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**A single-ion conducting hyperbranched polymer as high
performance solid-state electrolyte for lithium ion battery**

Meng Zhang, Songrui Yu^{*}, Yiyong Mai, Shaodong Zhang and Yongfeng Zhou^{*}

*School of Chemistry and Chemical Engineering, State Key Laboratory of Metal
Matrix Composites, Shanghai Jiao Tong University,
800 Dongchuan Road, Shanghai 200240, China.
E-mail: yfzhou@sjtu.edu.cn; tracyyu@sjtu.edu.cn;*

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1. Methods

Chemicals. Poly(ethylene glycol) diglycidyl ether ($M_n \sim 500$) was purchased from Sigma-Aldrich. Ethylene glycol diglycidyl ether ($M_w=174.14$, epoxy value = 0.7), DL-cysteine ($\geq 97\%$) and Lithium hydroxide (LiOH, $\geq 99\%$) were purchased from Adamas. Poly(ethylene glycol) ($M_n \sim 2000, 6000, 10000, 20000$), Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI; $\geq 99\%$) and dimethylformamide (DMF, SuperDry, $\geq 99.8\%$) were purchased from J&K Chemical Ltd.. Ethyl ether ($\geq 98.5\%$) was purchased from Sinopharm Chemical Reagent Co. Ltd., N-methyl pyrrolidone (NMP, $\geq 99.0\%$), tetrahydrofuran (THF, $\geq 99.0\%$) and ethanol ($\geq 99.7\%$) were from General Reagent. Poly(vinylidene fluoride-hexafluoro propylene) (PVDF-HFP, Knyar 2801) was purchased from Elf Atochem. Conductive carbon black(super P) was purchased from TIMCAL Graphite and Carbon. Lithium iron(II) phosphate (LFP, $>97\%$) was purchased from Aldrich. PVDF-HFP, carbon black and LFP were dried in vacuum at $110\text{ }^\circ\text{C}$ for 24h before use. The other chemicals were used as received unless otherwise specified.

Instruments and measurements

Nuclear Magnetic Resonance (NMR): ^1H NMR, ^{13}C NMR spectra were recorded on Varian Mercury Plus 400 (400 MHz) and Bruker AVANCE III HD 500 (500 MHz) spectrometer, respectively, with D_2O as solvent at 298K.

Differential Scanning Calorimeter (DSC): DSC analyses were carried out on a TA Q2000 apparatus under nitrogen flow. Three cycles were performed for each sample to eliminate thermal history. Cycle I: increasing temperature from $40\text{ }^\circ\text{C}$ to $200\text{ }^\circ\text{C}$ with a heating rate of $20\text{ }^\circ\text{C}/\text{min}$, and isothermal 1 min; Cycle II: decreasing temperature from $200\text{ }^\circ\text{C}$ to $-80\text{ }^\circ\text{C}$ with a cooling rate of $20\text{ }^\circ\text{C}/\text{min}$, and isothermal 5 min; Cycle III: increasing temperature from $-80\text{ }^\circ\text{C}$ to $200\text{ }^\circ\text{C}$ with a heating rate of $20\text{ }^\circ\text{C}/\text{min}$. The 3rd cycle of data was used for comparison of glass transition and melting temperature.

Thermogravimetric Analysis (TGA): TGA were performed on a Discovery TGA550 apparatus from T.A. Instruments under nitrogen flow. The heating process started from $50\text{ }^\circ\text{C}$ to $800\text{ }^\circ\text{C}$ with a heating rate of $10\text{ }^\circ\text{C}/\text{min}$.

Gel Permeation Chromatography (GPC): The molar mass of HPCPEG and HPCEG were measured by GPC on a Waters Breeze2 system at $40\text{ }^\circ\text{C}$ with H_2O as mobile phase at a flow rate of $1.0\text{ mL}/\text{min}$.

Scanning Electron Microscopy (SEM): SEM measurements were performed on a FEI NOVA NANOSEM 450 operating with an accelerating voltage of 12 kV. The samples were coated with a thin film of gold (Au) before measuring.

Fourier-transform Infrared Spectroscopy (FTIR): Solid sample of DL-cysteine was

mixed with KBr salt and then compressed into pellets. Viscous PEGDGE and HPCPEG were firstly dissolved in ethanol and then casted onto pure KBr pellets. After fully dried, the pellets were ready for FTIR. FTIR spectra were recorded on a Perkin Elmer Spectrum 100 spectrophotometer in the range of 4000-450 cm^{-1} .

Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES): ICP was carried out on an avio 200 optical emission spectrometry (PerkinElmer, Inc., Spokane, WA, USA).

X-ray photoelectron spectroscopy (XPS): Hyperbranched polymer HPCPEG was firstly dissolved in water (10 mg/mL) and casted onto a silicon wafer. After thoroughly dried, the sample was tested on a Kratos Axis Ultra DLD X-ray photoelectron spectroscopy.

Ionic conductivity: The measurement of ionic conductivity (σ , in $\text{S}\cdot\text{cm}^{-1}$) of the polymer electrolyte was carried out on an Autolab PGSTAT302N electrochemical workstation (Metrohm, Switzerland) using electrochemical impedance spectroscopy (EIS) technique. The membranes of blended polymer electrolytes were sandwiched between a pair of stainless steel (ss) blocking electrodes and fabricated in an argon-filled glovebox ($\text{O}_2 < 0.1\text{ppm}$, $\text{H}_2\text{O} < 0.1\text{ppm}$) using CR2016 coin-type cells by a lamination process. Before measuring, the cells were heated at 60 $^\circ\text{C}$ for 2h for allowing good contact between electrolytes and electrodes. The ac impedance spectra were recorded in the frequency range from 0.01 to 10^6 Hz over the temperature range from 25 to 85 $^\circ\text{C}$. The cell was thermally equilibrated at each temperature for at least 2h prior to measurement. The temperature of the cell was accurately controlled in a drying oven.

Lithium-ion transference number: The lithium-ion transference number (t_{Li}^+) was determined by using a symmetric cell of $\text{Li}|\text{SPE}|\text{Li}$ through a combination measurement of EIS and chronoamperometry (CA). (The cell was assembled in an argon-filled glovebox ($\text{O}_2 < 0.1\text{ppm}$, $\text{H}_2\text{O} < 0.1\text{ppm}$) using CR2016 coin-type cells by a lamination process. Before measurement, the cell was heated at 60 $^\circ\text{C}$ for 2 h for forming a stable interface between the electrolytes and electrodes. Then, the cell was applied a dc voltage of 10 mV until a steady current was obtained (usually 1~3 h in this study), and the initial and steady currents, which flow through the cell, were measured. This measurement was performed on the electrochemical workstation CHI 760e (CH instruments, China). Simultaneously, the same cell was also monitored in the frequency range from 0.01 to 10^6 Hz, by using EIS to measure the resistance of the electrolytes and the interface of electrolytes/Li metal electrodes, before and after the DC polarization. The measurement was also carried on an Autolab PGSTAT302N electrochemical workstation.

