

Supporting information

Metal organic frameworks MOF-808-based solid-state electrolytes for lithium-ion batteries

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Materials and methods

Chemicals. Zirconium Oxychloride Octahydrate ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, 99%), N, N-Dimethylformamide (DMF, 99.5%), lithium bis(trifluoromethanesulphonyl) imide (LiTFSI, 99.0%), carbon black and Ferrous lithium phosphate (LiFePO_4) were purchased from Macklin (Shanghai, China). Trimesic acid (98%) and lithium perchlorate (LiClO_4 , 98%) were purchased from Aladdin (Shanghai, China). Formic acid, absolute ethanol and acetonitrile were obtained from Acros Organics. Polyvinylidene difluoride (PVDF) and propylene carbonate (PC) were purchased from Shenzhen Kejing Star Technology Company. N-methyl-2-pyrrolidone (NMP) was purchased from Fu Chen (Tianjin, China). All chemicals were purchased as pure reagent grades and used without further purification.

Characterization. The structure and phase identification of the MOF-808, MOF-808-Li, Li/MOF-808-Li, were performed using X-ray diffraction (XRD, Brooker D8 Advance & Rigaku Ultima IV) with Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$, $2\theta = 5^\circ\text{-}50^\circ$), and the powder samples were evenly tiled on the slide during testing. Fourier transform infrared spectrometer (FT-IR, Nexus 8703040403) analyzed the chemical bond vibration of different functional groups, which tested from $400\text{-}4000 \text{ cm}^{-1}$. The scanning electron microscopy (SEM, Regulus 8200, detection voltage: 10.0 KV) analyzed the morphology of MOF-808, MOF-808-Li and Li/MOF-808-Li. X-Ray Photoelectron Spectroscopy (XPS, Escalab 250Xi3030708) analyzed the surface chemical properties of the MOF-808, MOF-808-Li and Li/MOF-808-Li. The content of lithium was analyzed by ICP-OES (PE Avio 200). Thermogravimetric analysis by TG-DTG (TGA/DSC3+) system under nitrogen atmosphere from room temperature to 800°C at a heating rate of $10^\circ\text{C min}^{-1}$. The specific surface area was tested by the N_2 adsorption isotherms at 77 K based on Brunauer-Emmett-Teller (BET) method with Quadrasorb-SI3030606.

1. Synthesis of MOF-808.

The preparation of MOF-808 was according to modified reported solvothermal method.^{1,2} In general, $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (0.7275 g, 2.25 mmol) and trimesic acid (0.315 g, 1.5 mmol) were added to 68 mL mixed solution of N, N-Dimethylformamide and formic acid (volume ratio of 1:1). The mixed solution was sealed into a teflon lined stainless steel autoclave and heated at 150°C for 48 h. After cooling down to room temperature, the product was recovered by centrifugation and washed with N,N-Dimethylformamide and absolute ethanol for 3 times, respectively. After removing the solvent by centrifugation and then heated in 150°C vacuum for 12 h.

2.Synthesis of MOF-808-Li.

1.0 g MOF-808 was added to acetonitrile solution of 1M LiClO_4 and stirred for 12 h at room temperature. Then the product was obtained by washing with acetonitrile for 3 times and heated in 100°C vacuum for 12 h.

3.Preparation of Li/MOF-808-Li electrolyte membrane.

The handled MOF-808-Li and LiTFSI were dried at 70°C under vacuum for 16 h before used. MOF-808-Li, LiTFSI and PVDF were mixed in a weight ratio of 1:1:0.7 with DMF as the solvent, and stirred for 12 h at room temperature.³ The dispersed mixture were poured into a petrie dish mold and dried in 100°C vacuum for 18 h to remove the leftover solvent. The as-prepared membrane was cut into free-standing and flexible sheets with 16 mm in diameter and kept in glove box filled with argon. The loading of Li/MOF-808-Li was 4.8 mg.

4.Preparation of cathode mixture.

