Electronic Supplementary Information

Constructing a stable interface between sulfide electrolyte and Li metal anode via a Li^+-conductive gel polymer interlayer

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Experimental section

Preparation of precursor solution of gel electrolyte interlayer (GPI):

The precursor solution of GPI was made by dissolving 2 mol L^{-1} lithium hexafluorophosphate ($LiFP_6$; Alfa Aesar, 98%) and 1 mol L^{-1} bis(trifluoromethane)sulfonimide lithium salt (LiTFSI; Sigma-aldrich 99.95% trace metals basis) into a 1, 3-dioxolane (DOL; Alfa Aesar, 99.5%, stab.) and 1, 2-dimethoxyethane (DME) (Alfa Aesar, 99+%) solvent (1:1, v/v) mixture. The decomposition of $LiFP_6$ triggers the ring-opening cationic polymerization of DOL monomer and thereby converting the precursor solution into GPI. All the preparation processes were conducted in an argon-filled glovebox (O_2< 0.1 ppm, H_2O < 0.1 ppm).

The assembly of symmetrical Li|LGPS|Li and blocking SS|LGPS|SS batteries:

About 80 mg of LGPS (Hefei Kejing Corp., 99.99%) powder was weighted and put into a battery mold (Zhongke Wanyuan Co. Ltd) with a diameter of 10 mm and then cold pressed under 360 MPa for 5 minutes.

And the Li foils (Φ8) were placed on the both sides of LGPS pellet followed by cold pressing under 100 MPa for 3 minutes. Similarly, blocking SS|LGPS|SS cells were prepared without Li foils, two stainless steel cylinders of the battery mold directly contact the LGPS pallet. All the assembled processes were conducted in an argon-filled glovebox (O_2 < 0.1 ppm, H_2O < 0.1

ppm).

The assembly of symmetrical Li|GPI-LGPS-GPI|Li batteries:

About 80 mg of LGPS powder was weighted and put into a battery mold with a diameter of 10 mm and then cold pressed under 360 MPa for 5 minutes. After that, 10 μL precursor solution was injected into the interface between LGPS pallet and Li foil. Subsequently, the assembled batteries were left to stand for a period of time to form GPI completely inside the battery. All the assembled processes were conducted in an argon-filled glovebox ($O_2 < 0.1$ ppm, $H_2O < 0.1$ ppm).

Materials characterization

The X-ray diffraction (XRD) patterns were collected on a Bruker D8 Advance diffractometer with Cu Kα radiation (λ = 1.5418 Å) in the 2θ range from 10° to 60° by using a sealed container to avoid oxygen. The morphology and element mapping were characterized by JEOL 6701F scanning electron microscopy (SEM) with an energy-dispersive X-ray spectroscopy (EDS) system. X-ray photoelectron spectroscopy (XPS) was recorded on AXIS Supra electron spectrometer using 150 W Al Kα radiation (hv = 1486.6 eV).

Electrochemical measurements

Electrochemical impedance spectroscopy (EIS) measurements were investigated over the frequency range from 1 MHz to 0.1 Hz with an amplitude of 10 mV on a Princeton PARSTAT MC 1000 multi-channel electrochemical workstation. The ionic conductivity σ was calculated based on the following equation

$$\sigma = \frac{L}{R_{SSE} \times S}$$

where L is the thickness of electrolytes, R_{SSE} is the resistance according to the EIS measurement, S is the effective contact area between electrolyte and stainless steel.

The galvanostatic polarization and cycling measurements were conducted using a LAND battery test system (LANHE Inc. CT2001A). Galvanostatic cycling performance of Li|Li cells were tested with current density 0.1 mA cm^{-2} and 0.5 mA cm^{-2} corresponding to areal capacity of 0.1 mAh cm^{-2} and 0.5 mAh cm^{-2}, respectively. For the critical current density tests, the initial current density is 0.1 mA cm^{-2}, the deposited capacity is 0.1 mAh cm^{-2}. After that, Li plating and stripping was tested at a fixed capacity of 0.1 mAh cm^{-2} but a step-increased current density from 0.1 mA cm^{-2} to 5 mA cm^{-2}.