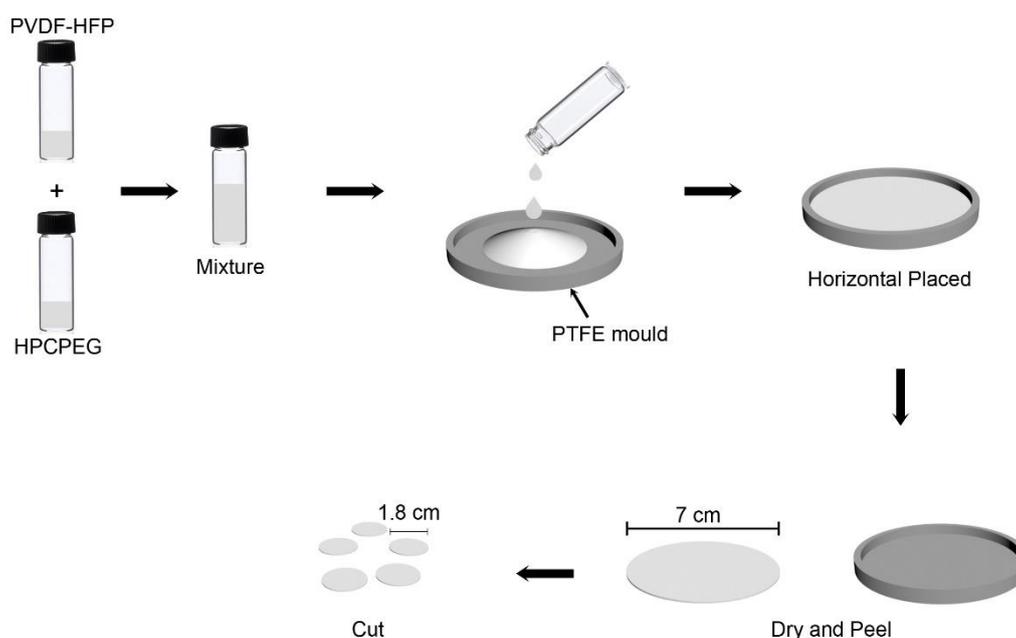
Linear sweep voltammetry (LSV) and cyclic voltammetry (CV): The electrochemical stability window of the polymer electrolytes was evaluated by linear sweep voltammetry (LSV) and cyclic voltammetry (CV) experiments using a $\text{ss}|\text{HPCPEG/PVDF-HFP SPE}|\text{Li}$ cell on the electrochemical workstation CHI 760e.

LSV was performed from 1.5 V to 7 V with a scanning rate of 0.5 mV/s, while CV was scanned from -0.5 V to 6 V with the same scanning rate.

Battery testing: The charge-discharge tests were performed at 0.1 C rate using an Land CT2001A (Land, China) in a potential window of 2.7 V to 4.2 V at 65 °C using a LiFePO₄|HPCPEG/PVDF-HFP SPE|Li cell. The LiFePO₄ (LFP) cathode electrode was prepared by mixing commercial LFP, HPCPEG and conductive carbon at a weight ratio of 5:4:1 in N-Methyl pyrrolidone(NMP) to form a uniform slurry. The slurry was cast on Aluminum foils and then dried under vacuum at 70 °C for 24 h. The active materials mass loading is 1.5-2.1 mg cm⁻². The Li | HPCPEG/PVDF-HFP/SPE | LFP cells were assembled in an argon-filled glovebox (O₂<0.1 ppm, H₂O<0.1 ppm) using CR2016 coin-type cells by a lamination process.

2. Preparation of polyelectrolyte films

In a typical preparation process, PVDF-HFP and HPCPEG were firstly dissolved in dry DMF separately with the final concentration both to be 0.04 g/mL. Then different volume of PVDF-HFP and HPCPEG solutions were mixed according to the HPCPEG content in targeted films. The total mass of both polymers in each film was constant to be 0.32 g. For example, in order to obtain the film with a HPCPEG content of 10 wt.%, 7.2 mL PVDF-HFP solution was mixed with 0.8 mL HPCPEG solution. After mixed, a transparent and homogenous solution was obtained. Then the solution was casted onto a PTFE round mould (diameter: 7 cm) with a flat bottom (Scheme S1). Subsequently, DMF was slowly removed under low vacuum at 75 °C and then free-standing films were obtained. The films were cut into small round pieces with a diameter of 1.8 cm for battery use. The average thickness of the resulted films was about 100 μm (measured by screw micrometer). The preparation of HPCEG/PVDF-HFP films followed the same procedure as described for HPCPEG/PVDF-HFP films, but replacing HPCPEG by HPCEG.



Scheme S1 Preparation process of HPCPEG/PVDF-HFP films for lithium battery use.

3. Synthesis and characterization of HPCPEG

HPCPEG polyelectrolytes was synthesized through click reaction between thiol and amino groups with epoxide groups.^{1,2} A brief procedure was as follows: Firstly, dissolve 3.63 g (0.03 mol) DL-cysteine in 150 mL ultrapure water, and adjust the pH of the solution to ~12 by adding 2M LiOH. Then, 23.0 g (0.045 mol) poly(ethylene glycol) diglycidyl ether (average $M_n \sim 500$) was added. The reaction was kept at 20 °C for 24 h and then at 40 °C for another 24 h. The two steps of reaction at different temperatures facilitated the reaction between thiol groups with epoxide groups at a lower temperature to avoid the formation of disulfide bonds, and ensured effective reaction between amine with epoxide groups at a higher temperature. Water was removed by rotary evaporation and the crude product was dissolved in ethanol. The insoluble precipitate was removed by filtration and the residual solution was concentrated by rotary evaporation. The concentrated solution was added dropwise to a large amount of cold ethyl ether to yield precipitate, which was collected and dissolved in ethanol. This purification process was repeated for three times and the final products were dried in vacuum at 60 °C. The product was highly viscous at room temperature and a yield of ~ 82% (21.8 g) was calculated.

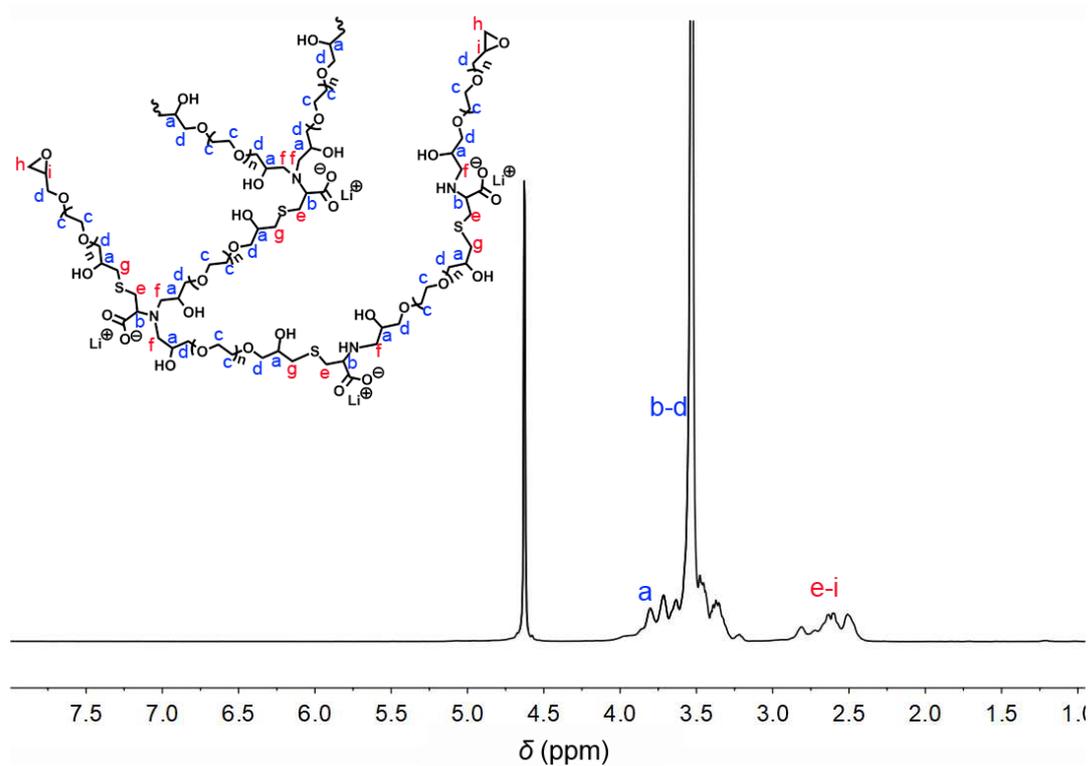


Fig. S1 ^1H NMR spectrum of hyperbranched HPCPEG (D_2O , 298K).

