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Critical Stripping Current Leads to Dendrite Formation on Plating in

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Lithium Anode Solid Electrolyte Cells

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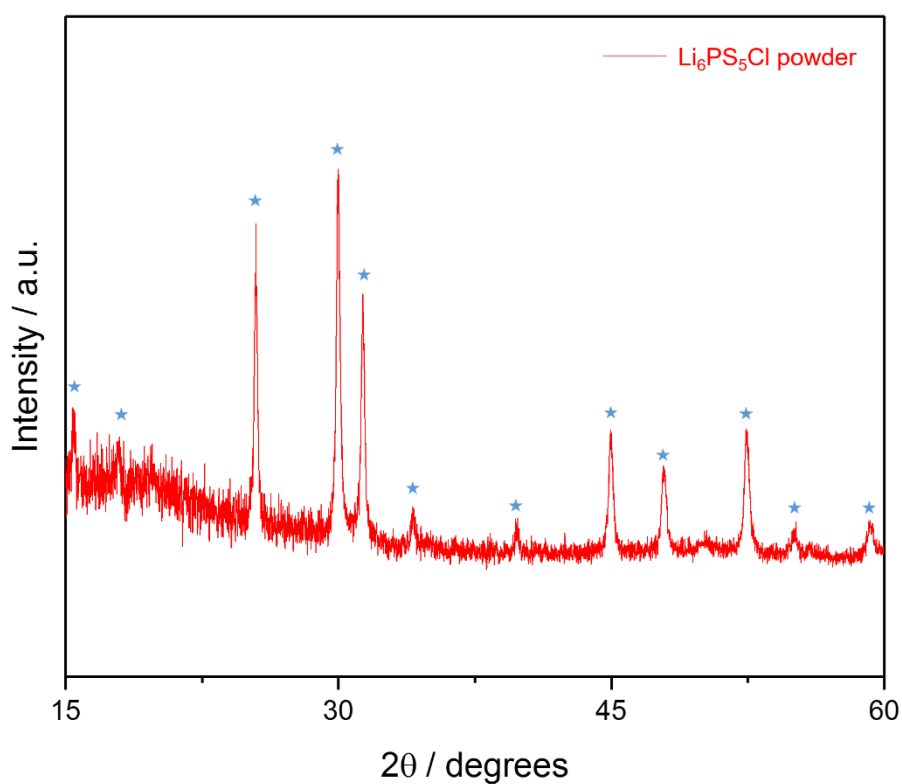
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Supplementary Information



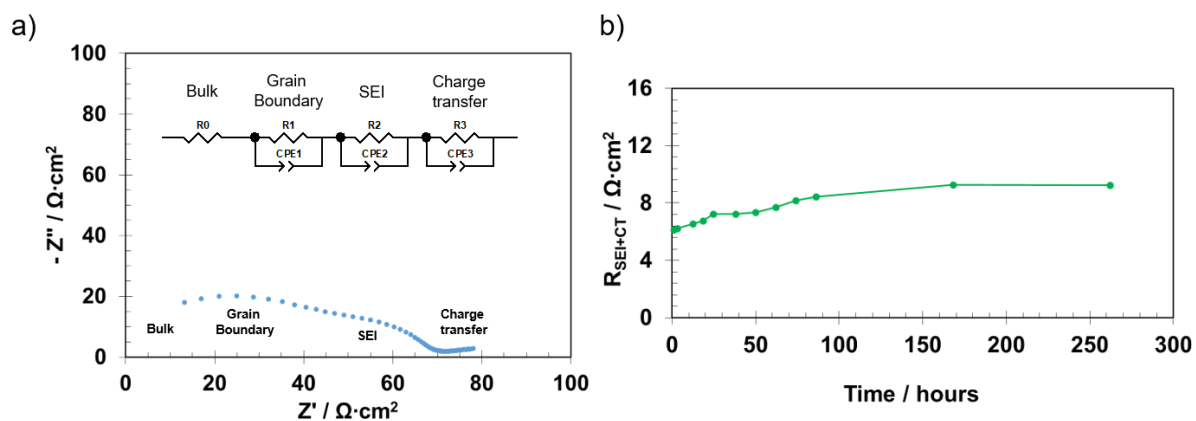
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Figure S1 | Powder X-ray Diffraction (PXRD) of $\text{Li}_6\text{PS}_5\text{Cl}$: after sintering at 300 °C

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★ indicates $\text{Li}_6\text{PS}_5\text{Cl}$ cubic phase.³²

