

## Supporting information

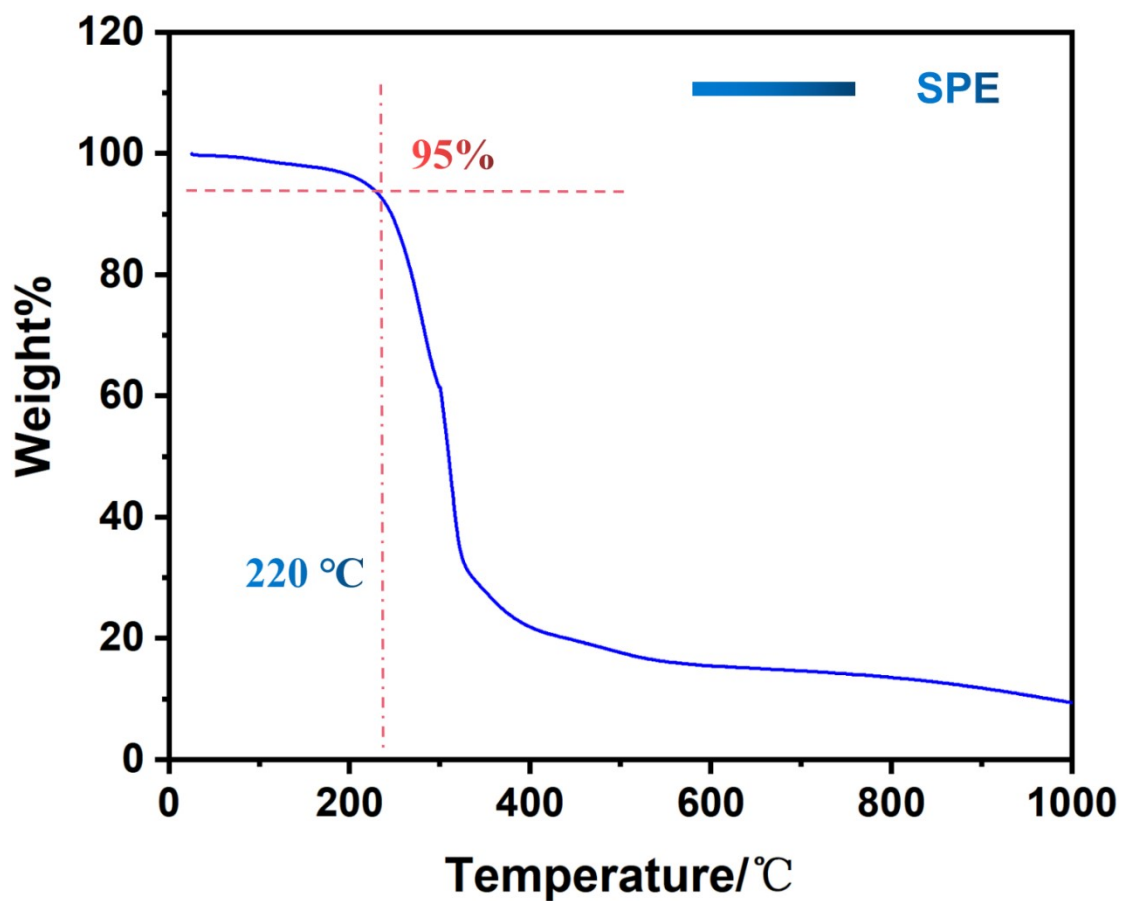


Figure S1. TGA curve of the PLAP membrane