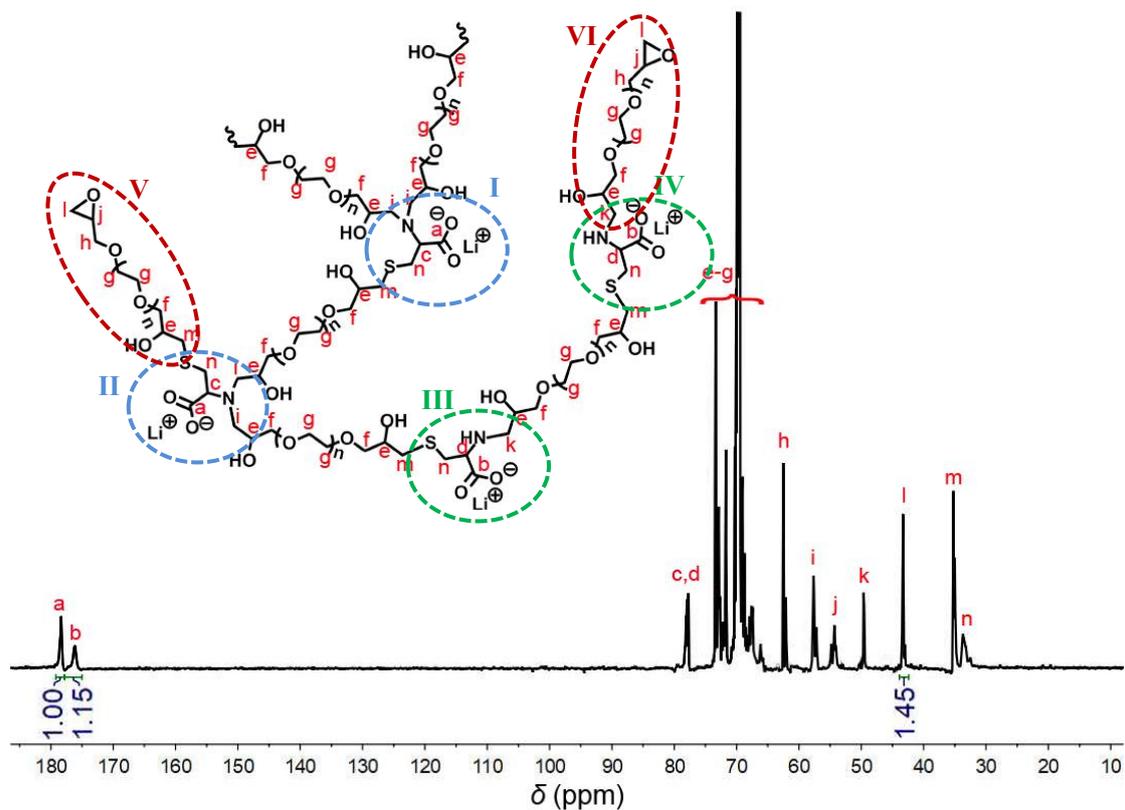


Fig. S2 ^{13}C NMR spectrum of hyperbranched HPCPEG (D_2O , 298K).

Degree of Branching (DB) of HPCPEG: To calculate the DB of HPCPEG, dendritic (D), linear (L) and terminal (T) units should be firstly identified. In HPCPEG, dendritic units are cysteine residues with tertiary amines (structures I & II in Fig. S2); linear units refer to cysteine residues with secondary amines (structures III & IV in Fig. S2); terminal units are PEGDGEs with un-reacted epoxide groups at one end of the polymer chain (structures V & VI in Fig. S2). The typical peaks for dendritic units (tertiary amines), linear units (secondary amines) and terminal units (epoxide groups) are a, b and l, respectively. According to the reported formula³:

$$DB = \frac{D + T}{D + L + T} \quad \text{..... (1)}$$

DB of HPCPEG could be calculated following the formula:

$$DB = \frac{A(a) + A(l)}{A(a) + A(b) + A(l)} \quad \text{..... (2)}$$

in which A(a), A(l) and A(b) represent the integration area of peak a, l and b in ¹³C NMR spectrum of HPCPEG, respectively (Fig. S2). Therefore, DB is calculated to be 0.68, which is a characteristic value for hyperbranched polymers.⁴

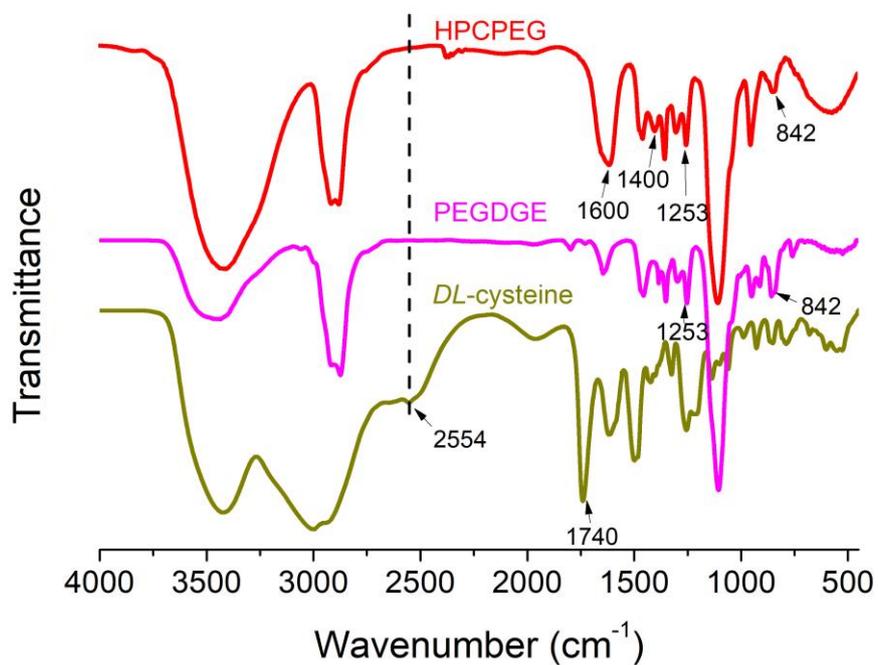


Fig. S3 FTIR spectra of HPCPEG.

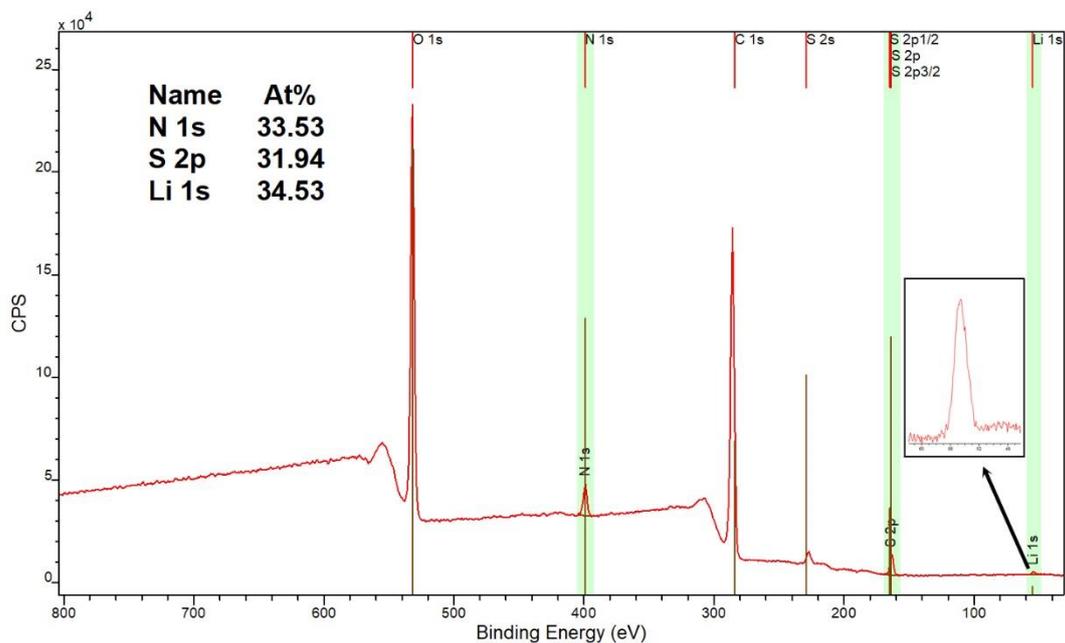


Fig. S4 XPS wide spectra of HPCPEG polymer. Inset shows a magnified Li 1s peak.

