

Supplementary Information

Growth of Lithium-Indium Dendrites in All-Solid-State Lithium-based Batteries with Sulfide Electrolytes

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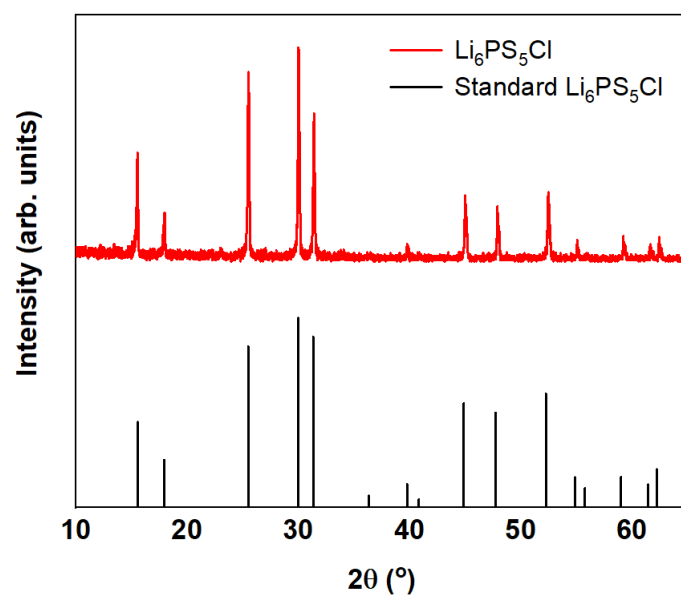
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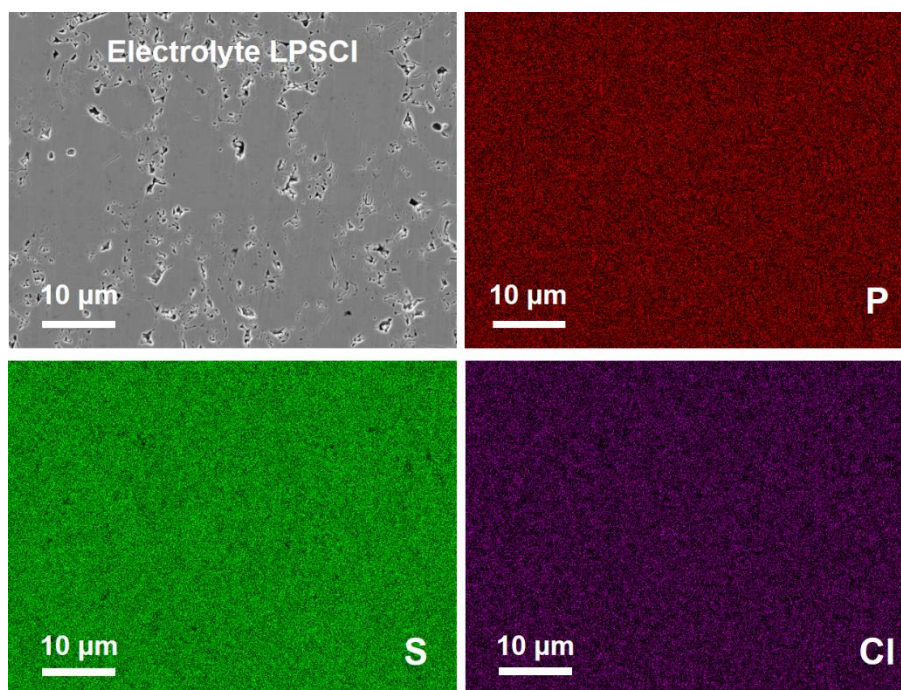
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Inventory of supplementary information