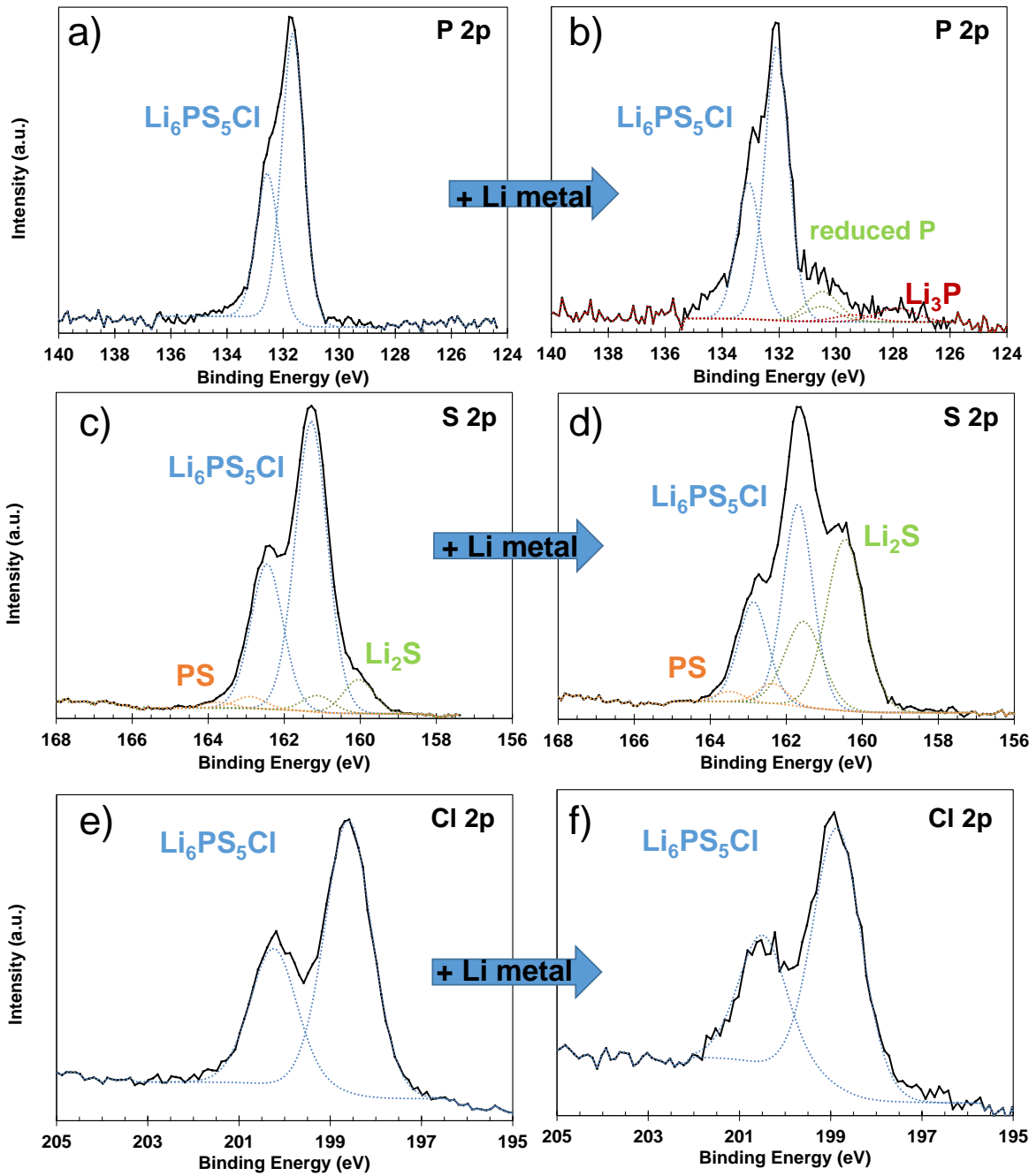


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2 **Figure S2 | AC Impedance data from the cell Li / Li₆PS₅Cl / Li:** (a) Nyquist plot at -1°C with the equivalent circuit
 3 (note that this equivalent circuit was also used to fit all room temperature EIS data), and b) the time-dependence
 4 plot of the interfacial resistances of the cell (the SEI and charge transfer) at 25°C.

