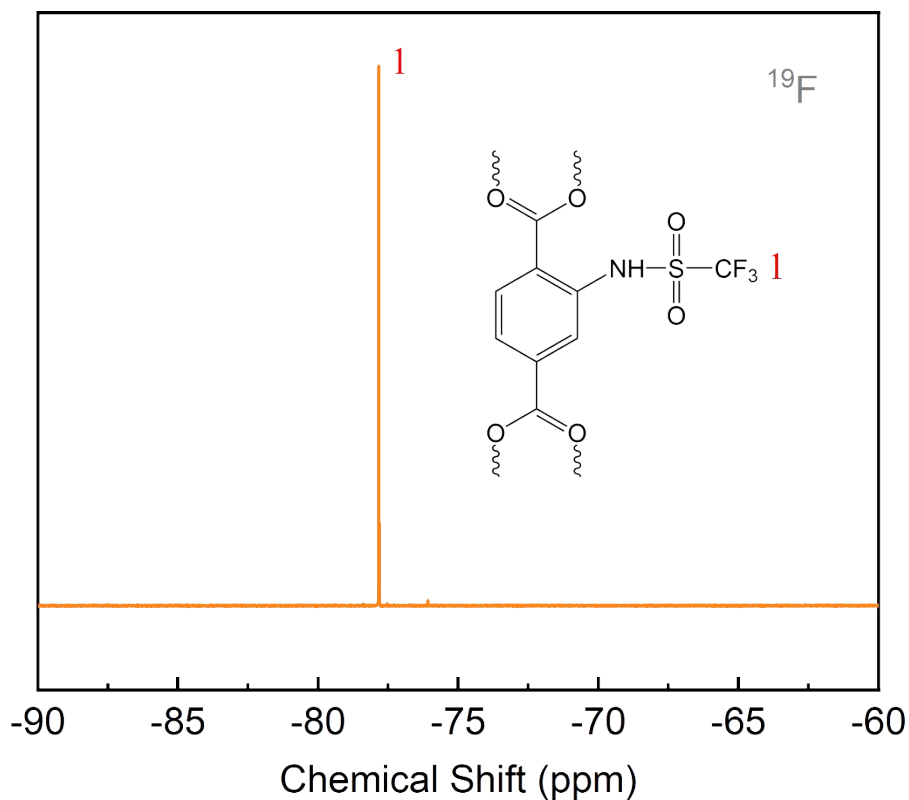


Fig. S4. ¹⁹F NMR spectra of the MIL-125-NHSO₂CF₃.

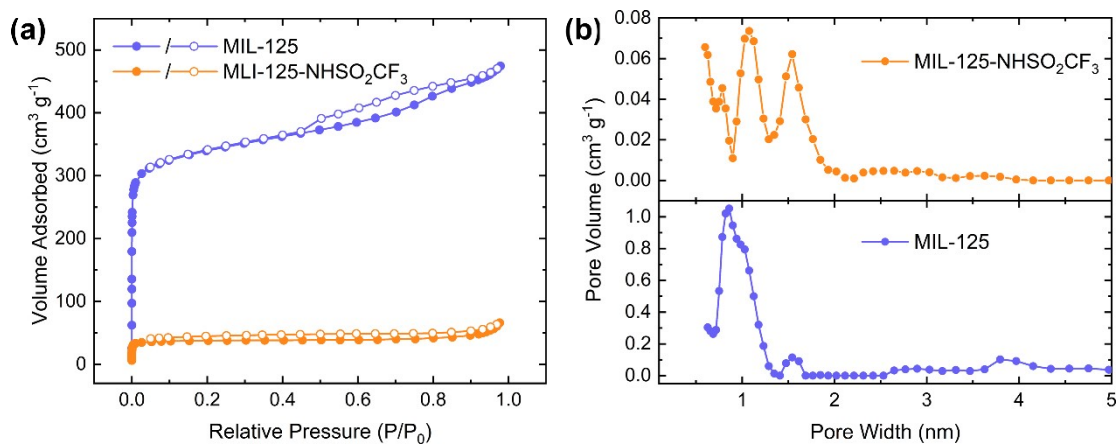


Fig. S5. (a) N_2 adsorption/desorption isotherm at 77 K and (b) corresponding BJH pore size distribution.

