

Supporting Information

The Effects of Fluorinated Metal-Organic Frameworks as Additives in Polymer-Based Electrolytes for All-Solid-State Lithium Batteries

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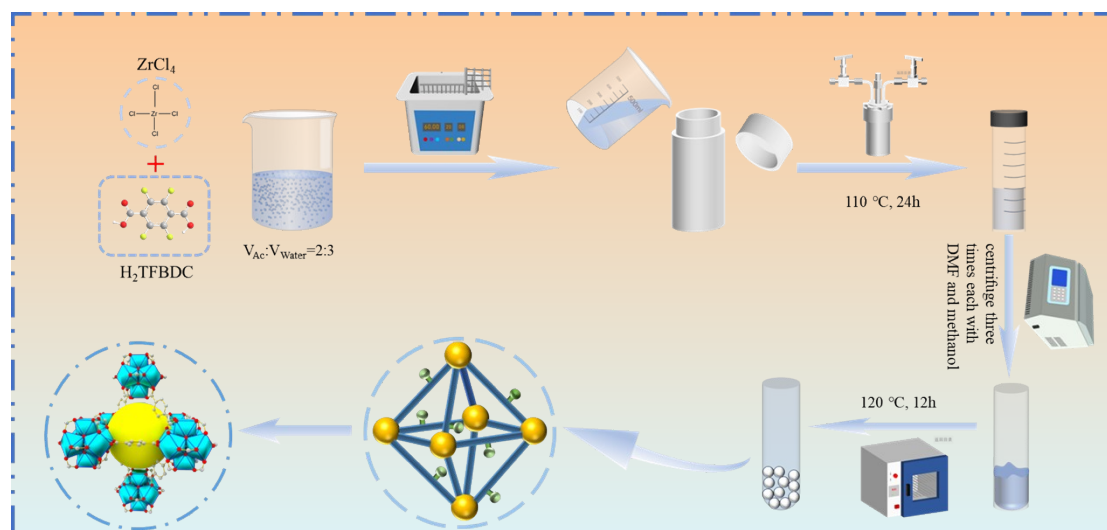
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1. Materials

Zirconium(IV) chloride (ZrCl_4 , 99.9%), N,N-dimethylformamide (DMF, 99.0%), Tetrafluoroterephthalic acid (H_2TFBDC), N,N-dimethylacetamide (DMAc, 99.0%), Methanol (99.7%), PVDF-HFP ($M_w \sim 400000$), Bis(trifluoromethane)sulfonimide lithium salt (LiTFSI, 99.0%) and 1-Methyl-2-pyrrolidone (NMP, 99.0%) were available from Aladdin; Acetic acid (99.5%), Acetone (99.0%), and Anhydrous ethanol (99.7%) were bought from Sinopharm.

2. Synthesis of UIO-66- $\text{F}_4(\text{Zr})$

UIO-66- $\text{F}_4(\text{Zr})$ was obtained by a simple solvothermal method (Scheme S1). Firstly, 5 mmol of ZrCl_4 and 5 mmol of H_2TFBDC were dissolved in 50 ml aqueous glacial acetic acid solution ($V_{\text{water}}: V_{\text{acetic acid}} = 3:2$) and sonicated for thirty minutes until the solution was clarified. The above solution was then transferred into a 100 ml Teflon autoclave and reacted at 110 °C for 24 h. After it was cooled to room temperature and centrifuged to obtain a white powder. The powder was washed three times with DMF and methanol, and finally dried at 80 °C overnight to obtain UIO-66- $\text{F}_4(\text{Zr})$ powder, which needed to be vacuum activated at 120 °C for 10 h.



Scheme S1. Schematic diagram for the preparation of UIO-66- $\text{F}_4(\text{Zr})$

3. Preparation of SCEs

A coating method was used to prepare the SCEs. Initially, different mass ratios of LiTFSI, UIO-66- $\text{F}_4(\text{Zr})$, and PVDF-HFP were dissolved in DMAc/Acetone

(V:V=2:1) and stirred for 3 h at 70 °C, then a homogeneous slurry was achieved by continuously stirred the mixture overnight at 40 °C. After that, the slurry was coated onto a polytetrafluoroethylene (PTFE) flat plate and vacuum dried at 60 °C for 12 h. Finally, the obtained film was punched into 18 mm diameter discs using a button cell punch and kept in the argon-filled glovebox. Table S1 shows the proportions of the various components in the SCEs, named SCE-0, SCE-1, SCE-2, and SCE-3, respectively.

