

# Temperature Dependence of Lithium Anode Voiding in Argyrodite Solid-State Batteries

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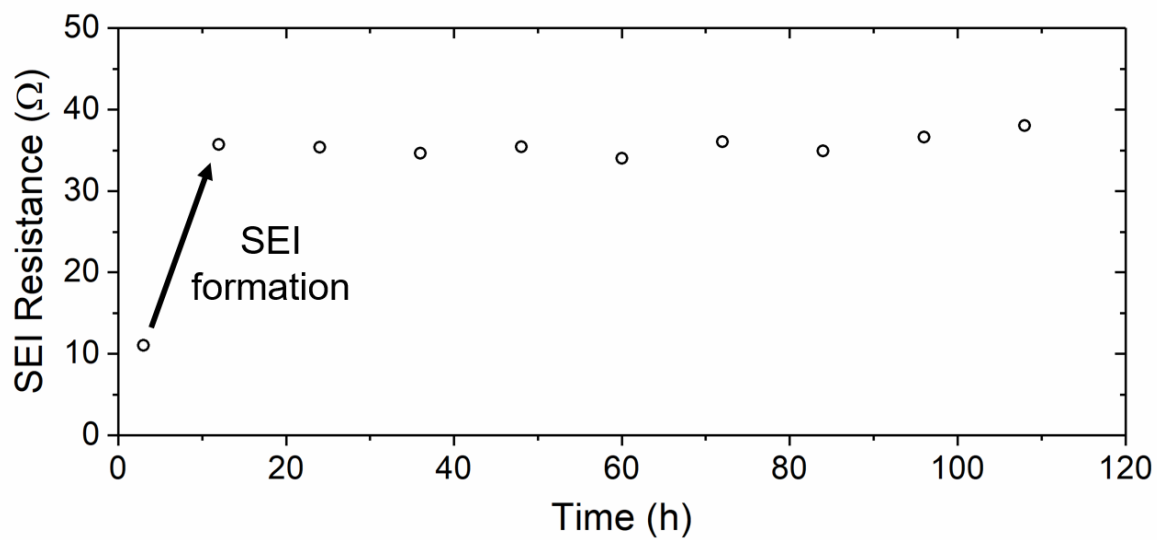
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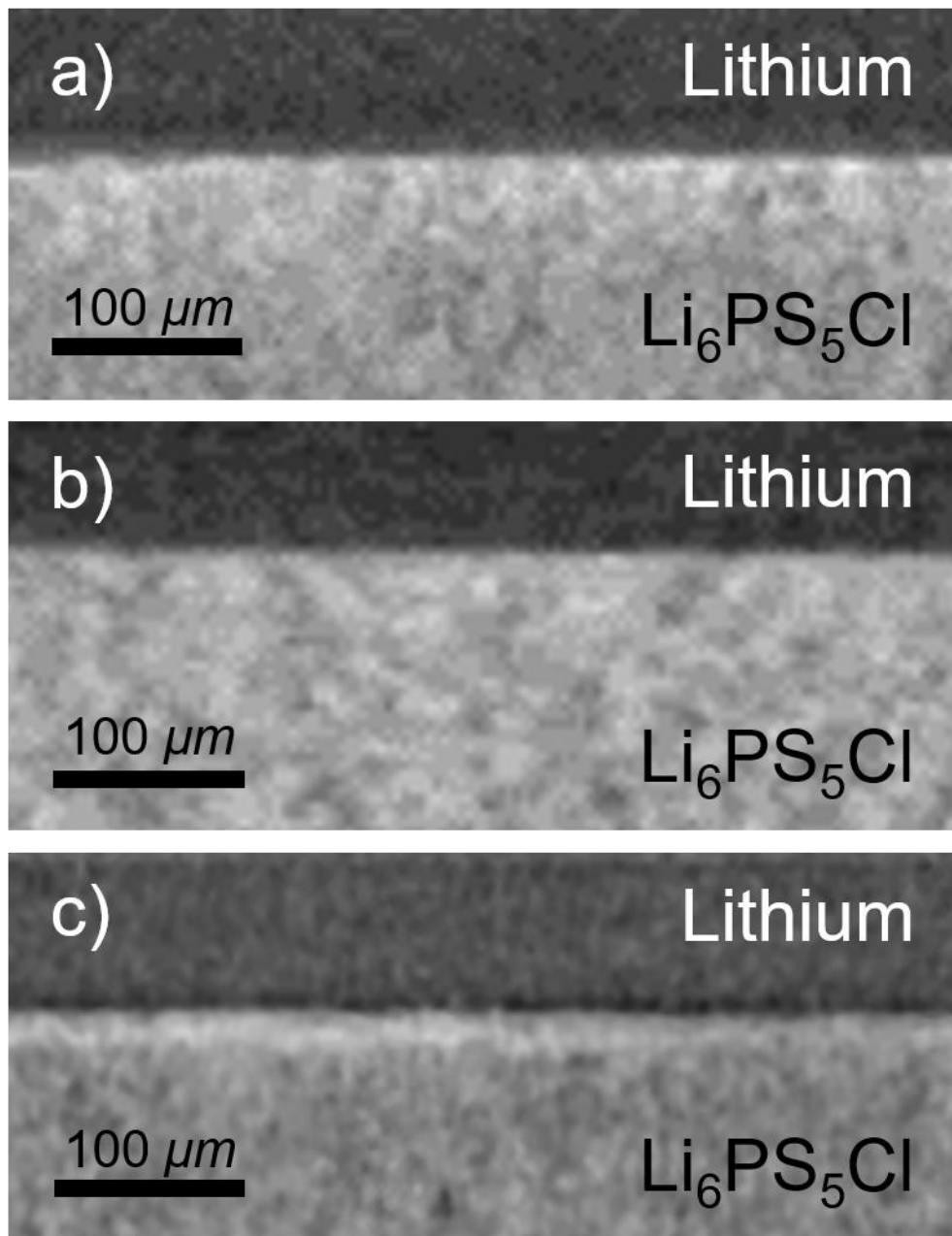
