Support Information

Catalysis of Rich-LiF SEI by the Aromatic Structure Modified Porous Polyamine for Stable All-Solid-State Lithium Metal Batteries

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Experimental section

Preparation of PAP:

The microporous polyamine network was obtained by one-step polycondensation of phenytoin with melamine, the microporous polyamine network was named PAP. A dry schlenker flask with a stirrer and condenser was degassed by using two evacuation-nitrogen backfill cycles. Under the condition of nitrogen flow, melamine (0.30 g, 2.4 mmol), Phenytoin (0.91 g, 3.6 mmol), and 15 mL dimethylsulfoxide (DMSO) were added and heated at 165 °C for 72 hours. No catalyst was added during the polymerization. Finally, the solid was separated and washed with dimethyl formamide (DMF), dichloromethane, and tetrahydrofuran (THF). The synthetic product was extracted in a Soxhlet unit with THF for 24 hours and dried to constant weight under vacuum at 120 °C. The yield of PAP powder is 70% and the color is faint yellow.

Preparation of PHD:

The microporous polyamine network was obtained by one-step polycondensation of hydantoin with melamine, the microporous polyamine network PHD. The method of

synthesizing PHD is the same as that of synthesizing PAP, only replacing Phenytoin (0.91 g, 3.6 mmol) with hydantoin (0.36 g, 3.6 mmol). The yield of PHD powder is 75% and the color is white (Fig. S1b).

Preparation of CPE:

CPE was prepared by dispersing anhydrous PEO and LiTFSI in acetonitrile (EO/Li+ = 10) and adding various amounts (1 wt%, 3 wt%, or 5 wt%) of PHD/PAP. PEOs containing x wt% (x = 1, 3, or 5) of PHD and PAP fillers were named CPE-x-PHD and CPE-x-PAP. PEOs without LiTFSI POP fillers were named PEO10. The PEOs without LiTFSI fillers were designated PEO10. After 24 hours of mixing, the PEOs were stripped by applying an oiled paper towel to the surface of the Teflon molds and then pouring in the liquid PEO mixture, which was allowed to dry. Finally, the CPE was vacuum dried at 60 °C for 24 hours to completely remove the acetonitrile solvent. It is then transferred to an argon filled glove box (O₂ and water on a ppm scale, typically less than 0.01 ppm).

Li/CSEs/Li symmetrical battery installation:

The details of the lithium-symmetric battery preparation conditions are as follows. By placing a piece of lithium metal in the cathode shell and subsequently covering the membrane with it, and then placing another piece of lithium metal on the other side of the membrane. The two pieces of lithium metal are aligned as much as possible.

Material characterization:

The composition of CPE was studied by X-ray diffraction (XRD). The range is 10-80°. Thermal gravimetric analyzer (TGA) was used to analyze the thermal stability of the polymer electrolyte at a scan rate of 10 °C min⁻¹ in a temperature range of 20-600°C under N₂ atmosphere. The Fourier transform infrared spectrum was obtained by Bruker Vertex 70 FT-IR spectrometer. The mechanical stability of CPE was measured by electronic tensile machine. X-ray photoelectron spectrometer (XPS, energy resolution is 0.6 eV) was utilized to investigate the elemental composition. The thermochemical properties of composite electrolyte films were tested by a differential scanning calorimeter under N₂ protection. The surface of the lithium anode and CPE was observed by scanning electron microscopy (SEM). **Electrochemical measurement:**

The electrochemical workstation (chi660e) was used to evaluate the ionic conductivity of CPE by electrochemical impedance technology, the temperature range was set at 30-60 °C and the frequency range was 10^{-2} - 10^{6} Hz. The CPE membrane was sandwiched between two parallel stainless steel discs. The ionic conductivity (σ) of the electrolyte membrane was calculated from equation (1), where R_b represents the resistance of the electrolyte, L represents the thickness of the solid electrolyte (cm), and S represents the area of the solid electrolyte (cm²):

$$\sigma = \frac{L}{R_b S} \tag{1}$$

The lithium-ion transfer number (t_{Li}^+) of CPE was measured in DC-polarized Li/CPE/Li cell, A voltage of 10 mV (Δ V) was applied, and EIS spectra of cell before and after polarization was obtained from 10⁻²-10⁶Hz. The (t_{Li}^+) of electrolyte membrane is calculated by equation (2):

$$t_{li}^{+} = \frac{I_{s}\Delta V - I_{0}R_{0}}{I_{0}\Delta V - I_{S}R_{S}}$$
(2)

Where I_0 and I_s are the initial current and steady-state current, and ΔV is the polarization potential at 10 mV. R_0 and R_s are the initial interface resistance and final interface resistance respectively.