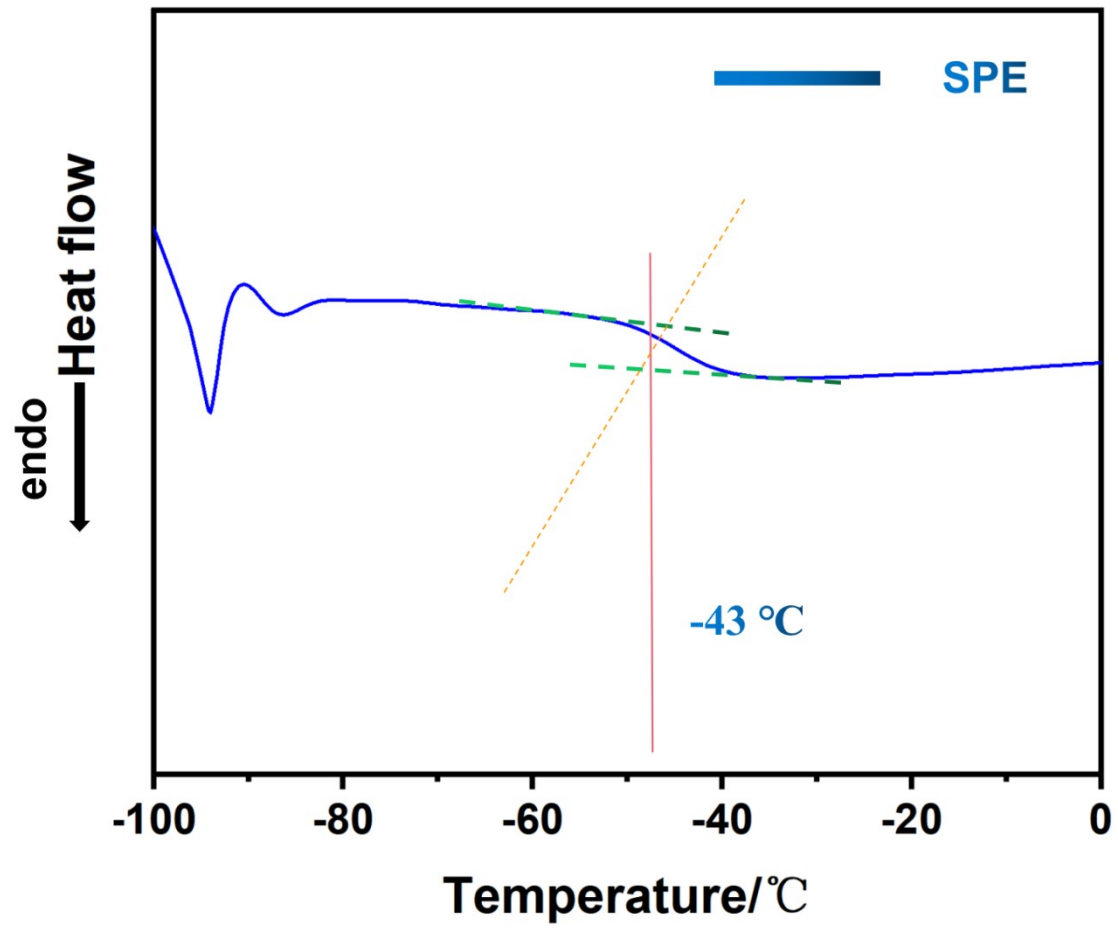


Figure S2. DSC curve of the PLAP membrane.

