Supporting Information

Fast ion-conduction in solid-state Li-S batteries realized by an interfacial-bridges strategy

Jing Yang, Yuxuan Li, Kangshuai zhu, Qinmin Pan*

State Key Laboratory of Space Power-Sources, MOE Engineering Research Center for Electrochemical Energy Storage and Carbon Neutrality in Cold Regions, School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin 150001, China

Keywords:

"Polymer in salt" electrolyte, interfacial bridges, in-situ polymerization, interfacial stability, room temperature solid-state lithium sulfur battery

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Experimental Section

Chemicals and materials

Polyacrylonitrile (PAN, Mw 150000) were purchased from Macklin Co.Ltd. Bistrifluoromethanesulfonimide lithium salt (LiTFSI, 99%), N, N-dimethylformamide (DMF, 99.5%), manganese (II) sulfate monohydrate (MnSO₄·H₂O, 99%), potassium acetate (CH₃COOK, 99%), potassium chlorate (KClO₃, 99.5%), acetic acid (CH₃COOH, 99.5%), (3-aminopropyl)trimethoxysilane (APTMS, 98%), sulfur (99.5%), 1,3-Dioxlane (DOL, 99.8%), lithium difluoro(oxalato)borate (LiDFOB, 99%) were purchased from Aladdin Co.Ltd. Acetylene carbon (AC) was purchased from Lion Co.Ltd. All chemicals were used as received without further purification.

Synthesis of MnO₂ nanowires

 $MnSO_4$ ·H₂O 4.0 mmol, KClO₃ 7.0 mmol and CH₃COOK 7.0 mmol were dissolved in a solution contained 3.2 mL of CH₃COOH and 80 mL of distilled water to form a solution. The resulting solution was transferred to a 100 ml autoclave and subjected to hydrothermal treatment at 160 °C for 12 h. Finally, brown cotton-like deposits were collected by freeze-drying, washed with distilled water and ethanol to obtain ultra-long MnO₂ nanowires.

Modification of MnO₂ nanowires with APTMS

 100 mg MnO_2 nanowires was dispersed in 10 ml distilled water in the presence of 120 μ L of APTMS. The dispersed mixture was then heated to 80°C for 12 h under stirring. The resulting MnO₂ nanowires was washed with distilled water and ethanol, then freeze-dried.

Preparation of PIS

A certain proportion of PAN, LiDFOB and LiTFSI were dissolved in DMF by stirring at 80 °C. Then AMW was ultrasonic dispersed in the above solution, poured into a PTFE mold, and dried at 80°C for 48 h in vacuum to obtain PIS films.

Preparation of PIS-PDOL

The preparation of PIS-PDOL was carried out in a glove box filled with argon gas, with both O₂ and H₂O contents kept 0.1ppm. PIS films were immersed in a DOL solution of 2M LiTFSI. After heat treatment at 60 °C for 12 hours, the DOL monomer was gradually transformed into PDOL. For comparison, PDOL was synthesized by directly dissolving 0.3M LiDFOB in precursor dissolution through the similar procedures.

Characterizations

Chemical structure of PIS-AMW, PIS-AMP, PIS were identified by using Fourier transform infrared spectroscopy (FT-IR, Alpha Platinum ATR, Bruker). PDOL was dissolved in dimethyl sulfoxide-d₆ for ¹H NMR analysis on a Bruker 600M. Microscopic morphology of the prepared materials was observed using a field emission scanning electron microscope (FE-SEM, S-4800, Hitachi). X-ray diffraction (XRD) analysis was conducted on a Rigaku SmartLab3. Thermogravimetric analysis (TGA) was performed using a TG/DTA7300 thermogravimetric/differential analyzer. The PDOL was dissolved in THF, and then the solution was eluted in a Waters ambient temperature GPC equipped with a triple detection function for absolute polymer molecular weight determination, and GPC measurement was performed with Agilent PL-GPC50. X-ray photoelectron spectroscopy (XPS) was performed on an Axis Ultra DLD Kratos AXIS SUPRA. The tensile and puncture stress-strain curves were measured by an INSTRON 5565 testing system. Electrochemical impedance spectroscopy (EIS, frequency range of 10^{6} – 10^{-2} Hz) tests were performed on an electrochemical workstation (CHI650e).