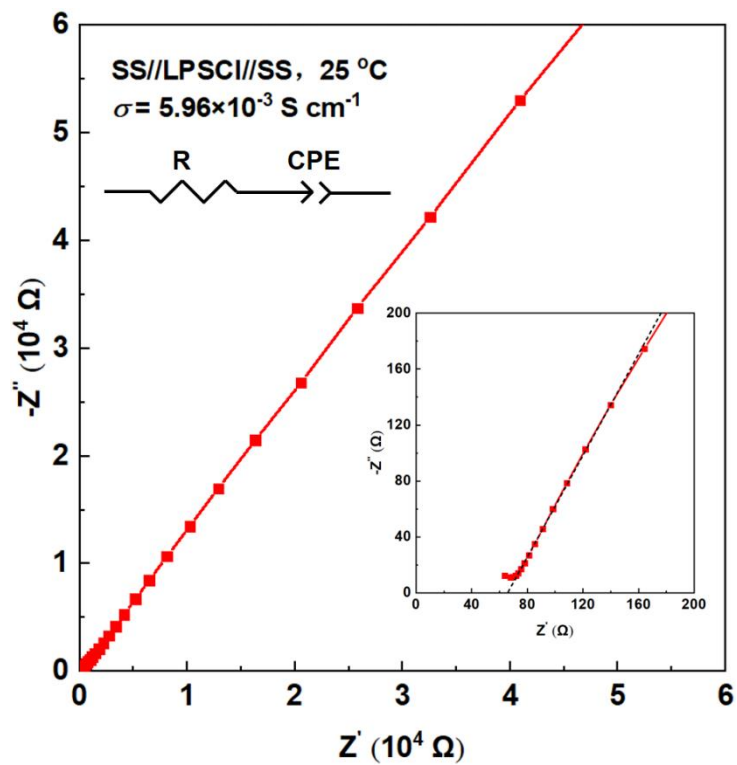
- S1** XRD patterns of the synthesized $\text{Li}_6\text{PS}_5\text{Cl}$ (LPSCl) and standard LPSCl.
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- S16** Ragone plots for the cells employing sulfide electrolytes cycled at closed room temperature.
- S17** Cycling performance of the cell Li|LPSCl|LNO@NCM622.



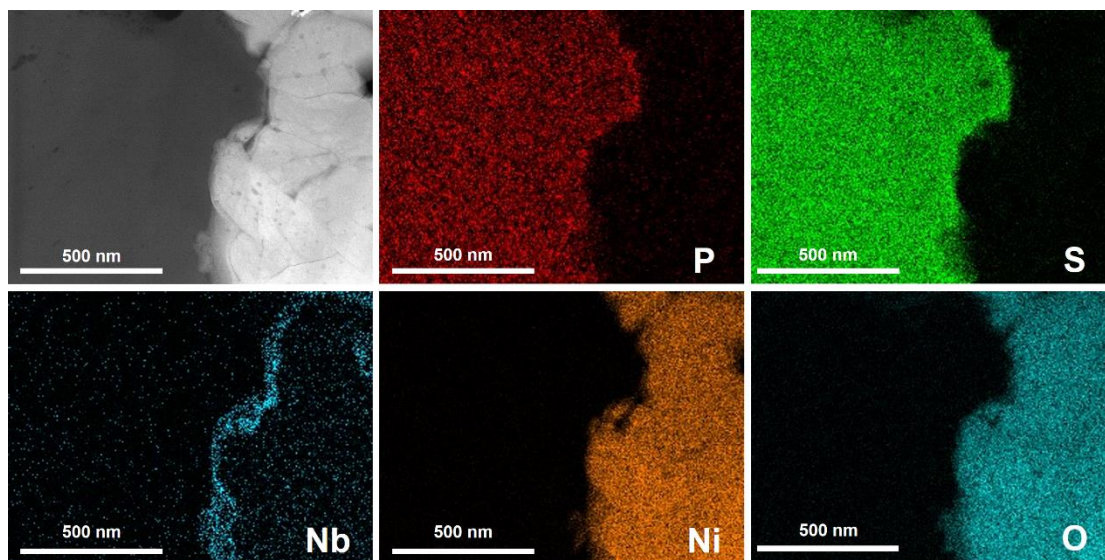
Supplementary Figure 1 XRD patterns of the synthesized $\text{Li}_6\text{PS}_5\text{Cl}$ (LPSCl) and standard LPSCl.



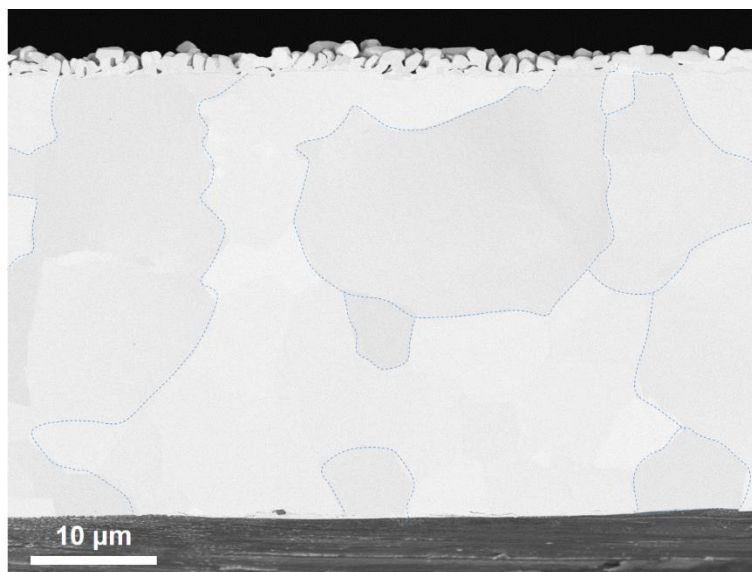
Supplementary Figure 2 SEM image and EDX mapping of P, S, Cl for electrolyte LPSCl.