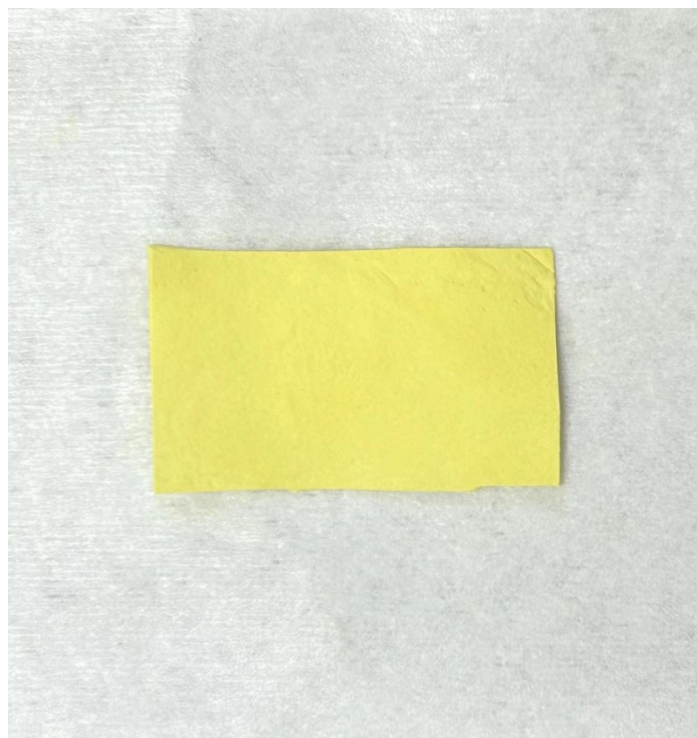


Fig. S6. Photograph of the free-standing M-NH SO_2CF_3 QSE membrane.

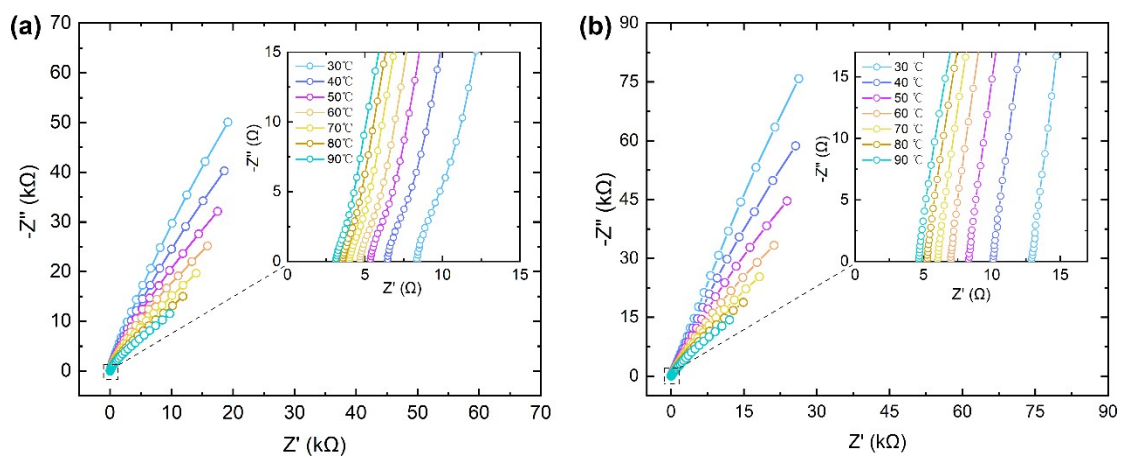


Fig. S7. EIS plots of (a) M-NHSO₂CF₃ and (b) M-125 QSEs from 30 to 90 °C.