The atomic concentration ratio between N, S and Li is close to 1:1:1, indicating the molar ratio between cysteine units and Li cations is close to unity.

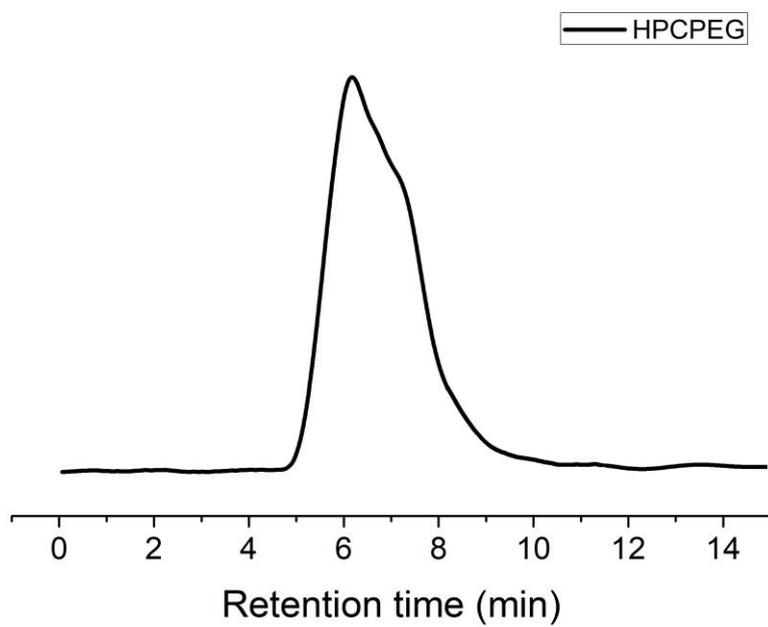


Fig. S5 GPC chromatogram of HPCPEG.

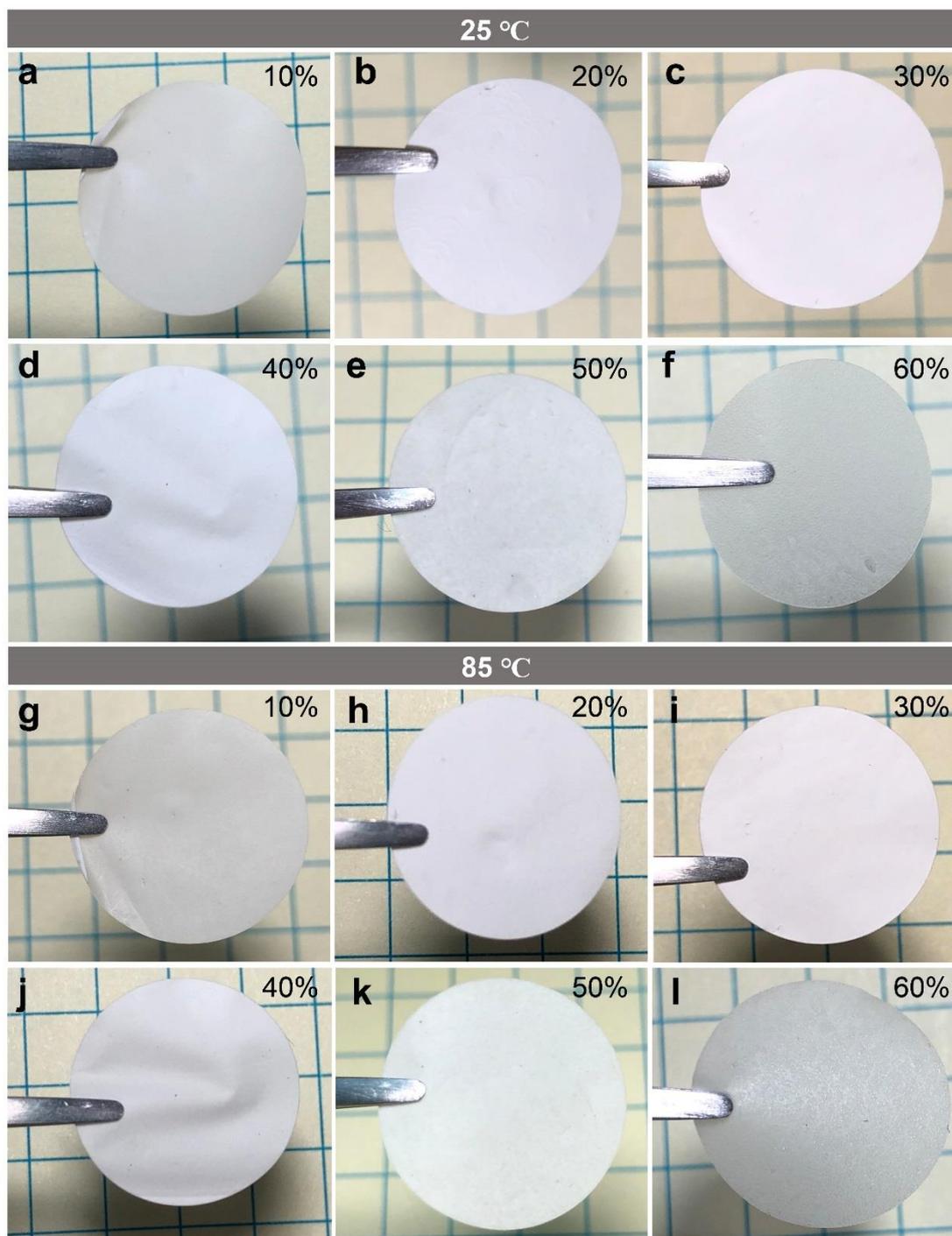


Fig. S6 Photos of free-standing SIPE films with different HPCPEG content at 25 °C (a-f) and 85 °C (g-l).

