

Supporting information

A Single Ion Gel Polymer Electrolyte based on Polyimide Grafted with Lithium 3-Chloropropanesulfonyl(Trifluoromethanesulfonyl)imide for High Performance Lithium Ion Batteries

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1. Experimental section

1.1 Materials

All the materials were purchased from commercial suppliers and used without further purification unless otherwise noted.

1.2 Characterization

FT-IR spectra were obtained on the Nicolet IS50 Fourier Transform Infrared spectrometer. ¹H NMR spectra were performed on a Bruker Advance NEO 500 NMR spectrometer. The surface area and pore size distribution were obtained with the Micromeritics ASAP 2020M Accelerated Surface Area and Porosimetry System. Scanning Electron Microscopy (SEM) was performed with a Hitachi SU8010 Field-emission Scanning Electron Microscope. Transmission Electron Microscopy (TEM) was performed with a JEM-2100 PLUS Transmission Electron Microscope. Mechanical properties were obtained with a Shimadzu AG-I 1kN Electronic Universal material testing machine. Thermal stability testing of the samples was performed on TAQ50 Thermal Gravimetric Analyzer (TGA) Instrument at a heating rate of 10 °C min⁻¹ from 30 to 700 °C under N₂ atmosphere. The gas flow rate was 60 mL min⁻¹.

1.3 Electrochemical measurements

The mass ratio LiFePO₄: Acetylene black: Polyvinylidene Fluoride (PVDF) =8:1:1 was mixed in NMP and coated on aluminum foil. After vacuum drying, it was stamped into wafers as the cathode. Lithium was used as the anode, and PI-SIGPE soaked in plasticizer (EC/DMC (1:1, volume ratio)) for 1 h before use was used as the separator to assemble a cr2025 button cell. All the above operations were carried out in the glove box. The active material content was approximately 6 mg cm⁻¹. Neware was selected as the test system.

The stainless-steel sheet (SS)/PI-SIGPE/SS battery was assembled and used to test

the ionic conductivity of the separator with the electrochemical workstation (Autolab PGSTAT302N). The test frequency range was 1~10⁶ Hz, and the disturbance voltage was 10 mV. The intersection of the impedance spectrum in the high-frequency region and the real axis was the bulk impedance of the electrolyte R_b. The conductivity was calculated by the formula:

$$\sigma = \frac{l}{R_b S}$$

where l represented the thickness of the single-ion electrolyte (cm), R_b represented the bulk impedance (Ω) of the single-ion electrolyte, and S represented the actual effective contact area between the electrolyte and the steel sheet (cm²).

The Li/PI-SIGPE/Li battery was assembled and used to calculate the transference number of lithium ions with the electrochemical workstation (Autolab PGSTAT302N). The symmetrical battery was polarized at a disturbance voltage of 10 mV (ΔV) at 25 °C. t_{Li+} was calculated according to the following formula:

$$t_{Li^+} = I_{ss} (\Delta V - I_0 R_0) / I_0 (\Delta V - I_{ss} R_{ss})$$

Among them, I₀ and I_{ss} was the current before and after polarization respectively; R₀ and R_{ss} was the voltage before and after polarization respectively. Electrochemical impedance (EIS) was tested by electrochemical workstation (Autolab PGSTAT302N). The frequency range was 0.1-10⁶ Hz, and the disturbance voltage was 10 mV in the AC impedance.

Linear sweep voltammetry (LSV) was by an electrochemical workstation (Autolab PGSTAT302N). The voltage range was 3-5V and the sweep speed was 1 mV s⁻¹. Steel sheet (SS) was employed as the working electrode, and the lithium sheet was used as the reference electrode, the ionic gel polymer electrolyte was employed as an electrolyte diaphragm to assemble a "SS/PI-SIGPE/Li" battery,

1.4 Synthesis process

1.4.1 Synthesis of lithium 3-chloropropyltrifluoromethanesulfonimide (LiCPSI)

Under argon atmosphere and ice-water bath conditions, 2.9818 g of trifluoromethylsulfonamide and 0.479 g of anhydrous LiOH were added to a 100 mL round bottom flask, and 20 mL of anhydrous acetonitrile solvent was added. 3.541 g of 3-chloropropanesulfonyl chloride was added to the above solution. Subsequently, the reaction mixture was warmed to room temperature to continue the reaction for 24 h, the product was filtered off, and a white solid was precipitated in dichloromethane, which was dried in vacuum at 60 °C for 24 h to obtain a pure white solid, namely 3-chloropropyltrifluoro. The yield of lithium methylsulfonimide (LiCPSI) was about 60%.

The FT-IR spectrum of lithium 3-chloropropyltrifluoromethanesulfonimide in Figure S2(b) can help prove the synthesis of its structure. The peaks of 1314 cm^{-1} , 1184 cm^{-1} and 1125 cm^{-1} were respectively Corresponding to the asymmetric and symmetric stretching of $-\text{SO}_2-$, S-N- and -S-N-S-.