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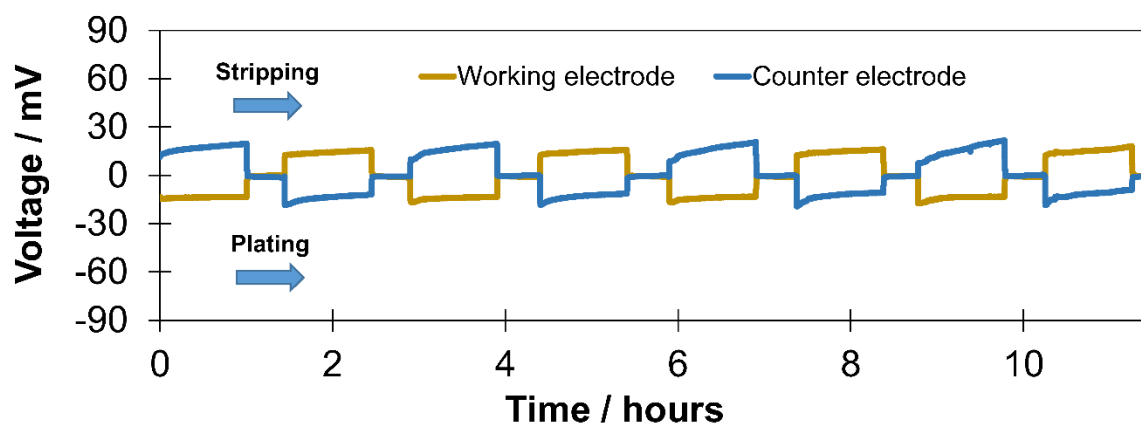
2 **Figure S3 | XPS spectra of the $\text{Li}_6\text{PS}_5\text{Cl}$ pellet surface: P 2p** a) pristine b) exposed to Li metal for 250 h, **S 2p**
 3 c) pristine d) exposed to Li metal for 250 h, **Cl 2p** e) pristine f) exposed to Li metal for 250 h.

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2 **Figure S4 | Voltage vs time for a 3-electrode cell**, the voltage of the Li working and counter electrodes were
 3 collected simultaneously at a current density of $1.0 \text{ mA}\cdot\text{cm}^{-2}$, capacity of $1.0 \text{ mAh}\cdot\text{cm}^{-2}$ on each $\frac{1}{2}$ cycle, pressure
 4 3 MPa .