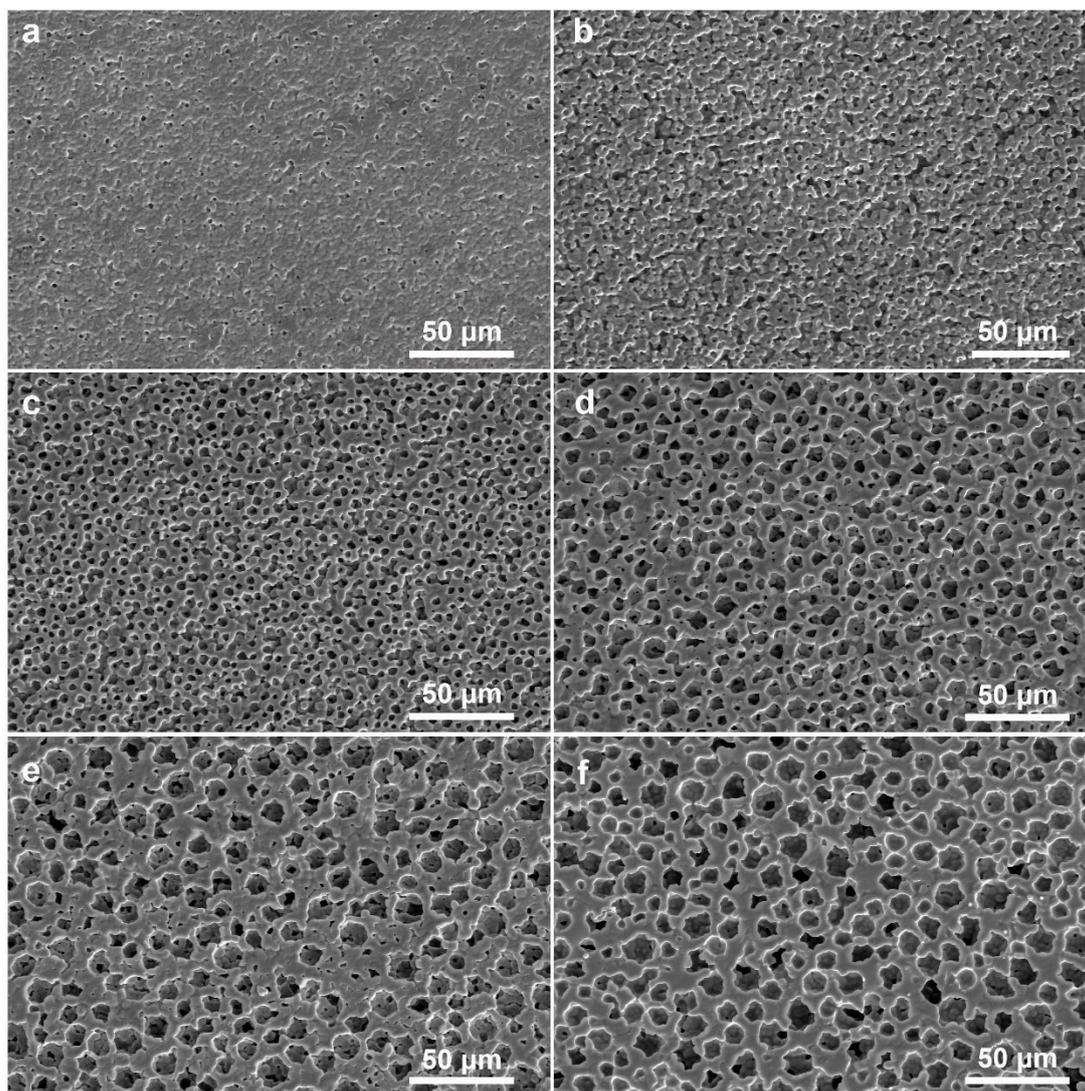


Fig. S7 SEM images of surface of polyelectrolyte films with different content of HPCPEG. The content of HPCPEG in **a-f** is 0%, 10%, 20%, 30%, 50% and 60% (w/w), respectively.

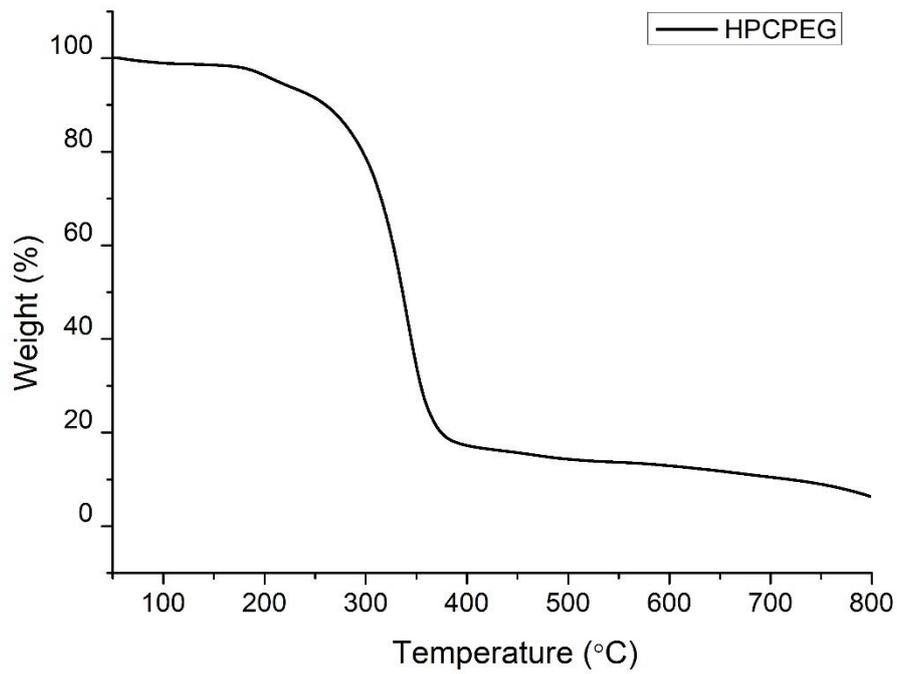


Fig. S8 TGA spectra of HPCPEG.

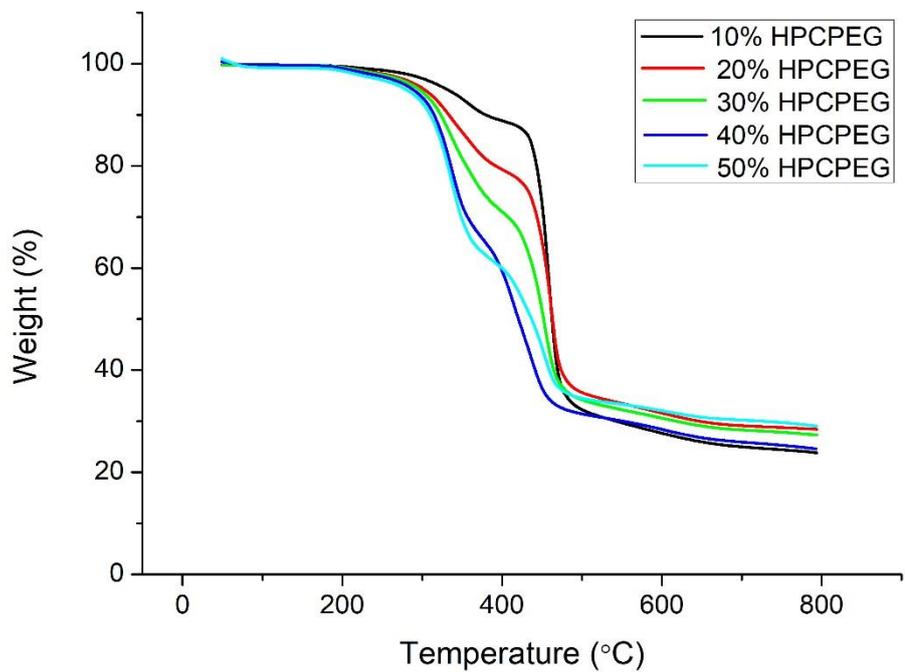


Fig. S9 TGA spectra of SIPE films with different HPCPEG content.

