Supporting Information

A Near-room Temperature Solid Composite Electrolyte Enabled by Lithiated Sulfonated Covalent Organic Frameworks

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Experimental Section

Materials

Materials form Aladdin: 2,5-diaminobenzene-1,4-disulfonic acid ($Pa(SO_3H)_2$), 2,4,6-Trihydroxybenzene-1,3,5-tricarbaldehyde (Tp), PVDF-HFP (Mw-4000), dioxane, benzaldehyde, acetic acid (99.5%), mesitylene, bis(trifluoromethane)sulfonimide lithium salt (LiTFSI, 99.0%), N,N-dimethylacetamide (DMAC, 99.0%), and1-methyl-2-pyrrolidone (NMP, 99.0%). Materials from Sinopharm: anhydrous ethanol (99.7%) and acetone (99.0%).

Structural characterization

Scanning electron microscopy (SEM) was employed to examine the morphologies of the TpPa-$(SO_3Li)_2$ and SCEs films. The crystal structure of TpPa-$(SO_3H)_2$ and TpPa-$(SO_3Li)_2$ samples were observed by using X-ray diffraction (XRD) between the range of 3° to 30° at 10°/min. Elemental compositions of (TpPa-$SO_3H)_2$ and (TpPa-$SO_3Li)_2$ powders were obtained via X-ray photoelectron spectroscopy (XPS). Additionally, the

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elemental distribution uniformity of the SCEs was observed through energy-dispersive X-ray spectroscopy (EDS).

Synthesis of TpPa-$(SO_3Li)_2$

As shown in Fig. S1, firstly, 10.5 mg 1,3,5-triformylphloroglucinol (TP) and 20 mg of Pa$(SO_3H)_2$ were dissolved in a Pyrex tube containing 0.1 mL of mesitylene, 0.4 mL of 1,4-dioxane, 0.1 mL of 6 mol/L aqueous acetic acid, and 2 μL of benzaldehyde. Sonicate the mixture for 10 min, then heat it at 120 °C for three days. Subsequently, the product was washed by sequential centrifugation three times with acetone, deionized water, and DMAC, then dried overnight at room temperature to obtain TpPa-$(SO_3H)_2$ powder.

Place the obtained COF powder in a 1 M lithium nitrate solution for ion exchange, repeating the process three times. Centrifuge to collect the lithium-doped COF powder, and dry it under vacuum at room temperature overnight to obtain TpPa-$(SO_3Li)_2$ powder.

Preparation of SCEs

A coating method was used to prepare the SCEs. Initially, PVDF-HFP, LiTFSI, and COF (TpPa-$(SO_3H)_2$/TpPa-$(SO_3Li)_2$) were added at a fixed mass ratio of 6:3:1 and dissolved in DMAC/Acetone (V:V = 1:2) and stirred at 70 °C for 5 h, then a well-mixed slurry was achieved by continuously stirred the mixture overnight at 40 °C. After preparation, the slurry was cast onto a PTFE plate and subjected to vacuum drying (60 °C, 12 h). The resulting film was subsequently punched into 18 mm diameter discs using a button cell punch and kept in the argon-filled glovebox.

Cathode preparation and cell assembly

Firstly, to prepare the LFP cathode slurry, the active material, conductive carbon black, and polyvinylidene fluoride (PVDF) binder were combined in a weight ratio of 7:2:1 and uniformly dispersed in N-methyl-2-pyrrolidone (NMP). After achieving uniform dispersion, the slurry was uniformly coated onto an aluminum foil current collector and dried for 6 h at 60 °C. To eliminate any residual NMP solvent, the coated aluminum foil was then placed in a vacuum oven at 120 °C overnight. Subsequently, coin cells were constructed sequentially using a lithium metal anode, a LFP cathode, and SCEs. In addition, control cells with analogous structures, including Li||Li, SS||Li, and SS||SS, were fabricated in a glove box under the same experimental conditions to facilitate subsequent performance comparison and analysis.

