Three-in-One C₆₀-Integrated PEO-Based Solid Polymer Electrolyte Enables Superior All-Solid-State Lithium-Sulfur Batteries

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Experimental Section

1. preparation of solid polymer electrolyte

The dried PEO was mixed with LiTFSI with a molar ratio of 20:1 in CH₃CN, and the mixture was stirred at 60°C for 24 h. The C_{60} was added with different weight ratio and stirred at 60°C for 100 h, and the mixture colloidal was casted onto the Teflon substrate dried at room temperature.

2. Material Characterization

The crystal structure of electrolyte was detected by a bruker D8 Advanced X-ray diffraction analyzer (Cu K α , $\lambda = 0.154056$ nm). The surface states were analyzed by X-ray photoelectron spectroscopy (XPS) using an ESCALADE Xi⁺ with a monochromatic Al K α X-ray source. Raman measurement was carried out with LabRAM HR Evolution. Scanning electron microscope (SEM, TESCAM MIRA3) was used to examine the morphology and microstructure of sample. Fourier Transform InfraRed (FT-IR) spectrum was collected from Nicolet iS50R (Thermo Scientific) in the range of 400 to 4000 cm⁻¹.

3. Electrochemical measurements

The SS/electrolyte/ SS structured CR2032 type coin cells were assembled and their

ionic conductivity were measured by alternating-current (AC) impedance spectroscopy instrument (CHI760E Electrochemical Workstation) in the frequency range of 100 KHz-0.1 Hz with an AC amplitude of 10 mV at temperatures ranging from 70 to 30 °C with 10 °C steps. The cell was kept at the specific temperature for 2 h prior to the measurement.

Ionic conductivities were calculated using the following equation:

 $\sigma = L/(R * S)$

where σ is the ionic conductivity (S cm⁻¹), R is the resistance (Ω), L is the thickness (cm), and A is the area (cm⁻²) of the electrolyte membrane. The interface stability was measured by Li/electrolyte/Li symmetric cells at current density from 0.05 to 0.2 mA cm⁻². The cycle test is carried out at current density of 0.05 mA cm⁻² with capacity of 0.1 mAh cm⁻² and 0.2 mA cm⁻² with capacity of 0.2 mAh cm⁻².

For the sulfur/carbon cathode, sulfur was mixed with KB with a weight ratio of 7:3 or 8:2, and then heat at 155°C for 10 h. The cathode was prepared by mixing sulfur/carbon, super P, and PVDF with weight ratio of 8:1:1, which is casted on carbon-coated Al foil. The sulfur mass loading is 0.8-1 mg cm⁻² with N/P ratio of 190-135. The ASSLSBs was assembled with Li metal as anode, electrolyte as separator, and electrode as cathode. Galvanostatic charge/discharge tests were carried out in the voltage range of 1.6 to 2.7 V at rate from 0.1 to 0.5 C. CV tests were conducted at a scan rate of 0.1 mV S⁻¹ using CHI760E. The galvanostatic intermittent titration technique (GITT) was performed under constant-current density of 0.1 C for 0.5 h followed by a relaxation period of 2 h during the discharge/charge process. All the ASSLSBs were tested at 55 °C, and were preserved at 55 °C for 72 h before electrochemical measurements.

4. Computational method

The calculations reported in this work were performed using the Vienna Ab initio

Simulation Package (VASP), which is based on density functional theory (DFT)^[1]. The exchange-correlation interactions were described in the generalized gradient approximation (GGA) with the functional parameterization of Perdew-Burke-Ernzerhof (PBE)^[2]. The projected augmented wave (PAW) approach was used to describe the ionic-electron interactions. The energy cutoff was fixed at 400 eV. The DFT-D3 empirical correction method was employed to describe van der Waals interactions. Geometry optimizations were performed with the force convergency smaller than 0.05 eV/Å. Monkhorst-Pack k-points of $2\times2\times1$ and $1\times1\times1$ were applied for graphene and C₆₀, respectively. All atoms were relaxed in the present calculations. The graphene model was built by a 5×5 graphene supercell (lattice parameter: a =14.75999 Å, b = 14.75999 Å, c = 20.000 Å, $\alpha = \beta = 90^{\circ}$, $\gamma = 120^{\circ}$). The C₆₀ was a spherical structure composed of 60 carbon atoms (lattice parameter: a =b = c = 25.000 Å, $\alpha = \beta = \gamma = 90^{\circ}$). The Gibbs free energy (Δ G) for each electrochemical process can be calculated as:

$\Delta G = \Delta E + \Delta E Z P E - T \Delta S$

where the value of ΔE , $\Delta EZPE$ and ΔS denotes the changes of DFT energy, the zeropoint energy and the entropy at 300K, resepctively.