Table S1 Melting enthalpy of HPCPEG/PVDF-HFP films with different composition

	HPCPEG (wt.%)	PVDF-HFP (wt.%)	Enthalpy (J/g)
Film-A	10	90	28.8
Film-B	20	80	26.1
Film-C	30	70	22.7
Film-D	40	60	16.8
Film-E	50	50	14.6
Film-F	60	40	12.1

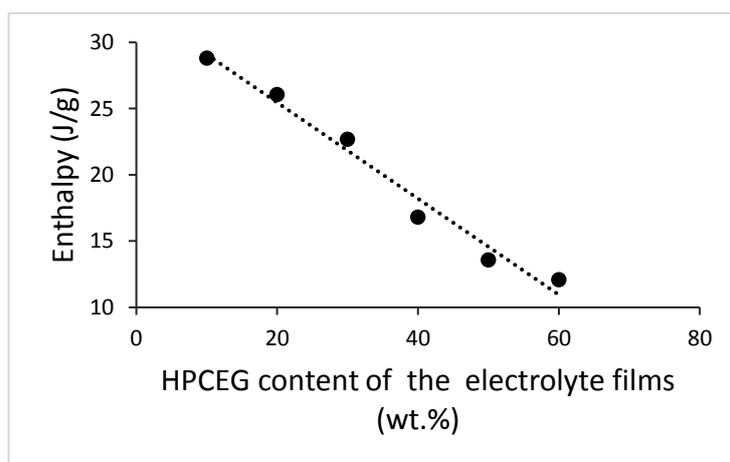


Fig. S10 Change of melting enthalpy of polymer electrolyte films as a function of HPCPEG content (wt.%).

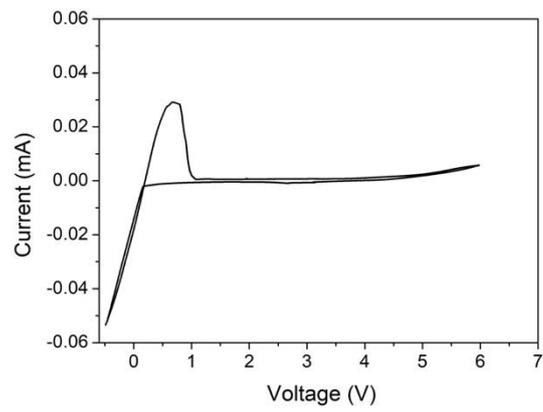


Fig. S11 Cyclic voltammogram of HPCPEG/PVDF-HFP (HPCPEG content: 60%) on ss | HPCPEG/PVDF-HFP SPE | Li at 65 °C under 0.5 mV s⁻¹.

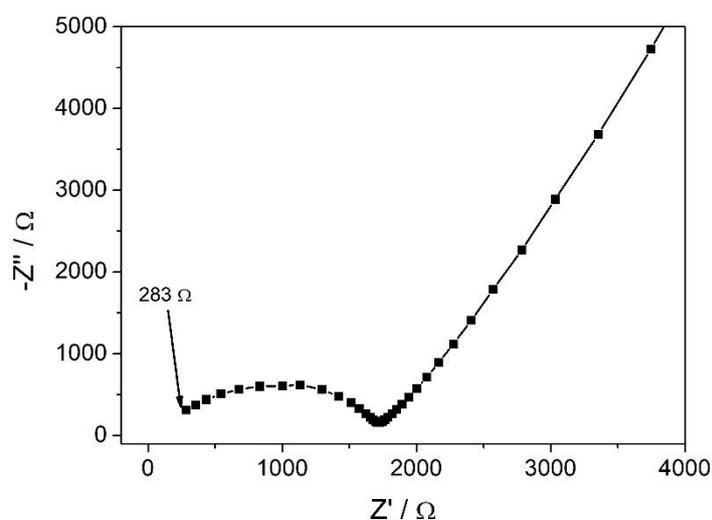


Fig. S12 Impedance spectra for HPCPEG/PVDF-HFP (HPCPEG content: 60%) SPEs on the ss | SPEs | ss cell at 25 °C.

Calculation of ionic conductivity (σ): The values of ionic conductivity were derived from the measured resistance by using the equation of $\sigma = l/(A \cdot R)$, where l (cm) is the thickness of membranes, A (cm^2) is the area of stainless-steel blocking electrode, and R (Ω) is the resistance determined from the Nyquist plot (Fig. S10). The average thickness of the SPE films is about 100 μm (measured by screw micrometer). The area of stainless-steel blocking electrode is 1.77 cm^2 .

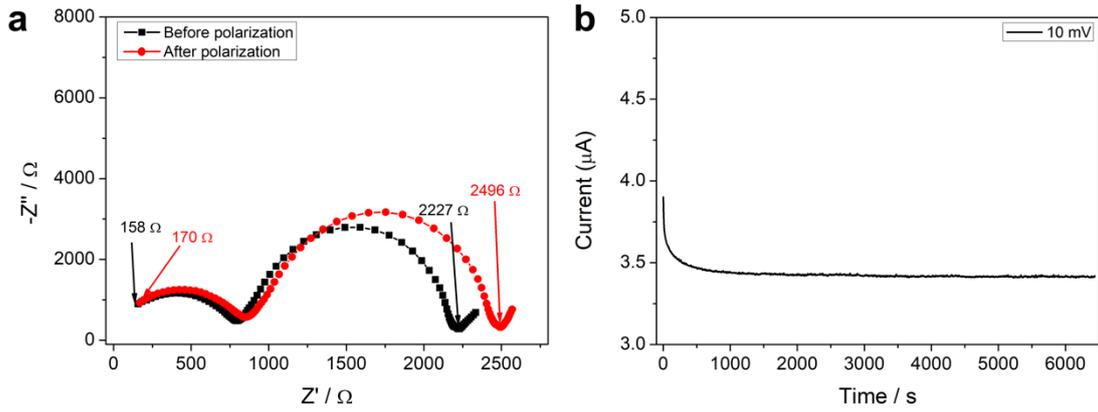


Fig. S13 Impedance spectra (a) and time-dependence response of polarization (b) for HPCPEG/PVDF-HFP (HPCPEG content: 60%) on the Li | SPEs | Li cell at 25 °C, polarized with a potential of 10 mV.

Calculation of Li^+ transference number (t_{Li}^+): The Li^+ transference number (t_{Li}^+) was determined by using a symmetric cell of Li | HPCPEG/PVDF-HFP SPE | Li through a combination measurement of electrochemical impedance spectroscopy (EIS) and chronoamperometry (CA).^{5,6} The equation was given as:

$$t_{Li}^+ = \frac{I_s R_b^s (\Delta V - I_o R_i^o)}{I_o R_b^o (\Delta V - I_s R_i^s)} \dots\dots\dots (3)$$

ΔV was a 10 mV voltage bias applied to polarize the SPE. I_o was the initial current, and I_s was the current in steady-state after 2-hour polarization. R_b^o and R_b^s were the initial and final resistances of the electrolytes. R_i^o and R_i^s were interfacial resistances in initial and steady state, respectively. For example, impedance spectra and time-dependence response of dc polarization for the HPCPEG/PVDF-HFP SPE with HPCPEG content of 60% at 25 °C were shown in Figure S10. The parameters of I_o , I_s , R_b^o , R_b^s , R_i^o and R_i^s could be read and then t_{Li}^+ can be calculated to be 0.86 according to formula (3).

