

## Electronic Supporting Information: ESI

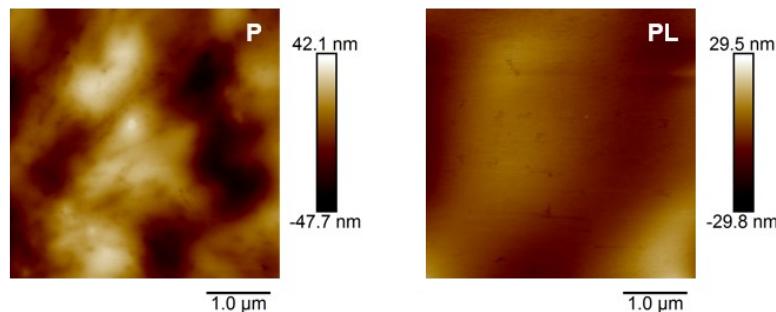
### Utilizing $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as Multifunctional Filler of Composite Solid Electrolyte for All-Solid-State Lithium Metal Battery

Yubo Xu,<sup>a</sup> Xiaosong Xiong,<sup>a</sup> Jun Peng,<sup>b</sup> Qi Zhou,<sup>a</sup> Wenzhuo Wu,<sup>c</sup> Wanjie Gao,<sup>a</sup> Yi Peng,<sup>a</sup> Tao Wang,<sup>a\*</sup> Faxing Wang,<sup>a</sup> and Yuping Wu <sup>\*a,b,c</sup>

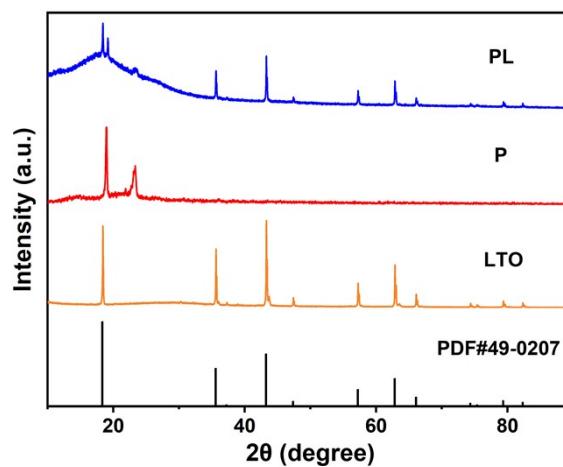
<sup>a</sup>Confucius Energy Storage Lab, School of Energy and Environment & Z Energy Storage Center, Southeast University, Nanjing 211189, China.

<sup>b</sup>School of Energy Science and Engineering, Nanjing Tech University, Nanjing 211816, China.

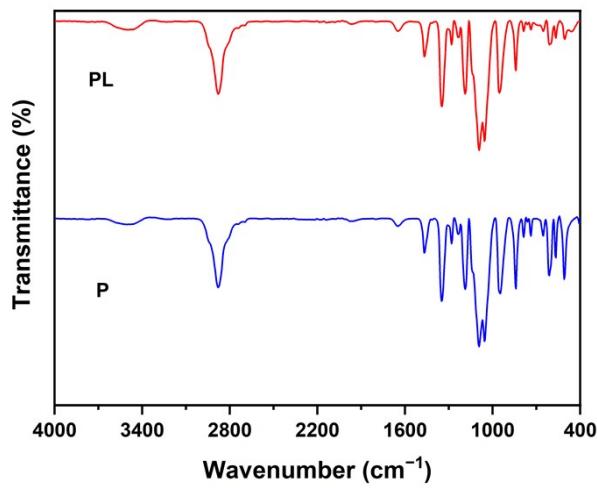
<sup>c</sup>R & D Center, DKJ New Energy Tech Co Ltd, Shaoxing 312365, China.



