Solid-state Dendrite-free Lithium-Metal Battery with Improved Electrode Interphase and Ion Conductivity Enhanced by Bifunctional Solid Plasticizer

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1 Experimental Details

2 Preparation of composite electrolytes

Polyethylene oxide (PEO, $M_w = 6 \times 10^5$, Sigma Aldrich) was dried for 48 h at 45 °C in a vacuum 3 oven overnight. Lithium bis(trifluoromethanesulfonyl) imide (LiTFSI, >99%, battery grade, 4 Sigma Aldrich) was dried for 24 h at 60°C. Lithium Aluminium Germanium Phosphate (LAGP, 5 Li_{1.5}Al_{0.5}Ge_{1.5}(PO₄)₃, MTI Kejing Group). Succinonitrile (SN, From Macklin) was dried for 12 h 6 at 60°C. All materials stored in a glove box ($H_2O < 0.5$ ppm, $O_2 < 0.5$ ppm). The solid organic-7 8 inorganic composite polymer electrolyte (SPE) was prepared by dissolving PEO and LiTFSI in 9 acetonitrile ($H_2O < 0.003\%$, Aladdin) with a PEO/LiTFSI mole ratio of 18:1. And then, different amount of LAGP powders and SN were added to the white slurry, the slurry was laid flat on the 10 PTFE doctor by a delayed flow method. It was dried in an Ar-filled glove box (with H₂O and O₂ 11 contents below 0.5 ppm, respectively) for about 12.0 h, then dried in vacuum oven for additional 12 12.0 h to completely remove the solvent. This free-standing film can be peeled off and cut into 18 13 mm used as diaphragm and electrolyte. The formed SPEs are denoted as SPE-X-Y (X = 8, 14 and 14 23, Y= 5, 15, 25), where x indicates the weight percentage of LAGP, Y indicates the weight 15 percentage of SN. 16

17 Sample characterizations

The particle size distribution was tested by Zeta Plus (Brookhaven) laser particle size analyzer, ethanol was used as solvent. The morphology and phase were characterized by Hitachi S-4800 scanning electron microscopy (SEM) and X-ray power diffraction (Ultima IV, $2\theta = 10^{\circ}-90^{\circ}$). Differential scanning calorimetry (DSC) analyses of SPEs were obtained in a NETZSCH DSC equipment. The samples were heated from -60 °C to 100 °C at a heating rate of 10 °C min⁻¹. Fourier transform infrared (FTIR) spectra of the samples were recorded on the Nicolet 380 in the range of

500-3000 cm⁻¹ sandwiched between two BF₂ windows. The ionic conductivities of PPEs were 1 determined via electrochemical impedance spectroscopy (EIS). Imposed an AC amplitude of 10 2 mV, the measurements were achieved with a frequency from 10⁵ to 10 mHz at various 3 temperatures from 20 to 90 °C. Ionic conductivity σ was calculated based on the following 4 equation: 5

8

7 where R_b represents the resistance according to EIS measurement, l represents the thickness of SPE membrane, and S represents the cross-section area.

 $\sigma = \frac{l}{R_b \bullet S} \quad (1)$

The Li-ion transference number measurement was conducted with a Li| SPE|Li symmetrical cell 9 system, polarized with a DC voltage of 10 mV, 40 °C. t_{Li}^{t} was calculated by the following 10 equation: 11

$$t_{Li}^{+} = \frac{I_{S}(\Delta V - I_{0}R_{0})}{I_{0}(\Delta V - I_{S}R_{S})}$$
(2)

Electrochemical windows of the SPEs were measured by LSV using Li |SPE|SS button cells with 13 the scan from 2.0 to 7.0 V at a scan rate of 1 mV s⁻¹, 40 °C. 14

Electrochemical techniques for investigating the formation of lithium dendrites 15

The linear sweep voltammogram (LSV) curves of Li electrodeposition on the Li anode were 16 obtained in a Li/SPEs/Li symmetrical cell with a CHI660D electrochemical station (Chenhua, 17 China) at a scan rate of 2 mV s⁻¹, 40 °C. The interface compatibility and stability between SPEs 18 19 and Li metal anodes were examined by recording the variation tendency of interfacial resistance (Ri) for Li|SPE|Li symmetric cells, following continuously increasing storage time at 40 °C. The 20

diffusion coefficients of Li⁺ (D_{Li+}) were obtained in a Li |SPEs |Li symmetrical cell at a potential
 step of 0.2 V, and get the result according to the formula:

