

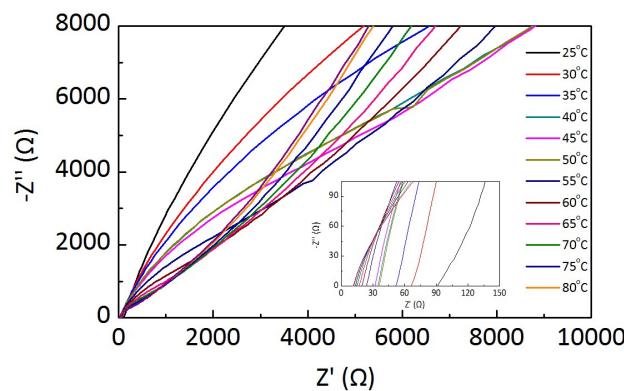
## Electronic supplementary information

### Advanced Construction Strategy of All-solid-state Lithium Batteries with Excellent Interfacial Compatibility and Ultralong Cycle Life

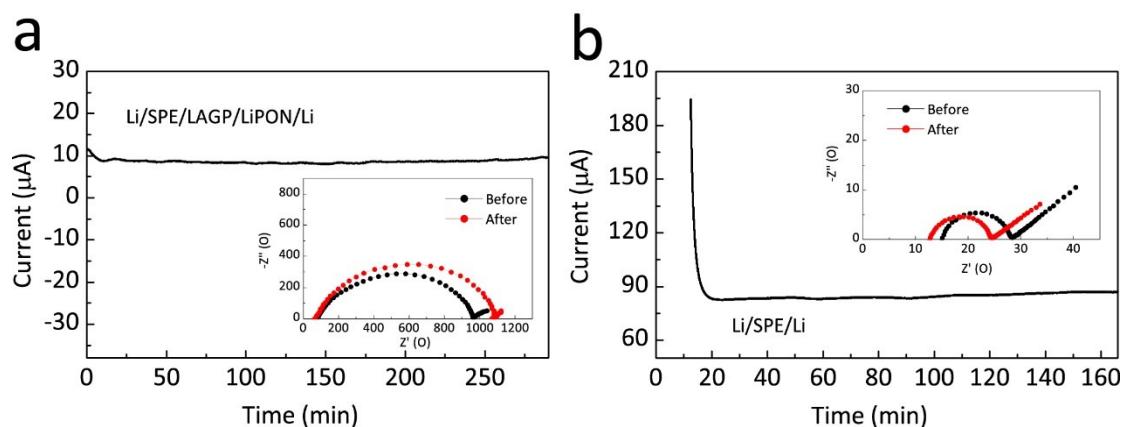
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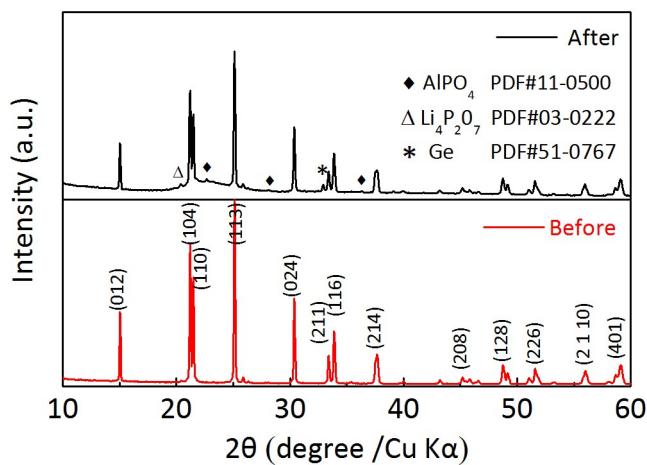
<sup>b</sup> University of Chinese Academy of Science, 100049 Beijing, PR China



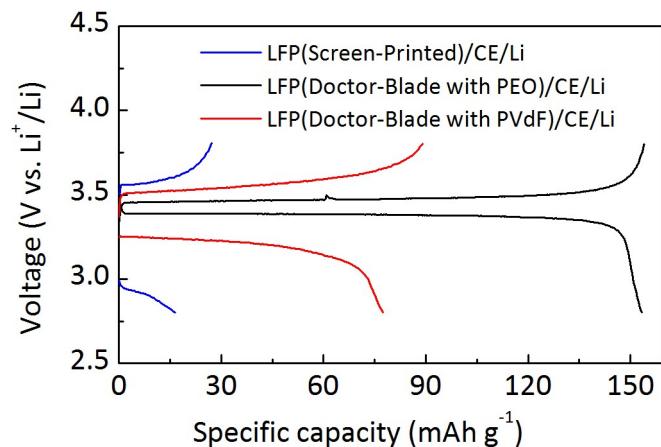
**Fig. S1** EIS plots of CE at different temperatures.