Ionic conductivity measurements

Ionic conductivity of the as-prepared electrolytes was determined by EIS on the electrochemical station CHI660D in the frequency range of 10^{6} – 10^{-2} Hz with an AC amplitude of 5 mV in the temperature range from 20 °C to 80 °C. The ionic conductivity was calculated by the following equation:

$$\sigma = \frac{d}{R \times A}$$

where R, d and A are the bulk resistance, thickness, surface area of the electrolytes, respectively.

The activation energies of the electrolytes were fitted by the Arrhenius equation: $\sigma = Aexp(-E_a/RT)$

where A is the pre-exponential factor, E_a is the activation energy, R is the molar gas constant (8.314 J mol⁻¹ K⁻¹), T is the absolute temperature.

Li-ion transference number measurements

The Li-ion transference number (t_{Li}^+) was obtained by a chronoamperometry test with a voltage amplitude of 0.01 V via using symmetric Li cells with the as-prepared electrolytes. The EIS tests were conducted on the cells before and after DC polarization. The value of t_{Li}^+ can be calculated according to equation:

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

where I_0 and I_{ss} are the initial and steady-state DC currents, R_0 and R_{ss} are the initial and steady-state interfacial resistances, and ΔV is the applied potential, respectively.

Li-ion diffusion coefficient measurements

The Li-ion diffusion coefficient of the electrolytes was estimated using the method proposed by Ma et al.^[48] The symmetric Li cells with the electrolytes are polarized at 5 mV before the potential is interrupted. Once the potential was interrupted, the cell was kept at OCP until a stable state was achieved. Later, the profiles are plotted as the natural logarithm of potential (V) versus time (t). The D_{Li}^+ values were calculated from the slope of the linear curves using the following equation:

$$Slope = -\frac{\pi^2 \times D_{Li}}{L^2}$$

where *L* is the thickness of the electrolytes.

Electrochemical stability window measurements

Electrochemical stability window of the electrolytes was estimated by linear sweep voltammetry (LSV) test with Li|electrolytes|steel cells at a scan rate of 0.1 mV s⁻¹ from OCP to 5.5 V at room temperature.

Galvanostatic Li plating/stripping test

The Galvanostatic Li plating/stripping test was conducted with the Li|electrolyte|Li cells under constant current density and capacity at room temperature. The Li dendrite suppression capability of solid electrolyte was defined in the critical current density (CCD) test, in which a current density from 0.1 to 2.0 mA cm⁻² with a step of 0.1 mA cm⁻² with a fixed capacity from 0.1 to 2.0

mA cm⁻², respectively, was conducted on Li|electrolyte|Li cell.

Preparation of sulfur cathodes

For the Li-S cell performance tests, the cathode slurry was prepared by dispersing AC@S, PIS electrolytes, acetylene black and PVDF (6: 2: 1: 1, in mass ratio) in NMP under stirring for 8 h. The slurry was coated onto an Al foil and then dried at 60°C for 12 h under vacuum. The resulting foil was punched into circle disks with diameters of 14 mm.

Electrochemical performance testing of Solid-state Li-S cells

Solid-state Li-S cells were assembled with AC@S Cathodes, lithium foils and the as-prepared electrolytes in an argon filled glove box. The mass loading of sulfur was 1.5-2.0 mg cm⁻². The galvanostatic discharge/charge, rate capability and cycling stability of the batteries were tested on a Neware battery testing system in a voltage range of 1.5–3.0 V.