Table S1. The specific values of resistances and the calculation result of ionic conductivity of Figure 2b, Figure S2b.

	Thickness (cm)	Effective area (cm^2)	R_b (Ω)	R_{gb} (Ω)	R_{SSE} (Ω)	Ionic conductivity (mS cm^{-1})
LGPS	0.0593	0.785	-	-	14.437	5.23
LGPS-DME	0.0589	0.785	24.8	27.5	52.3	1.43
LGPS-DOL	0.0595	0.785	24	25.6	49.6	1.53
LGPS-DOL/DME (v:v, 1:1)	0.0580	0.785	-	-	38.9	1.89

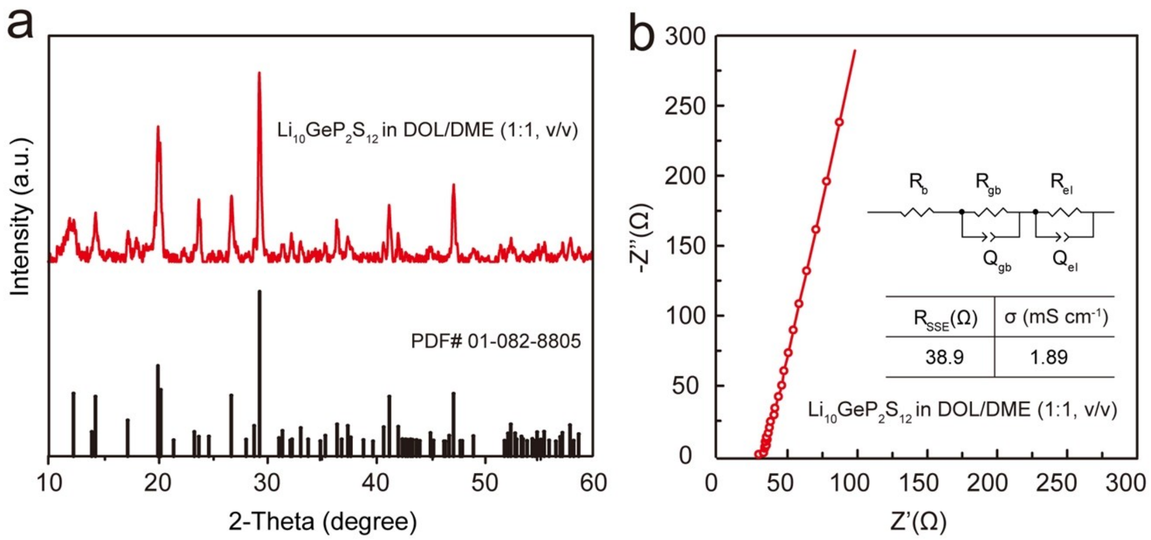

Figure S1. (a) XRD pattern and (b) EIS spectrum of LGPS in DOL/DME (v:v, 1:1) after 24 hours.

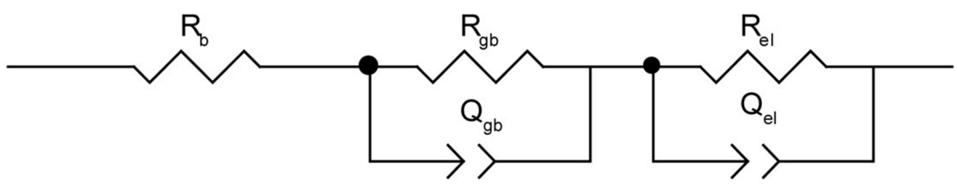

Figure S2. Detailed equivalent circuit of Figure 2b, where R_b is the bulk resistance, R_{gb} is the grain-boundary resistance of LGPS powder and R_{el} is the resistance of blocking electrode. Each constant phase element (CPE) describes the capacitance of the corresponding process.