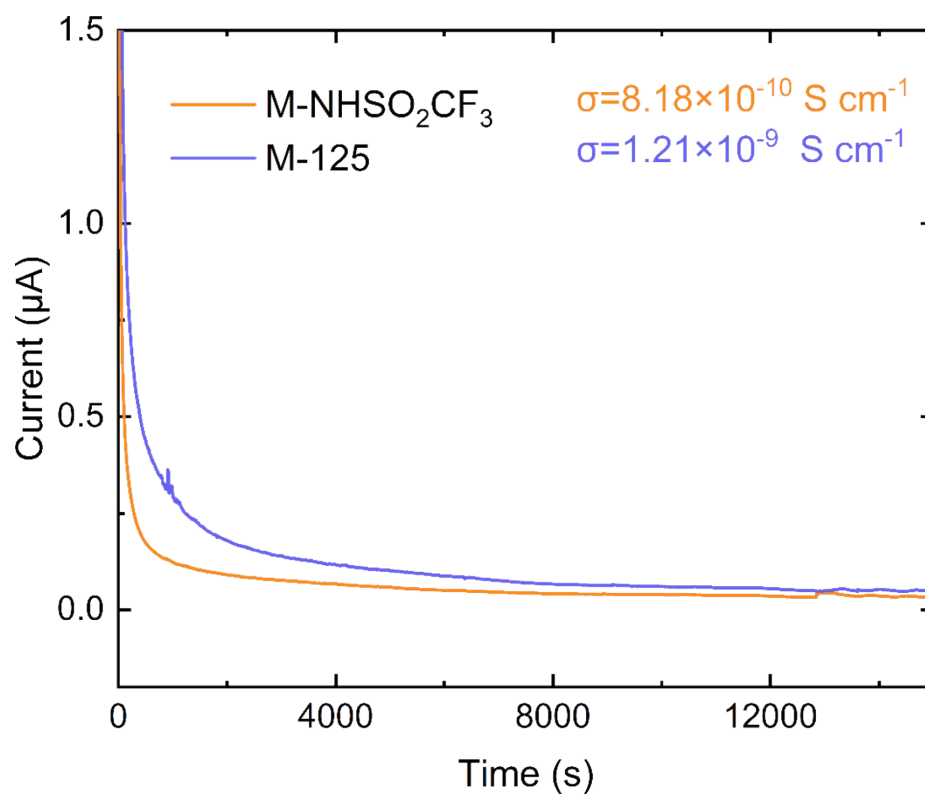


Fig. S8. Electronic conductivity measurement of the QSEs using a two-blocking-electrode cell. The bias voltage is 1.0 V.

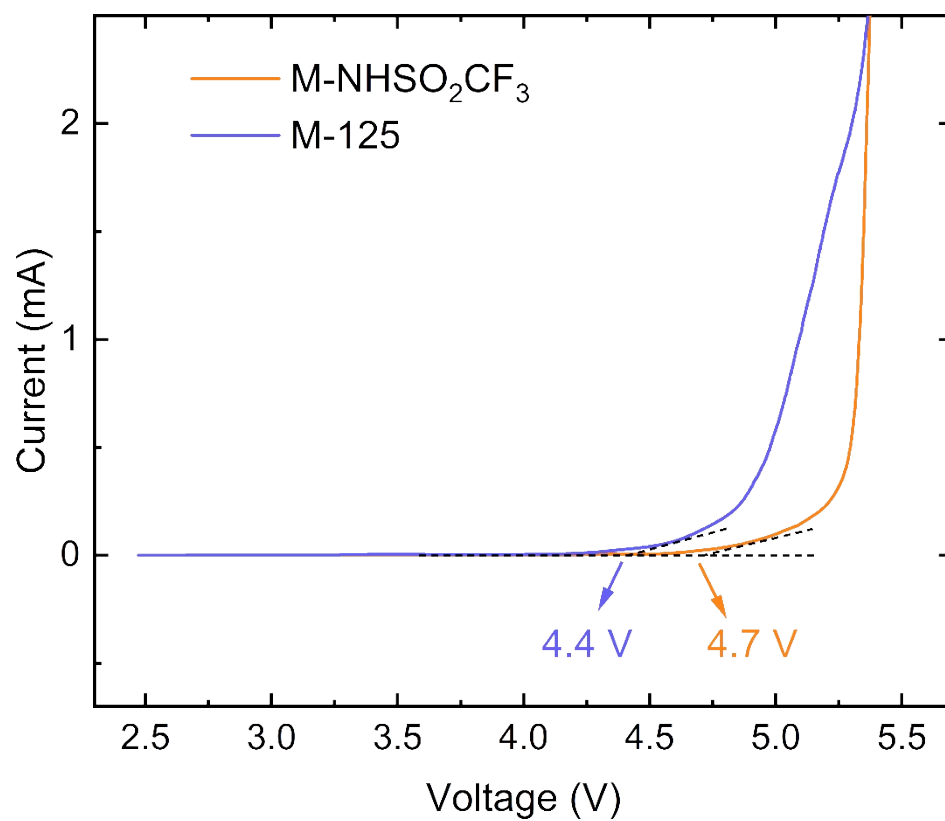


Fig. S9. LSV curves of different QSEs.