Theoretical calculation

The theoretical calculations were performed with periodic boundary conditions used Materials Studio 2020 (Accelrys Inc.). One-dimensional Six-polymer connected PAN chain and One-dimensional three-polymer connected PDOL chain were used to contact with sulfur species (Li_2S_x , $4 \le x \le 8$). The spin-polarized first-principles calculations were performed based on density functional theory (DFT) as implemented in the Dmol3 module with the Perdew-Burke-Ernzerhof (PBE) functional method. The cut-off energy for the basis function was 300 eV. Structural relaxations were performed until all the residual forces on atoms were less than 0.02 eV·Å⁻¹. The convergence criteria for the energy calculation and geometric optimization were set as below: a maximum force tolerance of 10^{-6} eV and an energy tolerance of 10^{-5} eV.

The coupling behaviors of Li⁺-TFSI⁻ and Li⁺-PAN and Li⁺-PDOL in PIS-PDOL system were illustrated by molecular dynamics (MD) simulation, in which universal forcefield of Materials Studio with Forcite module was employed to describe the intermolecular interaction forces.[1] For composite electrolyte system, the simulation box with a size of 45 Å×45 Å×45 Å consists of 116 molecules of LiTFSI, 38 molecules of LiDFOB, 4 units of one-dimensional fifty-polymer connected PAN chain and 3 units of one-dimensional twenty-five-polymer connected PDOL chain. A periodic boundary condition (PBC) and cutoff energy of 400 eV were applied to the box. After establishing the box with optimized configuration, an anneal procedure from 300 to 400 K in 1.0 atm was carried out for 2 ns to reach equilibrium state with minimum local energy according to a conjugate gradient method. Afterwards, a dynamic procedure was also conducted with NVT ensemble for 1 ns to relax, and MD simulation was then continued with additional simulation time of 2 ns (the time step was set to 1 fs) to transform from NVT ensemble to NVE to collect molecular/ion coupling data. Notably, all the temperature is controlled with Nose thermostat.[2] Radial Distribution Function (RDF) of Li⁺ and N atom of TFSI⁻, PAN as well as Li⁺ and O atom of TFSI⁻, DFOB⁻, PDOL were also calculated employing MD simulation. Mean squared displacement (MSD) was recorded every time step to acquire Li⁺ diffusion dynamics at different location of composite electrolyte. The average MSD was defined by equation as following:

$$MSD = \langle |r(r(t_0 + t) - r(t_0)|2 \rangle = \frac{1}{N} \sum_{i=1}^{N} |r_i(t_0 + t) - r_i(t_0)|^2$$

where vector $r_i(t)$ represents ith-ion position at the time t, and N corresponds to the total number of species in the simulation box. The corresponding Li⁺ diffusion coefficient was determined as the linear slope of averaged MSD with regards to MD time based on following Equation:

$$D_{Li^{+}} = \frac{1dMSD}{6 dt}$$



Figure S1. Schematic diagram of the polymerization mechanism of PDOL.

LiDFOB undergoes thermal decomposition to form BF₃, which receives lone pair electrons from O in DOL to provide cationic sites, and triggers DOL ring opening and chain growth.



Figure S2. Digital images before and after polymerization.



Figure S3. GPC curves of PIS-PDOL.



Figure S4. SEM images of PIS.

(a)Top and (b) cross-sectional images.



Figure S5. SEM images of PIS-PDOL.

(a)Top and (b) cross-sectional images.



Figure S6. Tensile stress-strain curves of (a) PIS and (b) PIS-PDOL electrolytes.



Figure S7. (a) Ionic conductivity and (b, c) corresponding EIS plots of PDOL at different polymerization times.

The ionic conductivity of PDOL electrolytes only slightly decreases during the initial 12 h of polymerization. However, when the polymerizing time reaches 24 h, the ionic conductivity decreases to ~ 10^{-5} S cm⁻¹. After 48 h of polymerizing, the ionic conductivity remained at 4×10^{-6} S cm⁻¹.



Figure S8. (a) Ionic conductivity and (b) corresponding EIS plots of PIS-PDOL at different polymerization times.