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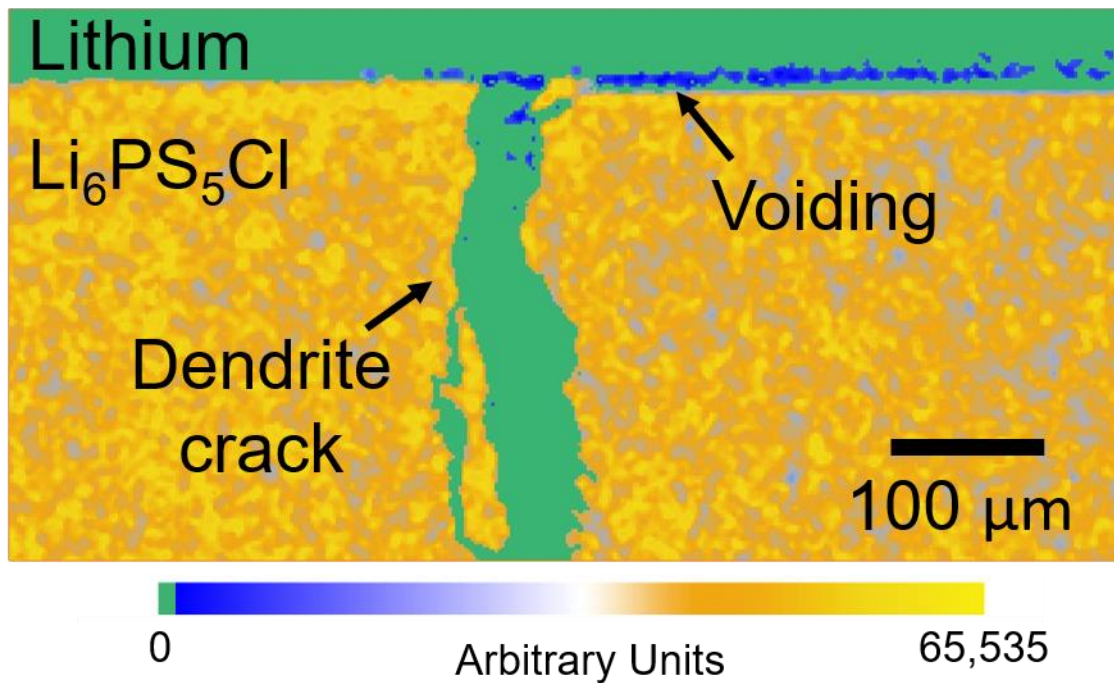
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**Figure S1:** Graph showing the change in SEI resistance with time from PEIS. PEIS was carried out using a voltage perturbation of 5 mV in a frequency range of 1 MHz to 1 Hz, collecting 10 points per decade.