LiFePO₄ powders, carbon black and PVDF were mixed in a weight ratio of 8:1:1 with NMP as the solvent.³ After stirring for 12 h, the obtained slurry was coated on the aluminum foil and dried vacuum at 110°C for 12 h. Then cut into sheets with 11 mm in diameter under pressed at 8 MPa. CR2032 type coin batteries were fabricated in an argon-filled glove box, and the charge and discharge tests of the batteries. The loading of LiFePO₄ was 1.5 mg.

5.Electrochemical measurements and cells assembly.

Ionic conductivity is an important prerequisite for becoming an electrolyte material and can significantly affect the power output of batteries.⁴ Ionic conductivity σ (S cm⁻¹) of the electrolyte membrane (Li/MOF-808-Li) were tested by electrochemical impedance spectroscopy (EIS) with the frequency ranging from 0.1 Hz to 1 MHz at various temperatures between 25°C and 70°C. The solid electrolyte membrane was sandwiched between two stainless steel block electrodes. And the ionic conductivity (σ) was calculated as the following formula:

$$\sigma = \frac{L}{R \times S} \quad (1)$$

Where L (cm), R(Ω), and S (cm²) are the thickness, bulk resistance, and the area of the membrane, respectively.⁵ In order to obtain activation energy (Ea), the traditional Arrhenius shown as:

$$\sigma = A e^{\frac{-Ea}{kT}} \quad (2)$$

Where σ (S cm⁻¹) is ionic conductivity, A is pre-exponential factor, Ea is the activation energy, k is the Boltzmann constant, T is the Kelvin temperature.⁶ The Li⁺ transference number (t_{Li^+}) with the Bruce-Vincent-Evans method used lithium symmetric battery with polarization voltage of 10 Mv.⁷ In order to improve interface contact, dropping 5 μ L of PC

solvent on the interface between Li/MOF-808-Li and electrode.⁸ Then the transference number be calculated as the following equation:

$$t_{\text{Li}^+} = \frac{I_{ss}(\Delta V - I_o R_o)}{I_o(\Delta V - I_{ss} R_{ss})} \quad (3)$$

Where ΔV is polarization voltage, I_o , I_{ss} are the initial current and steady state current; R_o , R_{ss} are the interfacial impedance before and after polarization, respectively. The electrochemical window was determined by linear sweep voltammograms (LSV) using stainless steel|electrolytes|Li cells, and the scanning rate of 1 mV s^{-1} over the range of 1 V-6 V. Lithium stripping and plating was implemented on a lithium symmetrical cell with 5 μL PC solvent using a LAND battery cycler. LiFePO_4 was used as the cathode material of LIBs, and assembled with electrolyte membrane and lithium metal into Li|Li/MOF-808-Li|LiFePO₄. The charge and discharge performances of LIBs were tested on LAND test system at room temperature.

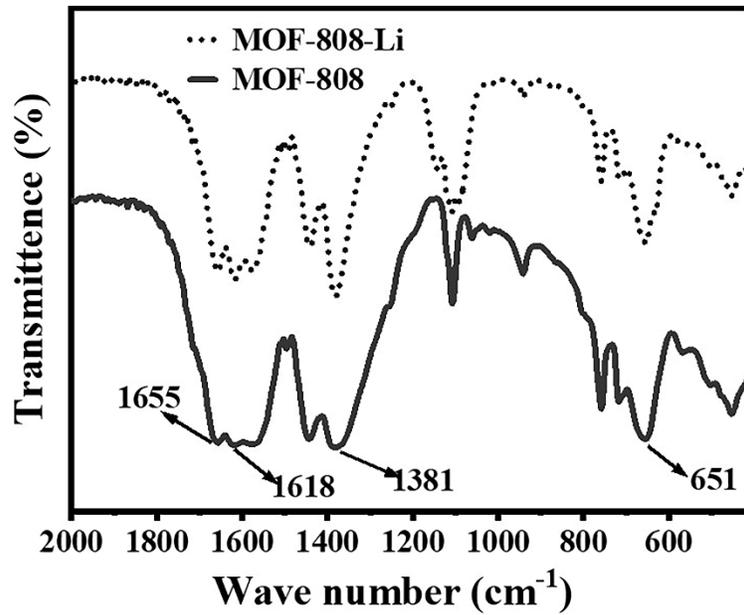


Figure S1 The FT-IR of MOF-808 and MOF-808-Li.

