

Supporting Information

Interface-Enabled Ion Conduction in $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ - Polyethylene Oxide Hybrid Electrolytes

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EXPERIMENTAL SECTION

Scanning electron microscopy (SEM): The SEM measurements were carried out with a Zeiss Ultra Plus Field Emission Scanning Electron Microscope (acceleration voltage: 0.02 kV-30 kV). The surface of the sample was coated with a thin Au layer before measurement to improve electron conductivity.

Li-ion transference number (T_{Li^+}): The T_{Li^+} was calculated based on the Bruce–Vincent–Evans equation below:¹

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

where I_0 and I_s are the initial and steady-state currents, R_0 and R_s are the initial and steady-state interfacial resistances between the electrolyte and electrodes, and ΔV is the applied polarization voltage, 10 mV.

The electrolyte films were sandwiched with Li foils as electrodes. The potentiostatic measurements of the symmetric cells were performed on a Gamry Reference 600+ with a DC polarization voltage of 10 mV.

Differential scanning calorimetry (DSC) and Thermogravimetric analysis (TGA):

The DSC and TGA measurements were performed on an SDT Q600 (TA Instruments). The chamber was purged with Ar gas and the temperature was continuously increased from room temperature to 500 °C with a heating rate of 10 °C min⁻¹.

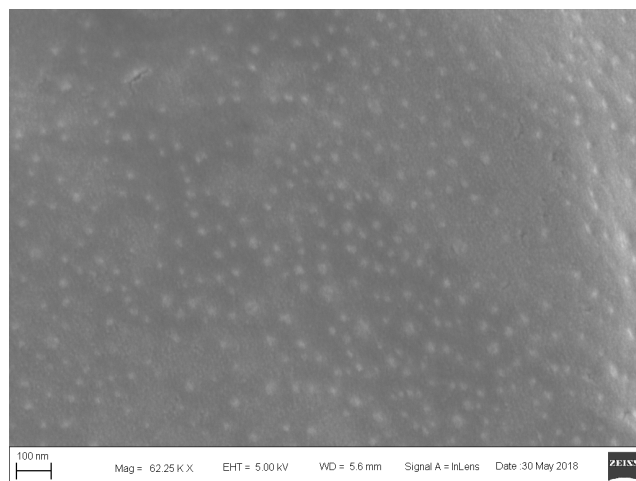


Figure S1. The SEM image of the 70 wt% LGPS-PEO (LiTFSI) (9:1) hybrid film.

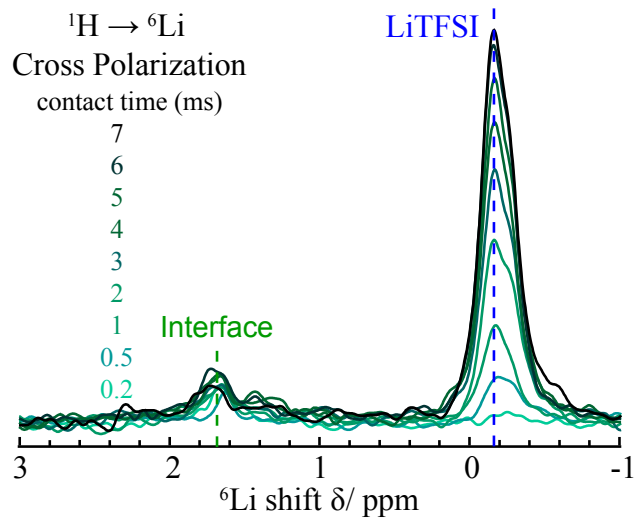


Figure S2. ^1H - ^6Li cross polarization NMR of 70 wt% LGPS-PEO (LiTFSI) (EO: Li=9: 1).

Table S1. Parameters for ^6Li NMR fitting.

