Supporting Information

Self- healing solid polymer electrolyte based on imine bond for high safety and stable lithium metal batteries

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Experimental Section

Materials

Diglycidyl ether of bisphenolA (DGEBA), terephthalaldehyde (TPA), bis(trifluoromethane)sulfonimide lithium salt (LiTFSI) were purchased from Energy Chemical and were dried under vacuum. Polyoxyethylenebis(amine) (NH_2-PEG-NH_2)（average molecular weight of 2000）was supplied by Shenzhen Meiluo Technology Co., Ltd., Acetonitrile (AR) were provided by Sinopharm Co., Ltd., Metal lithium foils with a thickness of 1.0 mm and a diameter of 16 mm, lithium iron phosphate cathode with a thickness of ~16 μm were obtained from Guangdong Canrd New Energy Technology Co., Ltd., All chemicals were used as-is for purification and dewatering operations.

Synthesis of self-healable solid polymer electrolytes

The self-healable solid polymer electrolytes (ShSPE) were prepared through the cross-linking reaction of NH_2-PEG-NH_2, TPA and DGEBA, which was stirred in acetonitrile solvents at room temperature for 4 h. In the cross-linking reaction, the molar ratio of TPA, DGEBA and NH_2-PEG-NH_2 is 1/2/(1 ~ 3).The molar ratio of EO/Li^+ was kept at 16:1. According to the above principles, the mass ratios of TPA, DGEBA, NH_2-PEG-NH_2 and LiTFSI were 0.0335, 0.1702, (0.5/1/1.5) and (0.1974/0.3947/0.5921). The formed self-healing polymer electrolytes were named ShSPE-1, ShSPE-2 and ShSPE-3, respectively. When the solution became homogeneous and transparent, it was transferred to a polytetrafluoroethylene (PTFE) mold slowly using a pipette to minimize air bubble formation. After the evaporation

of acetonitrile, the solution gradually turned to be viscous at room temperature. The samples were dried under vacuum at 80°C ～120°C for 48 h to remove the acetonitrile residue and water vapor. At last, the flexible and adhesive ShSPE were obtained.

In order to further study the relationship between lithium salt and conductivity, TPA, DGEBA and NH_2-PEG-NH_2 (1/2/3) are fixed and EO/Li^+ is 8/16/24 with the mass fraction of lithium salt is 41%/25%/18%, respectively.

Synthesis of semi-interpenetrating self-healable polymer

The semi-interpenetrating self-healable solid polymer was synthesized in the same way as the ShSPE just without the addition of lithium salts, which was labeled as ShSP-1, ShSP-2 and ShSP-3 for contrast.

Characterization of the polymer electrolytes

Infrared spectroscopy was performed on a Shimadzu IR Prestige-21 Fourier Transform Infrared spectrum-photometer over the range of 4,000-400 cm^{-1}. Thermodynamic properties of the polymer and electrolytes were characterized with a Q20 analyser manufactured by Thermogravimetric instruments in the range of 50°C–600°C at a heating rate of 10°C min^{-1} under N_2 atmosphere. Differential scanning calorimetry (DSC) measurement was performed on a TA DSC Q2000 differential scanning calorimeter for a temperature range of −80 to 100°C under an argon atmosphere at constant heating rate of 10°C min^{-1}. The morphology of the membranes was conducted on an Environmental Scanning Electron Microscope (ESEM, FEI Quanta 200). The XRD was tested on a Bruker D8 Focus X-ray

diffractometer.

Characterization of self-healing properties

The solid polymer electrolytes were cut with a razor blade into two pieces and the half membranes were re-attached at the cut-interface using a tweezer for a certain time. The healing speed was monitored under different temperatures. These samples were then subjected to tensile measurement using an electronic universal testing machine (Shanghai Xieqiang Instrument Co., Ltd. CTM2500) at a crosshead speed of 200 mm min^{-1}.