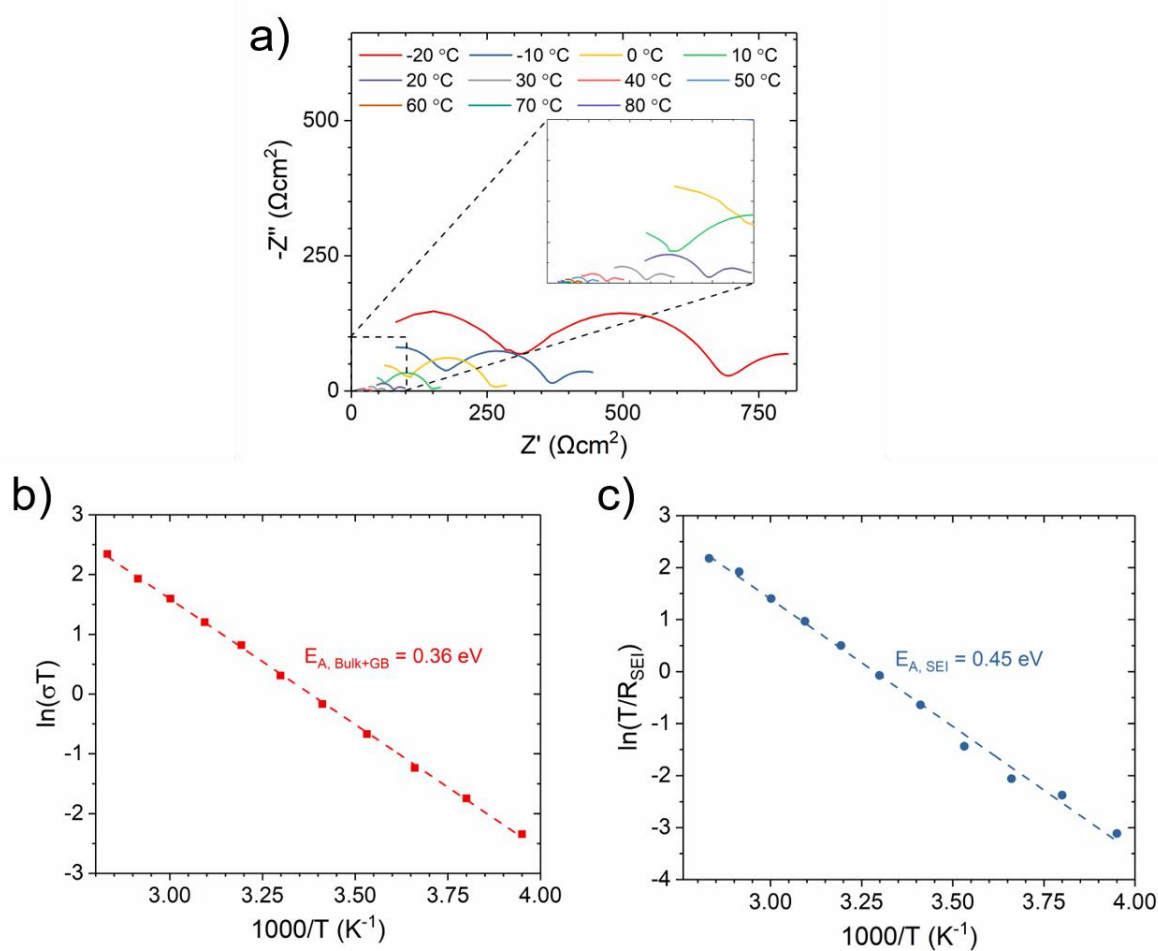


**Figure S2:** Unsegmented X-ray tomography cross-sectional images of the Li/Li<sub>6</sub>PS<sub>5</sub>Cl interface for a) a pristine cell and after cycling under 1 MPa stack-pressure at b) 0.5 mAcm<sup>-2</sup> and c) 0.75 mAcm<sup>-2</sup>.