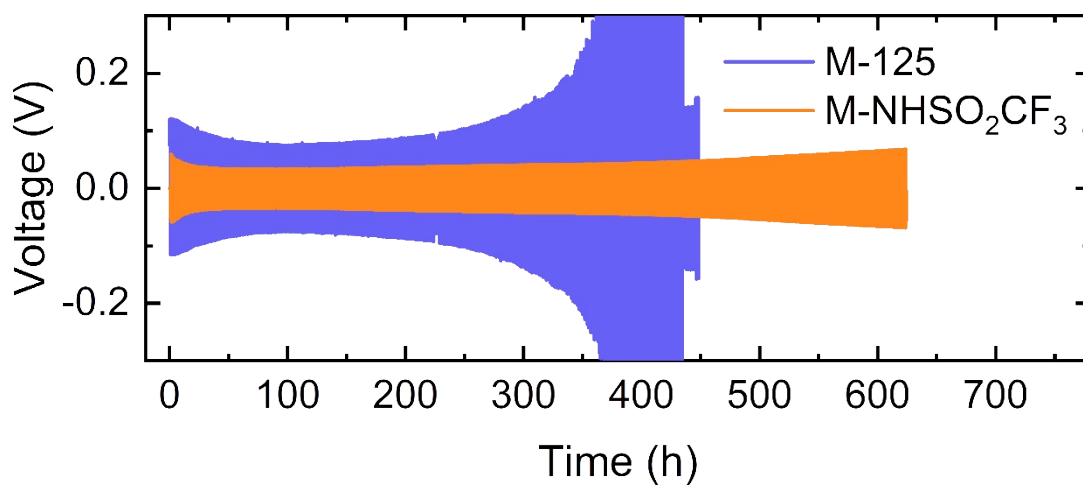


Fig. S10. Cycling performance of the Li symmetric cells with different QSEs under 0.5 mA cm^{-2} .

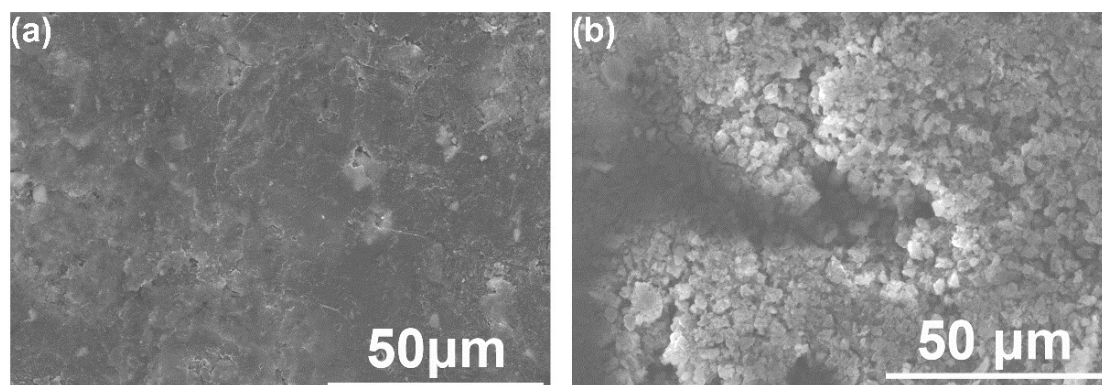


Fig. S11. SEM images of the cycled Li with (a) M-NHSO₂CF₃ and (b) M-125 QSEs.

