

Supporting Information

Spherulite-packed polymer electrolytes with high ion-selectivity for stable lithium–sulfur battery performance

Miaofa Yuan, Leyuan Ma, Kangdong Tian, Rtao Wang, Luyuan Zhang and Chengxiang Wang*

Shandong Provincial Key Laboratory of Electrochemical Catalysis and Conversion, School of Materials Science and Engineering, Shandong University, Jinan 250061, People's Republic of China. Email: wxmat@sdu.edu.cn.

1. Experimental Section

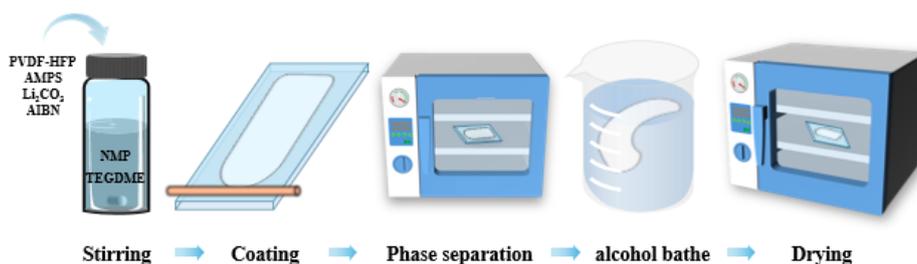
1.1 Chemicals and Reagents

All chemicals were used as received. Poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP, Mw400000,); 2-Acrylamido-2-methylpropane sulfonic acid (AMPS); Li_2CO_3 ; N-methyl-2-pyrrolidinone (NMP); tetraethylene glycol dimethyl ether (TEGDME, 99%); anhydrous ethanol.

1.2 Preparation of Spherulite-packing polymer electrolytes

SP-PHLS: A homogeneous solution was prepared by dissolving 0.5 g of PVDF-HFP in a mixture of 3 g of NMP and 0.5 g of TEGDME at 60 °C under stirring at 800 rpm for 6 hours, followed by cooling to room temperature. Separately, 0.5 g of AMPS, 0.089 g of Li_2CO_3 , and 0.01 g of AIBN (2 wt%) were dissolved in 0.5 g of NMP to form a clear solution. This solution was then added to the PVDF-HFP mixture and stirred at 300 rpm in a low-temperature water bath for 6 hours to obtain a homogeneous, transparent polymer electrolyte precursor.

The precursor solution was degassed via low-speed centrifugation and subsequently cast onto a clean glass substrate using a doctor blade with a 500 μm gap. The cast film was dried under vacuum at 70 °C for 6 hours, followed by washing with anhydrous ethanol to remove residual solvent, and further vacuum-dried to yield the freestanding SP-PHLS solid polymer electrolyte membrane. Finally, the membrane was transferred into an argon-filled glove box and punched into circular discs with a diameter of 16 mm for electrochemical testing.



SP-PH: Prepared using the SP-PHLS membrane fabrication procedure without the addition of AMPS, Li_2CO_3 , and AIBN.

S-PH: Prepared following the SP-PH membrane fabrication procedure with TEGDME replaced by glycerol.

D-PH: Prepared following the S-PH membrane fabrication procedure using only NMP as the solvent.

1.3 Manufacturing of CNTs/S Cathode

CNTs/S composites are prepared using the melt-diffusion method. The cathode slurry is obtained by mixing CNTs/S composite, Super P, and PVDF with a weight ratio of 8:1:1 in anhydrous NMP. The resulting slurry is then coated on carbon-coated aluminum foil and then dried for 12 h. The cathode sheets was cut circular pieces with a diameter of 10 mm, and the active material loading is 1.5 mg cm^{-2} .

1.4 Electrochemical Measurements

Electrochemical measurements were taken by using CR2025 coin cells or CR2032 coin cells. An electrochemical workstation ((CHI600E) was used for electrochemical impedance spectroscopy (EIS), lithium-ion transference number (t_{Li^+}) and linear sweep voltammetry (LSV).

Ionic conductivities of different gel electrolyte systems at room temperatures were measured by EIS. The ionic conductivity(σ) was calculated depending on Eq. (1):

$$\sigma = \frac{L}{RS}$$

where L is the thickness of the GPE electrolyte, S is the contact area between GPEs and SS electrode and R is the resistance measured from EIS in the frequency ranging from 0.1 Hz to 10 MHz with an AC amplitude of 10 mV. The Li^+ transference number, t_{Li^+} , was determined by a combined method of chronoamperometry and AC impedance spectroscopy with a Li||Li symmetric cell, according to Eq. (2):

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

where I_0 and I_s are the initial and steady-state currents measured by chronoamperometry under a small polarization potential (10 mV), and R_0 and R_s are the resistances of the symmetric cell before and after polarization. LSV was studied between 1.0 and 6.0 V versus Li/Li⁺ at a scan rate of 10 mV s⁻¹ with a Li|SS asymmetric cell to measure the electrochemical window.