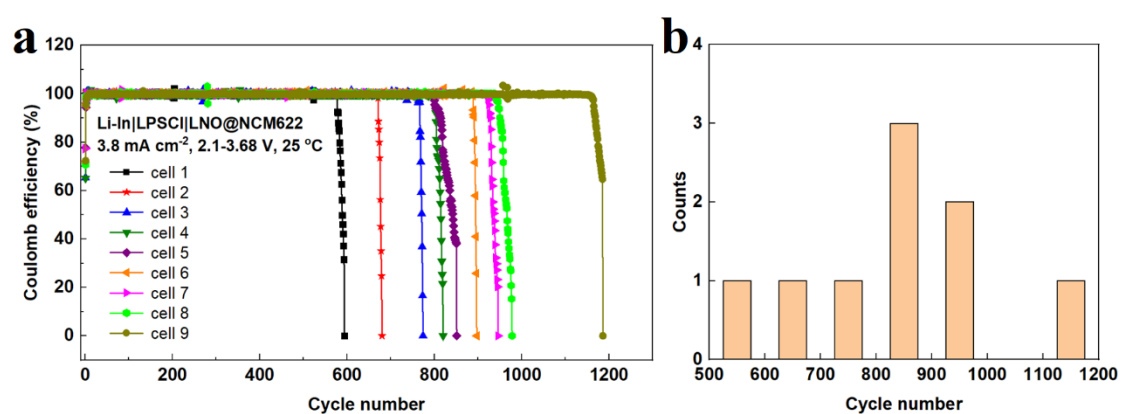
Supplementary Figure 3 Nyquist plot of the synthesized LPSCl solid electrolyte at 25 °C.



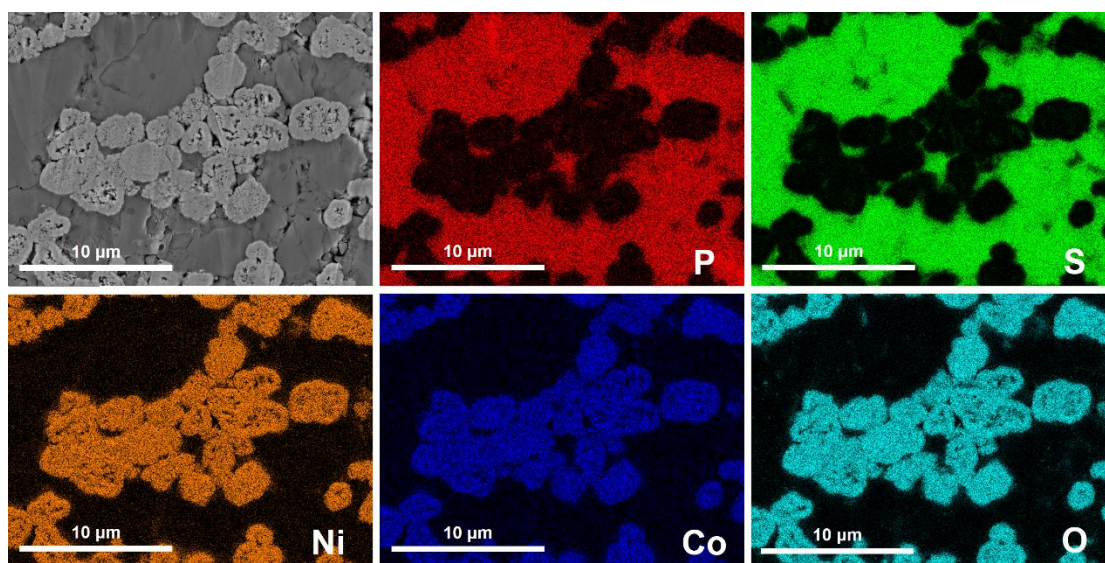
Supplementary Figure 4 STEM image and EDX mapping of a thin sheet of LNO@NCM622.