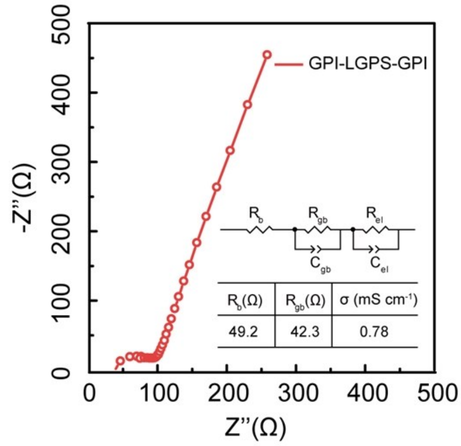

Figure S3. EIS spectrum of GPI-LGPS-GPI composite electrolytes.

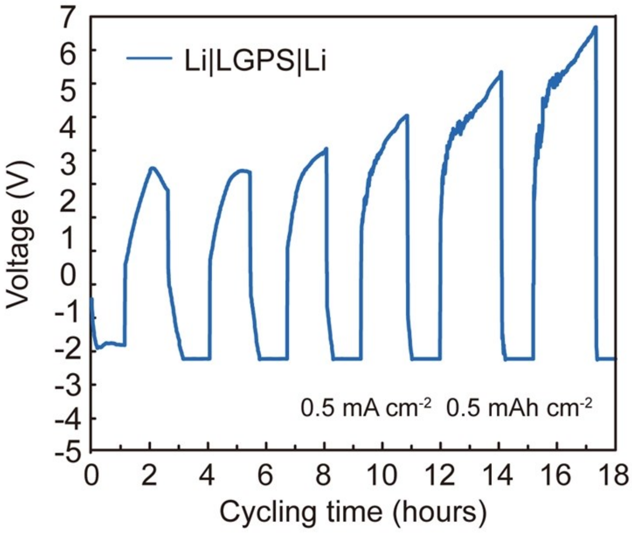

Figure S4. Galvanostatic Li plating/stripping overpotential profiles of symmetrical Li|LGPS|Li cells at current density of 0.5 mA cm^{-2} with a fixed capacity of 0.5 mAh cm^{-2} at room temperature.

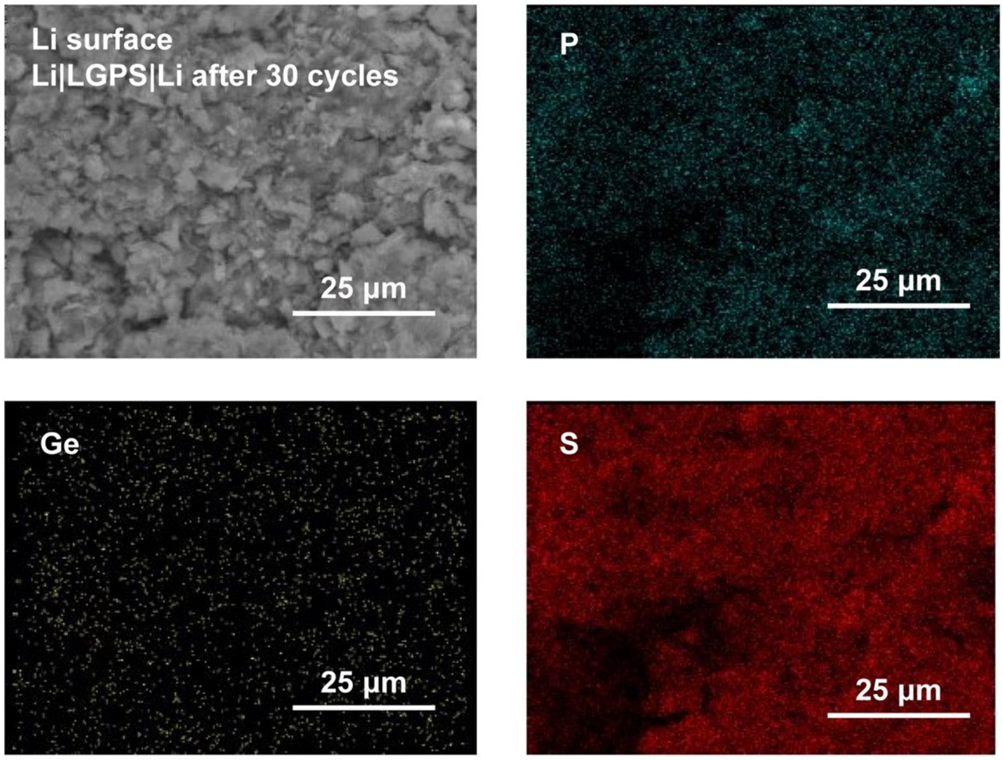

Figure S5 The EDS elemental mapping images of Li anode in Li|LGPS|Li system after 30 cycles.