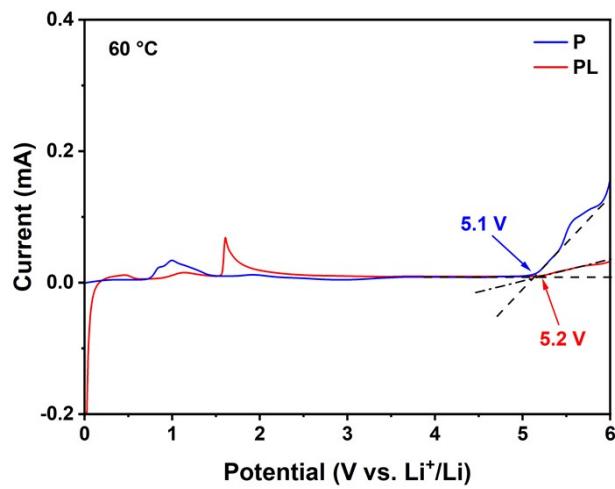
**Fig. S1** AFM surface topographies of P and PL membrane.



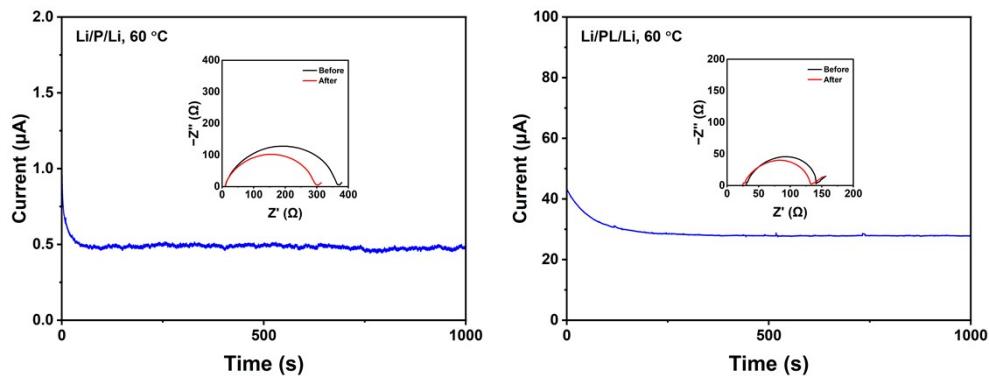
**Fig. S2** XRD spectra of P and PL membrane.



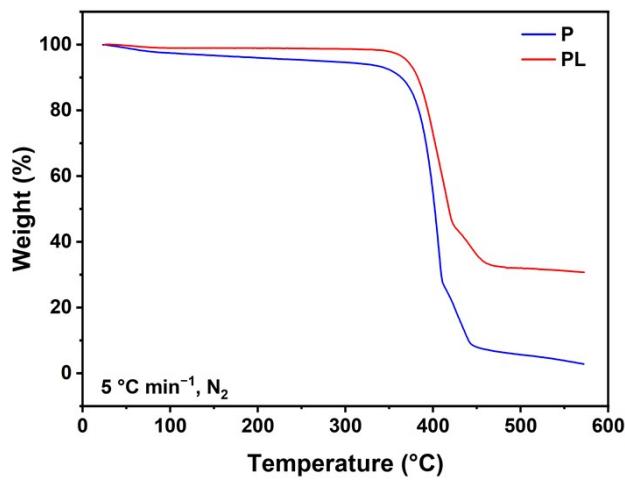
**Fig. S3** FTIR spectra of P and PL membrane.