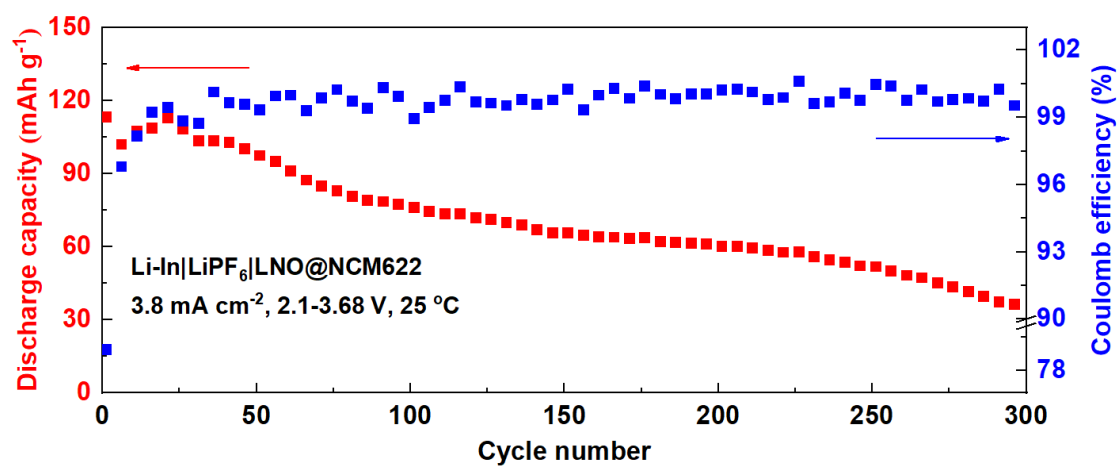
Supplementary Figure 5 Cross-sectional SEM image of the prepared Li-In alloy anode.



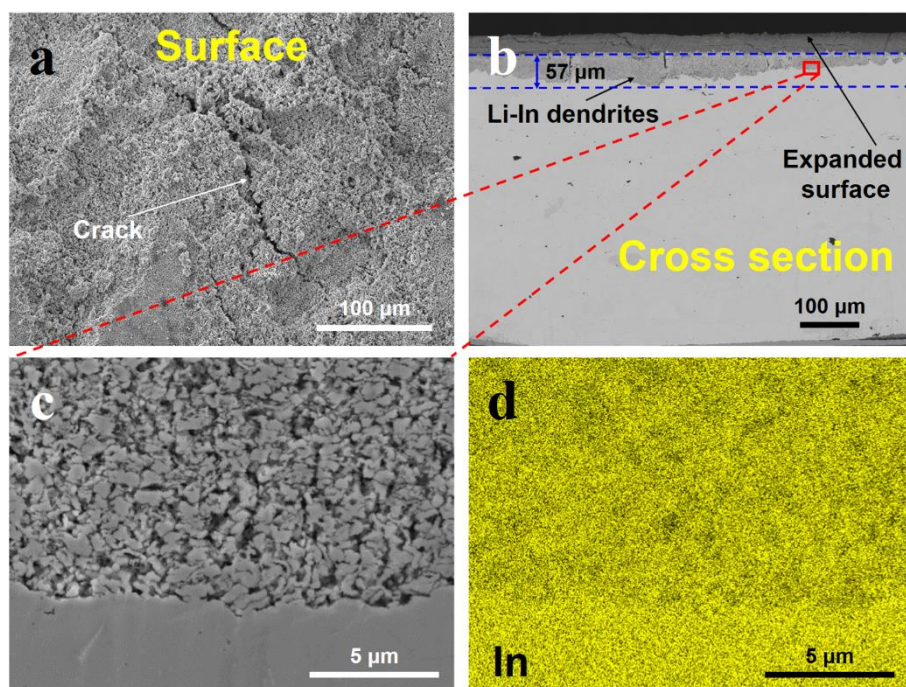
Supplementary Figure 6 Nine sets of repeated experiments for the cells Li-In|LPSCI|LNO@NCM622. **a** Long cycling performance at 3.8 mA cm⁻² at 25 °C. **b** Distribution of cycling life for the nine cells.



