Supporting Information

Zwitterion metal covalent organic framework constructed from lithium salts to reinforce Poly(ethylene oxide)/Poly(propylene carbonate) composite solid electrolytes

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1. Synthesis and characterization.

1.1 Process synthesis of HUT4

Squaraine-based zwitterionic covalent organic framework nanosheet (HUT4) was prepared by conventional solvothermal synthesis method. The squaric acid monomer (205 mg, 1.8 mmol) and melamine monomer (277 mg, 2.2 mmol) were weighed and dissolved in n-butanol (8 mL) and mesitylene (4 mL), and reacted for 72 h under 120°C argon atmosphere. After the reaction, the reactants were filtered. Then the obtained powders were then washed and filtered with anhydrous ethanol dichloromethane and tetrahydrofuran for three times. Finally, the light yellow powder was vacuum dried at 60°C for 12 h to obtain HUT4 with a yield of about 62%.

1.2 Synthesis of HUT4Li

Put HUT4 (20 mg) and CH_3COOLi (60 mg) into a dry ball milling tank and dissolve them in anhydrous methanol solution (3 mL). Run for 6 h according to the four-step setting procedure of forward rotation (30 min), intermittent (2 min), reverse rotation (30 min) and intermittent (2 min). Transfer the system to the Buchner funnel, wash and filter it with dry anhydrous methanol (200 mL), and vacuum dry it for 6 h at 45°C to obtain light white solid powder (HUT4Li), with a yield of about 72%.
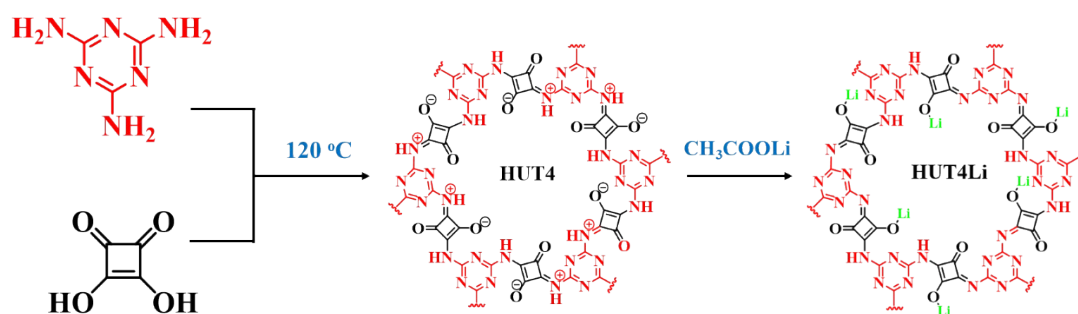
1.3 Preparation of PEO-xHUT4Li (x=5,10,15,20) composite polymer electrolyte

The composite polymer electrolyte is prepared by solution pouring method. Before using PEO (molecular weight 600000) and LiTFSI, it is necessary to dry at 60°C and 100°C for 24 h respectively. First dissolve PEO and LiTFSI into anhydrous acetonitrile (n(EO)/n(Li⁺)=20:1), then add HUT4Li materials with different proportions (5%, 10%, 15%, 20 wt% of PEO) into the solution, and place them at room temperature and stir for 48 h. Pour the obtained solution onto the

polytetrafluoroethylene plate for molding, dry it in vacuum at 60 °C for 3 days, cool it to room temperature and place it in the glove box for 4 days, finally obtain a thickness about 90 μm The PEO-xHUT4Li (x=5,10,15,20) electrolyte is cut into a film with a diameter of 19 mm and stored in a glove box before use.

1.4 Preparation of PPC-xHUT4Li (x=5,10,15,20) composite polymer electrolyte

The preparation process is similar to PEO-xHUT4Li polymer electrolyte. Before using PPC (molecular weight 120000) and LiTFSI, it is necessary to dry at 80°C and 100°C for 12 h and 24 h respectively. First, dissolve PPC and LiTFSI into N, N-dimethylacetyl, then add HUT4Li materials with different proportions (5%, 10%, 15%, 20 wt% of PPC) into the solution, and stir at room temperature for 48 h. Pour the obtained solution onto a cut round Tp with a diameter of 24 mm, and place it at room temperature for 24 h to volatilize the excess solvent. Finally, vacuum dry the semi-dry film at 60 °C for 3 days, and place it in a glove box for 4 days to obtain a thickness of about 70 μm of polymer electrolyte, cut it into a film with a diameter of 19 mm, and store it in a glove box before use.