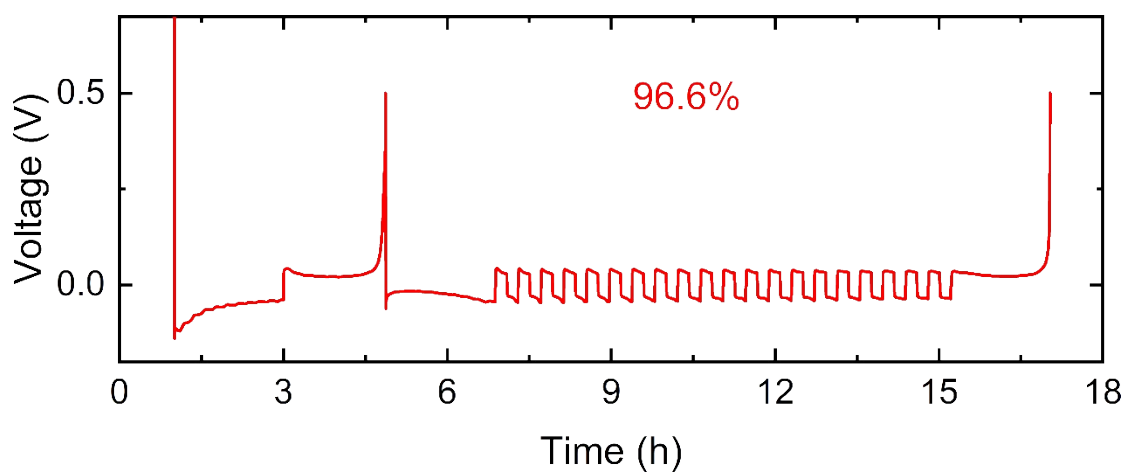


Fig. S12. Average Coulombic efficiency test of liquid cells.

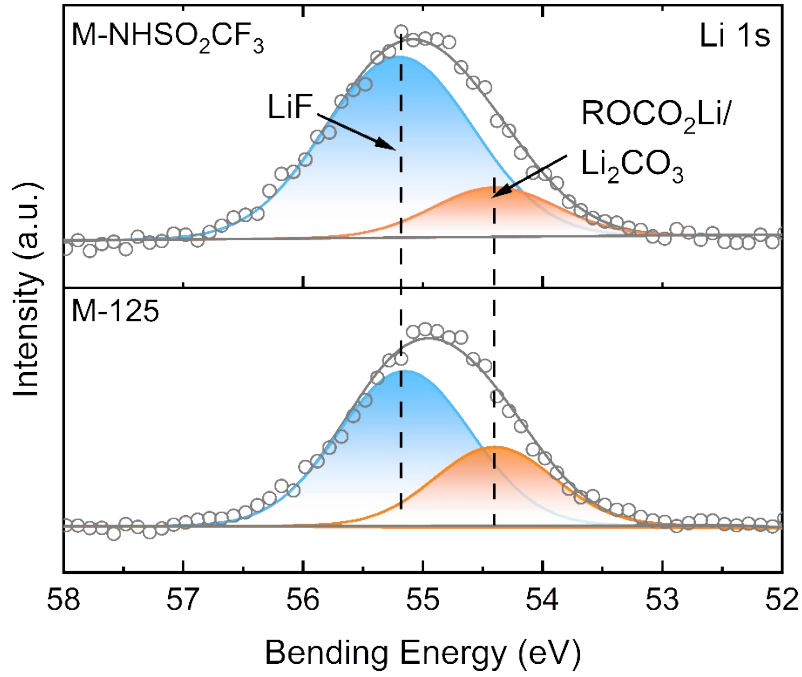


Fig. S13. Li 1s XPS spectra of the deposited Li with different QSEs.