	LGPS				Modified LGPS				LiTFSI			
	δ /ppm	LB	GB	%	δ /ppm	LB	GB	%	δ /ppm	LB	GB	%
50 wt% LGPS-PEO (LiTFSI) (EO: Li=9: 1)	1.70	7.2	2.0	89.2	1.40	8.9	5.2	3.1	-0.16	4.7	4.6	7.7
70 wt% LGPS-PEO (LiTFSI) (EO: Li=9: 1)	1.70	10.0	4.0	60.9	1.60	6.6	6.0	36.7	-0.16	2.6	19.3	2.4
70 wt% LGPS-PEO (LiTFSI) (EO: Li=9: 1) $^6\text{Li} \rightarrow ^7\text{Li}$ replaced	1.70	10.3	4.2	15.2	1.50	34.0	10.0	79.7	-0.20	40.0	5.0	5.1
90 wt% LGPS-PEO (LiTFSI) (EO: Li=9: 1)	1.70	4.4	3.8	94.7	1.40	13.1	11.5	4.3	-0.10	7.3	12.7	1.0
70 wt% LGPS-PEO (LiTFSI) (EO: Li=6: 1)	1.70	5.2	3.2	90.5	1.40	11.1	9.1	3.9	-0.14	6.9	6.6	5.6
70 wt% LGPS-PEO (LiTFSI) (EO: Li=18: 1)	1.70	4.2	3.6	97.4	--	--	--	0	-0.10	3.0	19.0	2.6

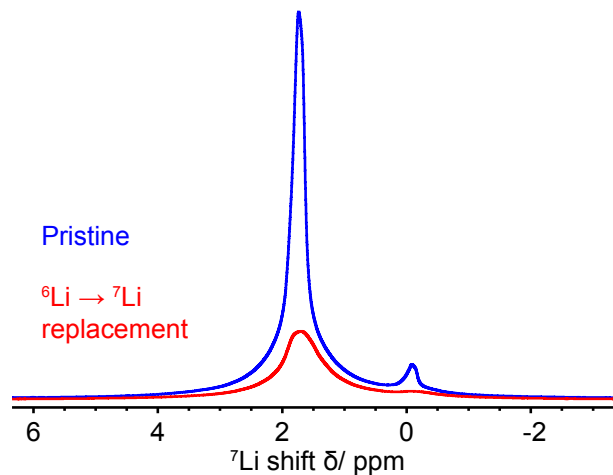


Figure S3. ^7Li MAS NMR comparison of pristine and $^6\text{Li} \rightarrow ^7\text{Li}$ replaced 70 wt% LGPS-PEO (LiTFSI) (EO: Li=9: 1) samples.

Table S2. The volume percent (vol.%) of LGPS, PEO and LiTFSI in hybrid electrolytes, using the densities of LGPS, PEO and LiTFSI are 2.00 g cm^{-3} , 1.21 g cm^{-3} and 1.33 g cm^{-3} , respectively.²

	20 wt% LGPS-PEO (LiTFSI) (9:1)	50 wt% LGPS-PEO (LiTFSI) (9:1)	60 wt% LGPS-PEO (LiTFSI) (9:1)	70 wt% LGPS-PEO (LiTFSI) (9:1)	80 wt% LGPS-PEO (LiTFSI) (9:1)
LGPS (vol.%)	8.5	26.7	35.3	46.0	59.3
PEO (vol.%)	55.9	44.2	39.0	32.5	24.5
LiTFSI (vol.%)	35.6	29.1	25.7	21.5	16.2
	90 wt% LGPS-PEO (LiTFSI) (9:1)	70 wt% LGPS-PEO (LiTFSI) (18:1)	70 wt% LGPS-PEO (LiTFSI) (12:1)	70 wt% LGPS-PEO (LiTFSI) (6:1)	
LGPS (vol.%)	76.6	51.5	48.6	41.5	
PEO (vol.%)	14.1	36.5	34.4	29.4	
LiTFSI (vol.%)	9.3	12.0	17.0	29.1	

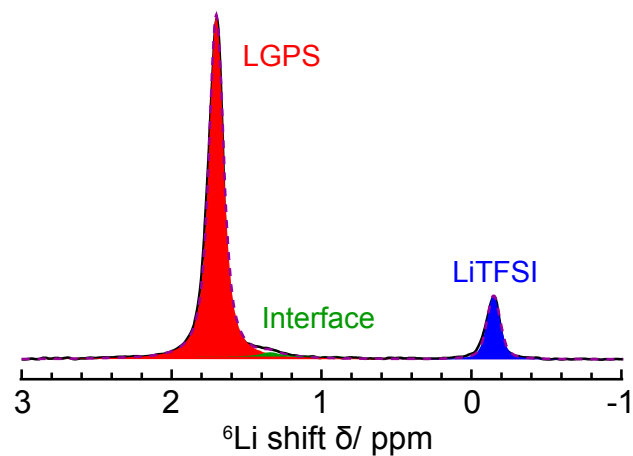


Figure S4. ^6Li MAS NMR of the remade 50 wt% LGPS-PEO (LiTFSI) (9: 1) sample.