Interfacial stability of electrolyte/electrodes

The interfacial stability between the electrode and the electrolyte was investigated by measuring the SEM of the Li/$LiFePO_4$ full cells cross section after the cycle. The cross-section was obtained by breaking the electrode/electrolyte cell in a liquid nitrogen atmosphere.

Electrochemical characterization measurements

The ionic conductivity of the as-prepared solid polymer electrolyte was measured by electrochemical impedance spectroscopy (EIS) using a CHI 660 electrochemical workstation (CH Instruments). The measurements were carried out from 20 °C to 80 °C in a frequency range of 1 Hz up to 100 KHz with amplitude of 5 mV for open circuit potential at various temperatures. The electrolytes were sandwiched between a pair of stainless-steel blocking electrodes. The SS/electrolyte/SS symmetrical cells were kept at each temperature for 1 h to achieve thermal equilibrium. The ionic conductivities of the electrolytes were calculated by the equation: $\sigma = {}^{d}/_{SR_b}$. Where

d is the vertical distance between the two electrodes, S and R_b is the bulk resistance and the activity area of the ShSPE, respectively. The electrochemical stability window of polymer electrolytes was determined by linear sweep voltammetry (LSV) at scan rate of 10 mV s^{-1} from 1.0 to 7.0 V vs. Li^+/Li. The cell was assembled by sandwiching ShSPE between a lithium metal and stainless steel as the reference/counter electrode and working electrode, respectively. The lithium transference number (t_{Li^+}) was determined by using a combination method of ac impedance and dc polarization measurements. The coin cells with Li/ShSPE/Li structure were accomplished in an argon gas-filled glove box and the dc voltage pulse applied to the cell was 10 mV. The equation $t_{Li}^{+} = I_s(\Delta V - I_0R_0)/I_0(\Delta V - I_sR_s)$ was used to calculate the t_{Li^+}. Where ΔV is the potential applied across the cell, I_0 is the initial current, I_s is the steady-state current, R_0 and R_s is the charge transfer resistance before the polarization and the steady-state charge transfer resistance after the polarization, respectively.

Assembly of Li/$LiFePO_4$ full cells

The electrochemical performance of ShSPE was measured using CR2025 coin-type battery. A purchased $LiFePO_4$ as cathode electrode sheet, ShSPE as electrolyte separator and lithium metal as anode were assembled to form $LiFePO_4$ ||ShSPE||Li cell. The CR 2025 coin battery was assembled in an argon-filled glove box. The experiments were conducted in automatic galvanostatic charge–discharge unit, LAND CT2001A testing system, over the range of 2.5-4.2 V at 60 ºC**.**

Supplementary data

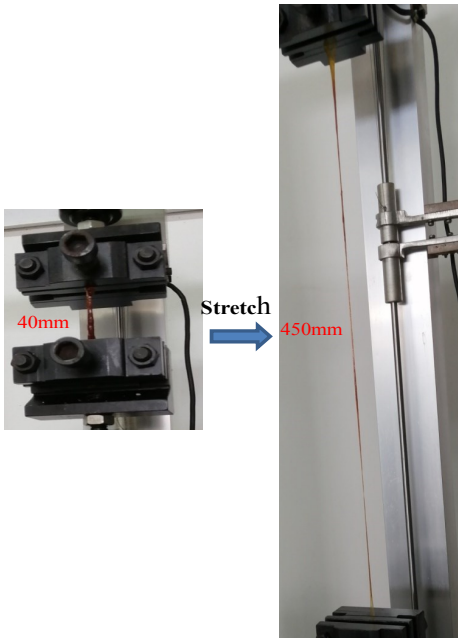

Figure S1.The stretchability test of ShSPE-3.