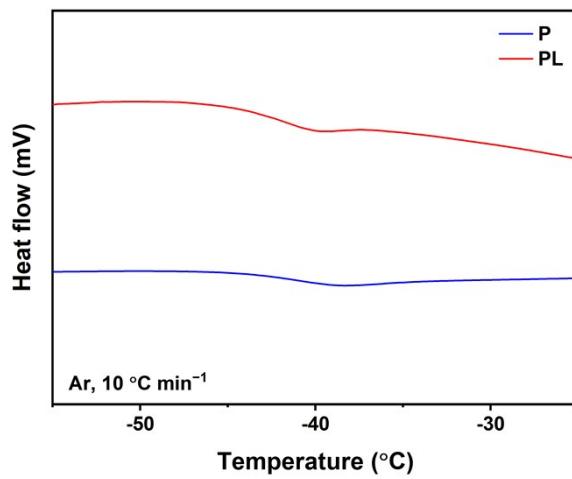
**Fig. S4** LSV curve of P and PL membrane.



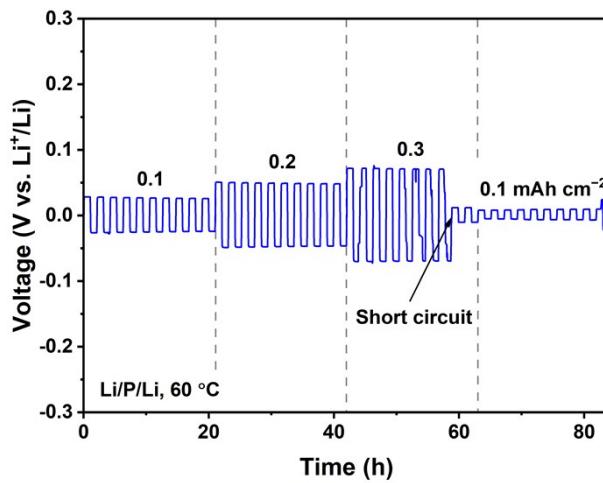
**Fig. S5**  $\text{Li}^+$  transference number of P and PL membrane.



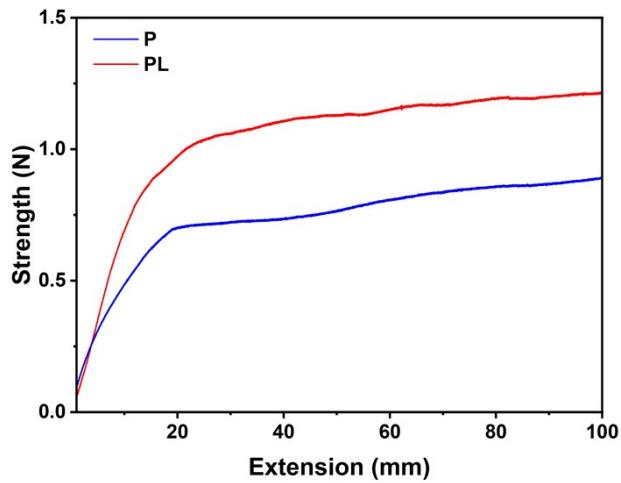
**Fig. S6** TG curve of P and PL membrane.



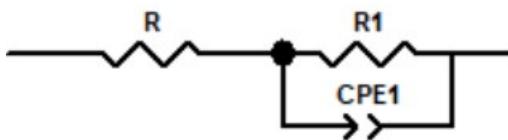
**Fig. S7** DSC curve of P and PL membrane.



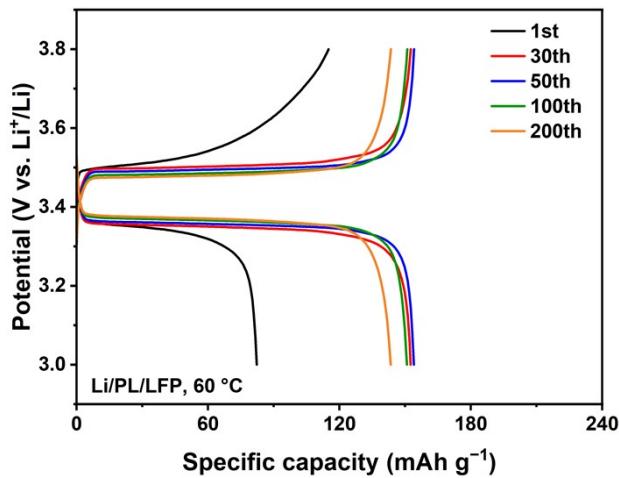
**Fig. S8** Rate performance of Li/P/Li cells with stripping/plating of 1h.