Electrochemical characterization

The electrochemical impedance spectroscopy (EIS) measurements of the fabricated SS/SCEs/SS batteries were systematically investigated over a temperature range of 27–90 °C utilizing a CHI660E electrochemical workstation. For the EIS tests, a sinusoidal voltage perturbation of 10 mV was employed, covering frequencies from 106 Hz down to 0.1 Hz. Subsequently, the ionic conductivity (σ) was determined using formula (1).

$$\sigma = \frac{L}{R \cdot S} \tag{1}$$

SS||Li symmetrical cells were constructed to investigate the electrochemical stability windows of the as-prepared SCEs, and the potential was swept from 2 to 7 V at a scan rate of 1 mV/s using linear sweep voltammetry (LSV). Subsequently, to characterize the interfacial resistive behavior, Li||Li symmetrical cells were fabricated. The initial interfacial resistance (R0) was measured via EIS at 30 °C, followed by re-testing to obtain the steady-state interfacial resistance (RSS). Finally, the tLi^{+} was obtained according to formula (2), where ΔV represents the direct current (DC) voltage of 10 mV, I0 means the initial current, and ISS stands for the steady-state current.

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

In this study, cyclic voltammetry (CV) was conducted using a CHI660E electrochemical workstation to assess the electrochemical stability of the as-prepared LFP cathode sheets and polymer electrolyte membranes in a Li/LFP full cell configuration. The specific test parameters were set as follows: the scanning voltage range was controlled at 2.6–4.0 V, the scanning rate was maintained at 0.1 mV/s, and a total of four scanning cycles were applied.

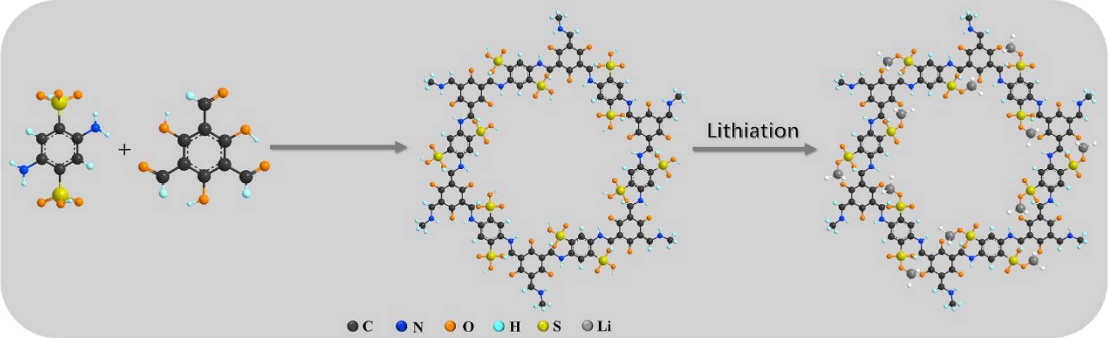

Figure S1. Schematic illustration of the synthesis routes for TpPa-$(SO_3H)_2$ and TpPa-$(SO_3Li)_2$.

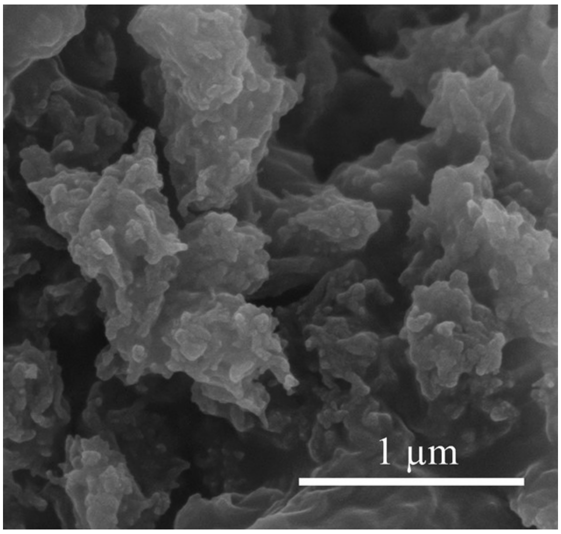

Figure S2. SEM images of TpPa-$(SO_3Li)_2$ powder.