Figure S1. The Nyquist plots of stainless steel/electrolyte/stainless steel of (a) PEO-1% C_{60} , (b) PEO-2% C_{60} , (c) PEO-3% C_{60} , and (d) PEO.



FigureS2. XRD patterns of PEO and PEO-LiTFSI.



Figure S3. FT-IR spectra of the PEO-based electrolytes at ranges of 1450-1485 cm⁻¹.



Figure S4. F1s XPS spectra of PEO-x% C_{60} (x=0, 1, 2, and 3) electrolyte.



Figure S5. Chronoamperometry profiles of Li/Li symmetrical cells for (a) PEO and (b) PEO-1% C_{60} under a polarization voltage of 10 mV. The inset is the EIS curves before and after the polarization.



Figure S6. The voltage profiles of Li symmetric cells with PEO-2%C₆₀ and PEO-3%C₆₀.



Figure S7. The critical current density of PEO and PEO-1%C₆₀.



Figure S8. The first four CV cycles of ASSLSBs with PEO.



Figure S9. Onset potentials of PEO-1%C $_{60}$ and PEO.



Figure S10. (a) Galvanostatic charge/discharge curves after different resting time. Nyquist plots of (b) pristine lithium sulfur batteries and (c) after different preserved time.



Figure S11. Rate capability of PEO-1% C_{60} with sulfur content of 64%.



Figure S12. Voltage-times curves obtained from GITT with PEO.



Figure S13. Voltage-times curves obtained from GITT with PEO-1%C₆₀.



Figure S14. Part of GITT profiles.



Figure S15. the Li ion diffusion coefficients of ASSLSBs with PEO and PEO-1% C_{60} obtained via the GITT technique during the second discharge-charge process.

Ionic Conductivity (S cm ⁻¹)	T(°C)					
	30	40	50	60	70	
PEO	4.81×10 ⁻⁶	8.71×10 ⁻⁶	2.22×10 ⁻⁵	5.76×10 ⁻⁵	1.09×10 ⁻⁴	
PEO-1%C ₆₀	5.44×10 ⁻⁶	1.79×10 ⁻⁵	4.83×10 ⁻⁵	1.27×10 ⁻⁴	2.04×10 ⁻⁴	
PEO-2%C ₆₀	5.52×10 ⁻⁶	1.39×10 ⁻⁵	3.77×10 ⁻⁵	1.27×10 ⁻⁴	1.84×10 ⁻⁴	
PEO-3%C ₆₀	1.65×10 ⁻⁶	4.97×10 ⁻⁵	1.62×10 ⁻⁵	5.62×10 ⁻⁵	8.12×10 ⁻⁵	

Table S1. Ionic conductivity of PEO-based solid polymer electrolytes.

Table S2. Cycling performance of Li-S batteries using PEO-based solid polymer electrolytes.

Electrolyte	Sulfur content (%)	Capacity (mAhg-1)/Current	Temperature (°C)	Reference
PEO-LLZO-LiCLO ₄	49	900/0.05mA cm ⁻² (0.02 C)	37	[3]
PEO-LiFTFSI	40	1000/0.1C	70	[4]
PEO-BN-LiTFSI	40	1162/0.1C	55	[5]
PEO-LiN ₃ -LiTFSI	40	800/0.1C	70	[6]
PEO-LITCM	40	900/0.1C	70	[7]
PEO-Al ₂ O ₃ -LiTFSI	25	630/0.05C	55	[8]
PEO-PVDF-BN-LiTFSI	40	790/0.1C	70	[9]
PEO-LLZTO-LiTFSI	56	833/0.2C	60	[10]
PEO-LLZTO-Mg(TFSI)2-LiTFSI	45	877/0.1C	50	[11]
	56	1125/0.1C	55	This work
PEO -C ₆₀ -LiTFSI	64	873/0.1C	55	This work

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