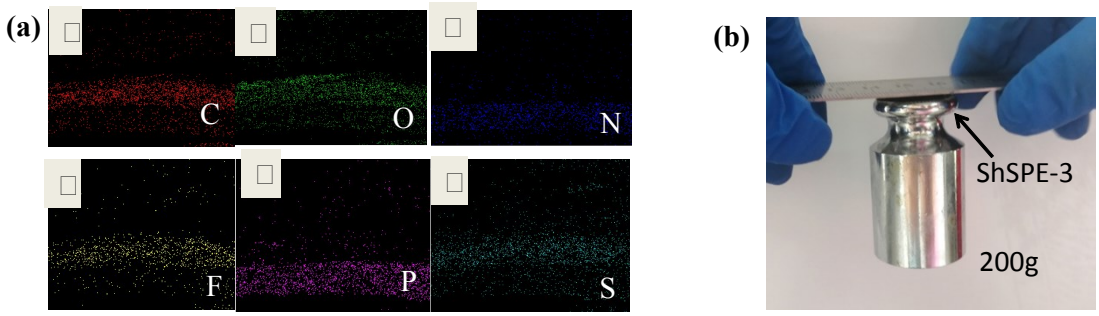

Figure S2.Elemental mapping images of i :C, ii :O, iii:N, iv:F, v :P and vi:S in the Li metal anodes after 5 cycles of deposition/stripping (a) and demonstration of the ShSPE-3 attached to a metal surface to completely support 200 g of mass (b).

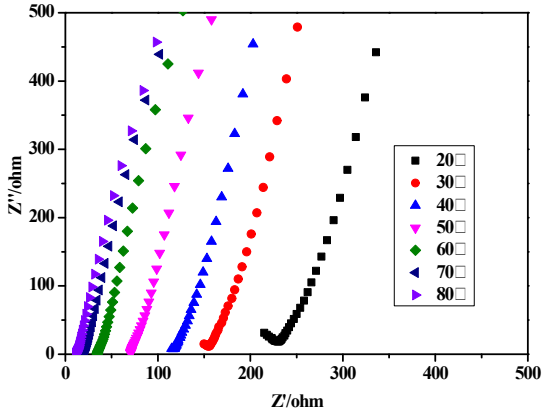

Figure S3. EIS plots of SS/ ShSPE-3/SS at different temperatures

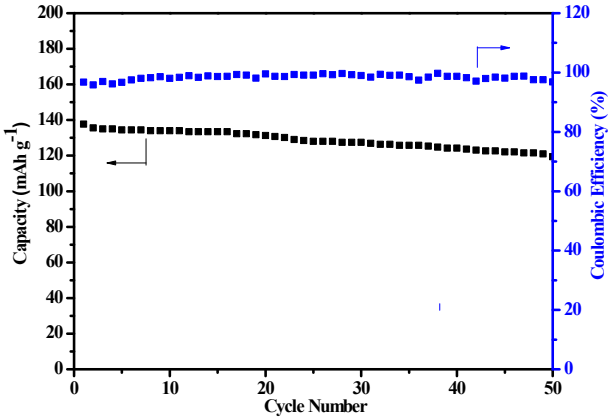

Figure S4. The LFP battery with healed ShSPE-3 at 0.1C

Table S1 Comparison of electrochemical performance of Li/$LiFePO_4$ batteries assembled with different types of PEG-doped LiTFSI to form an all-solid-state polymer electrolyte at different temperatures

Polymer matrix	Temp.[a] (℃)	Ion conductivity (S cm^{-1})	Temp[b]. (℃)	Discharge Capacity (mAh g^{-1})at 0.1C	Coulombic efficiency (%)	Ref.
3PEG-SSH	80	1.78 10^{-4} ,	60	135	97.5	[1]
PEO- Cs^{+}	60	1.9×10^{-4}	25	163	98.2	[2]
PEG5–UPy	30	2.1×10^{-5}	60	157	99.2	[3]
PEG600	30	1.99×10^{-3}	40	155	98.9	[4]
PEG-UPy	30	8.01×10^{-5}	60	145(0.2C)	99.1	[5]
PEG	40	3.6×10^{-5}	90	163	98.4	[6]
PEG	25	1.9×10^{-4}	25	147.9	~100	[7]
PEG	60	1.67×10^{-4}	60	141.3	96.8	This paper

[a]Acronyms: Test temperature of ion conductivity

[b]Acronyms: Temperature for testing battery cycle performance and rate performance

References

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