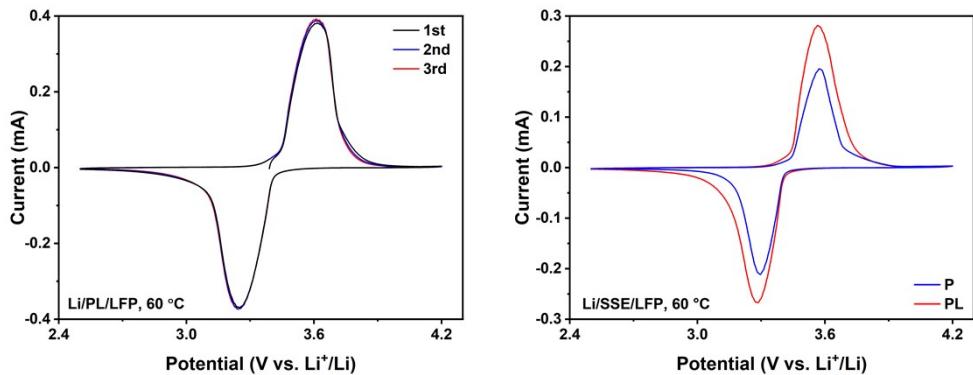
**Fig. S9** Stretch Curve of P and PL membrane.



**Fig. S10** Equivalent circuit of Li/Li symmetric cells.



**Fig. S11** Voltage-capacity curve of Li/PL/LFP cells at 0.5 C with different cycle



**Fig. S12** CV curve of Li/LFP cells.

**Table S1** The particle size distribution of LTO.

Item	Unit	Spec.
D10	μm	0.2~0.6
D50	μm	0.8~1.6
D90	μm	≤10

**Table S2** Activation energy of PEO-x%LTO membrane.

Sample	Activation energy (kJ mol <sup>-1</sup> )	
	30~60 °C	60~80 °C
PEO-0%LTO	81.0	58.0
PEO-20%LTO	118.8	87.7
PEO-40%LTO	122.8	81.6
PEO-60%LTO	89.5	34.0
PEO-80%LTO	97.3	28.1
PEO-100%LTO	90.2	53.7

**Table S3** Assignment for FTIR bands of PL membrane.

Wavenumber (cm <sup>-1</sup> )	Assignment
3460	O-H stretching of PEO
2880	C-H asymmetric stretching of PEO
1465	CH <sub>2</sub> scissoring of PEO
1350	CH <sub>2</sub> asymmetric bending of PEO
1281	CH <sub>2</sub> symmetric bending of PEO
1232	CH <sub>2</sub> symmetric twisting of PEO
1187	CF <sub>3</sub> asymmetric stretching of LiTFSI
1093	C-O-C stretching of PEO
1056	C-O-C stretching of PEO
955	C–O stretching with some CH <sub>2</sub> asymmetric rocking of PEO
840	C–O stretching of PEO
787	S-N-S asymmetric and symmetric stretching of LiTFSI
738	S-N-S asymmetric and symmetric stretching of LiTFSI
567	CF <sub>3</sub> asymmetric bending of LiTFSI
520	CF <sub>3</sub> asymmetric bending of LiTFSI
449	Ti-O bending vibration of Li <sub>4</sub> Ti <sub>5</sub> O <sub>12</sub>

**Table S4** Electronic conductivity of P, PL and lithiated PL membrane.

Sample	Electronic conductivity (S cm <sup>-1</sup> )
P	2.97E-10
PL	4.12E-10
Lithiated PL	4.76E-10