The galvanostatic charging–discharging of battery cells was performed in LAND CT2001A. As for symmetrical Li cells, the current density is 1 mA cm⁻². Li-S cells were cycled with cutoff voltages of 1.7–2.8 V.

1.5 Characterizations

X-ray diffraction (XRD) patterns were collected on Rigaku D/Max-KA X-ray diffractometer equipped with a Cu K α source ($\lambda = 1.5406 \text{ \AA}$). The surface or fracture section morphologies of the SGPE electrolyte and deposited Li were characterized by field emission scanning electron microscopy (FESEM, SU-70), with energy-dispersive spectrometer (EDS) to characterize the elemental distributions of the materials. Fourier transform infrared spectroscopy (FTIR) tests by Bruker spectrometer TENSOR 27.

The wetting ability was evaluated using static contact angle (CA) measurements (KRÜSS GmbH). In the swelling ratio test, the mass of the hydrogel was recorded every two hours until it reached a constant value, m. The swelling ratio (w, %) was calculated using the following Eq. (3): where m_0 is the initial mass of the dry hydrogel.

$$w = (m - m_0)/m_0 \times 100\%$$

2. Supplementary Figures

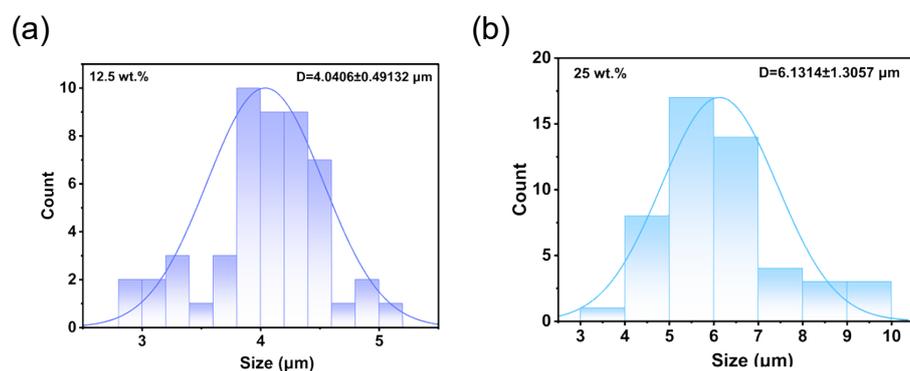


Figure S1. Particle size and distribution, (a)12.5 wt.% TEGDME in NMP, (b)25 wt.% TEGDME in NMP.

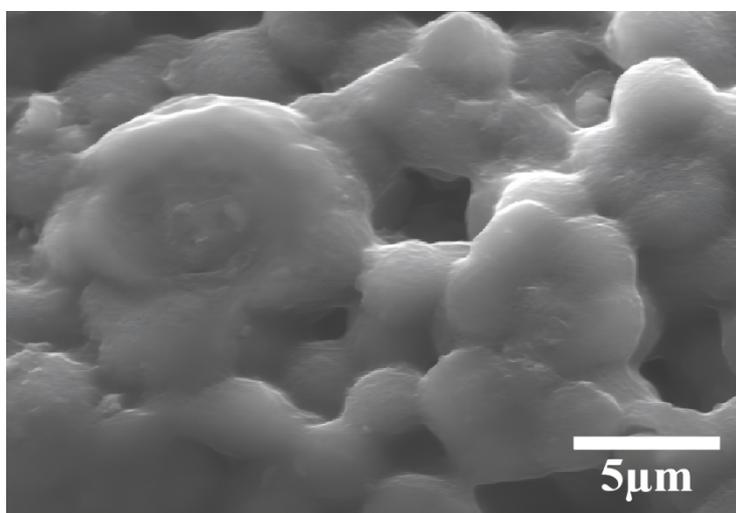


Figure S2. SEM image of S-PH with 25% TEGDME in NMP.

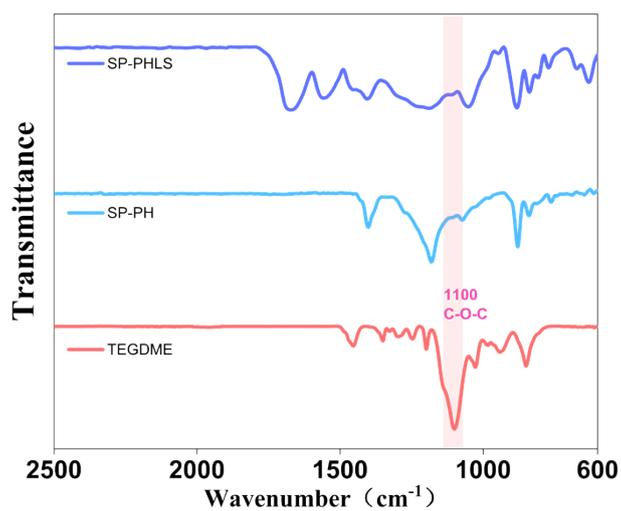


Figure S3. FT-IR spectra of TEGDME、SP-PHLS and SP-PH.