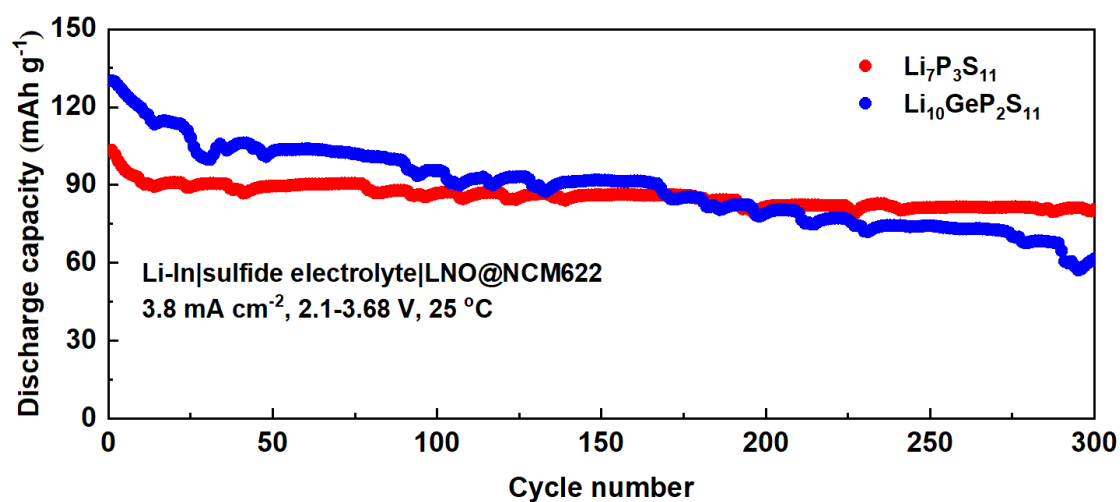
Supplementary Figure 7 SEM image and EDX mapping of P, S, Ni, Co and Mn for cathode-electrolyte interface for the cell with 897 cycles.



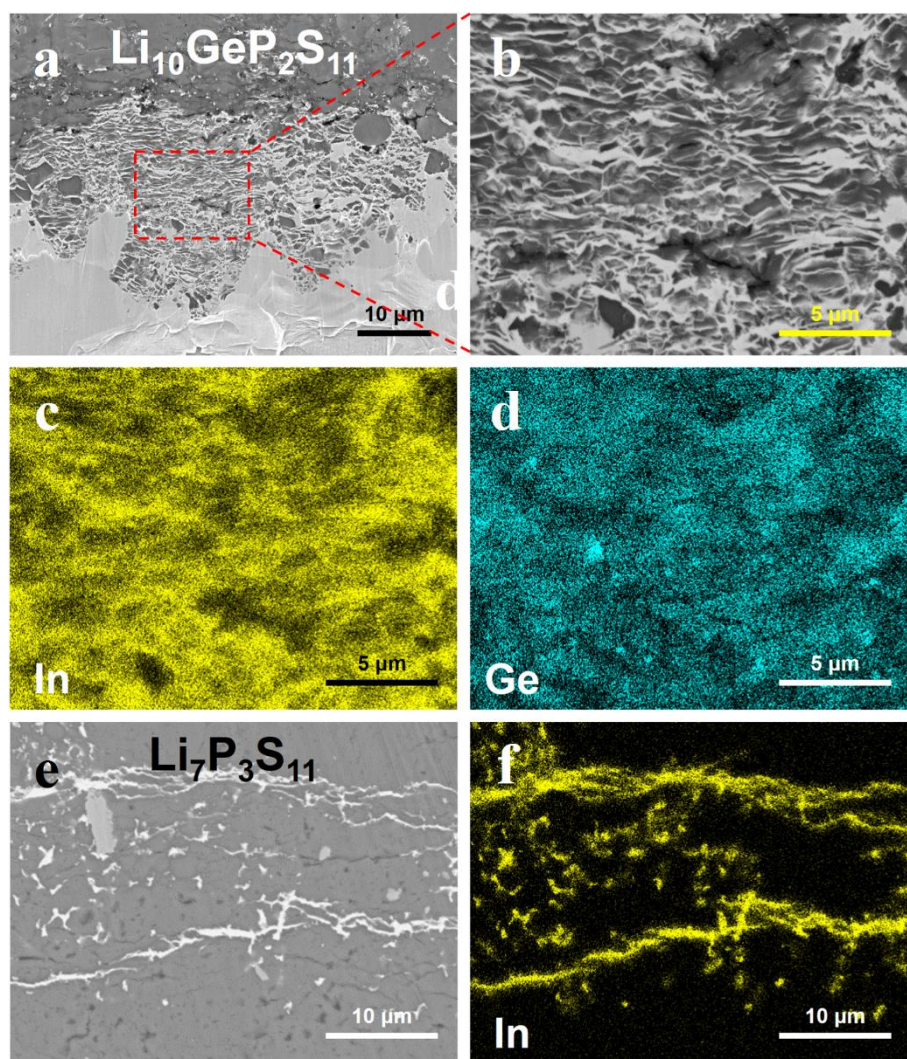
Supplementary Figure 8 Long-term cycling performance of the liquid cell Li-In|LiPF₆|NCM622 at 3.8 mA cm⁻² at 25 °C.