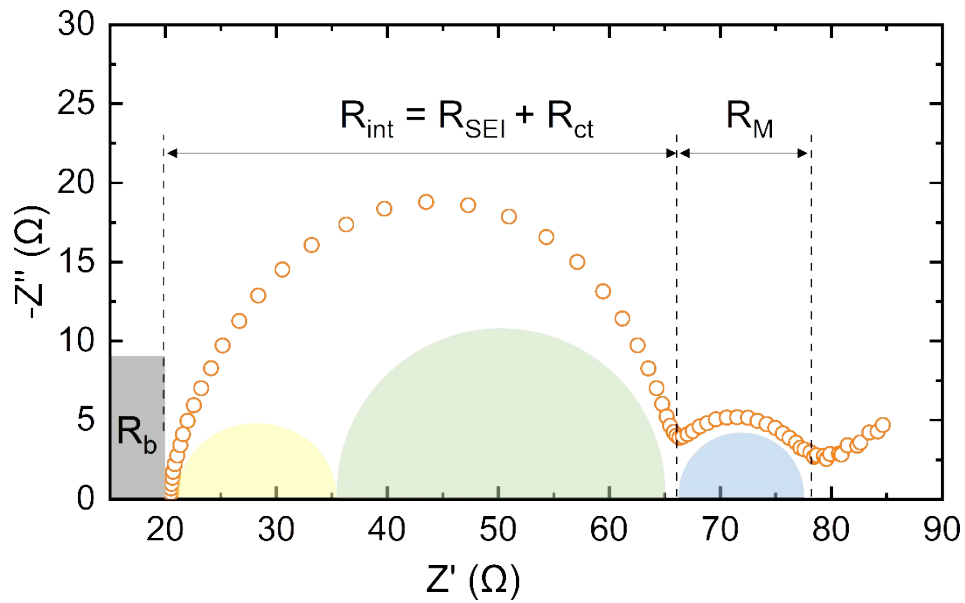


Fig. S14. Typical Nyquist plot of the resistance of the Li|M-NHSO₂CF₃|Li cell. R_b, R_{int}, R_{SEI}, R_{ct}, and R_{SM} represent bulk, interfacial, SEI, charge transfer, and sacrificed MOF layer resistance, respectively.

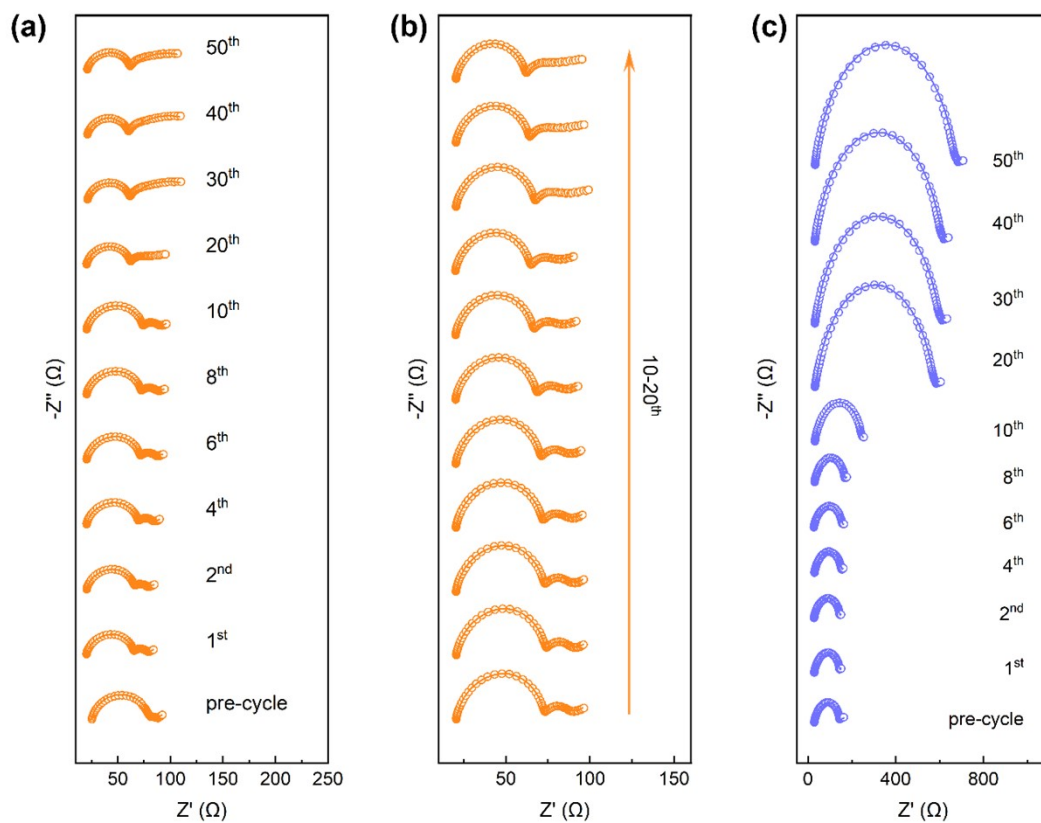


Fig. S15. EIS evolution of the Li symmetric cells with (a, b) M-NHSO₂CF₃ and (c) M-125 QSEs during cycling.