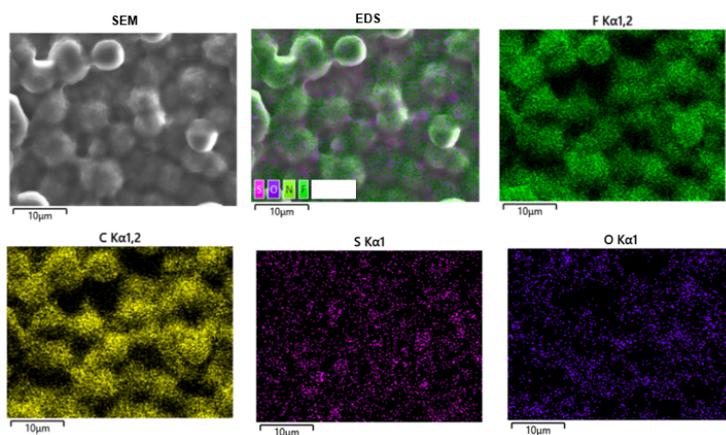


Figure S4. (A) SEM image of SP-PHLS, (B-F) Corresponding EDS element mapping images of SP-PHLS.

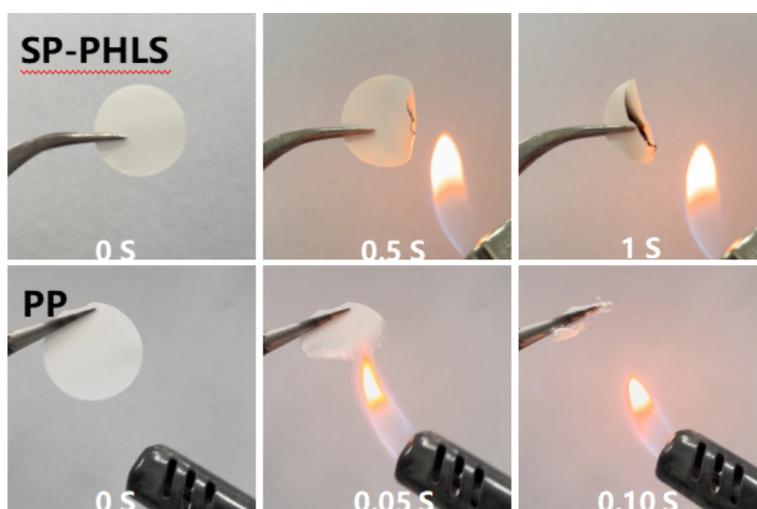


Figure S5. Ignition test of SP-PHLS and PP.

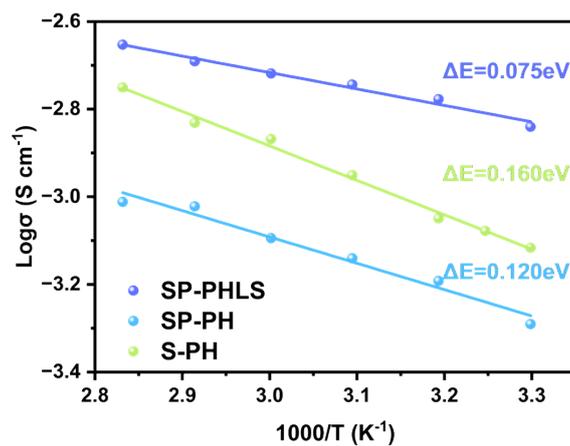


Figure S6. Arrhenius plots of SP-PHLS, SP-PH, and S-PH electrolytes at different temperatures.

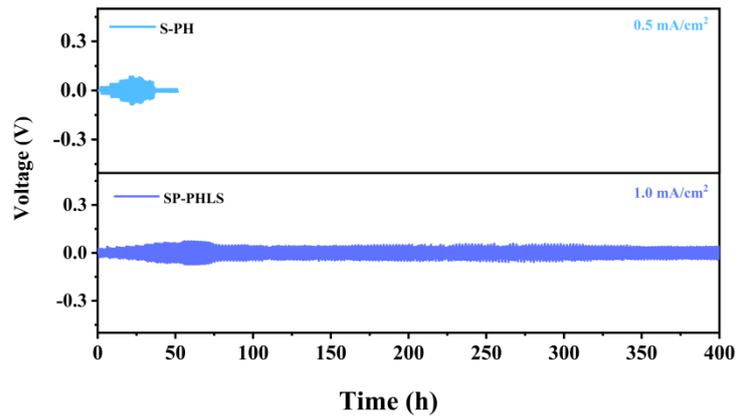


Figure S7. Constant current cycling curves at 1 mA cm^{-2} .