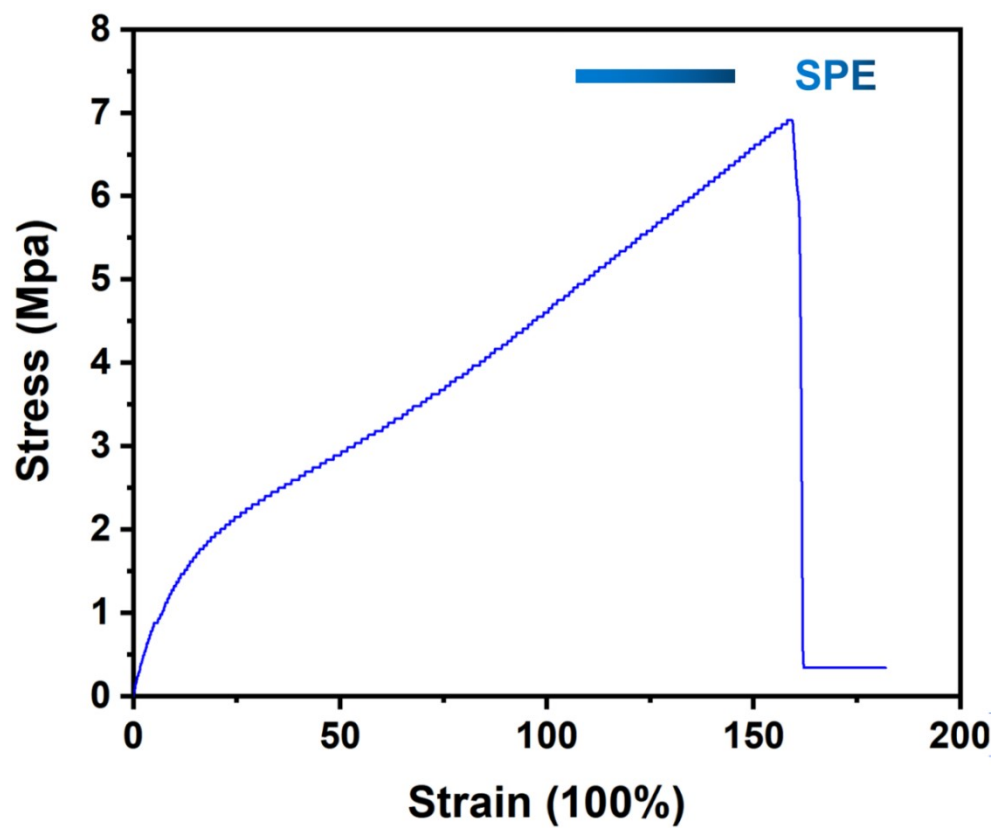
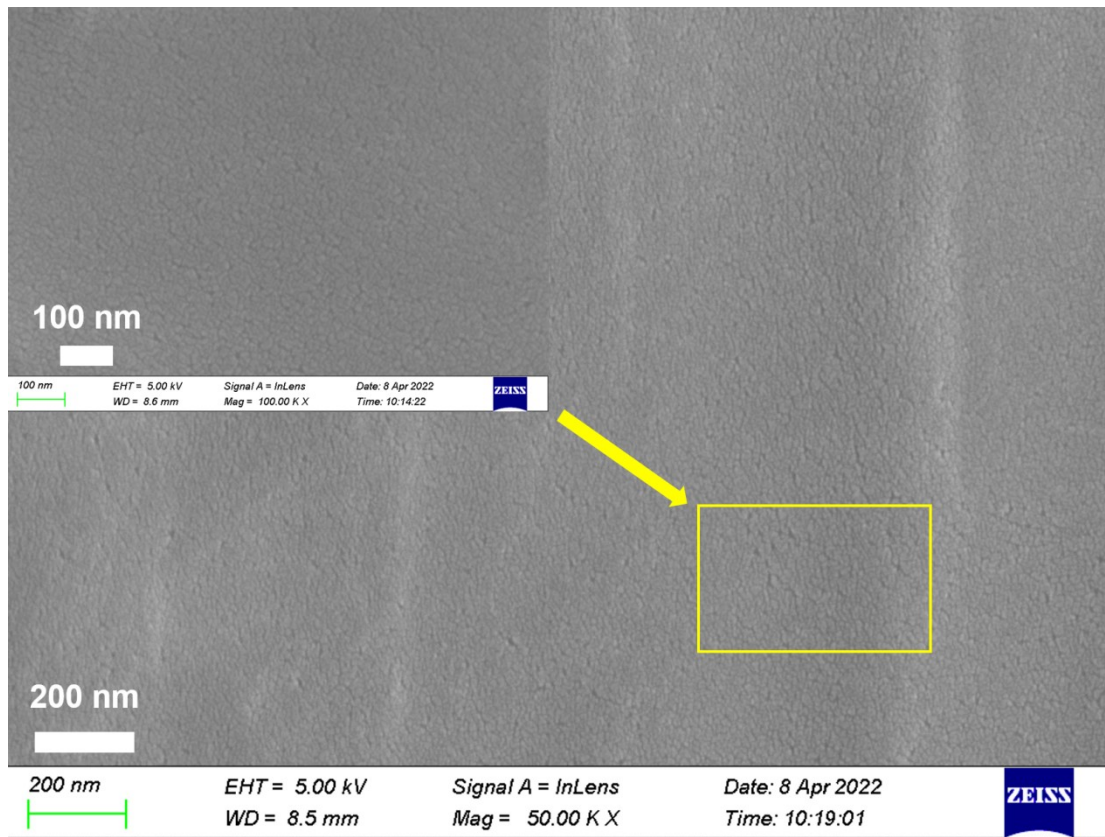