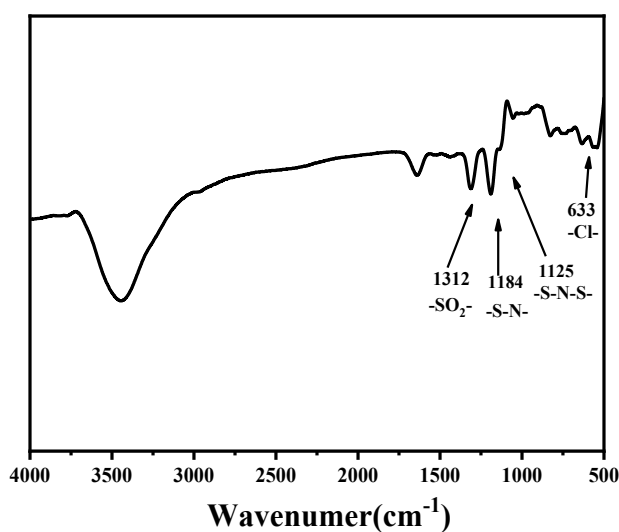


Fig. S1 FT-IR spectrum of LiCPSI.

1.4.2 Characterization of hydroxyl-containing polyimide

2,2'-bis(3-amino-4-hydroxyphenyl) hexafluoro (BNHPFP), 4,4'-Oxydiphthalic anhydride (ODPA), 4,4'-oxobiphenyldiamine (ODA) was added to the round bottom flask at a molar ratio of 7:3:10. The m-cresol was used as the reaction reagent, and the solid content of the monomer in the m-cresol reagent is 25%. Under a nitrogen atmosphere, the reaction was carried out at 80 °C for 4 h, and isoquinoline containing 10% m-cresol was added as a catalyst, and then stirred at 180 °C for 18 h. Finally, the reaction solution was poured into a large amount of ethanol to obtain a light-yellow fiber, which was exchanged and washed with ethanol and deionized water 3 times to remove residual solvents and unreacted monomers. Finally, PI-OH₇₀ was dried in a vacuum at 80 °C for 24 hours to obtain high-purity PI-OH₇₀.

1.4.3 Preparation and structural characterization of single ionic polymer by Williamson reaction

A three-necked round-bottomed flask was connected with a double-row tube and a nitrogen ball at the same time, filled with nitrogen three times, and baked with a baking gun to remove the water vapor in the bottle. Under a nitrogen atmosphere, 1.133 g of PI-OH₇₀ was dissolved in 22 mL of dry dimethyl sulfoxide, stirring at 60°C to form a clear solution. Then 0.159 g of LiH was added, and the reaction mixture was stirred at 60°C for 3 h, then 1.4772 g of LiCPSI was added, and the reaction mixture was further heated to 90°C for 48 h. The reaction solution was poured into ethyl acetate to obtain a brown solid. The material was washed with ethyl acetate and dried at 60°C for 24 h to obtain polyimide single ion polymer (PI-LiCPSI). The molecular weight of PI-

OH₇₀ was measured by Agilent Waters 515 HPLC Pump, a High-performance Gel Permeation Chromatograph. DMF was the solvent.

1.4.4 Preparation of polyimide single-ion gel polymer electrolyte

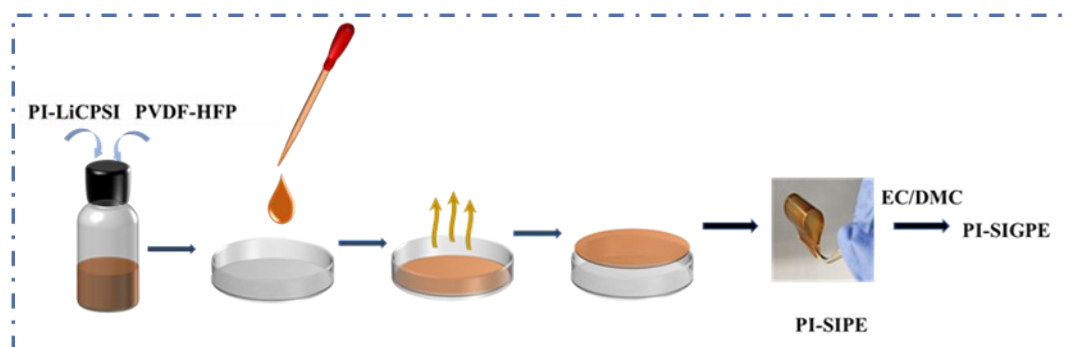


Fig. S2. Schematic diagram of membrane for PI-SIGPE.