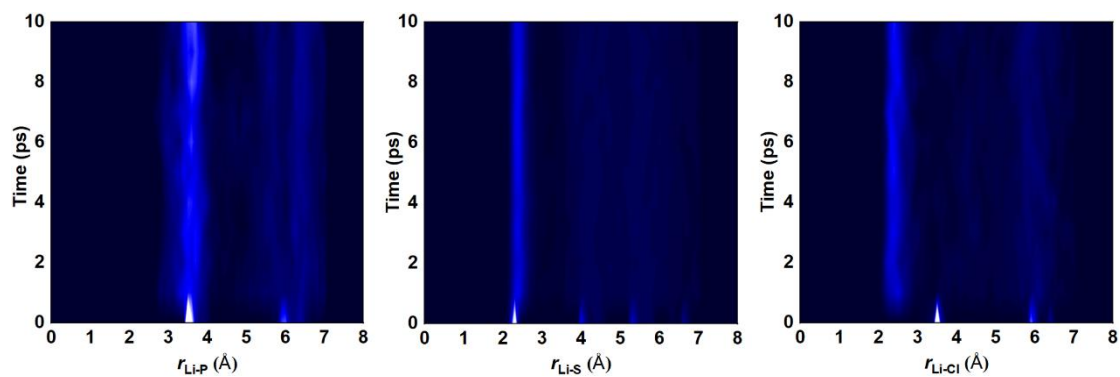
Supplementary Figure 9 SEM images for the Li-In anode cycled 300 times in liquid cell. **a** SEM image for the surface of Li-In anode. **b** SEM image for the cross section of Li-In anode. **c** Magnified SEM image of Li-In dendrites in red boxed area. **d** Corresponding EDX mapping of element In in red boxed area.



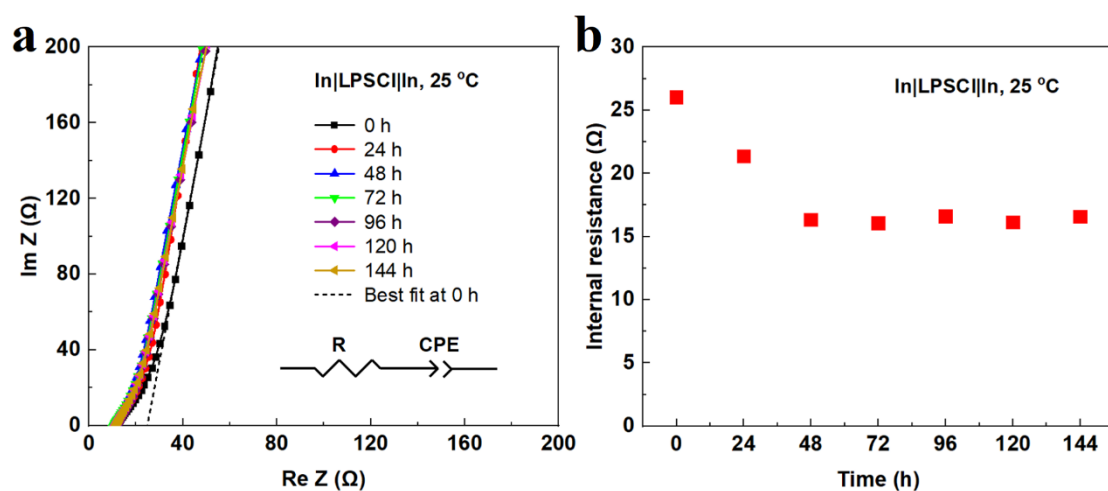
Supplementary Figure 10 Long-term cycling performance of the cells Li-In|LGPS|LNO@NCM622 and Li-In|LPS|LNO@NCM622 at 3.8 mA cm⁻² at 25 °C.