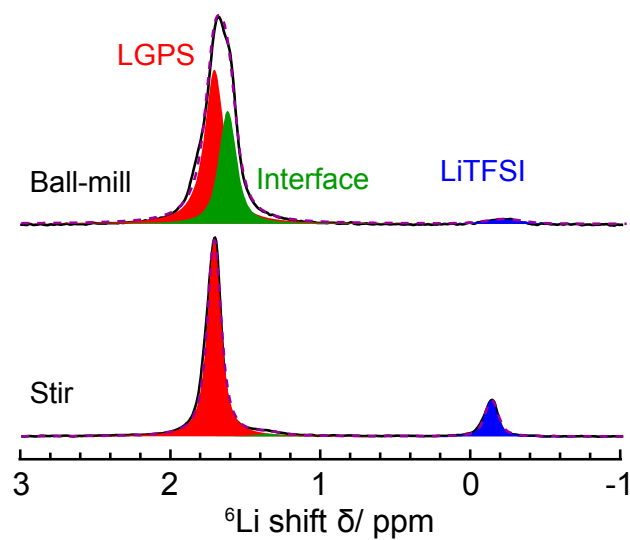


Figure S5. ^6Li MAS NMR comparison of 70 wt% LGPS-PEO (LiTFSI) (9: 1) hybrid films prepared through ball-milling (above) or stirring (bottom) for 2 h.