1.5 Preparation of S/CNT cathode

Weigh the sulfur powder and CNT powder in a 3:1 mass ratio and put them in an agate mortar for full grinding for 40 minutes, and then put S/CNT in the polytetrafluoroethylene reactor, fill the reactor with argon in the vacuum argon glove box and seal it. The hydrothermal reactor was heated in an oven at 155 °C for 12 h. After cooling to room temperature, the S/CNT, CNT and PVDF are added to the mortar at a mass ratio of 8:1:1 for grinding. Add an appropriate amount of NMP solvent into the mortar and continue to grind until a uniform black slurry is formed. Then, use the controllable scraper to evenly coat the ground slurry on the carbon-aluminum foil, and dry it for 12 h in a blast drying oven at 60 °C. Finally, the completely dried cathode is cut into a piece with a diameter of 10 mm for assembling the Li-S battery. The sulfur load of the cathode is about 1.29 mg cm^{-2}.

1.6 Assembly of Li-S battery

Assemble the CR2032 battery in a vacuum argon glove box with oxygen and water content less than 0.01 ppm. The cathode and anode of are S@CNT and metal lithium. Liquid electrolyte of which is 1 wt% LiNO$_3$ and 1.0 mol L^{-1} bis (trifluoromethane xanthyl) lithium (LiTTFSI) are dissolved in a mixed solution composed of 1,3-dioxane (DOL) and 1,2-dimethoxyethane (DME)

(volume ratio 1:1). CR2032 battery was assembled by cathode (S/CNT)/composite solid electrolyte /anode (Li) with 5 uL liquid electrolyte. The assembled battery needs to be placed in the glove box for 12 h before conducting a series of electrochemical tests.

1.7 Electrochemical performance characterization

Characterizations: The structure of HUT4Li was characterized by Fourier-transform infrared (FT-IR) spectrum (Vector-22 model, Bruker Co.) and solid-state nuclear magnetic resonance (NMR) spectrum (Agilent 600 M, Agilent Co.). The crystal structure of the samples was identified by X-ray powder diffraction (XRD, Bruker) at a scanning rate of 1° min^{-1} from 5° to 50°. An X-ray spectrometer and a transmission electron microscope (TEM) (Talos F200S, FEI Co.) were used. The surface morphology of the sample was observed with a Nova Nano SEM450 field-emission scanning electron microscope (FEI Co.). An SDT-TG Q600 thermogravimetric analyzer (TGA Instruments) was used to test the changing trend between sample quality and temperature. The electronic universal testing machine controlled by a CMT6104 microcomputer was used to detect the mechanical properties of the composite electrolyte membrane. The AA stacking structures of HUT4Li were simulated by Materials studio 7.0 (Forcite module), and its simulated PXRD was calculated by the PXRD diffraction module. Then, the PXRD refinements module refined the experimental PXRD by using Pawley refinements. Finally, the electrostatic potential (ESP) of HUT4Li that had been optimized at the r2scan-3c[1] level by using ORCA 5.0.1[2-4] software was calculated by Multiwfn 3.8 (dev.) [5].

A differential scanning calorimeter (DSC) was used to study the crystallinity of the composite material. The temperature was raised from −30 to 150 °C at a rate of 10 °C min^{-1}. The crystallinity (χ_C) was calculated by the following formula 1, where ΔH_m represents the melting enthalpy of the solid electrolyte, ΔH_{PEO} is 196.4 J g^{-1}, and f_{PEO} is the mass fraction of PEO.

$$\chi_C = \frac{\Delta H_m}{\Delta H_{PEO} f_{PEO}}$$

(1)

Ionic conductivity (σ)：The electrochemical impedance spectroscopy (EIS) was measured using the electrochemical workstation of CHI660E of Shanghai Chenhua Company. The measured temperature range was 30 °C~90 °C, the frequency range was 0.1 Hz~100 000 Hz, and the amplitude was 10 mV. In order to accurately measure the ionic conductivity of the polymer electrolyte membrane, the stainless steel （SS） symmetrical battery (SS/Electrolyte/SS) needs to be placed

at the corresponding measuring temperature for 1 h to reach the steady state. The conductivity is calculated by formula 2:

$$\sigma = \frac{L}{R * S}$$

(2)

Among them, σ is the ionic conductivity (S cm^{-1}), L is the thickness of the electrolyte (cm), S is the area of the electrolyte (cm^2), and R is the intrinsic impedance of the electrolyte.