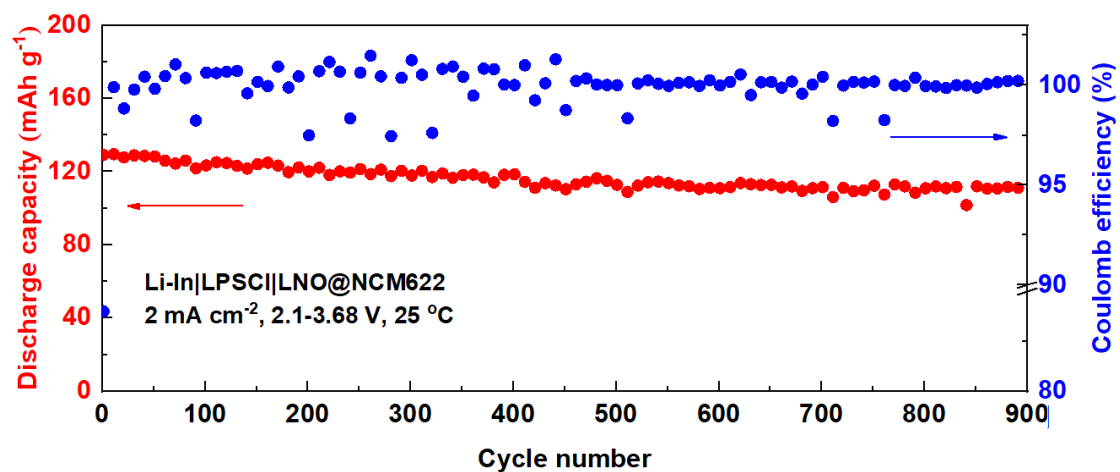
Supplementary Figure 11 Cross-sectional SEM images of the electrolyte-anode interface after 300 cycles. **a** Cross-sectional SEM image and **b** magnified SEM image of Li-In dendrites in LGPS electrolyte. EDX mapping of **c** In and **d** Ge in the red boxed area. **e** SEM image of Li-In dendrites in LPS electrolyte. **f** Corresponding EDX mapping of In.



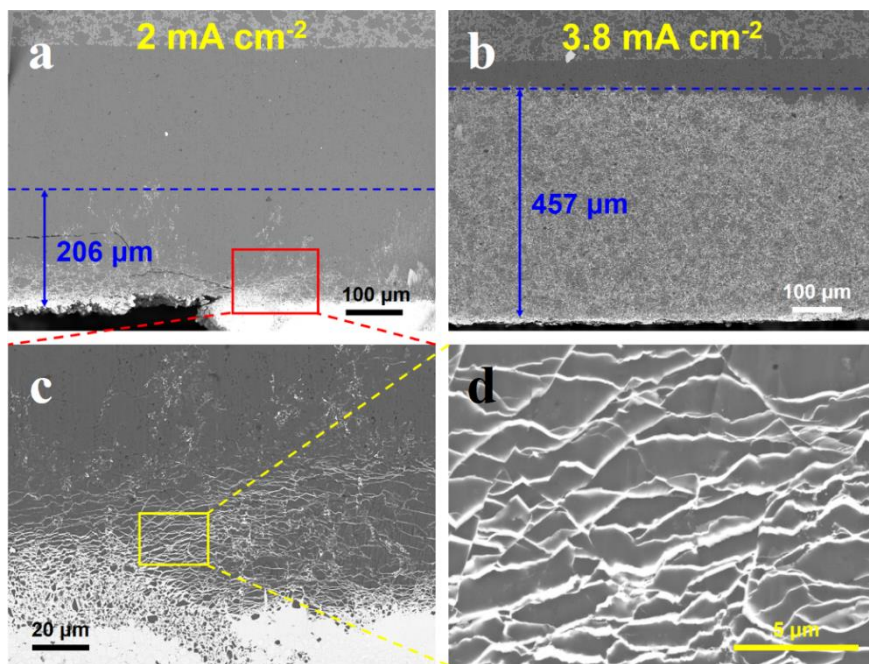
Supplementary Figure 12 Evolutions of the radial distribution functions (RDFs) vs. AIMD simulation time at room temperature (300 K), where RDFs of Li-P, Li-S and Li-Cl are at LPSCl-In interface.