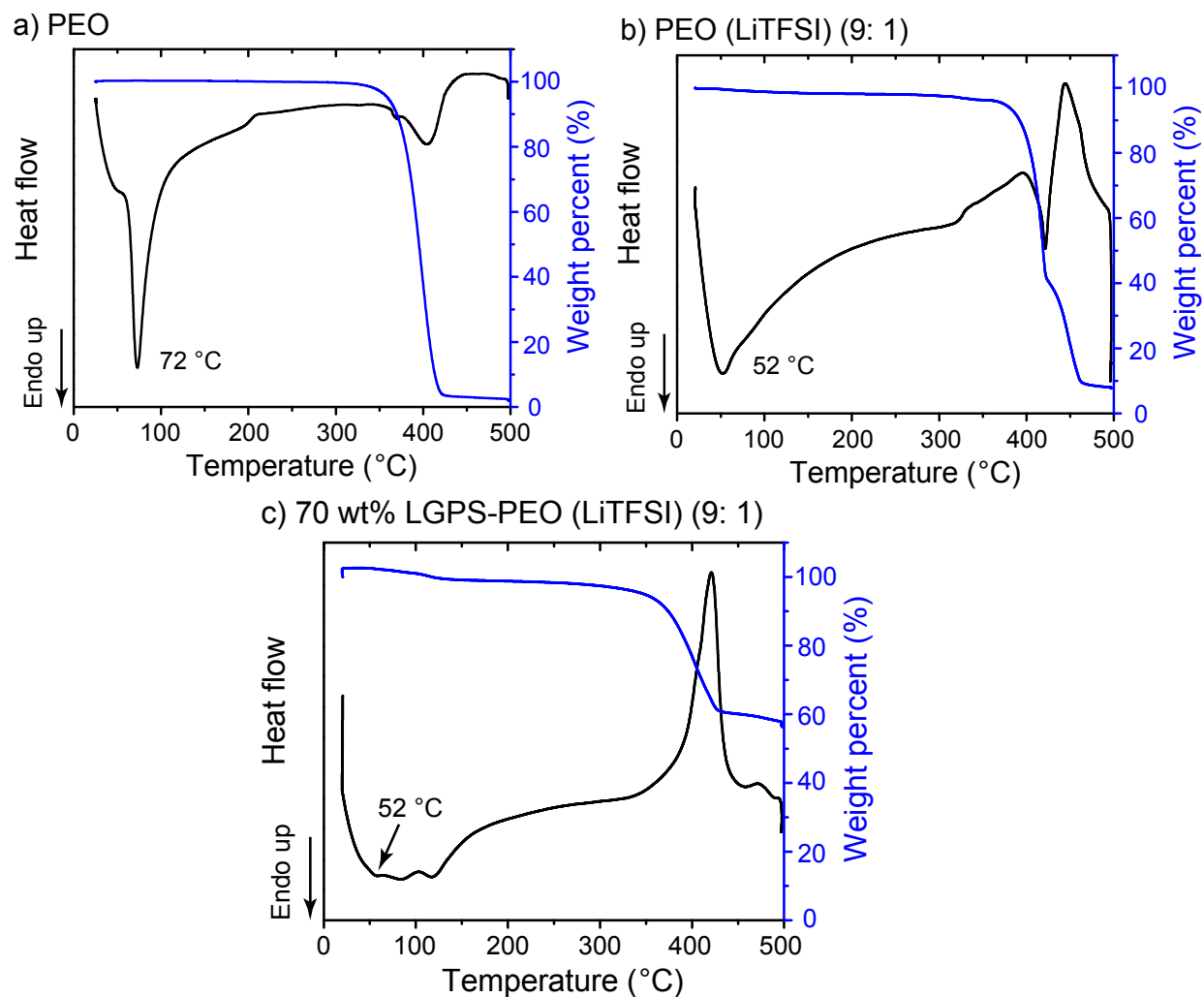


Figure S6. DSC (black) and TGA (blue) of pure PEO, PEO (LiTFSI) (9: 1) and 70 wt% LGPS-PEO (LiTFSI) (9: 1).

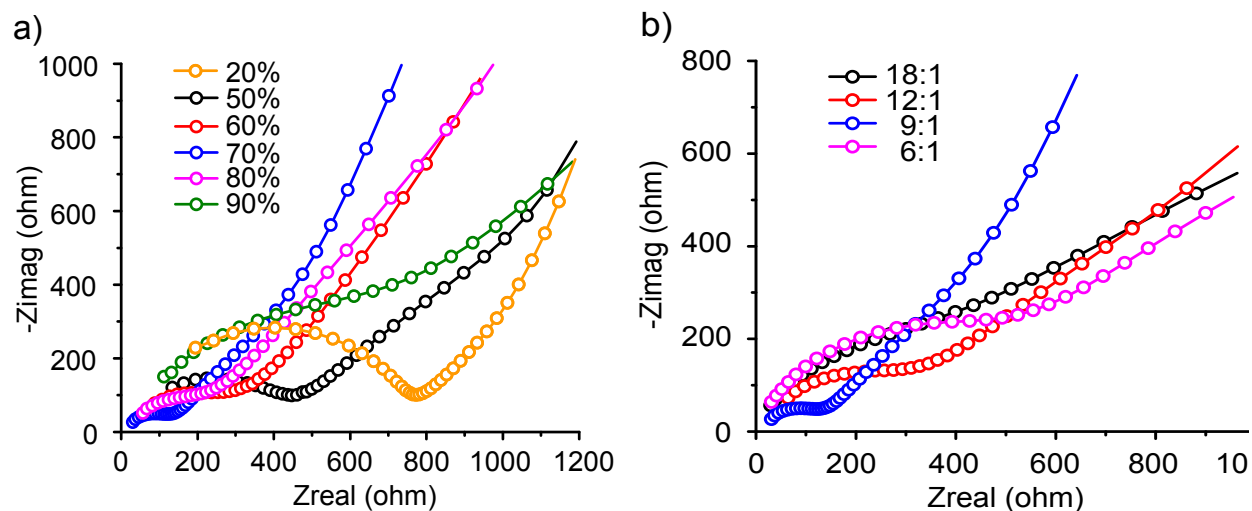


Figure S7. Electrochemical impedance spectroscopy (EIS) of LGPS-PEO (LiTFSI) as a function of wt% of LGPS (a) and the mole ratio of EO to Li (b).