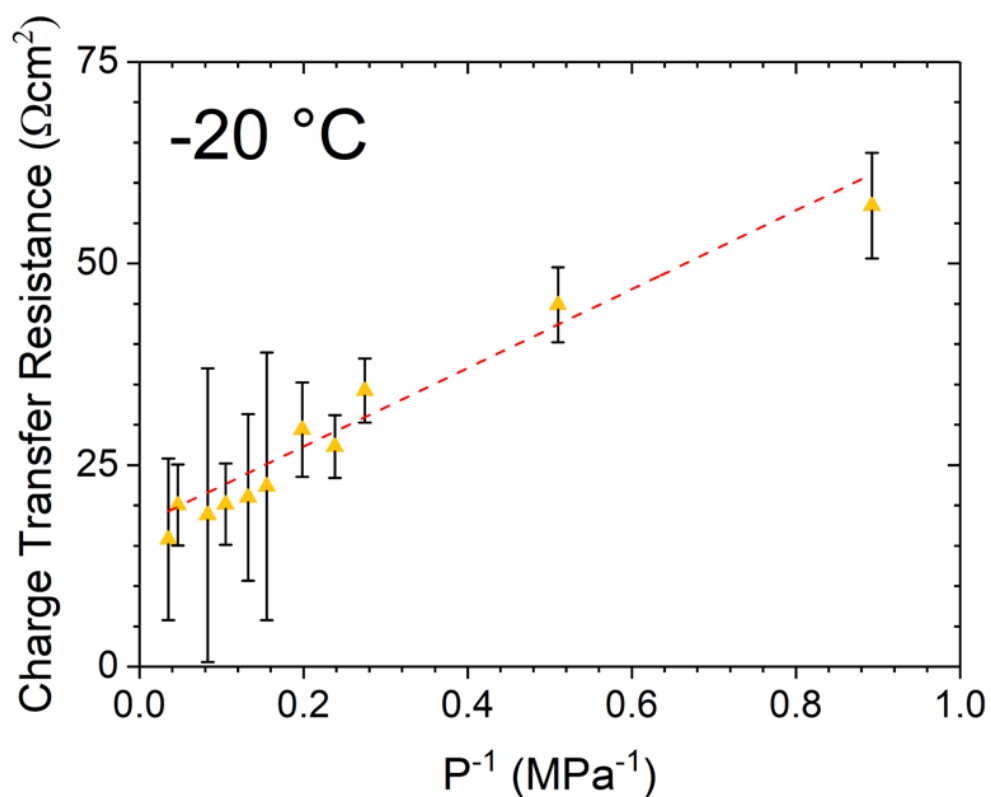


**Figure S3:** XCT cross-section showing dendrite crack through Li<sub>6</sub>PS<sub>5</sub>Cl electrolyte associated with the edge of an area of severe voiding in the Li anode. The cell failed after cycling at 0.75 mAcm<sup>-2</sup> at 80 °C under 1 MPa. Green, blue and orange/yellow indicate lithium, empty space (void) and Li<sub>6</sub>PS<sub>5</sub>Cl electrolyte respectively.

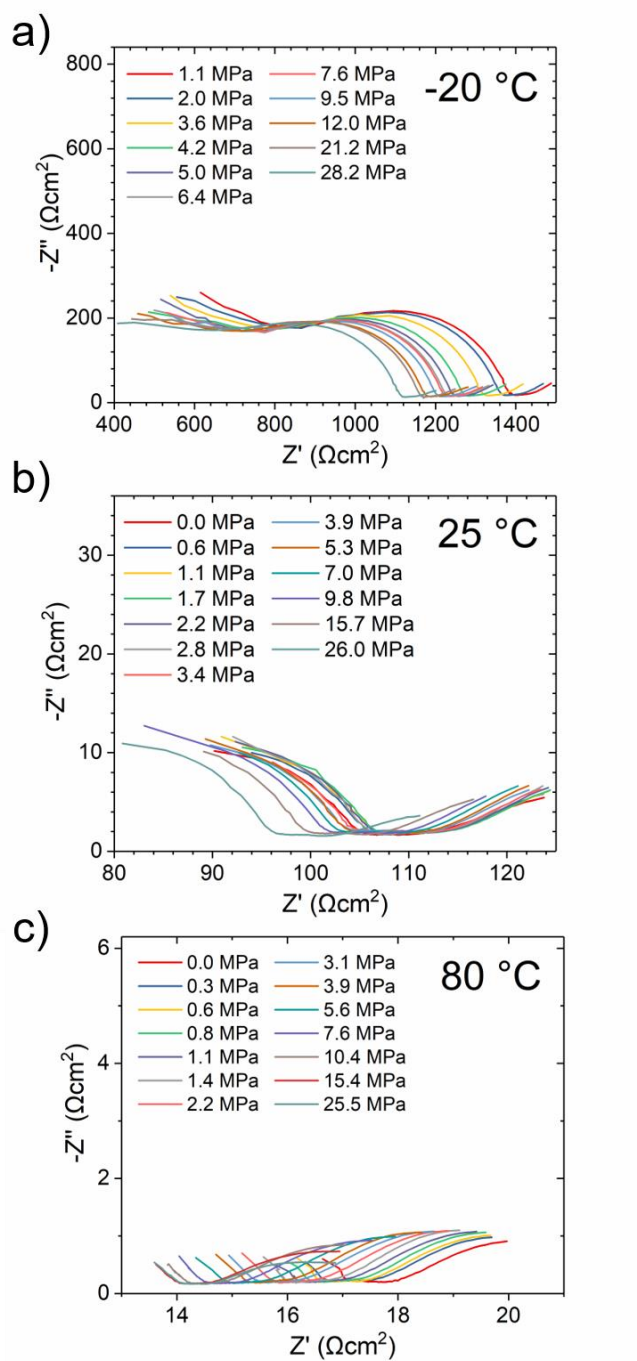
The physical meaning of the values in the XCT images are the grayscale intensity values in 16-bit, which depend on the electron density of the constituent atoms in a voxel. High grayscale intensity values correspond to heavier atoms, and lower values correspond to lighter atoms or empty space. To enhance the contrast between voids and lithium electrode, the grayscale of lithium metal was set to zero, as detailed in the experimental methods.