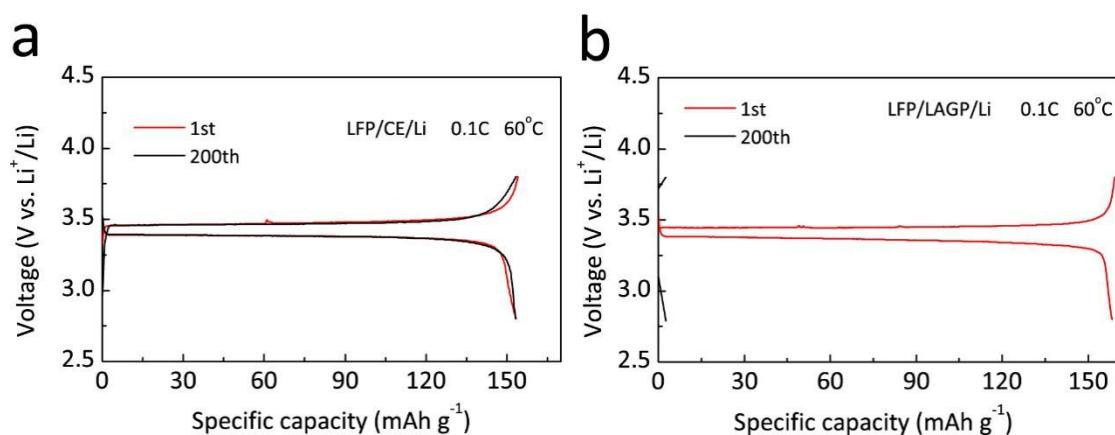
**Fig. S2** DC polarization of a) Li/SPE/LAGP/LiPON/Li cell and b) Li/SPE/Li cell. The inset shows EIS spectra before and after perturbation.



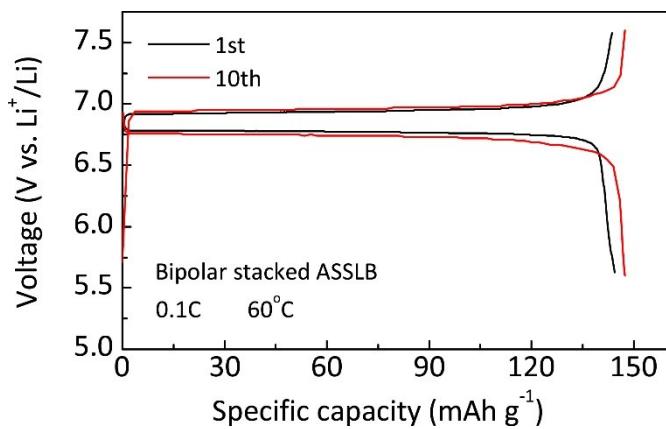
**Fig. S3** XRD pattern of LAGP pellets before and after being contacted with lithium metal for 72h at 60°C.



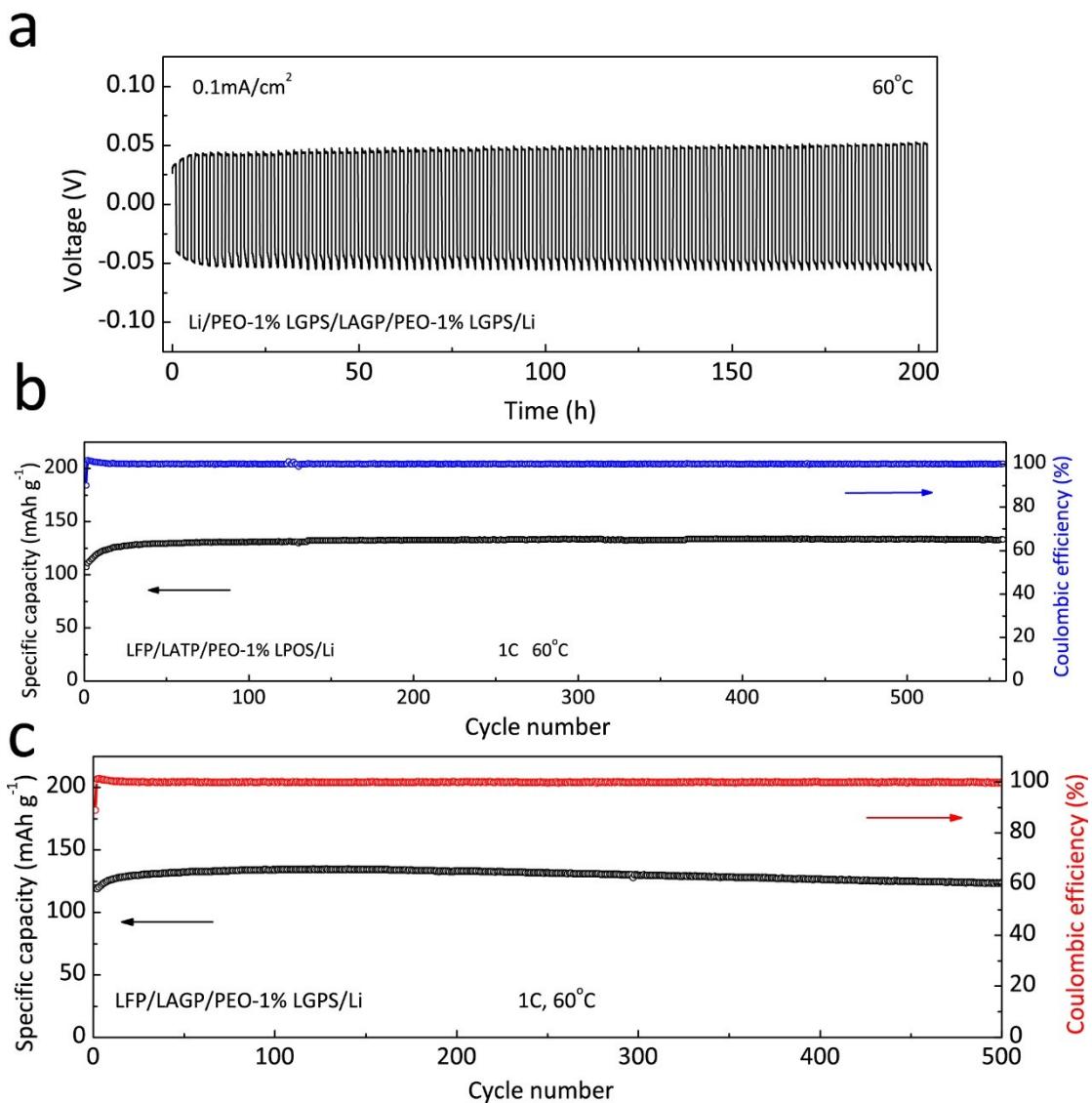
**Fig. S4** The initial charge-discharge curve of LFP/Li ASSLB with different cathode preparation methods.