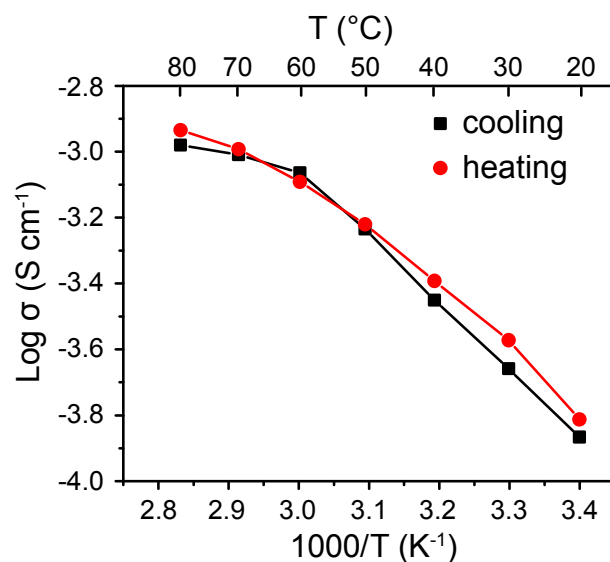


Figure S8. The comparison of conductivity measurements of 70 wt% LGPS-PEO (LiTFSI) (9: 1) hybrid electrolyte during cooling and heating.

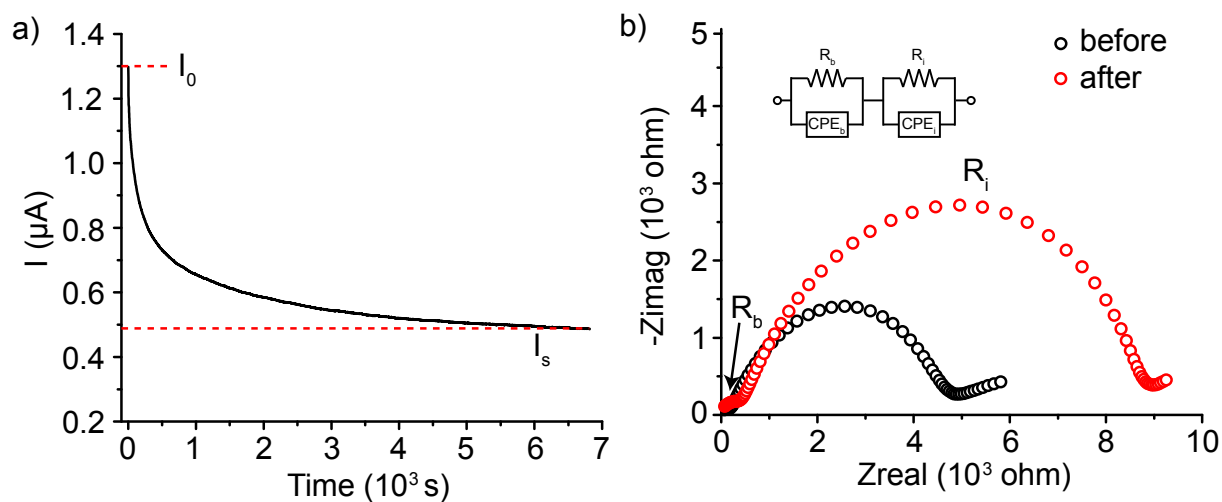


Figure S9. The transference number measurements of 70 wt% LGPS-PEO (LiTFSI) (9:1). (a) The current (I) under a 10-mV DC polarization potential as a function of time. (b) EIS of the electrolyte before (black) and after (red) polarization. The insert is the model to fit the EIS. R_b is the impedance of the bulk of the electrolyte, and R_i is the interfacial impedance between the electrolyte and Li metal electrodes.

Table S3. The transference number of Li^+ (T_{Li^+}) of LGPS-PEO (LiTFSI) hybrid electrolytes.

	50 wt% LGPS-PEO (LiTFSI) (9:1)	70 wt% LGPS-PEO (LiTFSI) (9:1)	90 wt% LGPS-PEO (LiTFSI) (9:1)	70 wt% LGPS-PEO (LiTFSI) (18:1)	70 wt% LGPS-PEO (LiTFSI) (6:1)
T_{Li^+}	0.14	0.41	0.91	0.45	0.69

REFERENCES

- (1) Evans, James; Vincent, Colin A. Electrochemical Measurement of Transference Numbers in Polymer Electrolytes. *Polymer* **1987**, 28, 2324–2328.
- (2) Wu, B.; Wang, S.; Evans IV, W. J.; Deng, D. Z.; Yang, J.; Xiao, J. Interfacial Behaviours between Lithium Ion Conductors and Electrode Materials in Various Battery Systems. *J. Mater. Chem. A* **2016**, 4, 15266–15280.