The solution casting method was used to prepare the single-ion polymer electrolyte. First, 0.1 g PI-LiCPSI and 0.1 g PVDF-HFP were added to 3.7 mL N-methylpyrrolidone (NMP) and stirred at 25 °C for 24 h to obtain a homogeneous solution. Insoluble impurities were then filtered with a filter cloth to obtain a unified solution, which was poured on a smooth glass plate with an area of 5×5 cm², and then gradually heated at 80 °C, 100 °C and 120 °C for 12 hours, and kept in vacuum at 120 °C for 12 hours to ensure that the solvent evaporates cleanly. The polyimide single-ion polymer electrolyte (PI-SIPE) obtained was cut into small discs with a diameter of 16 mm and stored in a glove box (O₂ <0.1 ppm, H₂O <0.1 ppm). Before assembling the battery, tested the thickness of PI-SIPE and immersed it in the plasticizer EC: DMC (V: V=1: 1) solution for 3 minutes, and wiped the surface to obtain a polyimide single-ion gel polymer electrolyte (PI-SIGPE), assembled the required batteries in the glove box.

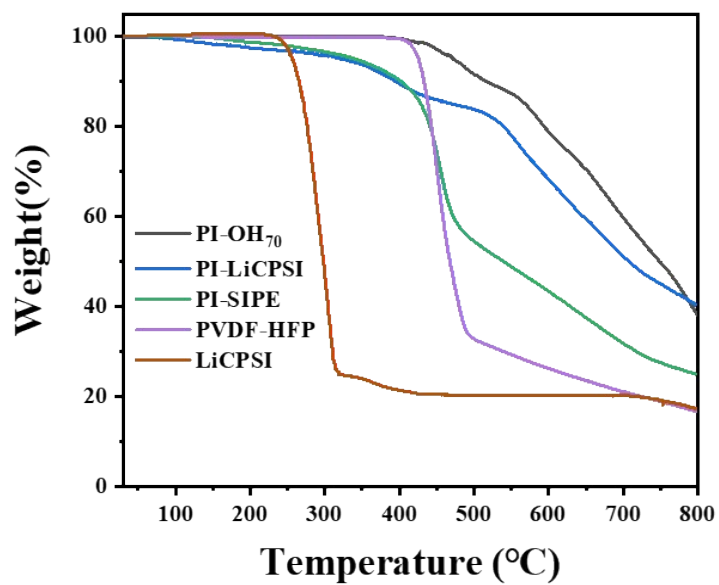


Fig. S3. TGA curves of PI-OH₇₀, LiCPSI, PI-LiCPSI, PVDF-HFP and PI-SIPE.



Fig. S4. The optical picture of PI-LiCPSI powder.

Table S1. T_5 and T_{10} of PI-OH₇₀, PI-LiCPSI, LiCPSI, PVDF-HFP and PI-SIPE.

Sample	T_5 (°C)	T_{10} (°C)
PI-OH ₇₀	412	459
PI-LiCPSI	323	395
LiCPSI	258	265
PVDF-HFP	425	434
PI-SIPE	334	395

T_5 and T_{10} represent the temperature of weight loss of 5% and 10%, respectively

Table S2. Tensile strength, elongation rate and modulus of PI-OH₇₀, PVDF-HFP and PI-SIPE.

Polymers	Tensile strength (MPa)	Elongation rate (%)	Modulus (MPa)
PI-OH ₇₀	85	3.8	2810
PVDF-HFP	24	21.9	722
PI-SIPE	30	7.2	1720

Table S3 Bulk impedance and ionic conductivity of PI-SIGPE at different temperatures.

PI-SIGPE	30 °C	40 °C	50 °C	60 °C	70 °C	80 °C	90 °C
Bulk impedance (Ω)	18.6	15.3	13.1	11.4	9.7	8.5	7.4
ion conductivity ($S\ cm^{-1}$)	1.4×10^{-4}	1.7×10^{-4}	1.9×10^{-4}	2.2×10^{-4}	2.6×10^{-4}	3.0×10^{-4}	3.4×10^{-4}

Table S4. t_{Li^+} of PI-SIGPE at 20 °C.

I_0 (mA)	I_S (mA)	R_0 (Ω)	R_S (Ω)	ΔV (mV)	t_{Li^+}
0.793	0.232	1048	1100	10	0.97

Table S5. Comparison of the main performance of LIBs based on SIGPE.

Sample	$t_{\bar{z}} +$	Electrochemical stability window	E_a (eV)	Ref.
HEC	0.570	-	0.016	[S1]
3D-BGPE	0.760	4.52	0.053	[S2]
SLIGPE-2	0.622	4.7	--	[S3]
LFP (asymmetric GPE)	0.660	--	0.105	[S4]
ACMC	0.902	4.5	0.046	[S5]
CCMNC-5	0.820	4.65	--	[S6]
OCMC-PVA	0.800	4.5	--	[S7]
ISGE	0.910	--	--	[S8]
PI-SIGPE	0.970	5.2	0.104	This work

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