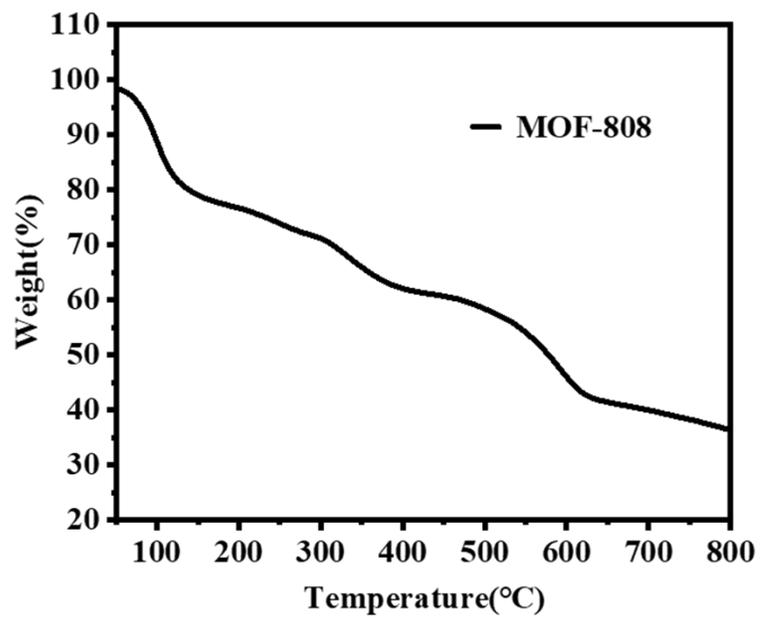


Figure S2 The TGA of MOF-808.

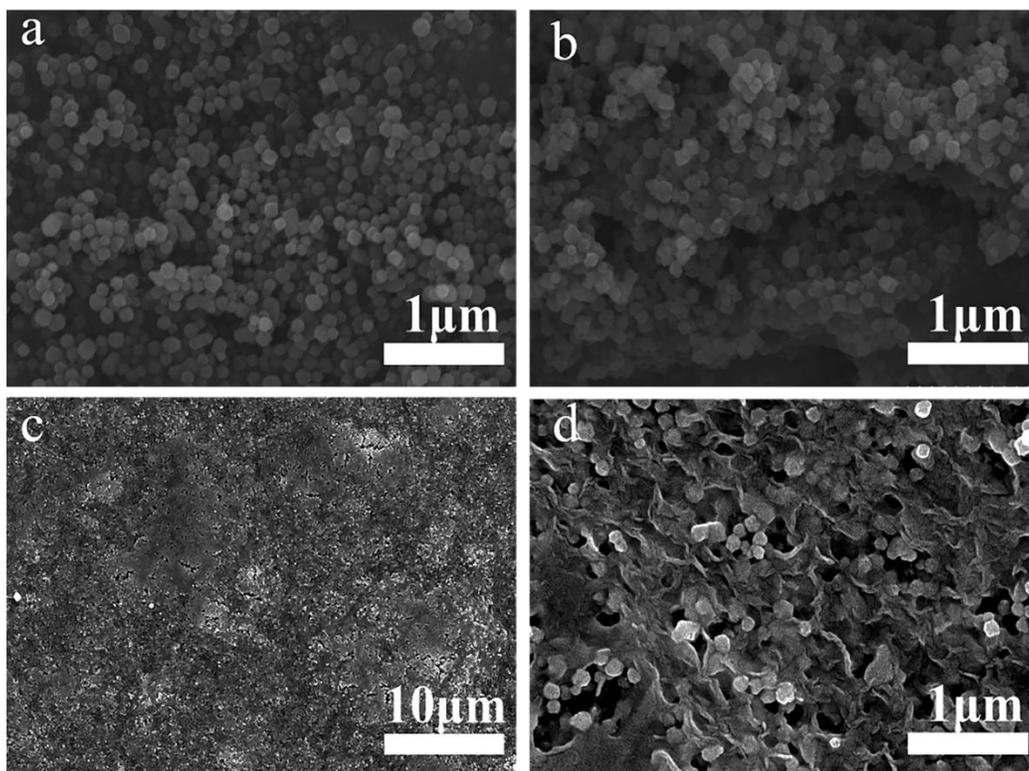


Figure S3 The SEM of (a) MOF-808; (b) MOF-808-Li; the SEM of Li/MOF-808-Li electrolyte membrane at the scale of (c) 10 μm and (d) 1 μm.