3

$$D_{Li^+} = -\frac{d \ln I 4 L^2}{d t_t \pi^2} \tag{3}$$

4

5 where *I* presents the current density, *L* presents the thickness of SPE membrane, and *t* represents
6 the process time of potential step. We use PEO (PEO-LiTFSI), PEO-LAGP (PEO-LiTFSI-14 wt.
7 % LAGP) and PEO-LAGP-SN (SPE-14-15) as compare samples, because the obvious different
8 performance of them.

9 Batteries test

LiFePO₄ cathodes and Li metal anodes were employed to assemble all-solid-state batteries. 70 % 10 11 LFP (MTI Kejing Group) powders, 10% LAGP powder, 10% super P carbon blacks, and 10 % 12 polyvinylidene fluoride (PVDF) binder were fully mixed in N-methyl-2-pyrrolidone (NMP) and the resultant slurry was coated on Al foil by using a doctor blade then dried in an oven at 110 °C 13 for 10 h. The LFP cathode foil was punched into 14 mm-diameter disks and the typical active 14 material loading was about $2\sim3$ mg cm⁻². Commercial Li metal foils were purchased from China 15 Energy Lithium Co., Ltd. All the batteries were assembled without using a separator or additional 16 liquid electrolyte in an Ar-filled glove box ($H_2O < 0.1$ ppm, $O_2 < 0.1$ ppm). The Li|SPEs|LFP 17 ASSLMBs cells were cycled in galvanostatic mode with voltage range of 2.8 - 3.8 V at 40 °C (1.0 18 C = 175 mA g⁻¹). We use PEO (PEO-LiTFSI), PEO-LAGP (PEO-LiTFSI-14 wt.% LAGP) and 19 PEO-LAGP-SN (PEO-LiTFSI-14 wt.% LAGP-15 wt.% SN, SPE-14-15) as compare samples, 20 because the obvious different performance of them. 21



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3 Figure S1. Size distribution of the LAGP particles determined by a laser particle size analyzer.



5 Figure S2. DC polarization result for Li | SPE | Li symmetrical cells under a potential step of 10
6 mV at 40 °C and EIS profiles of cells before and after polarization. (a) PEO, (b)PEO-LAGP, (c)
7 PEO-LAGP-SN.



Figure. S3 Voltage time traces of Li |SPE| Li symmetric cells at a current density of 0.2 mA
cm⁻² (0.2 mAh cm⁻²),40 °C. (a) Pure PEO₁₈-LiTFSI, (b) PEO₁₈-LiTFSI-14 wt.% LAGP, (c)

5 PEO₁₈-LiTFSI-15 wt.% SN.



5 Figure. S5 Exchange current densities of Li anodes in different SPEs at 40 °C as determined by





2 Figure. S6 Time dependence of interfacial impedance (Ri) with Li | SPE | Li cells using

3 different electrolytes at 40 °C.

4

1



6 Figure. S7 Galvanostatic stripping test of cells with different SPEs (0.5 mA cm⁻², 40 $^{\circ}$ C).



- 3 Figure S8 Impedance spectra of Li| SPEs| LFP cells use different electrolyte after 40 cycles.



- 7 Figure S9 SEM image of surface morphologies of Li anodes obtained from Li|SPE-14-15 | LFP
- 8 cell after 200 cycles at 0.5 C under 40°C.