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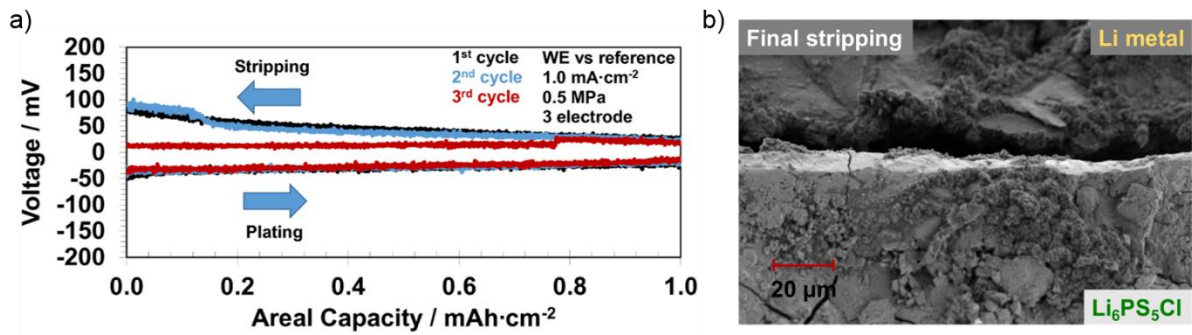
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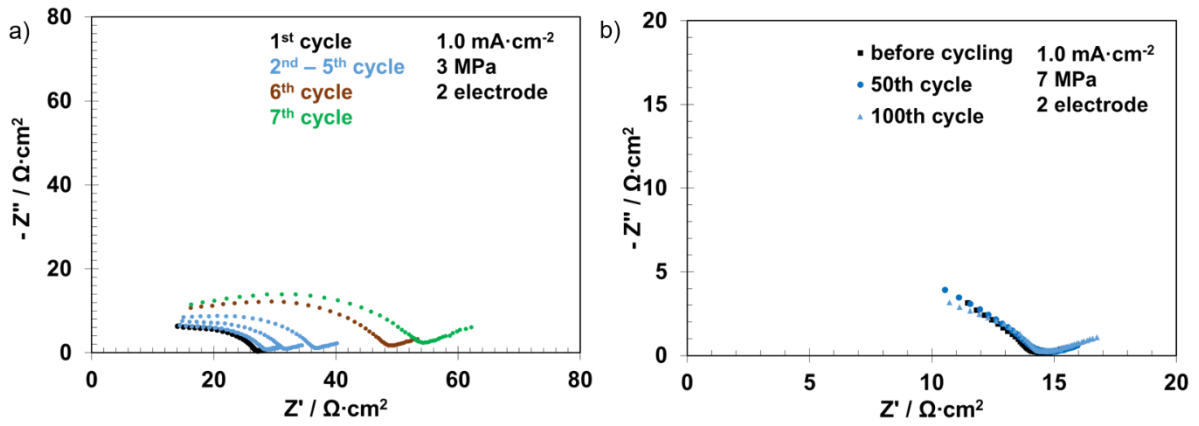
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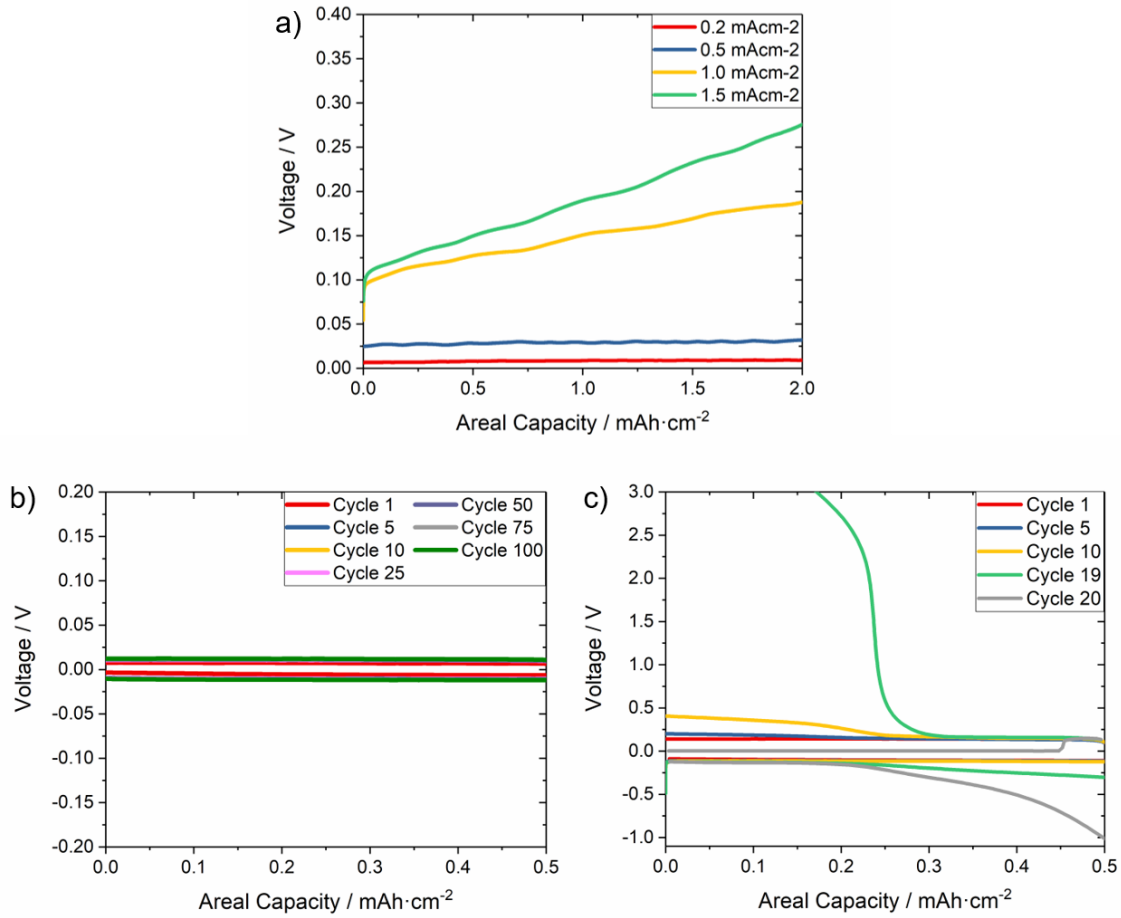
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Figure S5 | Cycling under 4 MPa pressure, (a) Voltage vs charge passed for a 3-electrode cell, Li metal plating and stripping at the Li / Li₆PS₅Cl interface at a current density of 1.0 mA·cm⁻² (b) SEM cross-section of the Li / Li₆PS₅Cl interface after the final stripping.



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Figure S6 | AC Impedance data measured from Li / Li₆PS₅Cl / Li, (a) cycled at $1.0 \text{ mA} \cdot \text{cm}^{-2}$ at 3 MPa for 7 cycles and (b) cycled at $1.0 \text{ mA} \cdot \text{cm}^{-2}$ at 7 MPa for 100 cycles. The impedance increases in (a) but not in (b) in accord with the data in Fig. 7, where the former showed an increase in polarisation but not the latter.



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Figure S7 | Voltage vs charge passed for Na / Na- β'' -Alumina cells, (a) 3-electrode cell, stripping at current densities of 0.2, 0.5, 1.0 and 1.5 mA·cm⁻² at 4 MPa pressure, (b) 2-electrode cell cycled at 0.1 mA·cm⁻² and 4 MPa for 100 cycles (below critical current for stripping) and (c) 2-electrode cell cycled at 1.5 mA·cm⁻² and 4 MPa for 20 cycles (above critical current for stripping) showing increasing polarisation and short-circuiting. Note that the polarisation was limited to 3 V.