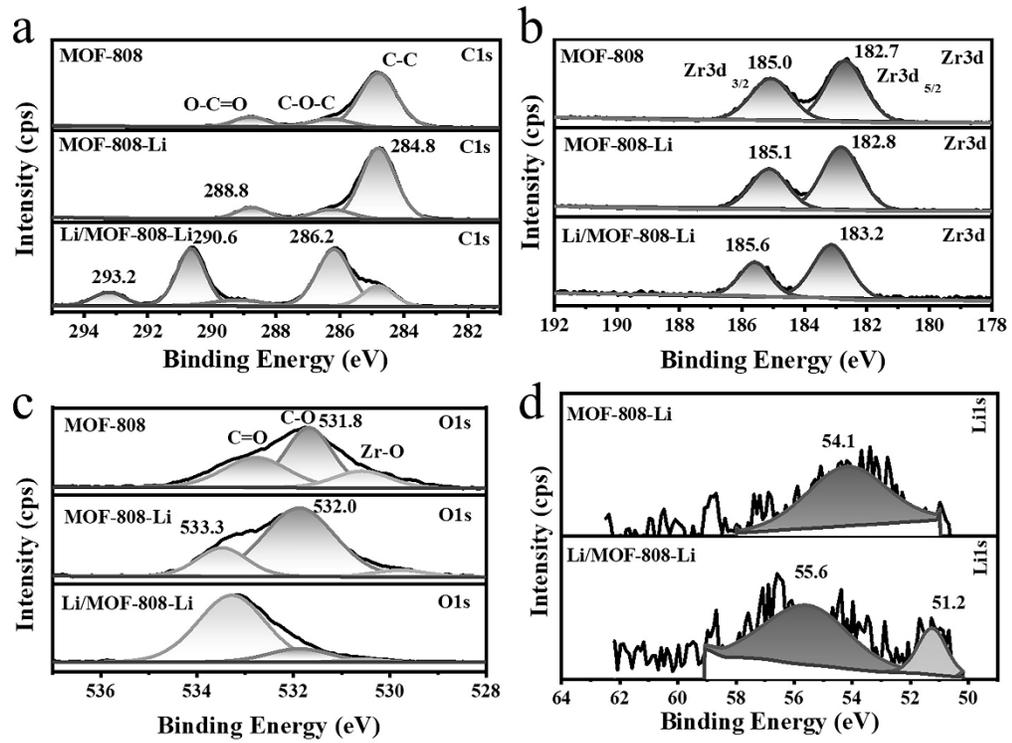


Figure S4 XPS narrow spectra of MOF-808, MOF-808-Li and Li/MOF-808-Li.

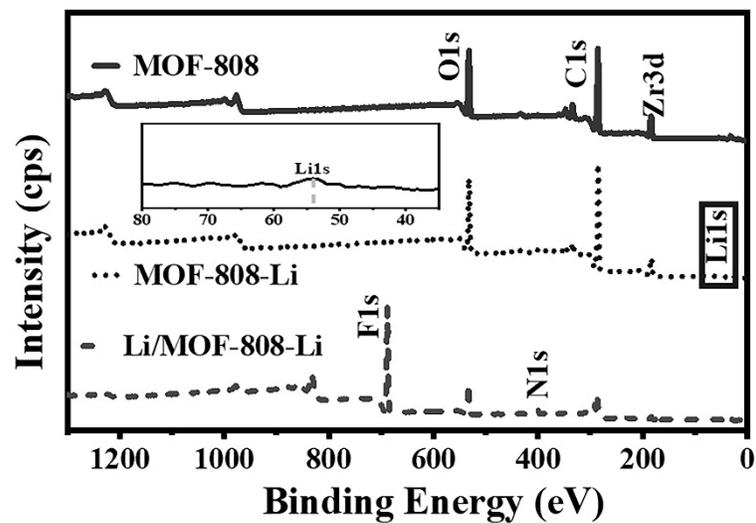


Figure S5 XPS full spectrum of MOF-808, MOF-808-Li and Li/MOF-808-Li.