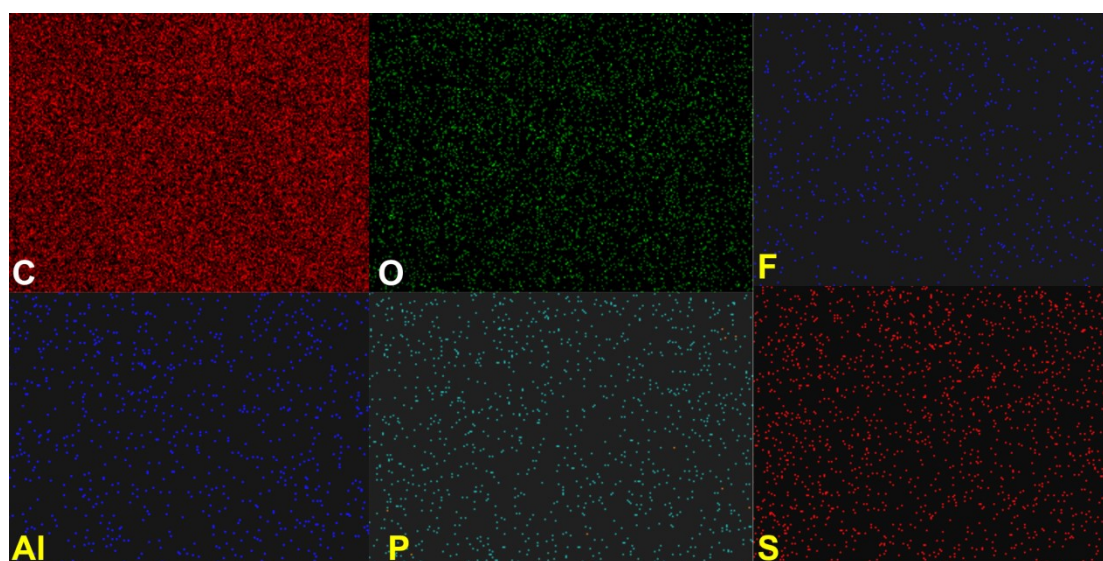