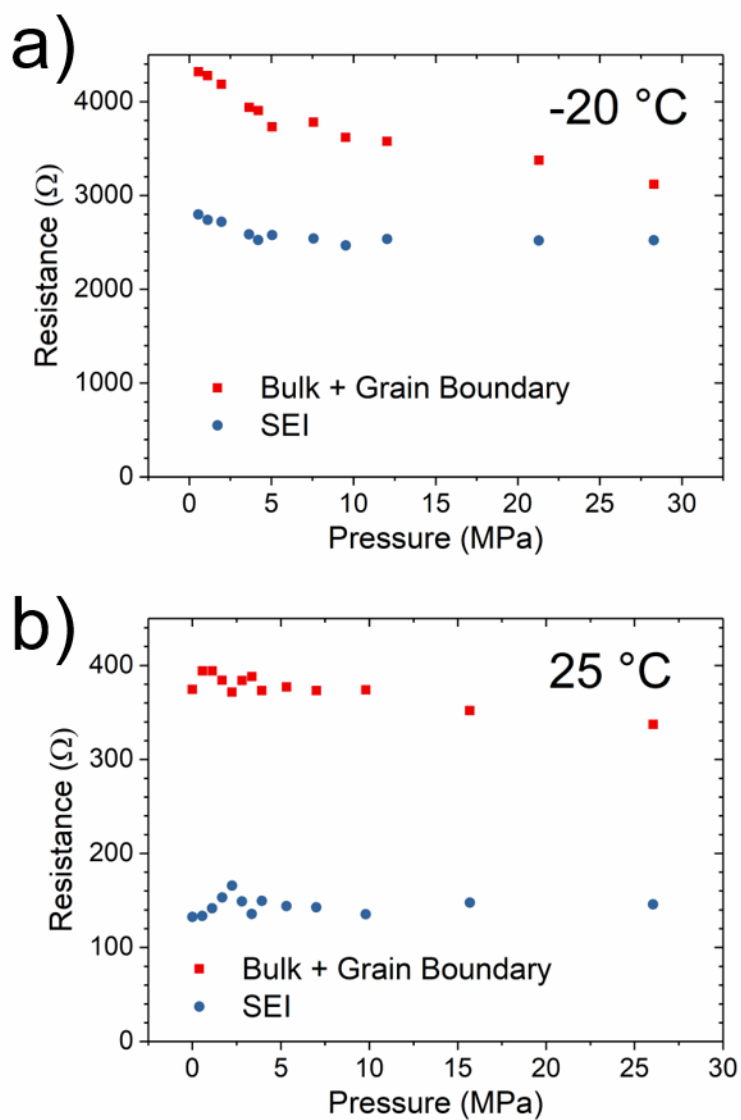
**Figure S4:** a) Nyquist plot showing PEIS at temperatures from -20 °C to 80 °C at 1 MPa stack-pressure; b) Arrhenius plot showing the calculated activation energy of  $\text{Li}_6\text{PS}_5\text{Cl}$  bulk + grain boundary conductivity; c) Arrhenius plot showing the calculated activation energy of  $\text{Li}/\text{Li}_6\text{PS}_5\text{Cl}$  SEI resistance. PEIS was carried out using a voltage perturbation of 5 mV in a frequency range of 1 MHz to 1 Hz, collecting 10 points per decade.