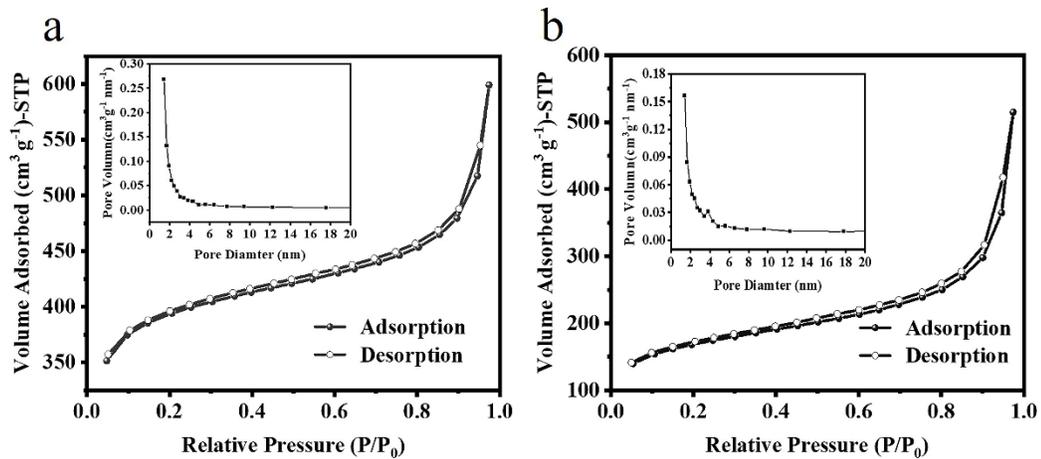


Figure S6 N₂ adsorption-desorption isotherm and pore diameter of (a) MOF-808; (b) MOF-808-Li.