Table S1 Components in different SCE membranes

SCEs	MOF/wt.%	PVDF-HFP/wt.%	LiTFSI/wt.%
SCE-0	0	70	30
SCE-1	5	65	30
SCE-2	10	60	30
SCE-3	15	55	30

4. Materials characterizations

The crystal structure of UIO-66-F₄(Zr) powder was analyzed using X-ray diffraction (XRD) over a range of 5° to 50° at 2°/min. The surface morphology of UIO-66-F₄(Zr) and SCEs films was characterized by a field emission scanning electron microscope. The elemental distribution uniformity of the SCEs films was observed by using energy-dispersive X-ray spectroscopy (EDS).

5. Cell assembly and test

First, the LiFePO₄ (LFP) cathode was obtained by mixing the active material, conductive carbon black, and PVDF in a 7:2:1 ratio, and NMP as the solvent. The homogeneous slurry was subsequent coated onto aluminum foil and dried for approximately 6 h at 60 °C, after which it was further dried overnight in a vacuum oven at 120 °C. Coin cells were sequentially constructed with LFP, SCEs, and lithium metal. Additionally, cells with similar structures such as SS||SS, SS||Li and Li||Li were put together in a glove box.

6. Electrochemical performance

The electrochemical impedance spectroscopy (EIS) of the assembled SS/SCEs/SS cells were tested on a CHI660E electrochemical workstation at different temperatures (30 °C-90 °C). The EIS parameters were set between a frequency range of 10^{-6} to 10^{-1} Hz at an amplitude of 10 mV. The ionic conductivity (σ) was then calculated using equation (1).

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

SS||Li cells were assembled, and the electrochemical window of the SCEs was studied by linear sweep voltammetry (LSV) under a scan rate of 1 mV/s and a voltage range of 2-7 V. Li||Li symmetrical cells were also assembled, and its initial interfacial resistance (R_0) was measured using EIS at 60 °C. Finally, the steady-state interfacial resistance (R_{SS}) was measured again using EIS. The lithium ion transference number (t_{Li^+}) was calculated using equation (2), where ΔV is the DC voltage of 10 mV, I_0 is the initial current, and I_{SS} is the steady-state current.

$$t_{Li^+} = \frac{I_{SS}(\Delta V - I_0 R_0)}{I_0(\Delta V - I_{SS} R_{SS})} \quad (2)$$

Table S2 EDX spectral scanning results

element	atomic number	normalized quality (%)	Atoms (%)
C	6	37.74	49.56
N	7	4.76	5.36
O	8	6.60	6.50
F	9	42.63	35.39
S	16	5.49	2.70
Zr	40	2.77	0.48
		100.00	100.00