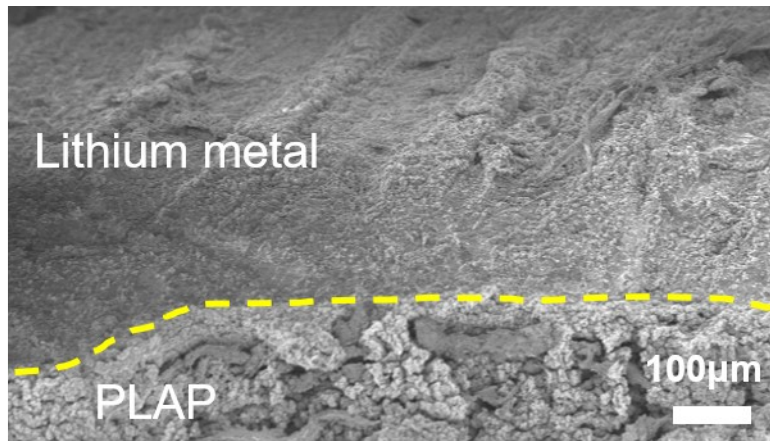
Figure S3. The stress-strain curve of as-prepared PLAP.



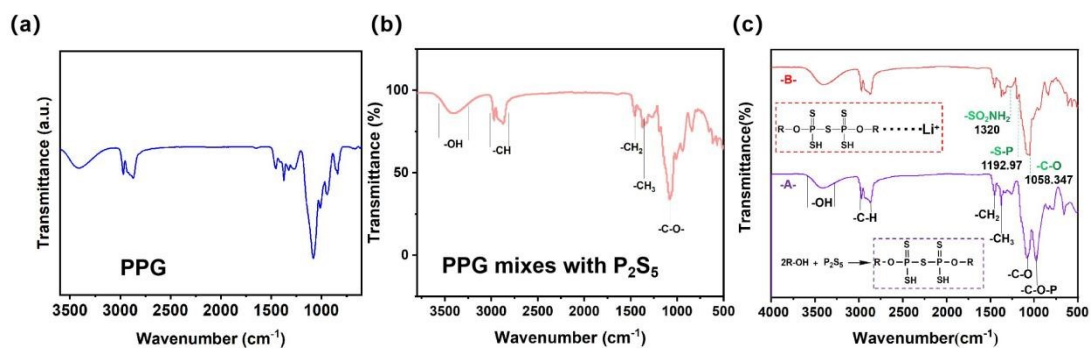
**Figure S4.** The surface morphology SEM image of PLAP.



**Figure S5.** The elements mapping of PLAP.



**Figure S6.** Cross-section SEM image of the interface between Lithium metal and PLAP.



**Figure S7.** Infrared spectrum of (a) PPG ;(b) mixed with P<sub>2</sub>S<sub>5</sub> before reaction and (c) after the reaction of PPG and P<sub>2</sub>S<sub>5</sub>.





**Table S1** Ionic conductivity of PU/LiTFSI–Al<sub>2</sub>O<sub>3</sub>–xP<sub>2</sub>S<sub>5</sub> (x =0.1, 0.4, 0.8, 1.0, 1.5, 2.0) system

Samples	PPG <sub>mol</sub> :P <sub>2</sub> S <sub>5</sub> mol	L <sup>a</sup> (thickness, um)	R <sup>b</sup> (Ω)	S <sup>c</sup> =πr <sup>2</sup> (r=0.05 cm)	Conductivity (S cm <sup>-1</sup> )
1	2:0.1	300	1274	π/4	3.0×10 <sup>-5</sup>
2	2:0.4	300	273	π/4	1.4×10 <sup>-4</sup>
3	2:0.8	300	106	π/4	3.6×10 <sup>-4</sup>
4	2:1.0	300	50	π/4	7.4×10 <sup>-4</sup>
5	2:1.5	300	50	π/4	7.4×10 <sup>-4</sup>
6	2:2.0	300	50	π/4	7.4×10 <sup>-4</sup>

<sup>a</sup> The samples thickness. <sup>b</sup> Electrolyte impedance value. <sup>c</sup> Electrolyte area.