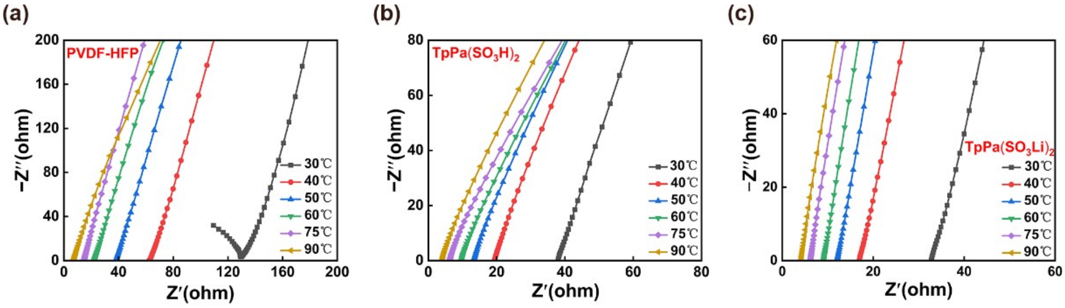

Figure S3. (a) EIS curves of SS//Li at different temperatures. (a) SCE of PVDF-HFP; (b) SCE of TpPa-$(SO_3H)_2$; (c) TpPa-$(SO_3Li)_2$ SCE.

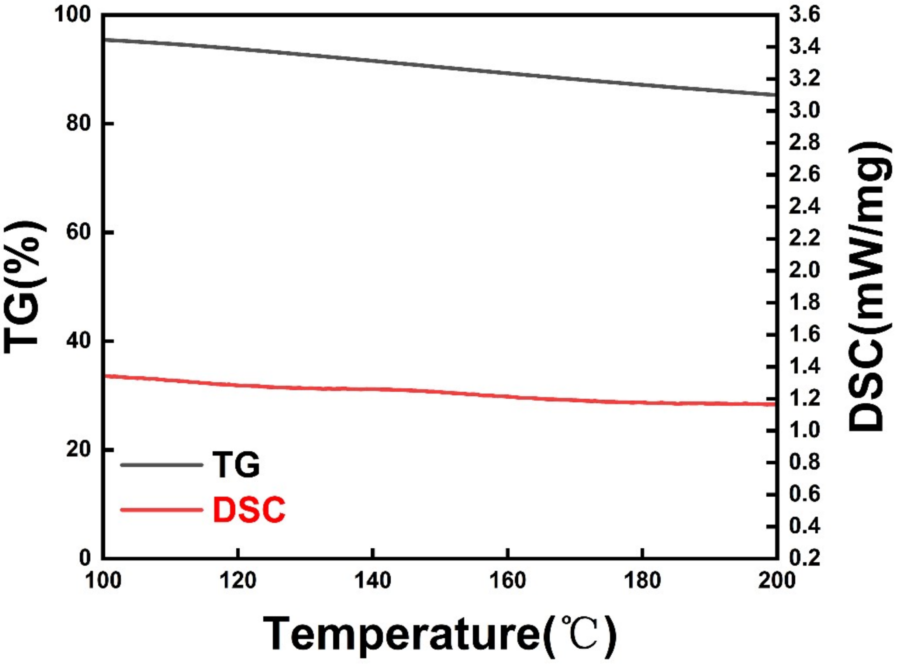

Figure S4. TG-DSC curves of TpPa-$(SO_3Li)_2$ SCEs.

