

## Supporting Information

### **Spatially isolating Li<sup>+</sup> reduction from Li deposition via Li<sub>22</sub>Sn<sub>5</sub> alloy protective layer for advanced Li metal anode**

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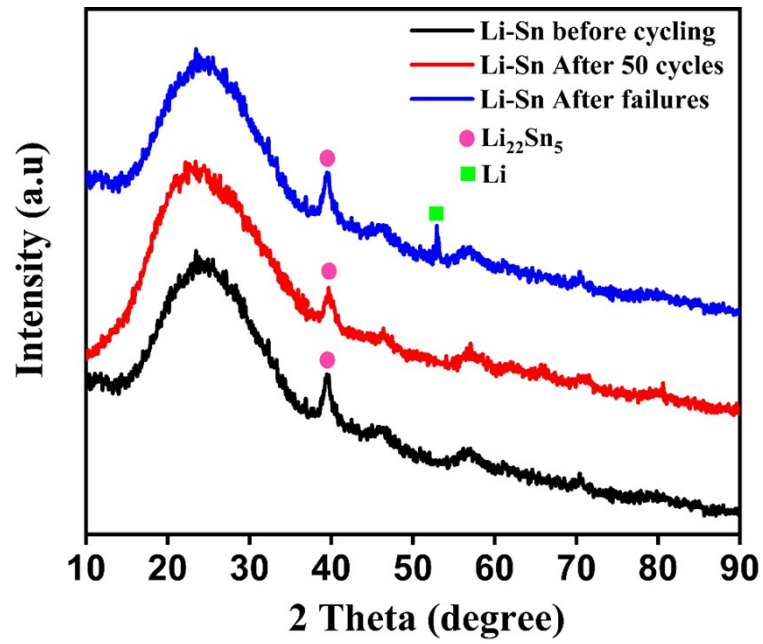


Figure S1. XRD profiles of the Li-Sn alloy layers detached by the adhesive tape from the coated Li foil metal after various cycles.

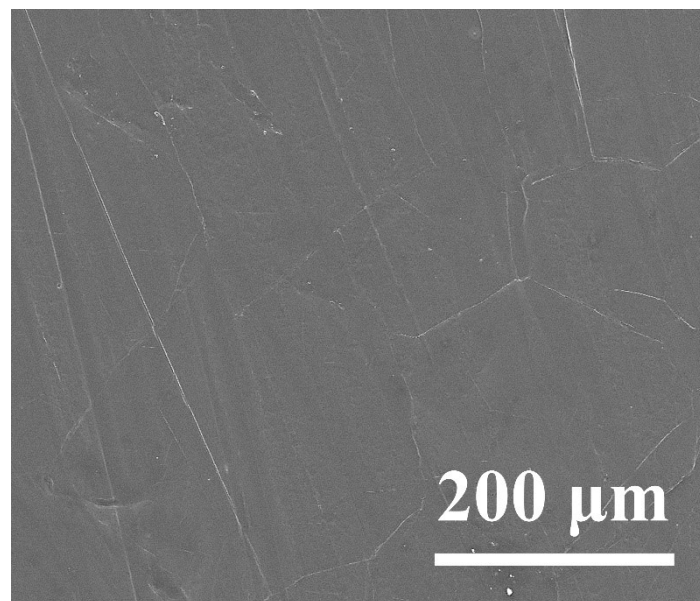


Figure S2. SEM image of the Li-Sn alloy protective layer fabricated by sputtering of Sn on Li foil and the subsequent alloying reaction between Sn and Li.