Lithium ion transfer number (t_{Li^+}): The t_{Li^+} of polymer electrolyte is measured by the combination of AC impedance method and direct-current (DC) polarization at 60 °C. The lithium-lithium symmetrical battery (Li/Electrolyte/Li) was assembled in an argon-filled glovebox. AC impedance is used to measure the resistance before polarization (R_0) and after polarization (R_S)with frequency range is 0.1 Hz~100 000 Hz and the amplitude is 10 mV. And the current values before polarization (I_0) and at steady state (I_S) were recorded with a voltage of 10 mV (ΔV). t_{Li^+} is calculated by formula 3

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

(3)

The Linear sweep voltammetry (LSV) was determined using a Li/Electrolyte/SS model from 0 to 6 V at a scan rate of 1 mV s^{-1}, and the measurement temperature is 60 °C. Electrochemical workstation of CHI660E of Shanghai Chenhua Company.

The Cyclic voltammetry (CV) curve using the electrochemical workstation of CHI660E produced by Shanghai Chenhua Company, with the scanning range of 1.6~2.8 V and the scanning speed of 0.1 mV s^{-1}.
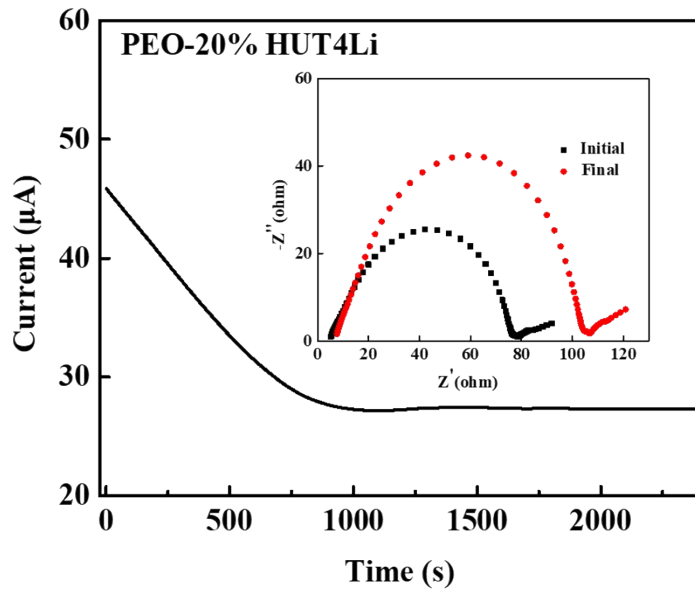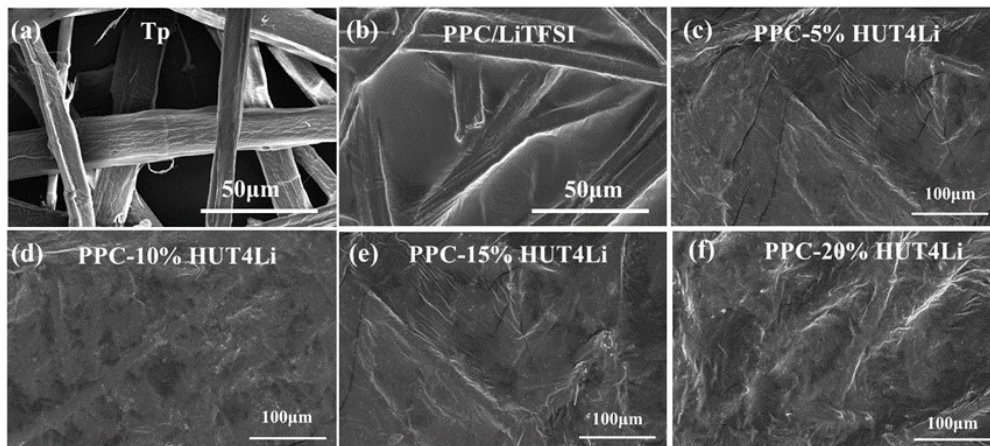
Figure S1 PEO-20%HUT4Li electrolytes.