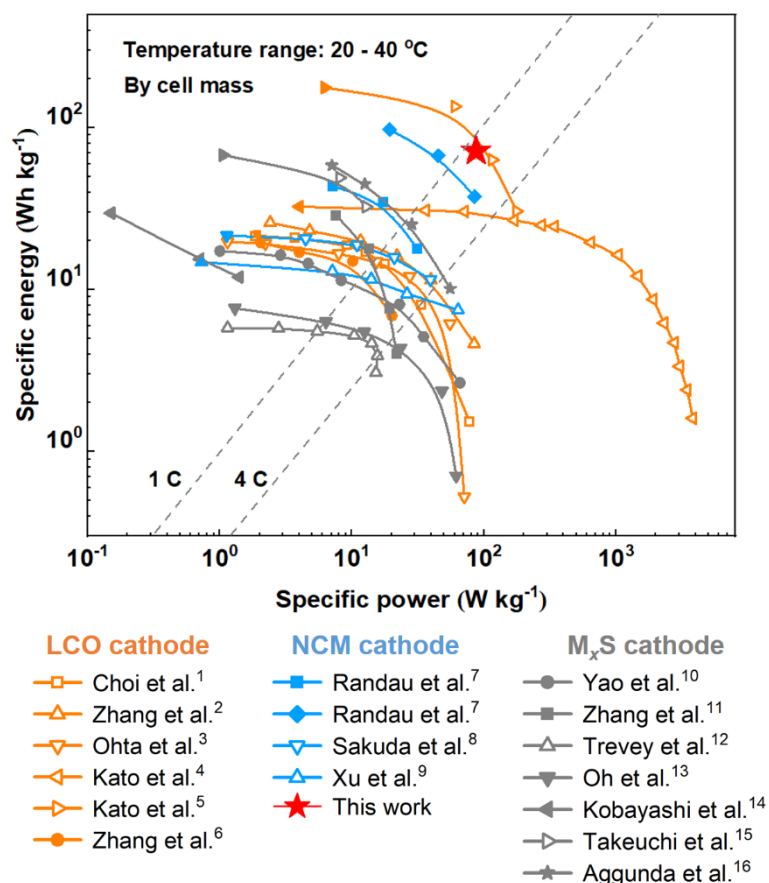
Supplementary Figure 13 Evolutions of electrochemical impedance spectrum and corresponding internal resistance of the cell In|LPSCl|In for one week. The equivalent circuit is shown in inset. The maximum error between the raw and fitted data is 2.6%.



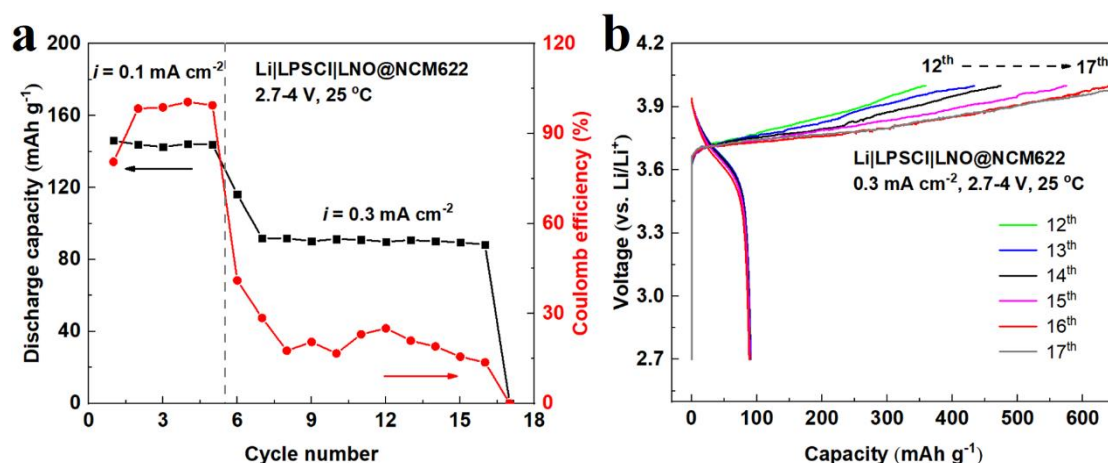
Supplementary Figure 14 Long-term cycling performance of Li-In|LPSCI|LNO@NCM622 at 2 mA cm^{-2} at 25 °C.



Supplementary Figure 15 Cross-sectional SEM images of the cells **a** at 2 mA cm^{-2} and **b** at 3.8 mA cm^{-2} , respectively. Magnified SEM images of **c** the red boxed area and **d** the yellow boxed area.



Supplementary Figure 16 Ragone plots for the cells employing sulfide electrolytes cycled at closed room temperature. The specific energy and power were delivered during discharging, normalized by the cell mass. ASSLBs with LiCoO₂ (LCO)¹⁻⁶, LiNi_xCo_yM_{1-x-y} (NCM)⁷⁻⁹ and M_xS (M = Co, Ni, Ti, Li, Fe, Cu)¹⁰⁻¹⁶ are compared. Filled symbol indicates that the cell was charged and discharged at equal current. Empty symbol indicates the cell was charged at a certain current and discharged at different rates.



Supplementary Figure 17 Cycling performance of the cell Li|LPSCI|LNO@NCM622.

a Variation of discharge capacity versus cycle number for the cell at 0.3 mA cm⁻² at 25 °C. **b** Galvanostatic charge-discharge profiles from the 12th to the 17th cycle.

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