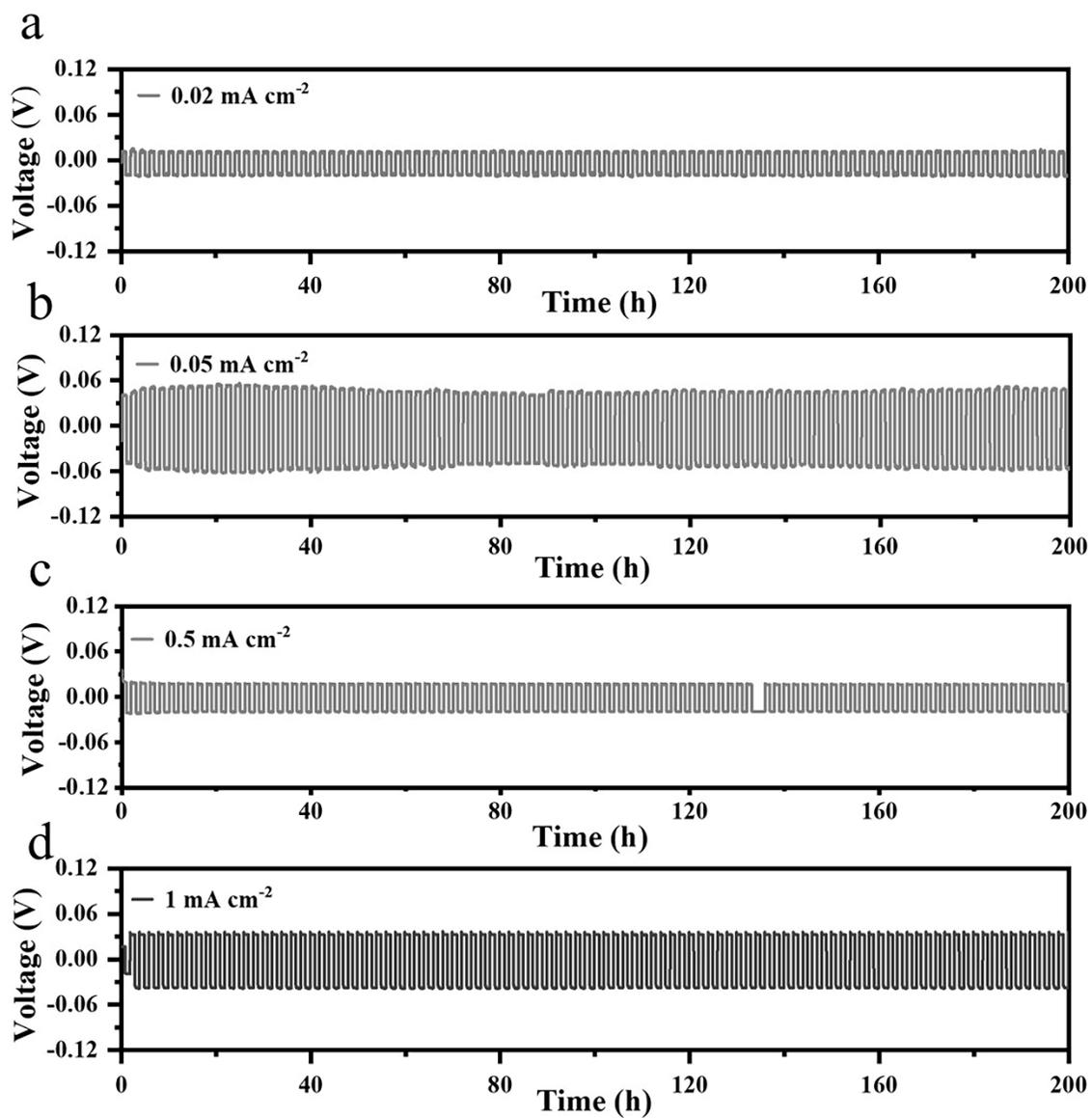


Figure S7 Li stripping and plating of the Li | Li/MOF-808-Li | Li cell at a current density of (a) 0.02 mA cm⁻²; (b) 0.05 mA cm⁻²; (c) 0.5 mA cm⁻²; (d) 1 mA cm⁻².

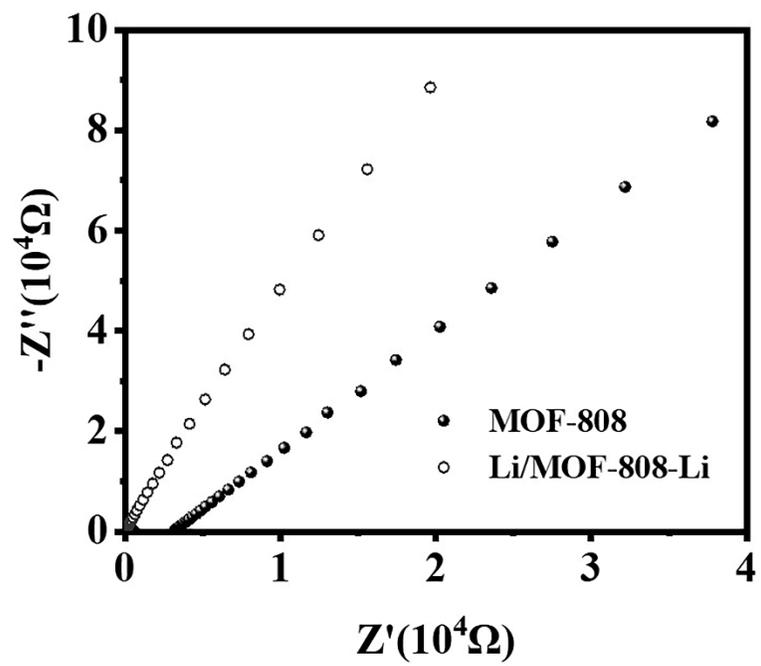


Figure S8 The pristine MOF and Li/MOF-808-Li electrolyte membrane resistance.

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