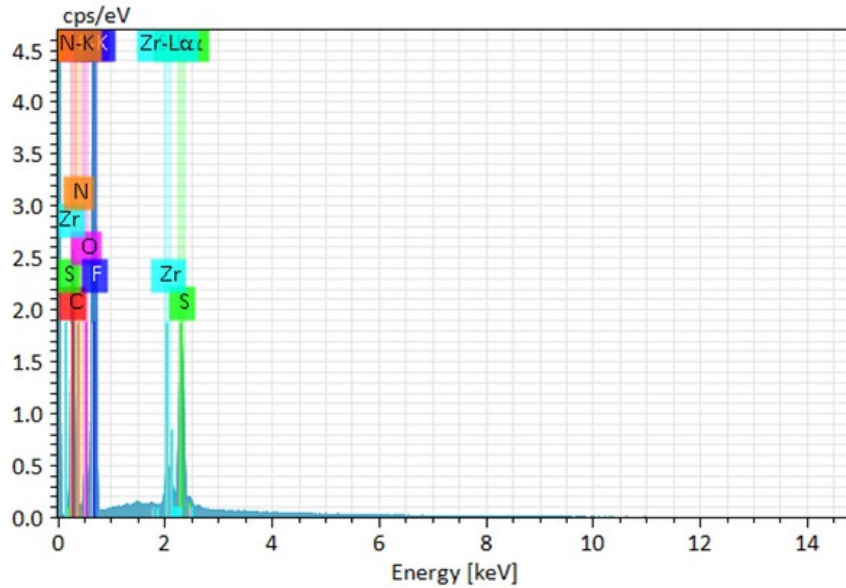


Figure S1. Individual elemental analysis diagram for EDX

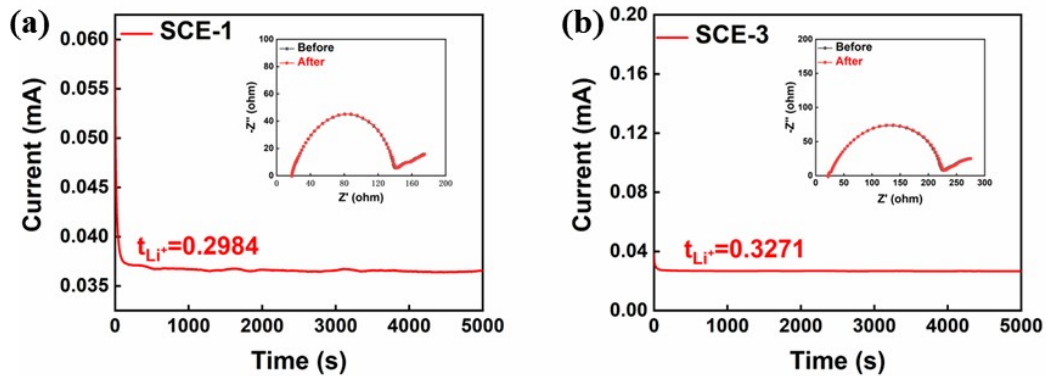


Figure S2. i-t profile of different SCEs-based symmetric Li/Li cells (the inset shows the electrochemical impedance spectroscopy curves before and after polarization). (a) SCE-1; (b)

SCE-3.

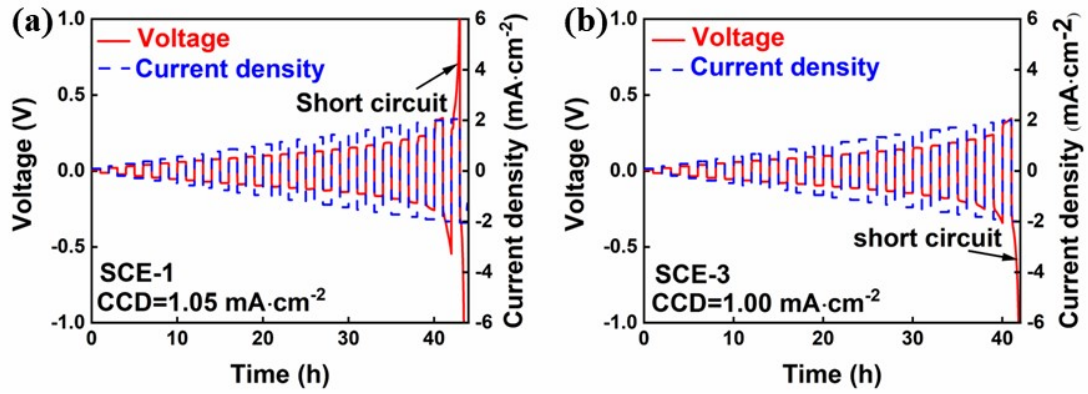


Figure S3. Galvanostatic cycling of (a) Li/SCE-1/Li and (b) Li/SCE-3/Li cells at step-increased current densities.