Figure S2 SEM image of (a) Tp; (b) PPC/LiTFSI; (c) PPC-5%HUT4Li; (d) PPC-10%HUT4Li; (e) PPC-15%HUT4Li; (f) PPC-20% HUT4Li.
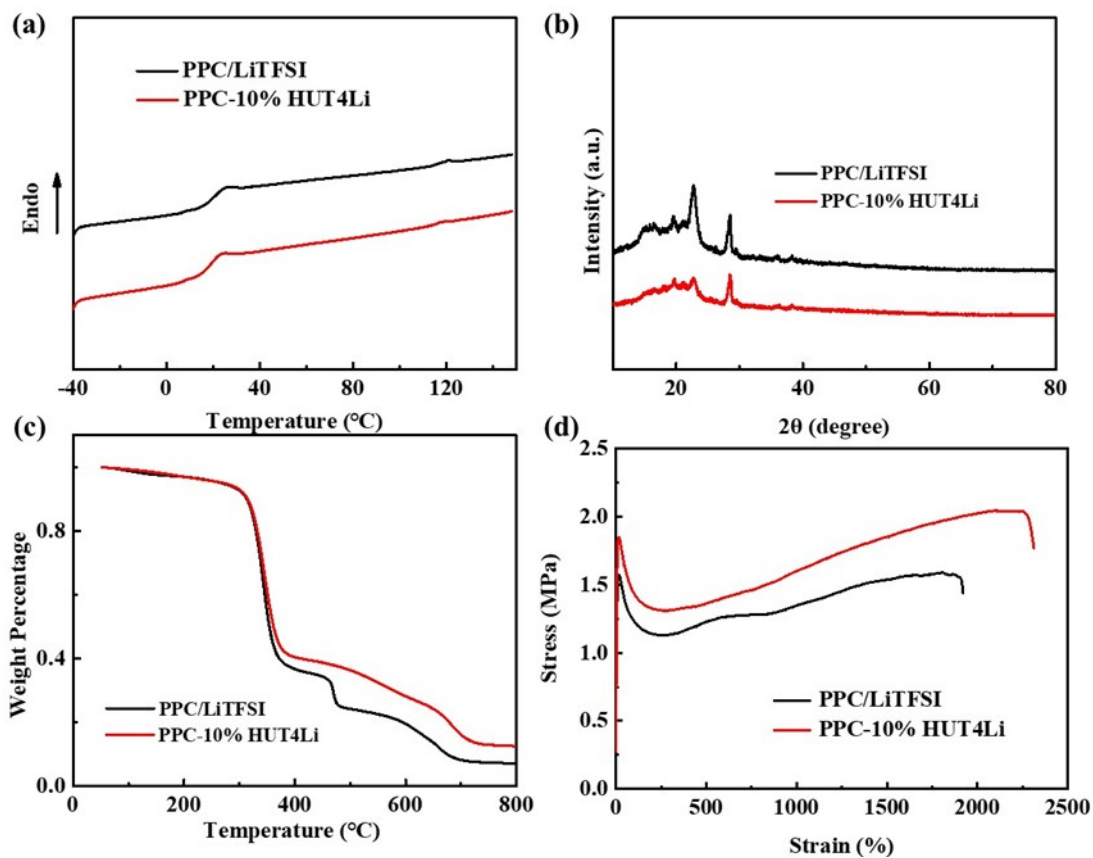
Figure S3 (a) DSC curve of two polymer electrolytes; (b) XRD patterns of PPC/LiTFSI and PPC-10%HUT4Li; (c) TGA of curves of two polymer electrolytes; (d) Tensile stress-strain curve of two polymer electrolytes.
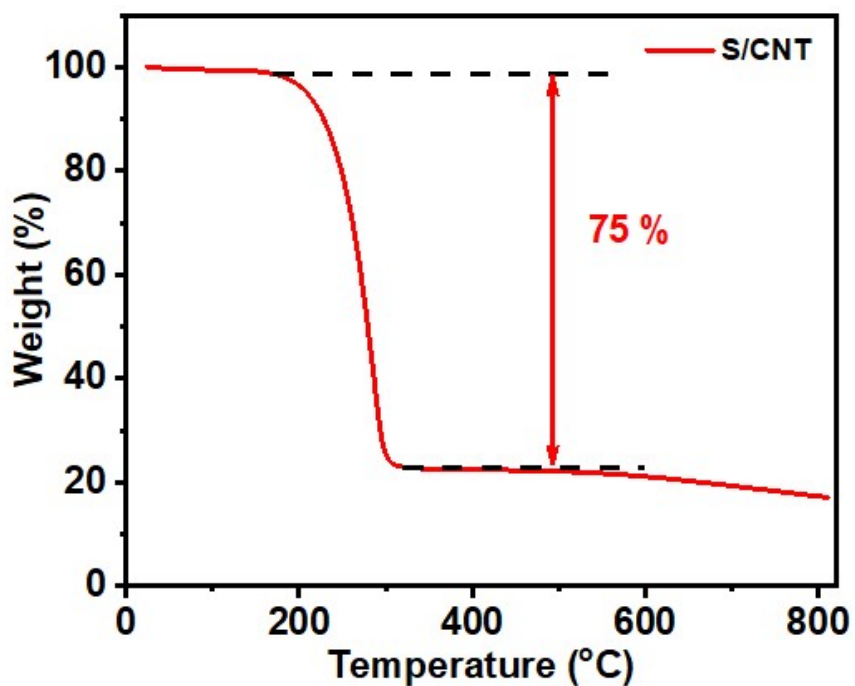

Figure S4 The sulfur content of S/CNT cathode.