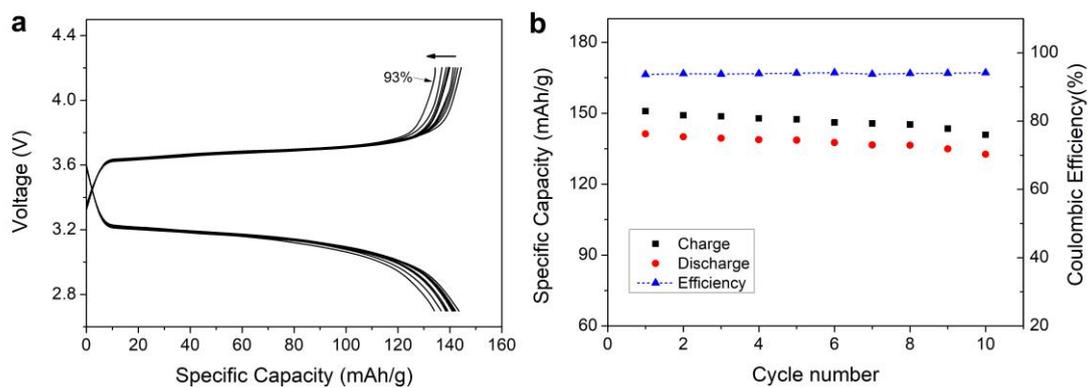
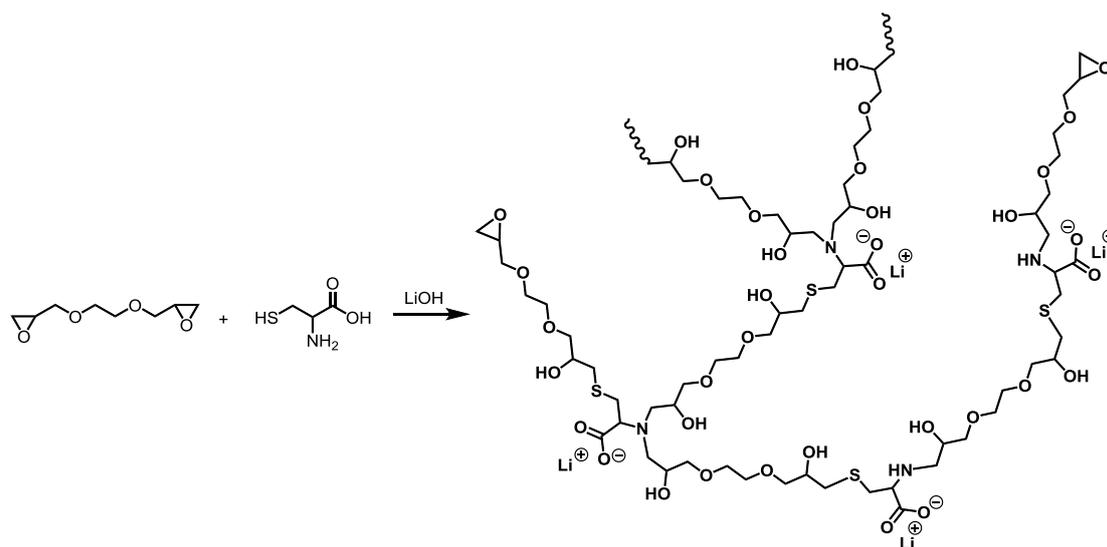


Fig. S14(a) Charge-discharge curves of an all-solid-state LFP | HPCPEG/PVDF-HFP SPE (HPCPEG content: 60%) | Li battery at a current intensity of 0.1 C in the voltage window of 2.7 to 4.2 V at 65 °C for ten cycles. (b) Cycling stability curves of the battery measured at 0.1C.

4. Synthesis and characterization of reference polymer HPCEG

The hyperbranched polymer of hyperbranched poly(cysteine-*co*-ethylene glycol diglycidyl ether) (denoted as HPCEG) was synthesized through click reaction similar to the synthesis of HPCPEG (Scheme S2). A brief procedure was as follows: Firstly, dissolve 2.42 g (0.02 mol) DL-cysteine in 50 mL ethanol/water (1:1, v/v), and adjust the pH of the solution to ~ 12 by adding 2 M LiOH. Then, 8.57 g (0.03 mol) ethylene glycol diglycidyl ether was added. The reaction was kept at 20 °C for 24 h and then at 40 °C for another 24 h. Ethanol and water were removed by rotary evaporation and the crude product was dissolved in water. The concentrated solution was added dropwise to a large amount of cold tetrahydrofuran to yield precipitate, which was collected and dissolved in water. This purification process was repeated for three times. The crude product was further dialyzed against (MWCO: 3500 Da) deionized water for three days. After removal of the water and dried in vacuum at 60 °C, the final light-yellow solid product of HPCEG was obtained with a yield of 70% (7.7 g).



Scheme S2 Synthesis of reference HPCEG.

Reference polymer HPCEG was successfully synthesized according to the ^1H NMR (Fig. S13), quantitative ^{13}C NMR (Fig. S14) and GPC results (Fig. S15). The peaks in NMR spectra are well assigned, and the GPC traces reveal a M_n of 12,500 g mol $^{-1}$ with molar mass dispersity (\mathcal{D}) of 2.0. The degree of branching (DB) of HPCEG is calculated to be 0.72, indicating a hyperbranched architecture. Similar molecular structure, comparable molecular weight and DB value of HPCEG to those of HPCPEG make it an ideal reference for comparison. Although alike in molecular structure, the glass transition temperature (T_g), however, increased to 20.5 °C in the case of HPCEG (Fig. S16). It may arise from the higher content of hydroxyl groups in HPCEG, which could form more hydrogen bonds and thus increase T_g .

DB of HPCEG: DB of HPCEG was calculated following the method described for the calculation of HPCPEG, based on the ^{13}C NMR spectrum (Fig. S10). Firstly, dendritic (D), linear (L) and terminal (T) units were firstly identified, as shown in Fig. S10. In summary, structures I & II are dendritic units; structures III & IV are linear units; structures V & VI are terminal units. The typical peaks for dendritic units (tertiary amines), linear units (secondary amines) and terminal units (epoxide groups) are a, b and l, respectively. According to formulas (1) and (2), DB of HPCEG is calculated to be 0.72.

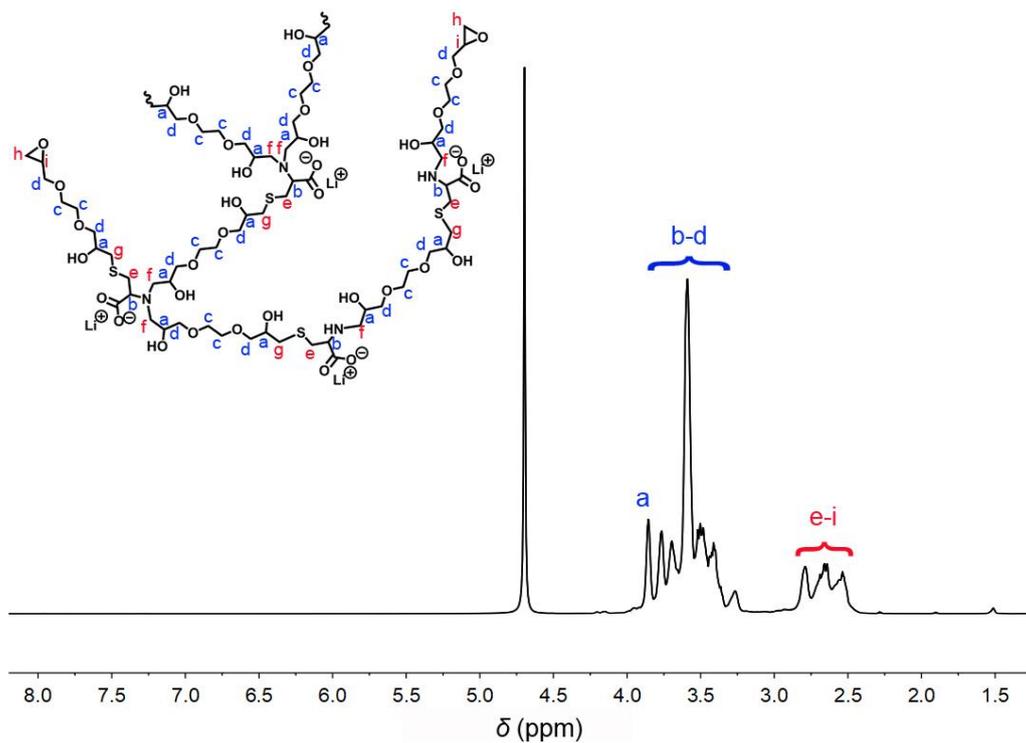


Fig. S15 ¹H NMR spectrum of reference HPCEG (D₂O, 298K).