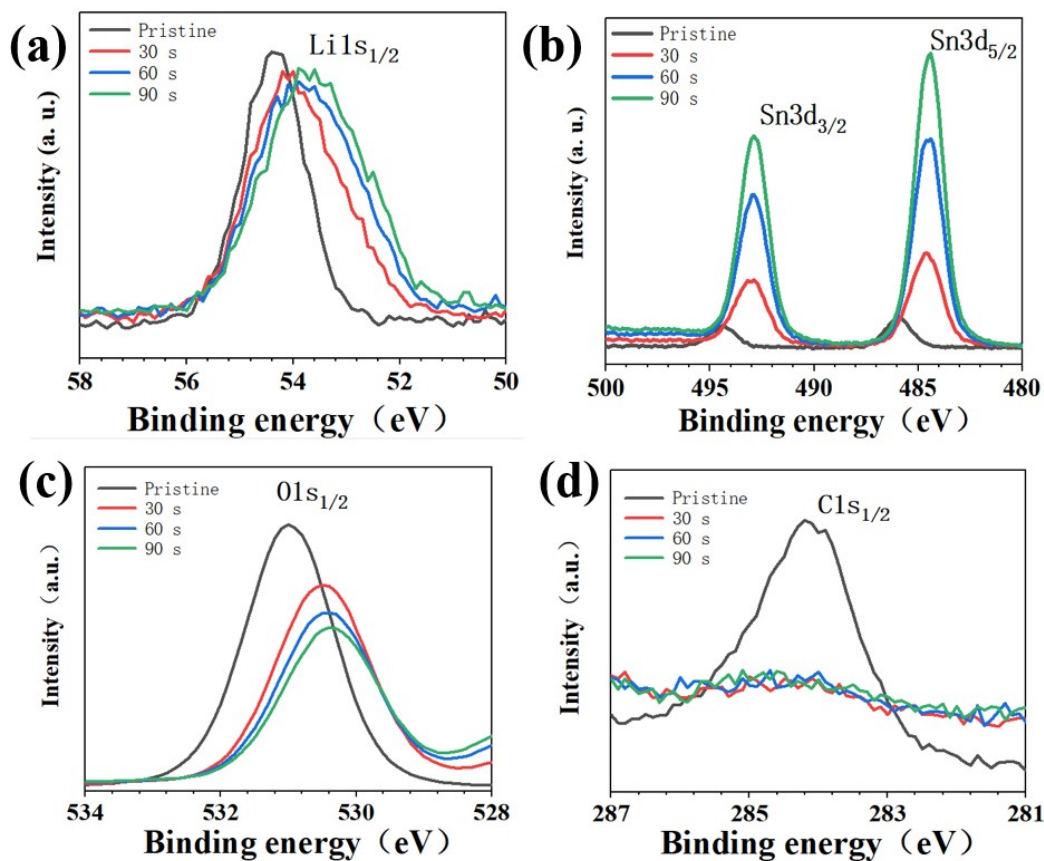


Figure S3. XPS spectra of Sn coated Li anode which was etched by ion beam for 0, 30, 60 and 90 s. (a) O1s; (b) Sn3d; (c) O1s; (d) C1s.

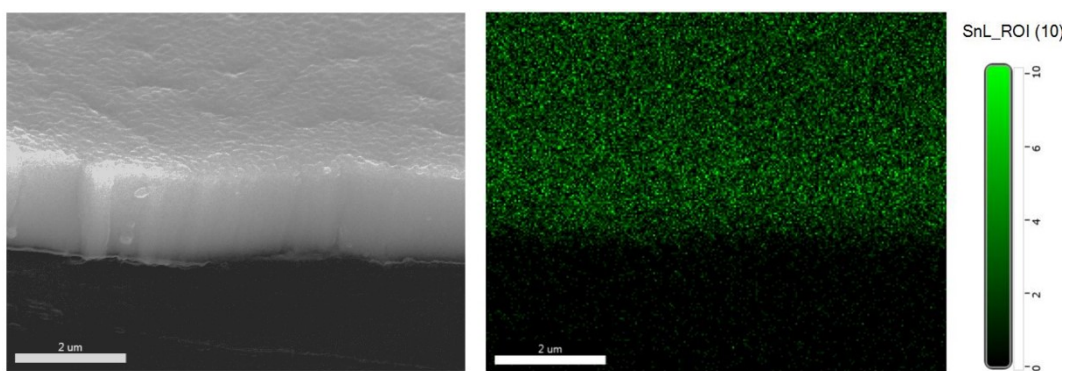


Figure S4. Side-view SEM image (left) and the corresponding EDS mapping image recorded in the vertical direction.

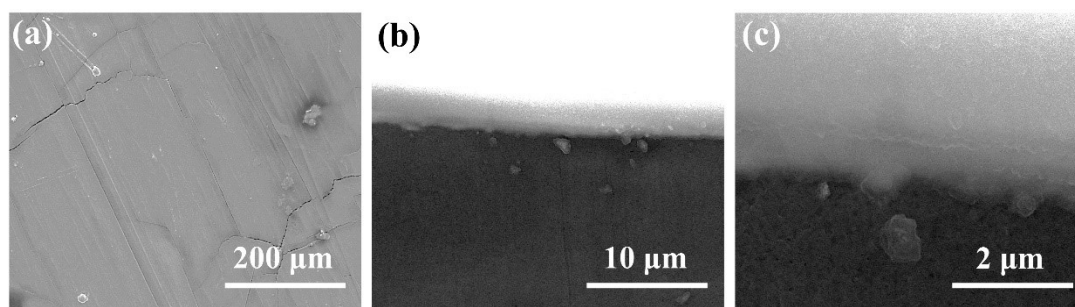


Figure S5. Top-view (a) and side-view (b-c) SEM images of the Li-Sn@Li electrode in the 1st Li plating process at  $0.1 \text{ mA cm}^{-2}$  and  $0.5 \text{ mA h cm}^{-2}$ .