The polymerization-time-dependent ionic conductivity of PIS-PDOL electrolyte was similar to that of PDOL. Although the ionic conductivity of PIS-PDOL (10^{-3} S cm⁻¹) is slightly lower than that of PIS (3×10^{-3} S cm⁻¹) at the beginning of polymerization, the stable ionic conductivity (6.3×10^{-4} S cm⁻¹) of the former is much higher than that of PIS after 48 h.



Figure S9. (a) Ionic conductivity and (b) corresponding EIS plots of PIS with different content of LiDFOB (wt.%) at 25 °C.



Figure S10. (a) Effect of content of DOL on Ionic conductivity of PIS-PDOL at 25 °C.(b) Corresponding EIS plots.



Figure S11. (a) Ionic conductivity of PIS and PIS-PDOL. Corresponding EIS plots of (b) PDOL, (c) PIS and (d) PIS-PDOL.



Figure S12. Li-ion diffusion coefficient of PDOL.



Figure S13. Chronoamperometry curves for (a) PDOL, (b) PIS and (c) PIS-PDOL with polarization voltage of 10 mV. Insets are EIS plots before and after the polarization.



Figure S14. The localized magnified images of the MD snapshots of (a) PIS and (b)

PIS-PDOL.



Figure S15. (a) Ionic conductivity and Corresponding EIS plots of (b) PIS and (c) PIS-PDOL with different concentrations of LiTFSI (wt.%) at 25 °C.



Figure S16. (a) Charge-discharge profiles of the solid-state Li|PIS|S cell at different current densities. (b) Charge-discharge profiles of the solid-state Li|PIS|S cell at 0.1 C and different cycles. (c) EIS plots of the solid-state Li|PIS|S cell after different cycles.
(d) The GITT measurement of the solid-state Li|PIS|S cell during the first discharge.



Figure S17. Charge-discharge profiles of Li|PIS-PDOL|S cell at 0.1C and different cycles.



Figure S18. Cross-sectional SEM image of Li|PIS-PDOL|S cell after 120 cycles.



Figure S19. Electrochemical performance of Li-S cells with PDOL at 25°C. (a) Cycling performance at 0.1C. (b) Charge-discharge profiles at 0.1C and different cycles. (c) EIS plots before and after cycle.



Figure S20. Molecular configuration of Li_2S_x (4 $\leq x \leq 8$) interact with PAN and PDOL.



Figure S21. Molecular configuration of Li_2S_x (4 ${\leq}x{\leq}8)$ interact with PAN.



Figure S22. E_{ad} of Li_2S_x (4 $\leq x \leq 8$) to PAN and PAN-PDOL.

Electrolyte	σ/ mS cm ⁻¹ (T/	Cycled capacity/	C-rate, T/		
	°C), t _{Li} +	mAh g ⁻¹ (Cycles)	°C	Reference	
PIS-PDOL	0.69 (25), 0.66	734 (120)	0.1, 25	This work	
PEO/LITFSI/PTE	0.138 (30), 0.415	774 (60)	0.1, 60	[3]	
PEO/LLTO	0.23(RT), /	415 (50)	0.05, RT	[4][4]	
PEO ₁₀ /30hc-SCP	0.087(50), 0.31	600 (100)	0.1, 70	[5]	
BN-PEO-PVDF	0.1 (60), 0.31	700 (50)	0.1, 55	[6]	
PEO-C ₆₀	0.127 (60), 0.21	1121 (24)	0.1, 55	[7][7]	
PVDF-LiTFSI-		610 (80)	0.1, 20	[8]	
LLBZTO	0.16 (23),7				
PEO-Li ₄ (BH ₄) ₃ I	0.41 (70), 0.45	967 (75)	0.12, 70	[9][9]	
PTFE@LLZO@PEO	0.25 (60), /	568 (100)	0.1, 30	[10]	
BNPs	0.1 (25), 0.94	873 (50)	0.05, 25	[11]	

Table S1. The ion-conductive properties of different solid-state electrolytes and the electrochemical performance of corresponding SSLSBs.