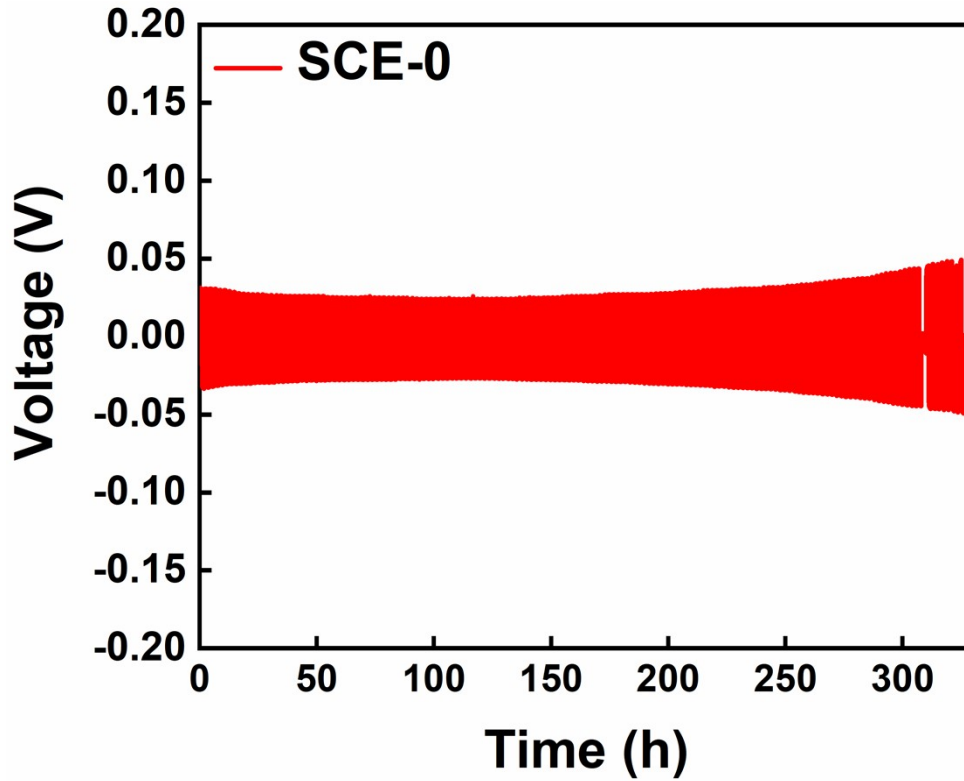


Figure S4 Constant current cycling curve of the Li/SCE-0/Li cell at 60°C with a current density of 0.1 mA cm^{-2} .

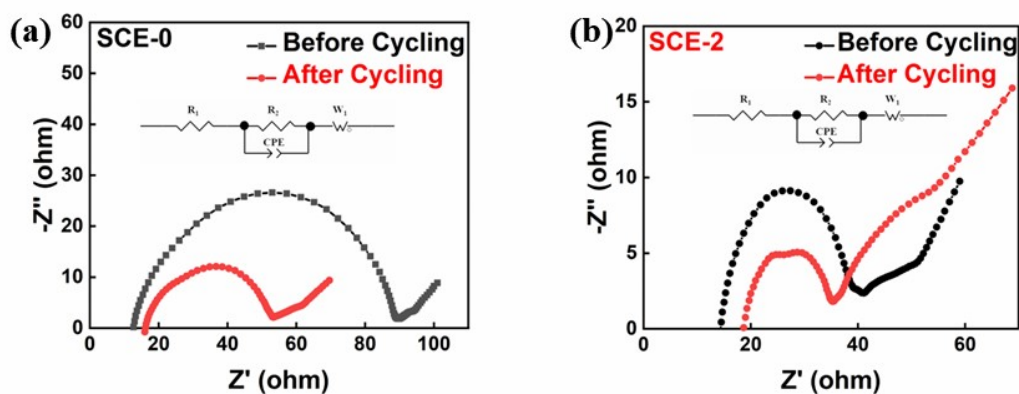


Figure S5. Nyquist plots of (a) SCE-0 and (b) SCE-2 batteries before cycling (black) and after 100 cycles (red) at 0.1 mA cm^{-2} at $60 \text{ }^\circ\text{C}$; the inset is the equivalent circuit.

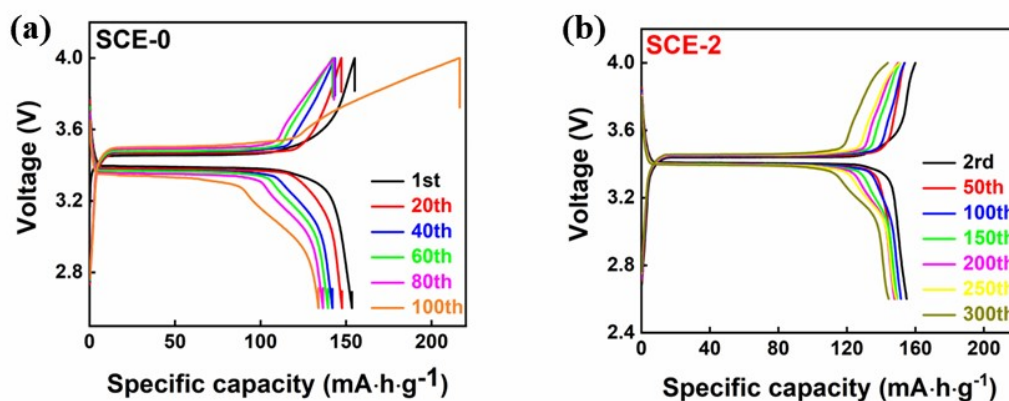


Figure S6. Voltage curves of charging-discharging processes in Li/SCEs/LFP cells at $60 \text{ }^\circ\text{C}$.
(a) SCE-0. (b) SCE-2.