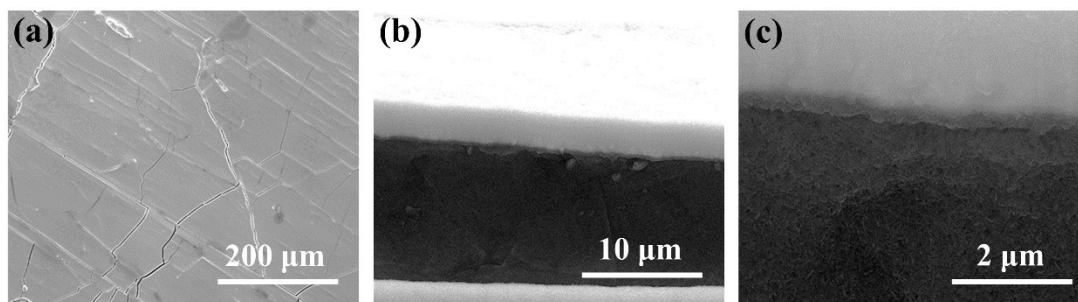


Figure S6. Top-view (a) and side-view (b-c) SEM images of the Li-Sn@Li electrode in the 1st Li plating process at  $0.5 \text{ mA cm}^{-2}$  and  $1 \text{ mA h cm}^{-2}$ .