	E _{polymer} /eV	E _{Li2Sx} /eV	E _{Total} /eV	E _{ad} /eV
Li_2S_4 to PAN	-27900.71	-43737.79	-71640.89	-2.39
Li_2S_6 to PAN	-27900.71	-65401.10	-93304.17	-2.36
Li_2S_8 to PAN	-27900.71	-87064.03	-114967.13	-2.39
Li ₂ S ₄ to PAN-PDOL	-49821.18	-43737.79	-93562.58	-3.61
Li ₂ S ₆ to PAN-PDOL	-49820.87	-65401.23	-115225.62	-3.52
Li ₂ S ₈ to PAN-PDOL	-49820.81	-87064.16	-136889.80	-3.83

Table S2. E_{ad} of Li_2S_x (4 $\leq x \leq 8$) to PAN and PAN-PDOL.

 $E_{ad} = E_{Total} - E_{polymer} - E_{Li2Sx}$

References:

- Rappe, A.K., et al., UFF, a full periodic table force field for molecular mechanics and molecular dynamics simulations. Journal of the American Chemical Society, 1992. 114(25): p. 10024-10035, https://doi.org/10.1021/ja00051a040.
- [2]. Nosé, S., A unified formulation of the constant temperature molecular dynamics methods. The Journal of Chemical PhysicsThe Journal of Chemical Physics, 1984. 81(1): p. 511-519, https://doi.org/10.1063/1.447334.
- [3]. Li, Y., et al., Interfacial chemistry and ion-transfer mechanism for a tailored poly(thioether)-enabled hybrid solid polymer electrolyte with electrochemical properties in all-solid-state lithium-sulfur batteries. JOURNAL OF MATERIALS CHEMISTRY A, 2023. 11(43): p. 23405-23417, https://doi.org/10.1039/D3TA04944B.
- [4]. Zhu, P., et al., Flexible electrolyte-cathode bilayer framework with stabilized interface for room-temperature all-solid-state lithium-sulfur batteries. ENERGY STORAGE MATERIALS, 2019. 17: p. 220-225, https://doi.org/10.1016/j.ensm.2018.11.009.
- [5]. Zhong, L., et al., Addressing interface elimination: Boosting comprehensive performance of allsolid-state Li-S battery. ENERGY STORAGE MATERIALS, 2021. 41: p. 563-570, https://doi.org/10.1016/j.ensm.2021.06.035.
- [6]. Yin, X., et al., Thermal Conductive 2D Boron Nitride for High-Performance All-Solid-State Lithium-Sulfur Batteries. ADVANCED SCIENCE, 2020. 7(19), https://doi.org/10.1002/advs.202001303.
- [7]. Wei, B., et al., A three-in-one C₆₀-integrated PEO-based solid polymer electrolyte enables superior all-solid-state lithium-sulfur batteries. JOURNAL OF MATERIALS CHEMISTRY A, 2023. 11(21): p. 11426-11435, https://doi.org/10.1039/D3TA01226C.
- [8]. Bag, S., et al., LiF modified stable flexible PVDF-garnet hybrid electrolyte for high performance all-solid-state Li-S batteries. ENERGY STORAGE MATERIALS, 2020. 24: p. 198-207, https://doi.org/10.1016/j.ensm.2019.08.019.
- [9]. Zhang, X., et al., Composite Electrolytes Based on Poly(Ethylene Oxide) and Lithium Borohydrides for All-Solid-State Lithium-Sulfur Batteries. ACS SUSTAINABLE CHEMISTRY & ENGINEERING, 2021. 9(15): p. 5396-5404, https://doi.org/10.1021/acssuschemeng.1c00381.
- [10]. Li, Z., et al., 3D porous PTFE membrane filled with PEO-based electrolyte for all solid-state lithium-sulfur batteries. RARE METALS, 2022. 41(8): p. 2834-2843, https://doi.org/10.1007/s12598-022-02009-x.
- [11]. Kim, B. and M.J. Park, All-solid-state lithium-sulfur batteries enabled by single-ion conducting binary nanoparticle electrolytes. MATERIALS HORIZONS, 2023. 10(10), https://doi.org/10.1039/D3MH00913K.