The S loading was calculated by the following formula (4):

$$\frac{(m_1 - m_2) \times 0.75 \times 0.8}{\pi r^2} = \rho_s \tag{4}$$

m_1 is the quality of cathode (mg), m_2 is the quality of the aluminum current collector (mg), r is the radius of cathode (cm).

Table S1. DSC datas of PEO-based electrolytes.

Electrolytes	$T_m/\,^oC$	$\Delta H_m/\ J\ g^{-1}$	$\chi_c\ /\ \%$
PEO/LiTFSI	60.87	60.27	40.78
PEO-5%HUT4Li	54.91	56.32	39.37
PEO-10%HUT4Li	**50.67**	**46.64**	**37.91**
PEO-15%HUT4Li	51.53	46.52	40.35
PEO-20%HUT4Li	51.39	45.33	40.62

Table S2. Data of SPEs by Tensile Measurement.

Electrolytes	Elastic Modulus/MPa	Tensile strength/MPa	Percentage of Breaking Elongation/%
PEO/LiTFSI	10.36	1.02	2463.52
PEO-5%HUT4Li	11.91	1.09	2374.25
PEO-10%HUT4Li	**17.46**	**1.37**	**2677.13**
PEO-15%HUT4Li	**16.93**	**1.29**	**2706.27**
PEO-20%HUT4Li	12.11	1.14	2529.14

Table S3 Ionic conductivity data of polymer electrolyte (S cm^{-1}).

Temperature	30°C	40°C	50°C	60°C	70°C	80°C	90°C
PEO/LiTFSI	6.1×10^{-6}	1.7×10^{-5}	1.4×10^{-4}	3.3×10^{-4}	4.6×10^{-4}	6.2×10^{-4}	9.7×10^{-4}
PEO-5% HUT4Li	1.2×10^{-5}	2.6×10^{-6}	1.8×10^{-4}	4.8×10^{-4}	6.4×10^{-4}	1.1×10^{-3}	1.4×10^{-3}
PEO-10% HUT4Li	$\mathbf{2.3\times10^{-5}}$	$\mathbf{5.9\times10^{-5}}$	$\mathbf{2.4\times10^{-4}}$	$\mathbf{7.4\times10^{-4}}$	$\mathbf{1.1\times10^{-3}}$	$\mathbf{2.5\times10^{-3}}$	$\mathbf{3.4\times10^{-3}}$
PEO-15% HUT4Li	1.5×10^{-5}	7.6×10^{-5}	2.7×10^{-4}	7.1×10^{-4}	1.1×10^{-3}	1.9×10^{-3}	2.7×10^{-3}
PEO-20% HUT4Li	1.1×10^{-5}	2.4×10^{-5}	1.3×10^{-4}	4.4×10^{-4}	6.3×10^{-4}	1.4×10^{-3}	1.9×10^{-3}

Table S4 Data of mechanical properties number of two polymer electrolytes.

Electrolytes	Elastic Modulus/MPa	Tensile strength/MPa	Percentage of Breaking Elongation/%
PPC/LiTFSI	7.49	1.59	1923.52
PPC-10%HUT4Li	15.96	2.07	**2311.43**

Table S5 Ionic conductivity data of polymer electrolyte (S cm^{-1}).

Temperature	30°C	40°C	50°C	60°C	70°C	80°C	90°C
PPC/LiTFSI	7.9×10^{-6}	1.9×10^{-5}	2.5×10^{-5}	5.1×10^{-5}	5.6×10^{-4}	6.2×10^{-4}	1.2×10^{-3}
PPC-10% HUT4Li	9.8×10^{-6}	2.4×10^{-5}	3.9×10^{-5}	5.9×10^{-5}	1.9×10^{-4}	6.3×10^{-4}	1.9×10^{-3}

Reference:

1.   Grimme, S.; Hansen, A.; Ehlert, S.; Mewes, *J Chem Phys* **2021**, *154*, 064103.

2.   Neese, F. *WIREs Computational Molecular Science* **2011**, *2*, 73-78,.

3.   Neese, F.; Wennmohs, F.; Becker, U.; Riplinger, C. *J Chem Phys* **2020**, *152*, 224108,.

4.   Neese, F. *Molecular Science* **2017**, *8*, doi:10.1002/wcms.1327.

5.   Lu, T.; Chen, F. *J Comput Chem* **2012**, *33*, 580-592,.