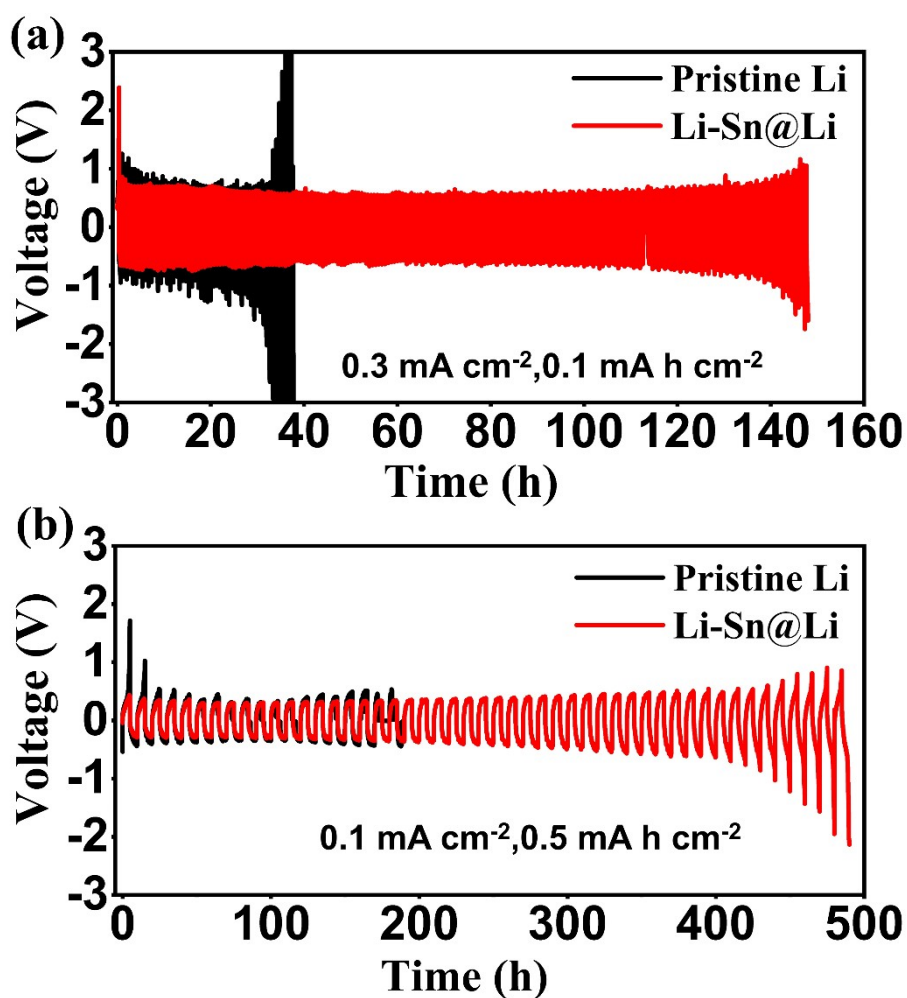


Figure S7. Cycling performance of Li/Li and Li-Sn@Li/Li-Sn@Li symmetric cells at (a)  $0.3 \text{ mA cm}^{-2}$  and  $0.1 \text{ mA h cm}^{-2}$ ; (b)  $0.1 \text{ mA cm}^{-2}$  and  $0.5 \text{ mA h cm}^{-2}$ .

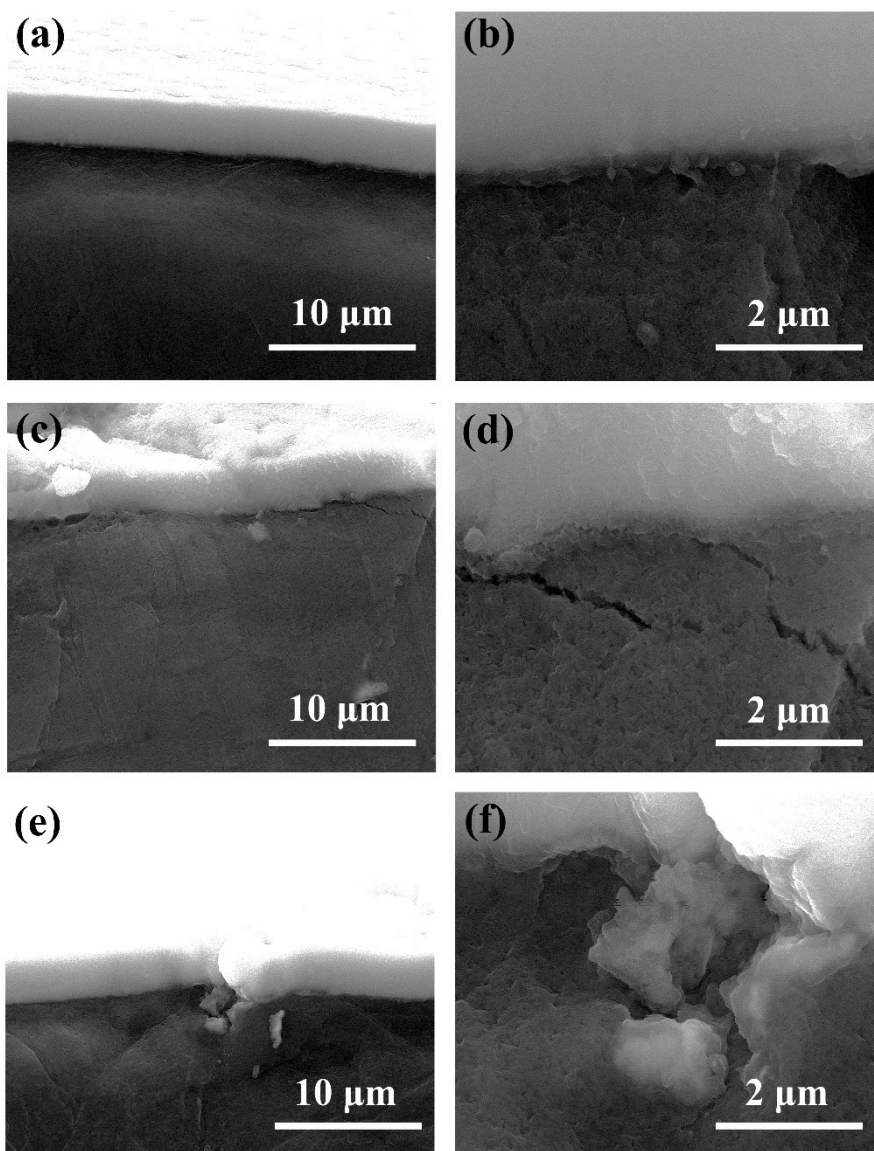


Figure S8. Side-view SEM images of the Li-Sn@Li electrode after 50 cycles at (a-b)  $0.1 \text{ mA cm}^{-2}$  and  $0.1 \text{ mA h cm}^{-2}$ ; (c-d)  $0.5 \text{ mA cm}^{-2}$  and  $0.5 \text{ mA h cm}^{-2}$ ; (e-f)  $1 \text{ mA cm}^{-2}$  and  $1 \text{ mA h cm}^{-2}$ .