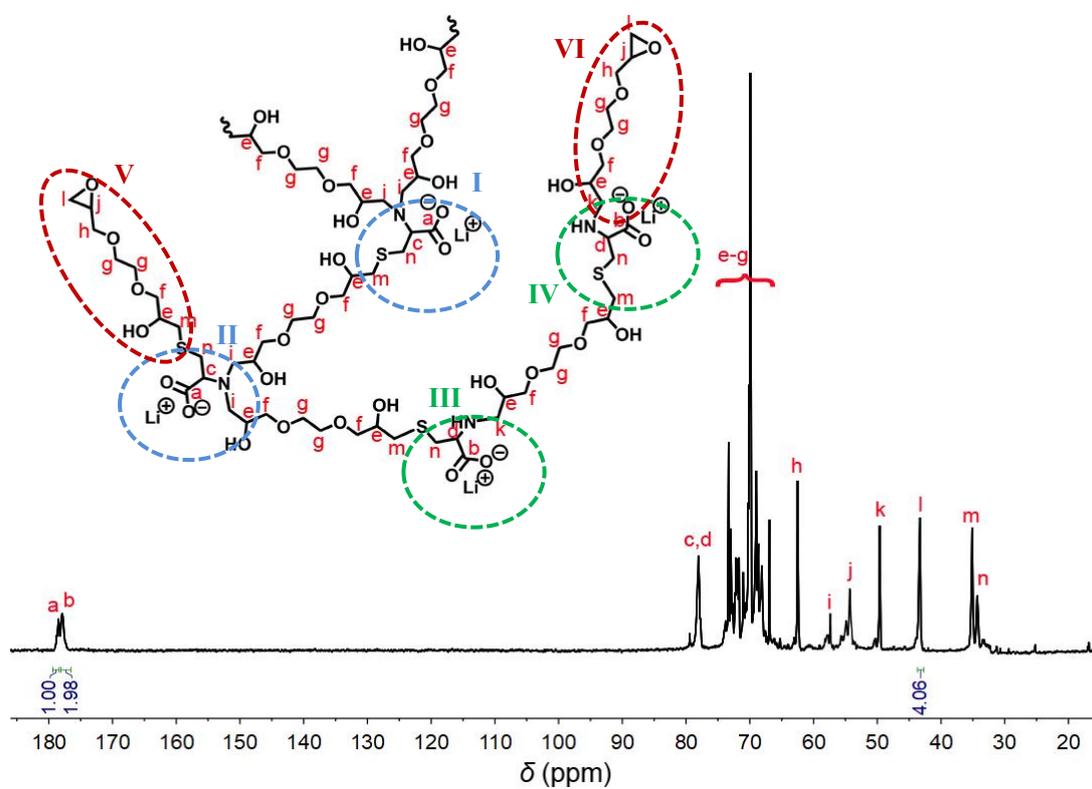


Fig. S16 Quantitative ¹³C NMR spectrum of reference HPCEG (D₂O, 298K).

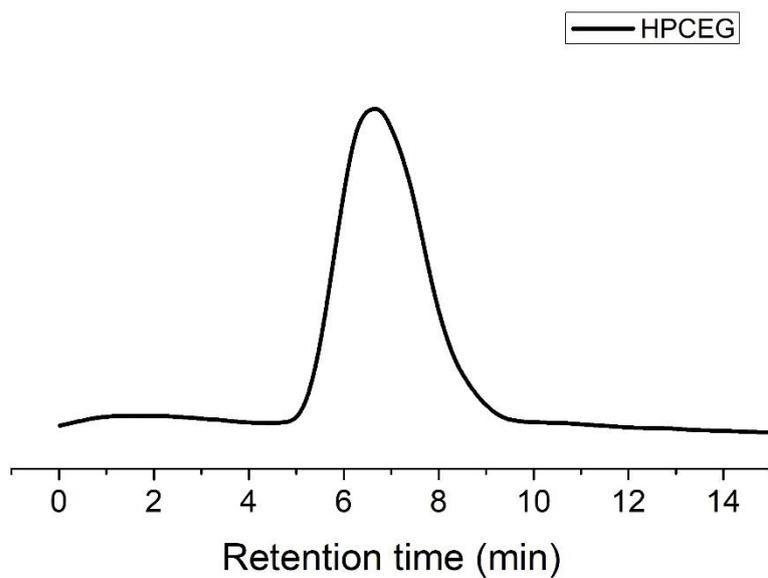


Fig. S17 GPC chromatogram of reference HPCEG.

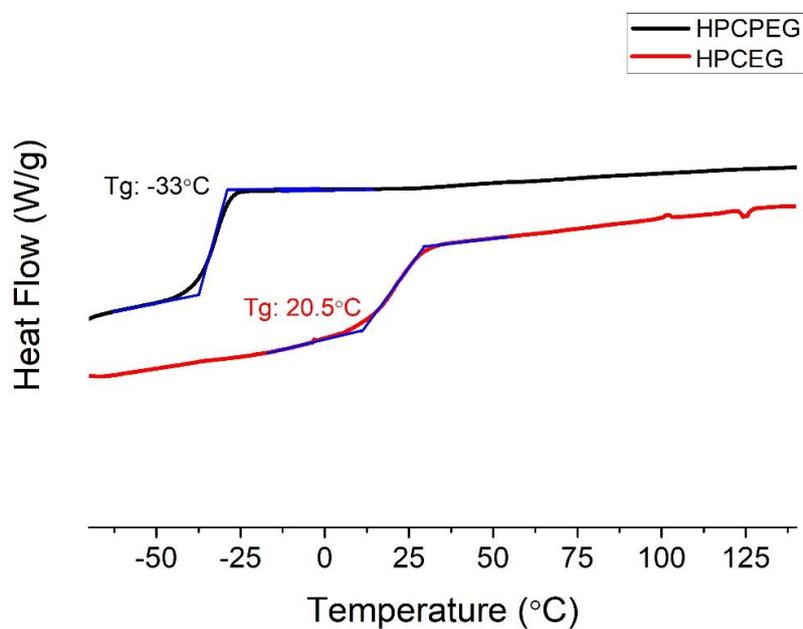


Fig. S18 DSC traces of polymer HPCPEG and reference polymer HPCEG.

Electrochemical performances: For comparison the electrochemical performances of reference polymer HPCEG with HPCPEG, HPCEG/PVDF-HFP films with HPCEG content of 40% were prepared under the same condition. The ionic conductivity (σ) and Li^+ transference numbers (t_{Li}^+) are determined in the same way described for the calculation of HPCPEG/PVDF-HFP films. The results are summarized in Table S2. The ionic conductivity of HPCEG/PVDF-HFP SPE was 2-3 orders of magnitude lower than that of HPCPEG/PVDF-HFP SPE. The t_{Li}^+ tested at 85 °C is 0.88 for HPCEG content of 40%, indicating its nature of single-ion polymer electrolyte. Therefore, compared with the SPEs prepared with reference polymer HPCEG, SPEs prepared with HPCPEG show much better electrochemical performances.

Table S2 Comparison of σ and t_{Li}^+ of HPCPEG/PVDF-HFP and HPCEG/PVDF-HFP polymer electrolytes

	σ (S cm ⁻¹)		t_{Li}^+
	25 °C	85 °C	
HPCPEG content: 40%	4.8×10^{-5}	1.2×10^{-4}	0.83 (25 °C)
HPCEG content: 40%	4.8×10^{-9}	2.7×10^{-7}	0.88 (85 °C)

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