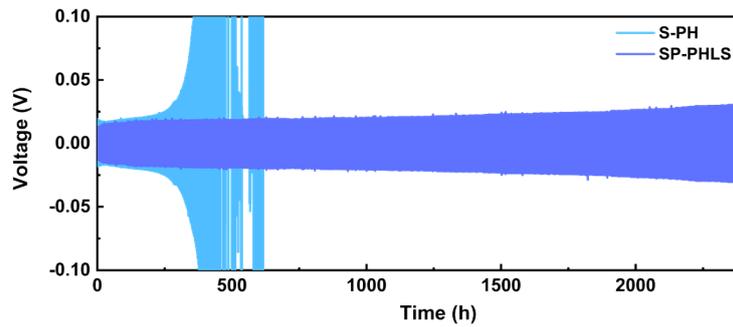


Figure S8. Constant current cycling curves at 0.1 mA cm^{-2} .

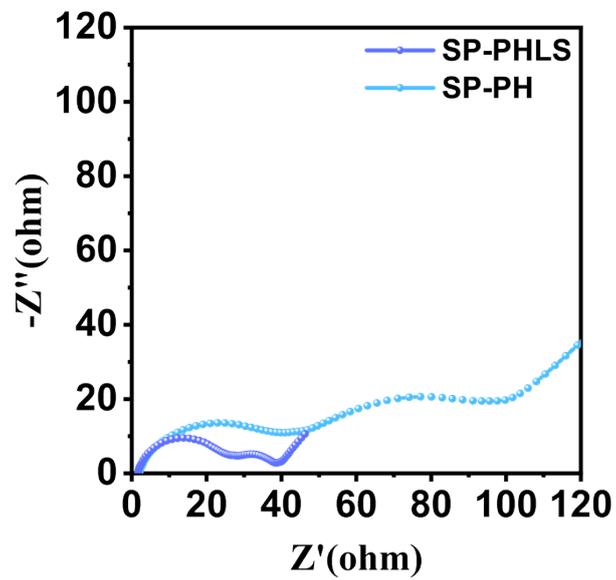


Figure S9. EIS plots after 300 cycles.

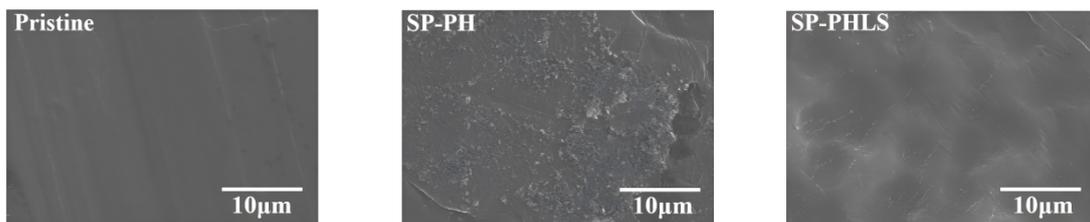


Figure S10. SEM images of Li deposition with different electrolytes.

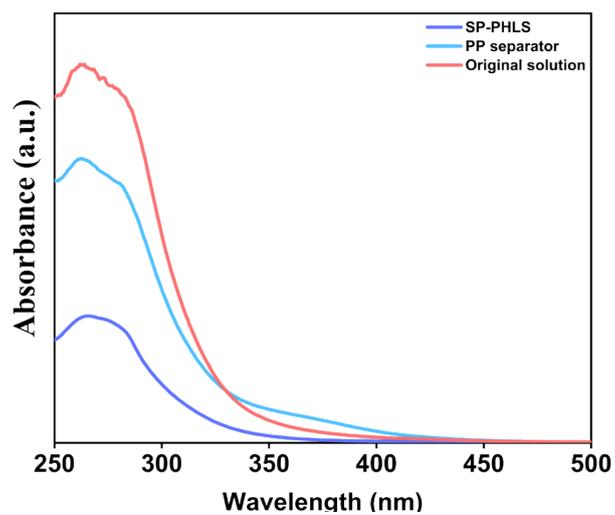


Figure S11. UV-Vis absorption spectroscopy of Li_2S_6 in DOL/DME solutions on the permeate side for SP-PHLS membrane and PP separator after 12 h of penetration.