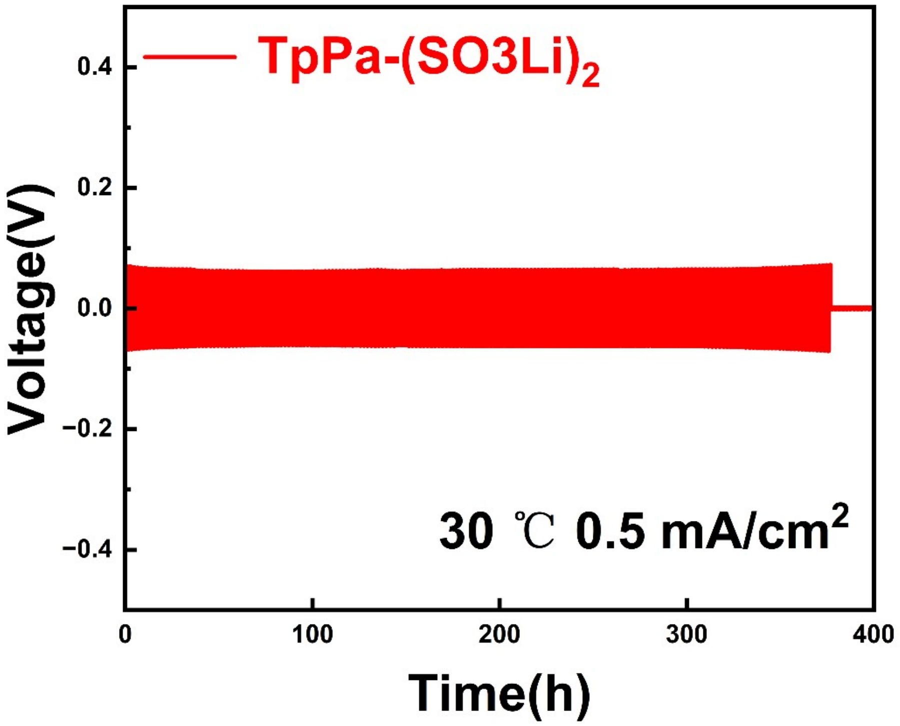

Figure S5. Long-term cycling performance of TpPa-$(SO_3Li)_2$ SCE at 0.5 mA/cm^2.

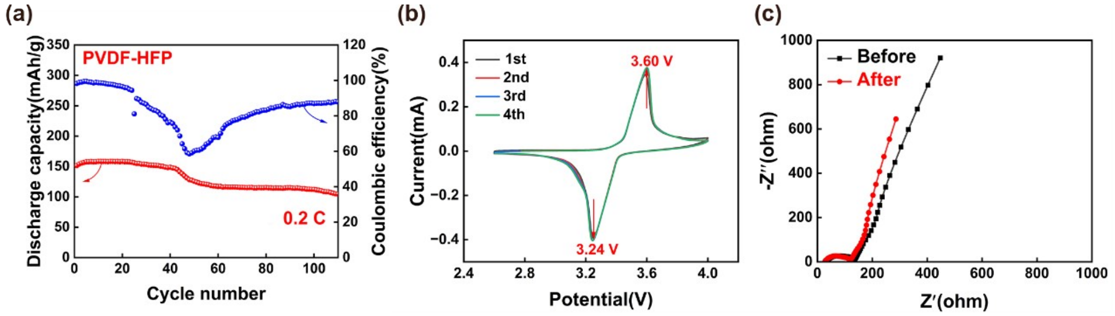

Figure S6. (a) The cycling performances of PVDF-HFP SCEs at 30 °C and 0.2 C. (b) CV curve of TpPa-$(SO_3Li)_2$ SCE at 30 °C. (c) Nyquist plot of TpPa-$(SO_3Li)_2$ SCE after 10 cycles.

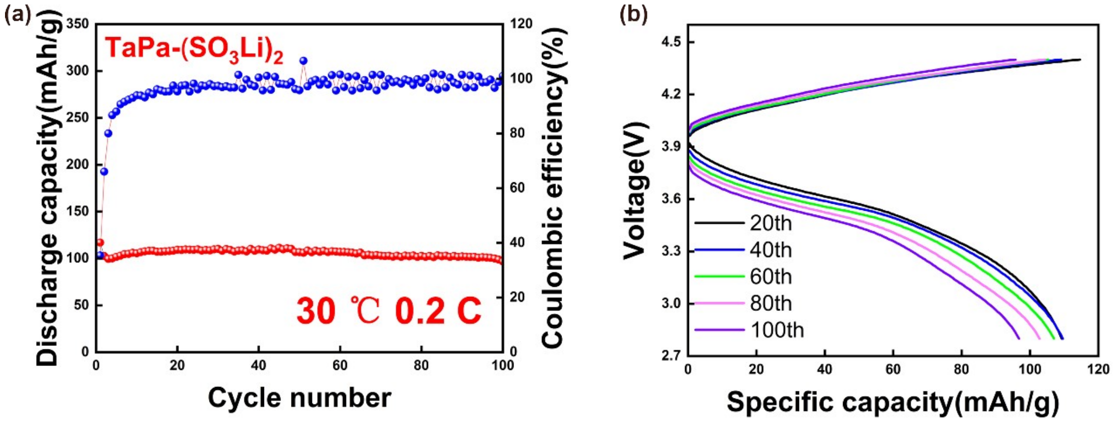

Figure S7. (a) The cycling performances of NCM |TpPa-$(SO_3Li)_2$ SCE| Li battery at 30 °C and 0.2 C .(b) Charge-discharge curves of NCM|TpPa-$(SO_3Li)_2$ SCE|Li batteries.