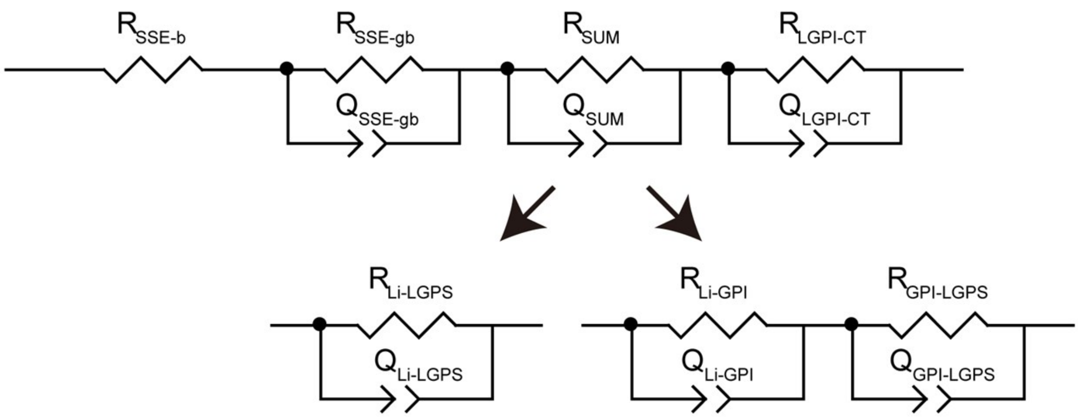

Figure S6. Detailed equivalent circuit of Figure 4c, d, where $R_{SSE\text{-}b}$ is the bulk resistance, $R_{SSE\text{-}gb}$ is the grain-boundary resistance of LGPS, $R_{Li\text{-}LGPS}$, $R_{Li\text{-}GPI}$, $R_{GPI\text{-}LGPS}$ is the Li/LGPS, Li/GPI, GPI/LGPS interphase resistance, respectively. $R_{LGPI\text{-}CT}$ is the electrochemical transfer polarization resistance of Li plating/stripping. Each constant phase element (CPE) describes the capacitance of the corresponding process.

Table S2. The specific values of resistances in Figure S4.

	R_b (Ω)	R_{gb} (Ω)	R_{SUM} (Ω)	$R_{LGPI\text{-}CT}$ (Ω)
Li-LGPS-Li Before cycle	69.91	-	68.01	149.5
Li-LGPS-Li After 30 cycles	-	-	70000	-
Li-GPI-LGPS-GPI-Li Before cycle	30.2	6.2	43.28	52.22
Li-GPI-LGPS-GPI-Li After 30 cycles	34.82	18.2	51.15	370