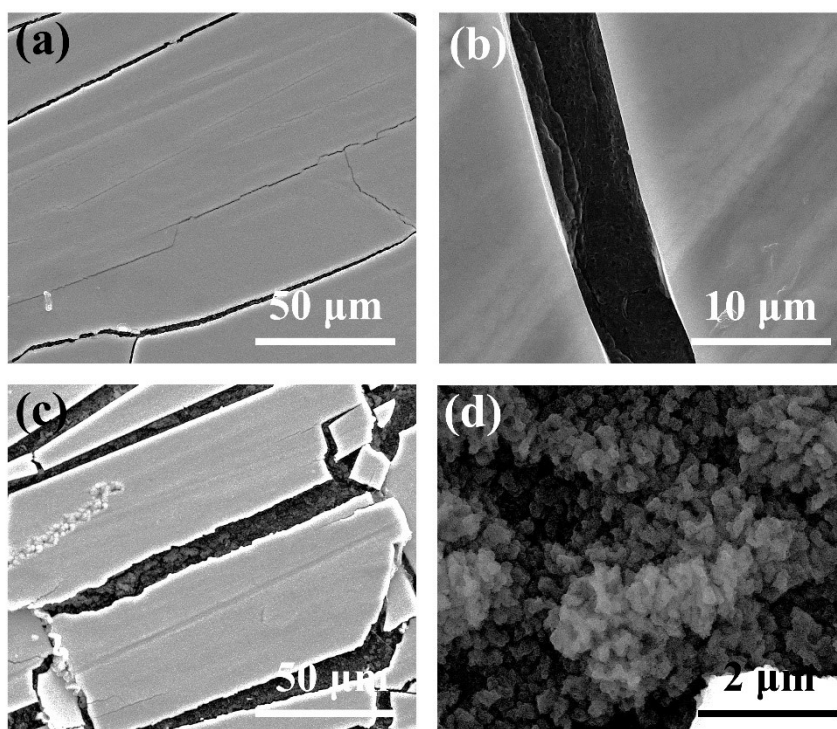


Figure S9. SEM images of the Li-Sn@Li electrode at  $0.1 \text{ mA cm}^{-2}$  and  $0.5 \text{ mA h cm}^{-2}$  after (a-b) 20 cycles and (c-d) 40 cycles.

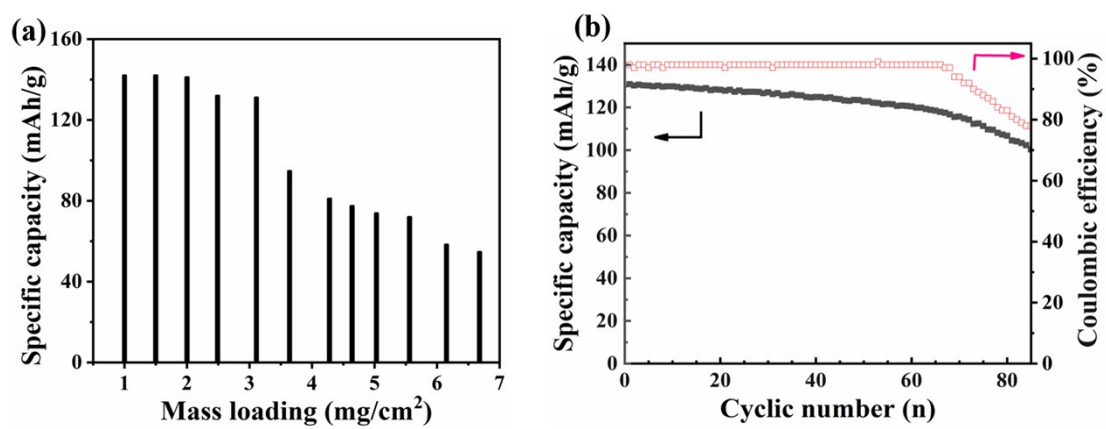


Figure S10. (a) The specific discharge capacity as a function of LFP mass loading; (b) The cyclic performance of LFP based full cell with the active material mass loading of  $3.1 \text{ mg/cm}^2$ .

Table S1. The performance comparison among the symmetric cells with the modified Li anodes and solid state electrolytes.