**Table S2.** Comparison of PU-based batteries

Polymer matrix	Lithium salt	Ionic conductivity	Mechanical strength	Thermal stability	Battery performance	Ref
This work (PLAP)	LiTFSI	7.4×10 <sup>-4</sup> (25 °C) 4.3×10 <sup>-3</sup> (80 °C)	7 Mpa	220	LiFePO <sub>4</sub> /Li :168 (0.2 C) (25 °C) 143 (5 C) (25 °C)	
PEUU	LiClO <sub>4</sub>	~10 <sup>-8</sup>	NA	NA	NA	[1]
PDXL-PU	LiClO <sub>4</sub> (O/Li = 12)	2 × 10 <sup>-5</sup>	NA	NA	NA	[2]
PE-BCPE	LiTFSI	~5.7 × 10 <sup>-4</sup>	~0.9 MPa (stress)	NA	LiFePO <sub>4</sub> /Li (1C, 133 mAh g <sup>-1</sup> )	[3]
LPU	LiClO <sub>4</sub>	2.7 × 10 <sup>-7</sup> (RT)	NA	NA	NA	[4]
HPU	LiClO <sub>4</sub>	1.51 × 10 <sup>-5</sup>	NA	NA	NA	[4]
NWPU	LiClO <sub>4</sub> (15 wt%)	5.44 × 10 <sup>-6</sup>	NA	176	LiFePO <sub>4</sub> /Li (0.02C, 134 mAh g <sup>-1</sup> )	[5]
WPU	LiTFSI (20 wt%)	7.3 × 10 <sup>-4</sup> (60. °C) 2.2 × 10 <sup>-3</sup>	0.5 MPa (stress)	~250	LiFePO <sub>4</sub> /Li (0.1C, 151 mAh g <sup>-1</sup> ) (2.2-4 V 60 °C)	[6]
PCPU	LiTFSI (20 wt%)	1.12 × 10 <sup>-4</sup>	6 MPa	306	LiFePO <sub>4</sub> /Li (1C, 134 mAh g <sup>-1</sup> )	[7]
PDMS-WPU	LiTFSI (20 wt%)	1.05 × 10 <sup>-5</sup>	NA	260	NA	[8]
SLICPs	NA	8.91 × 10 <sup>-7</sup>	NA	288	NA	[9]
SIPU	NA	9.8 × 10 <sup>-8</sup>	NA	200	NA	[10]
CL-PUA	LiClO <sub>4</sub>	~10 <sup>-8</sup>	> 0.7 MPa (neat PU)	> 400	NA	[11]
In-situ PUA	LiClO <sub>4</sub> (60 wt%)	3.72 × 10 <sup>-3</sup>	NA	NA	NA	[12]
PUA	LiPF <sub>6</sub>	4.5 × 10 <sup>-3</sup> (20 °C)	NA	NA	LiCoO <sub>2</sub> /graphite (0.2C, 147 mAh g <sup>-1</sup> ) (2.7-4.2 V 20 °C)	[13]
GPE-SN-IM	LiTFSI	1.63 × 10 <sup>-3</sup>	6.5 Mpa	NA	LiCoO <sub>2</sub> /Li	[14]
TPU-A	LiClO <sub>4</sub>	~3 × 10 <sup>-4</sup>	NA	NA	NA	[15]
Cellulose/PU	LiTFSI	4.8 × 10 <sup>-4</sup>	NA	NA	LiFePO <sub>4</sub> /Li	[16]
EPE-25	LiTFSI	>10 <sup>-4</sup>	~1.3 MPa	295	NMC622/Li	[17]

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**Table S3.** All the orbital comparisons of the elements

	Binding energy (eV) (before/ after)	Full width high maximum (eV)	Area (cps, eV)	Content (%) (before/ after)
<b>C 1s</b>				
<b>C-C</b>	<b>284.8 / 284.8</b>	1.25	34169.29	<b>34.75 / 37.6</b>
<b>C-O</b>	<b>286.42 / 286.4</b>	1.30	55410.43	<b>62.35/60.6</b>
<b>O-C=O</b>	<b>289.01 / 289.4</b>	1.06	1874.94	<b>2.9 / 1.8</b>

<b>O 1s</b>				
<b>C-O</b>	<b>530.95 / 531.0</b>	1.53	5714.34	<b>7.58 / 5.7</b>
<b>C=O/-OH</b>	<b>532.64 / 532.6</b>	1.53	85145.10	<b>92.42 / 94.3</b>
<b>S 2p</b>				
<b>-S- 2p<sub>3/2</sub></b>	<b>161.5 / 162.1</b>	1.34	1393.28	<b>31.5 / 30.3</b>
<b>-S- 2p<sub>1/2</sub></b>	<b>162.76 / 163.2</b>	1.34	709.57	<b>15.4 / 15.5</b>
<b>S=P 2p<sub>3/2</sub></b>	<b>163.53 / 163.6</b>	1.20	1004.46	<b>21.5 / 21.8</b>
<b>S=P 2p<sub>1/2</sub></b>	<b>164.83 / 164.7</b>	1.20	512.93	<b>11.31 / 11.2</b>
<b>O=S=O 2p<sub>3/2</sub></b>	<b>168.23 / 168.7</b>	1.17	651.91	<b>14.01 / 14.2</b>
<b>O=S=O 2p<sub>1/2</sub></b>	<b>169.3 / 169.8</b>	1.17	327.05	<b>6.93 / 7.0</b>
<b>P 2p</b>				
<b>P 2p<sub>3/2</sub></b>	<b>133.22 / 133.7</b>	1.65	1693.01	<b>56.01 / 56.5</b>
<b>P 2p<sub>1/2</sub></b>	<b>134.21 / 134.4</b>	1.79	1307.81	<b>43.32 / 43.5</b>
<b>Li 1s</b>				
<b>Li-S</b>	<b>55.4 / 55.4</b>	2.19	126.73	<b>100 / 100</b>