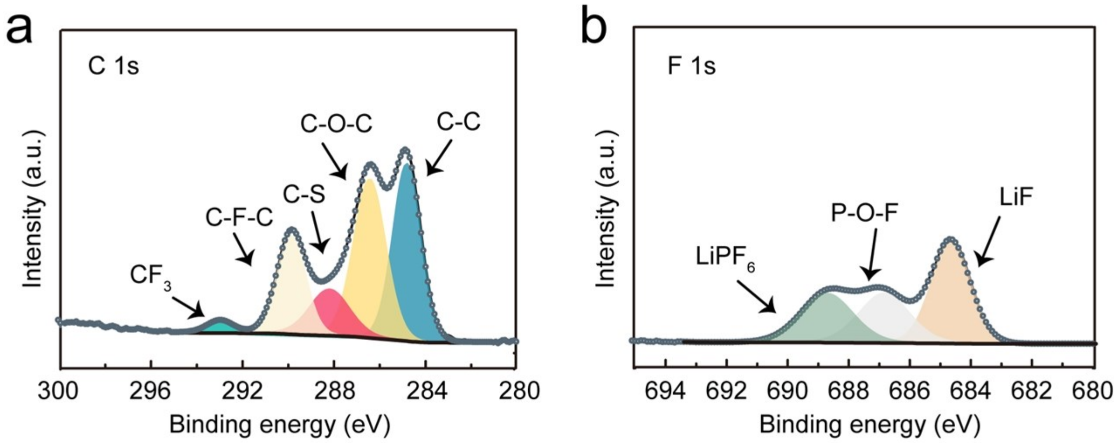

Figure S7. XPS of the cycled Li anode recovered from Li|GPI-LGPS-GPI|Li battery. The battery is tested for 30 cycles at current density of 0.1 mA cm^{-2} for 0.1 mAh cm^{-2} at room temperature.

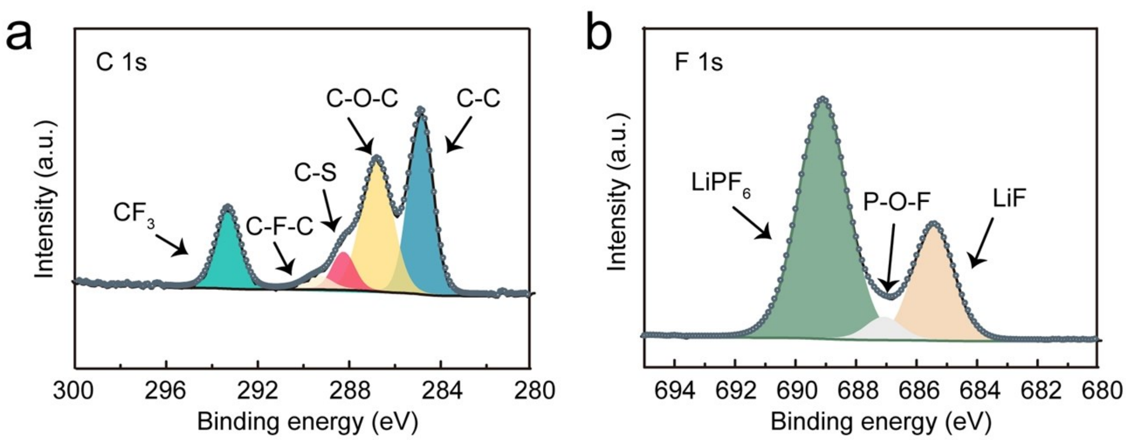

Figure S8. X-ray photoelectron spectroscopy of the LGPS pellet retreated from Li|GPI-LGPS-GPI|Li battery. The battery is tested for 30 cycles at current density of 0.1 mA cm^{-2} with a fixed plating/stripping capacity of 0.1 mAh cm^{-2} at room temperature.

Table S3. XPS binding energies with attributed species shown in Figure 5

Spectrum details	Binding energy (eV)		Attributed species
	$3d_{5/2}$; $2p_{3/2}$	$3d_{3/2}$; $2p_{1/2}$	
Ge 3d (Overlapping region F 2s)	30.66	31.24	Ge^{4+}
	28.85	29.43	Reduced Ge
	30.3 (F 2s)		LiF
P 2p (Overlapping region Ge 3p)	131.84	132.71	$P_2S_7^{4-}$
	132.86	133.73	PS_4^{3-}
	136.65	137.52	PF_5
	125.28	126.15	Li_3P
	122.98	127.08	Ge 3p
S 2p	161.34	162.50	PS_4^{3-}
	162.13	163.29	P=S
	159.66	160.82	Li_2S

Table S4. XPS binding energies with attributed species shown in Figure S7, S8.

Spectrum details	Binding energy (eV)	Attributed species
C 1s	284.71	C-C
	286.35	C-O-C
	288.02	S-C
	289.84	C-F-C
	292.95	CF_3
F 1s	684.64	LiF
	686.84	P-O-F
	688.72	$LiPF_6$