The electrochemical window of CPE was measured by linear sweep voltammetry (LSV) with electrolyte film. LSV was carried out at 60 °C on chi660e electrochemical workstation at a scanning rate of 1 mv s⁻¹.

The electrochemical test is carried out at 60 °C with a coin battery composed of lithium metal anode, CPE, and LiFePO₄ cathode (working electrode). The working electrode is made of 80 wt% LiFePO₄ (LFP), 10 wt% Super P, and 10 wt% PVDF dissolved in N-methyl-2-pyrrolidone (NMP). The slurry mixture was coated on the carbon-coated aluminum foil, and dried in a vacuum oven at 60 °C for 12 hours. The active material load was 1.5-2.2 mg cm⁻². The battery was assembled in a glove box filled with argon (O₂ and water at ppm level, usually < 0.01ppm) The land coin battery test system is used to charge/discharge Li/CPEs/LFP battery with a voltage of 2.5-4.1 V.



Fig. S1 Shows surface topography of PAP and PHD powders at higher magnification.



Fig. S2 X-ray diffraction data of PAP and PHD.



Fig. S3 Surface morphology: (a) CPE-3-PHD membrane. EDS mapping of CPE-3-PHD membrane: (b) C and (c) N.



Fig. S4 Surface morphology: (a) PEO_{10} membrane. EDS mapping of PEO_{10} membrane: (b) C and (c) N.



Fig. S5 Ionic conductivity as a function of temperature. (a) CPE-x-PAP(x=1, 3, 5), (b) CPE-x-PHD (x=1, 3, 5).

different tempera	tures.
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$\sigma \times 10^{-4} \text{ S cm}^{-1}$ PEO ₁₀ CPE-3-PAP CPE-3-PHD	σ×10 ⁻⁴ S cm ⁻¹	PEO ₁₀	CPE-3-PAP	CPE-3-PHD
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25 °C	0.012	0.249	0.0986
30 °C	0.77	0.39	0.213
35 °C	0.14	0.57	0.393
40 °C	0.4	0.1	0.567
45 °C	0.55	1.58	0.921
50 °C	0.59	2.21	1.55
55 °C	0.99	2.86	1.78
60 °C	1.11	3.32	2.07



Fig. S6 Chronoamperometry curve at 60 °C with polarization voltage of 10 mV and EIS plots before and after the polarization inset. (a) CPE-3-PHD, (b) PEO_{10} .



Fig. S7 Strain stress curve of CPE.



Fig. S8 TGA curves of CPE.



Fig. S9 EIS plots of the cells after different cycles. (a) Li/CPE-3-PAP/Li, (b) Li/CPE-3-PHD/Li.



Fig. S10 Cycling performance of the solid-state LiFePO₄/Li battery at 60 °C and

0.5 C.



Fig. S11 Charge-discharge curves of Li/CSEs/LFP batteries at 30°C.



Fig. S12 Cycle and charge/discharge profiles of pouch batteries with

Li/CSE/LFP high loads.



Fig. S13 Cycle and charge/discharge profiles of cell with Li/CSE/NCM811.

Temp	Specific discharge capacity after	Cycle Number	Rate	Ref.
eratur	Cycle		capability	
e				
80°C	116 mAh g ⁻¹	100th	1C	[42]
80°C	116 mAh g ⁻¹	100th	0.2C	[43]
150°C	147 mAh g ⁻¹	100th	1C	[44]
80°C	76 mAh g ⁻¹	100th	0.2C	[45]
80°C	132 mAh g ⁻¹	50th	0.1	[46]
120°C	105 mAh g ⁻¹	300th	0.2	[47]
120°C	145 mAh g ⁻¹	110th	1	[48]

Table S2. Cycling performance of different kinds of PEO-based SPE.

80°C	119 mAh g ⁻¹	100th	1C	[30]
100°C	146 mAh g ⁻¹	100th	1C	This work
100°C	103 mAh g ⁻¹	500th	1C	This work