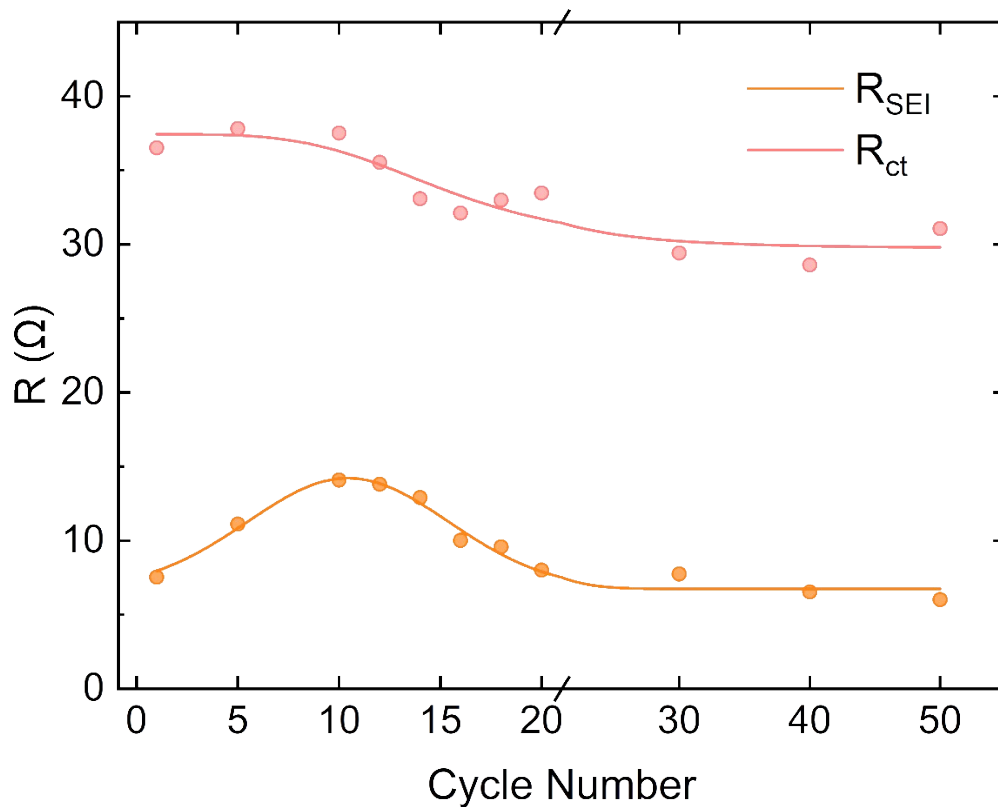


Fig. S16. The variation of R_{SEI} and R_{ct} of the Li|M-NHSO₂CF₃|Li cell with cycling.

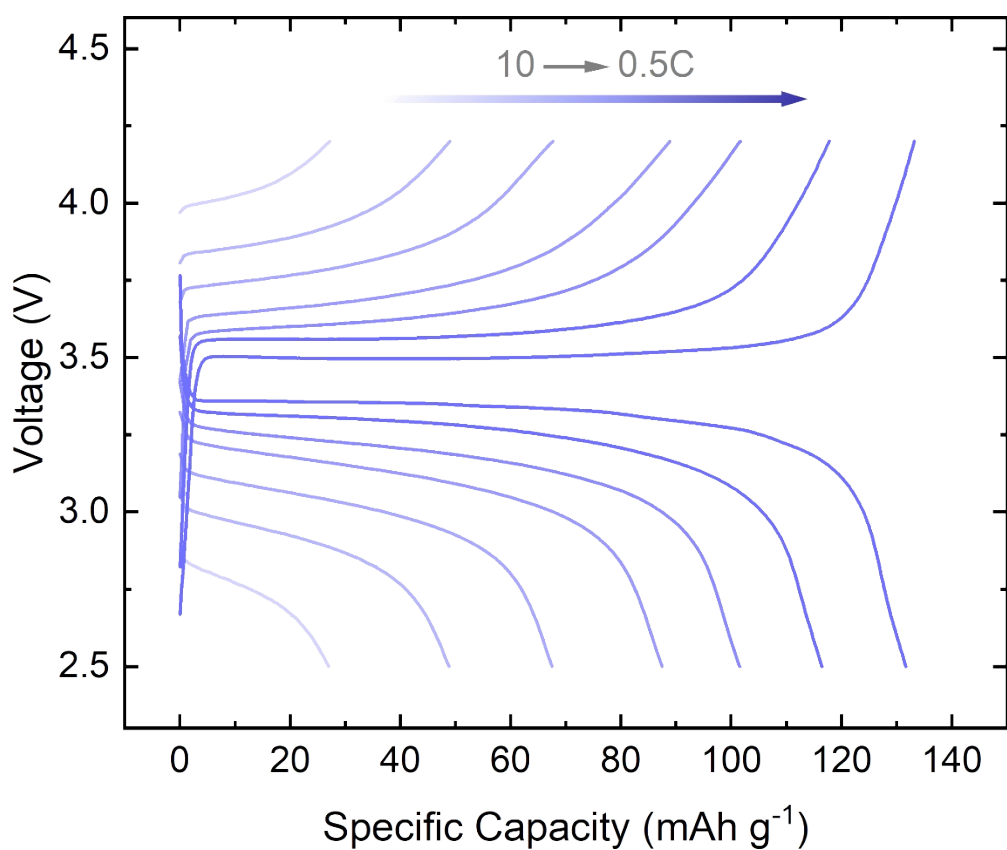


Fig. S17. Charge/discharge voltage profiles of the Li|M-125|LFP cells at different rates.