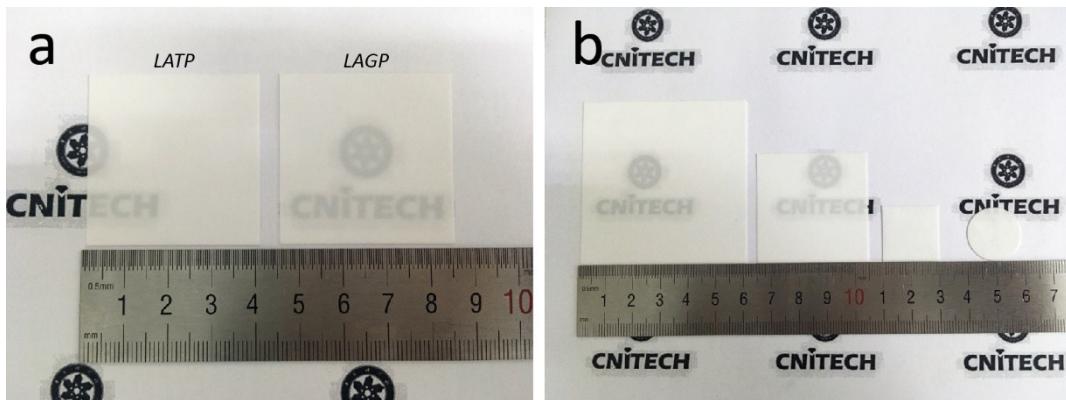
**Fig. S5** The charge/discharge curves of cell a) LFP/CE/Li and b) LFP/LAGP/Li at 0.1 C



**Fig. S6** The charge-discharge curve of bipolar stacked ASSLB



**Fig. S7** a) Voltage profiles vs. cycling time at  $0.1\text{mA cm}^{-2}$  of Li/PEO-1%LGPS/LAGP/PEO-1%LGPS/Li symmetric cell. The capacity retention of c) LFP/LATP/PEO-1%LPOS/Li cell c) LFP/LAGP/PEO-1%LGPS/Li cell at 1 C.



**Fig. S8** a) LATP and LAGP pellets. b) LAGP pellets with various shapes

**Table S1.** Thermal properties of PEO-x%LPOS polymer electrolyte ( $x=0, 1, 5, 10\text{wt}\%$ ).

Electrolytes	$T_g$ (°C)	$T_{m1}$ (°C)	$T_{m2}$ (°C)	$T_{5\%\text{weight loss}}$ (°C)
PEO-0% LPOS	-34.64	41.20	57.98	369.61
PEO-1% LPOS	-36.77	36.92	55.02	357.76
PEO-5% LPOS	-35.62	38.24	55.68	351.91
PEO-10% LPOS	-35.63	38.24	55.52	341.35

**Table S2.** Electronic conductivity and ionic conductivity of the LFP cathode with PVdF and PEO

	LFP cathode with PVdF		LFP cathode with PEO	
	$\sigma_{\text{Electronic}}$ (S cm <sup>-1</sup> )	$\sigma_{\text{Ionic}}$ (S cm <sup>-1</sup> )	$\sigma_{\text{Electronic}}$ (S cm <sup>-1</sup> )	$\sigma_{\text{Ionic}}$ (S cm <sup>-1</sup> )
25°C	$1.89 \times 10^{-3}$	$1.18 \times 10^{-4}$	$1.62 \times 10^{-3}$	$1.21 \times 10^{-4}$
60°C	$2.82 \times 10^{-3}$	$1.39 \times 10^{-4}$	$2.29 \times 10^{-3}$	$7.06 \times 10^{-4}$