Symmetrical cells	Current density (mA cm <sup>-2</sup> )	Areal capacity (mA h cm <sup>-2</sup> )	Temperatur e (°C)	Lifespan (h)	Ref.
Li/PEO-SCN-LLZTO/Li	0.2	0.1	60	50	[1]
Li/PEO-SCN-LAGP/Li	0.2	0.2	40	250	[2]
Li/PEO-SCN/Li	0.1	0.1	25	450	[3]
Li/PEO-SCN-GF/Li	0.1	0.1	25	500	[4]
Li-Ag/LLCZNO/Li-Ag	0.2	0.1	25	100	[5]
Li-Mg/LLZO/Li-Mg	0.1	0.02	25	37	[6]
Li-Si/PEO/Li-Si	0.5	0.5	60	1000	[7]
Li-Ge/LAGP/Li-Ge	0.1	0.1	25	200	[8]
LiCa <sub>2</sub> -LiFe/LLZTO/LiCa <sub>2</sub> -LiF	0.1	0.1	25	1000	[9]
Li-Al-Si/LLZTO/Li-Al-Si	0.1	0.1	25	1500	[10]
Li-Sn@Li/PEO-SCN/Li-Sn@Li	0.1	0.1	25	1300	This work
	0.1	0.5	25	500	This work

## References

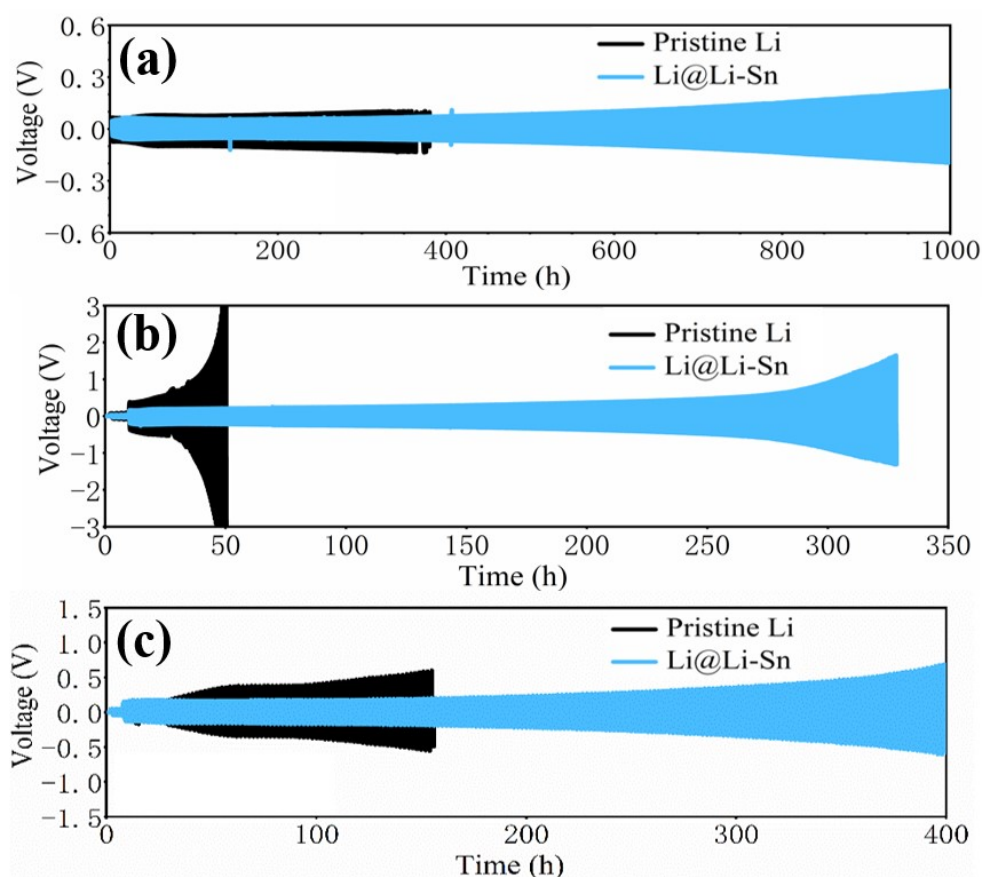
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**Figure S11.** Cycling performance of symmetric cells of Li/Li and Li-Sn@Li/Li-Sn@Li under 60 °C at (a) 0.1 mA cm<sup>-2</sup> and 0.1 mAh cm<sup>-2</sup>, (b) 0.5 mA cm<sup>-2</sup> and 0.1 mAh cm<sup>-2</sup>, (c) 0.3 mA cm<sup>-2</sup> and 0.3 mA h cm<sup>-2</sup>.