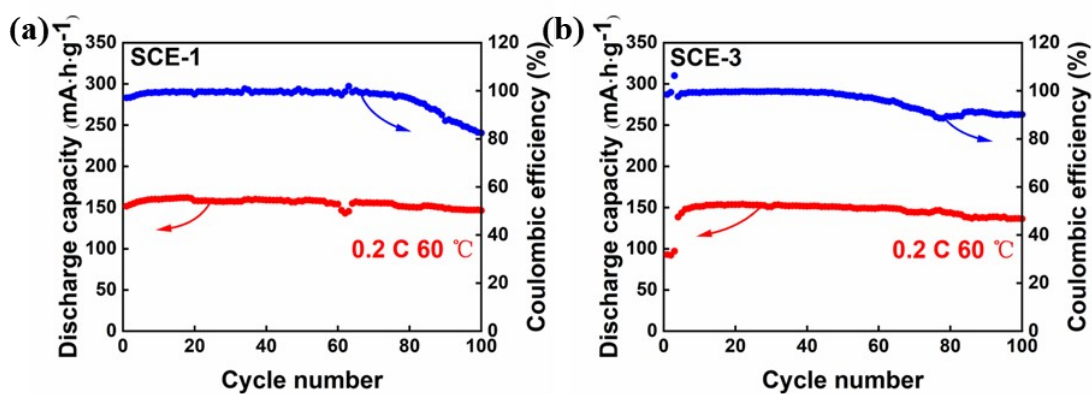


Figure S7. Full-cell cycling performance of SCEs at 0.2 C . (b) SCE-1; (c) SCE-3.

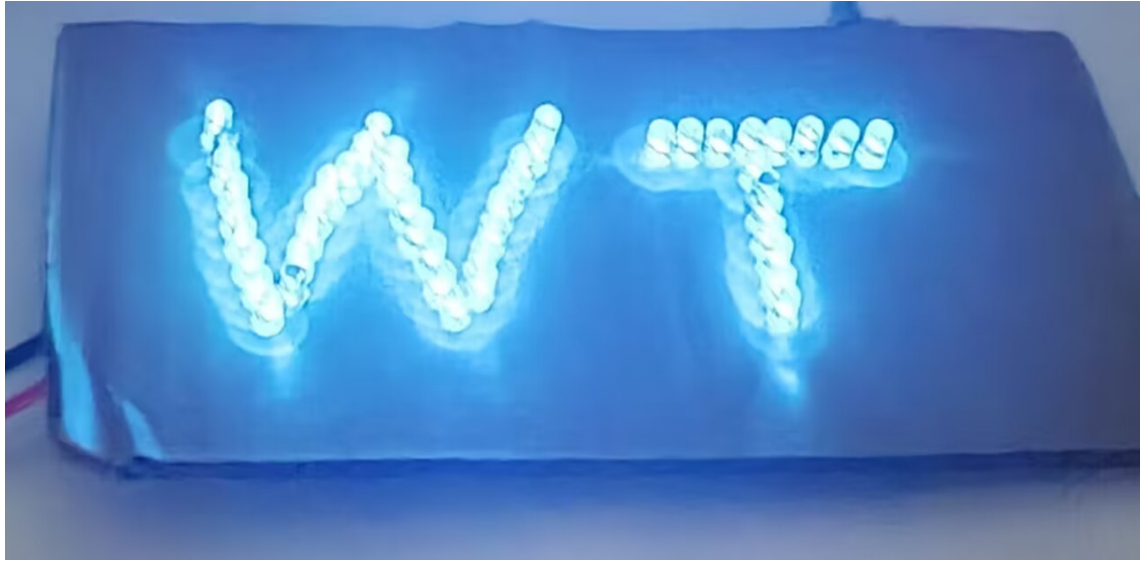


Figure S8. Optical photograph of SCE-2 powering an LED light.