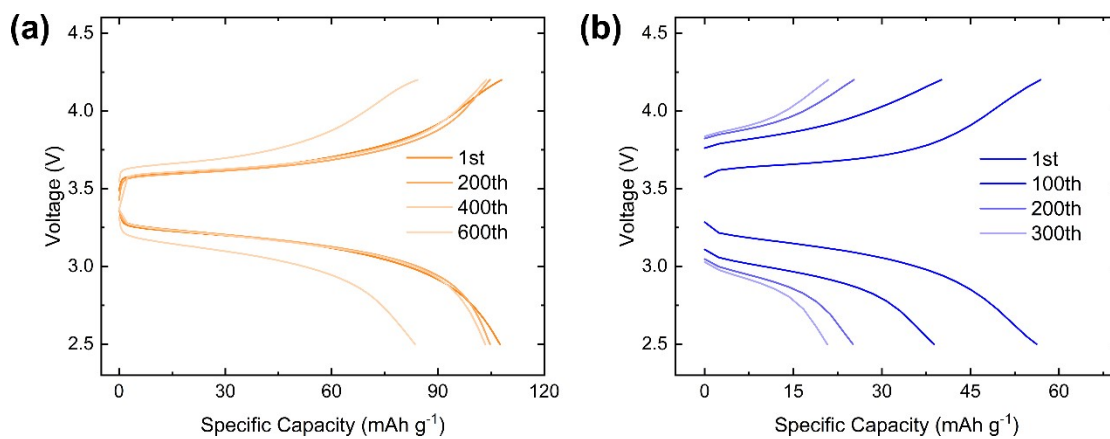


Fig. S18. Charge/discharge voltage profiles of the (a) M-NHSO₂CF₃ and (b) M-125 cells at 5 C.

Table S1. Comparison of the ionic conductivity of different MOF-based electrolytes.

Electrolytes	σ (S cm ⁻¹)	Description	Refs.
MOF-525(Cu)	3.0×10^{-4} (25 °C)	MOF+Li-IL	2
HKUST-1	1.2×10^{-4} (30 °C)	MOF+PEO+IL	3
ZIF-67	2.29×10^{-3} (30 °C)	MOF+Li-IL	4
PEO-n-UIO	1.3×10^{-4} (30 °C)	MOF+PEO+IL	5
UiO-66-LiSS	6.0×10^{-5} (25 °C)	MOF+DMSO	6
MIL-125	1.35×10^{-3} (25 °C)	MOF+LiTFSI+LiBF ₄	7
P-PETEA-ZIF-8	6.52×10^{-4} (25 °C)	MOF+PEGDA+ PETEA+LiTFSI	8
M-NHSO ₂ CF ₃	2.32×10^{-3} (30 °C)	MOF+LiTFSI+PC	This work

Table S2. Comparison of electrochemical performance of the Li|LFP cells with MOF-based electrolytes.

Electrolytes	Specific capacity (mAh g ⁻¹)	Cycling life	Refs
Li-IL@UiO-67/PVDF-HFP	118.1 (1C, 30 °C)	300	9
ZIF-8/PEO-LiTFSI	109 (1C, 60 °C)	350	10
UiO/Li-IL	119 (1C, 60 °C)	380	11
UiOLiTFSI/PVDF	132 (1C, 30 °C)	500	12
D-UiO-66NH ₂ /PEO	91.5 (1C, 60 °C)	60	13
UiO-67/PTFE	94 (1C, 30 °C)	500	14
ZIF-8/PEO	110 (1C, 30 °C)	300	15
MOF-CN/DPPG/PEGDE	126 (1C, 30 °C)	500	16
M-NHSO ₂ CF ₃ /PTFE	133.2 (1C, 30 °C)	1546	This work

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