Electrolyte	Tg / °C	Tm / °C	ΔHm / J g ⁻¹	χς %
РЕО	-	73.5	132.8	65.4
SN	-	58	50	-
PEO-LiTFSI	-40.6	54.1	65.29	32.16
PEO-LiTFSI-14 wt.%LAGP	-42.8	54.1	35.29	17.38
PEO-LiTFSI-14 wt.%LAGP-25 wt.% SN	-46.4	42.6	25.81	12.71
PEO-LiTFSI-14 wt.%LAGP-15 wt.% SN	-48.3	40.3	20.33	10.01
PEO-LiTFSI-14 wt.%LAGP-5 wt.%SN	-44.9	47.9	27.34	13.46

Table S1. The values of $T_g,\,T_m,$ and ΔH_m from DSC test and χ_c of samples

2 The crystallinities (χ_c) of the composite SPEs are calculated by Eq:

$$x_c = \frac{\Delta H_m}{\Delta H_{PEO}}$$

4 (where χ_c represents the relative percentage of crystallinity of the PEO-based polymer electrolyte, 5 and ΔH_{PEO} represents the ΔH_m of 100 % crystalline PEO (203 J g⁻¹)).

6

7

Table S2. The values of I_0 , Is, R_0 , Rs, and the calculated values of t_{Li^+} at 40 °C

Electrolytes	$I_0 / \mu A$	$I_s/\mu A$	R_0 / Ω	R_s / Ω	$\Delta V / mV$	t_{Li^+}
PEO	4.81	2.21	1425	1475	10	0.215
PEO-14 wt.% LAGP	8.98	5.36	400	450	10	0.506
PEO-14 wt.% LAGP-15 wt.% SN	8.09	4.53	280	300	10	0.501

^{8 (}Where I_0 and I_s represent the initial and steady polarization currents, R_0 and R_s represent the

⁹ initial and steady interfacial resistances.)

Electrolytes	$E_a / eV (25^{\circ}C-60^{\circ}C)$
PEO	1.01
PEO-14 wt.% LAGP	0.71
PEO-14 wt.% LAGP-15 wt.% SN	0.34

Table S3. The activation energy of SPEs.

Table S4. The fitted value of electrochemical impedance spectroscopy (EIS) about the

4 Li|SPE|LFP cell after 50th cycling.

SPEs	$Ri(R_2) / \Omega$
РЕО	506.4
PEO-14 wt.% LAGP	226.5
PEO-14 wt.% LAGP-15 wt.% SN	165.2

Electrolytes	Li-ion	Reversible	Capacity	Cycle	Working	Reference
	conductivity/S	capacity/	retention	number	temperature	
	cm ⁻¹	mAh g ⁻¹			/°C	
PEO-14 wt.%	1.26×10 ⁻⁴ (30°C	142.6	0.5 C	200	40	This
LAGP-15 wt.%)		91.2 %			work
SN						
PEO-LLZTO	1.12×10 ⁻⁵ (25°C	135	0.1 C	100	60	[13]
)		87 %			
PEO-LiTFSI-	5.53×10 ⁻⁵ (25°C	123	0.5 C	100	60	[16]
(5%) LLTO)		94 %			
nanowires						
PEO ₁₈ -LiTFSI-	1.19×10 ⁻⁴ (25°C	130.2	1 C	500	60	[17]
LLZO-SN)		80 %			
Sandwich-type	1. 6×10⁴(30°C)	99.1	0.1 C	200	30	[19]
PEO-LLZTO			82.4 %			
PEO-LiTFSI-	5.5×10 ⁻⁴ (30°C)	121	0.5 C	105	60	[20]
(7.5%) LLZO			89 %			
PEO-LGPS-SN	9.1×10 ⁻⁵ (25°C)	138.4	0.5 C	100	40	[22]
			87.65 %			
PEO-LLZO (40	2.1×10 ⁻⁴ (30°C)	118	0.1 C	200	60	[23]
nm)			90 %			
vertically aligned	1.1×10 ⁻⁴ (25°C)	120	0.6 C	400	60	[30]
ceramic LAGP-			87.4 %			
PEO						
PEO-vermiculite	1.89×10 ⁻⁴ (25°C	131	0.5 C	200	35	[34]

1 Table S5. Li|SPEs|LFP Performance comparison of this work and reported ASSLMBs.

sheets (VS))		82 %			
PEO-IL-LLZTO	2.2×10 ⁻⁴ (20°C)	120	0.5 C	150	25	[51]
			88 %			
PEO-LAGP	/	152	0.2 C	150	50	[52]
(LPON modified			98 %			
Li anode)						