**Figure S5:** Plot showing the linear dependence of the charge transfer resistance on the inverse of pressure. Error bars give error in the least-squares fitting of the interfacial resistance. Cells were placed under a formation pressure of approximately 25 MPa for 12 hours prior to the measurements.

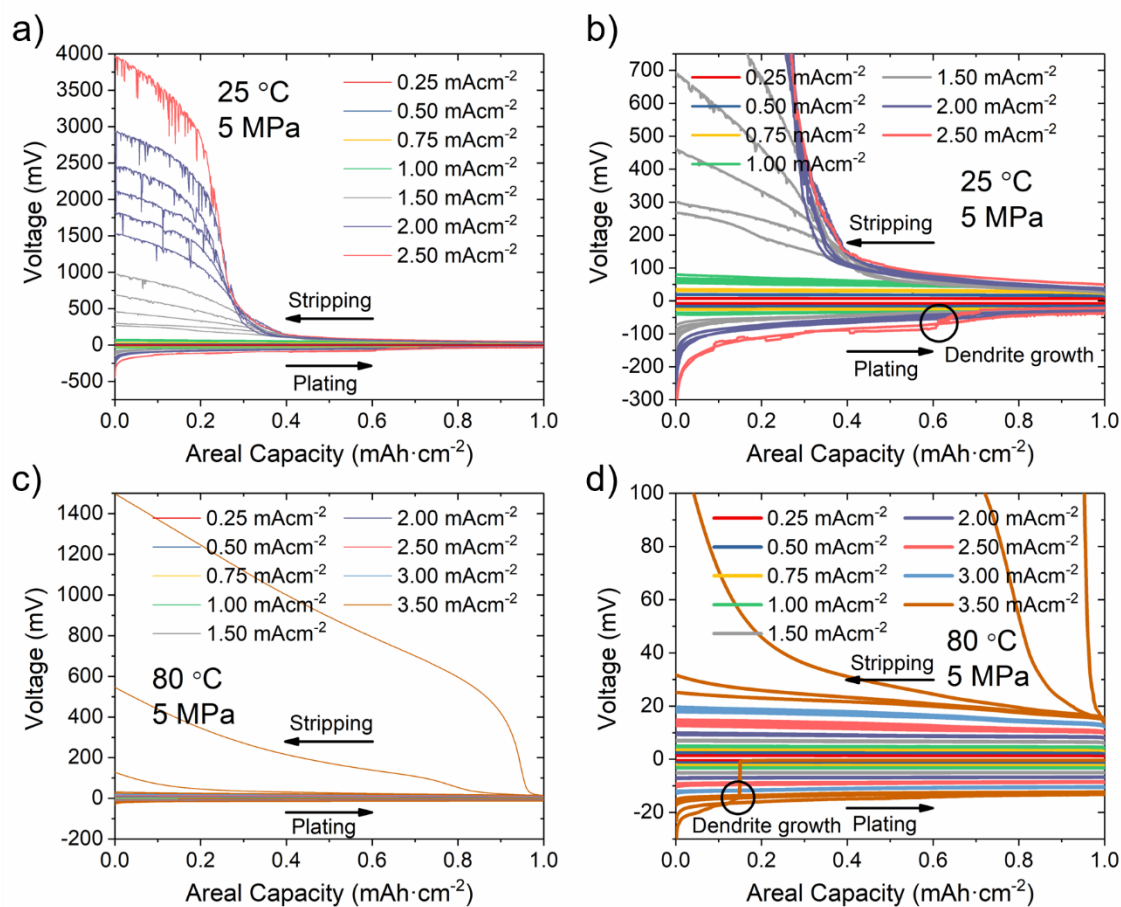


**Figure S6:** Nyquist plot showing the pressure dependence of cell impedance at a) -20 °C, b) 25 °C and c) 80 °C. Cells were placed under a formation pressure of approximately 25 MPa for 12 hours prior to the measurements. PEIS was carried out using a voltage perturbation of 5 mV in a frequency range of 0.4 MHz to 0.04 Hz, collecting 10 points per decade.

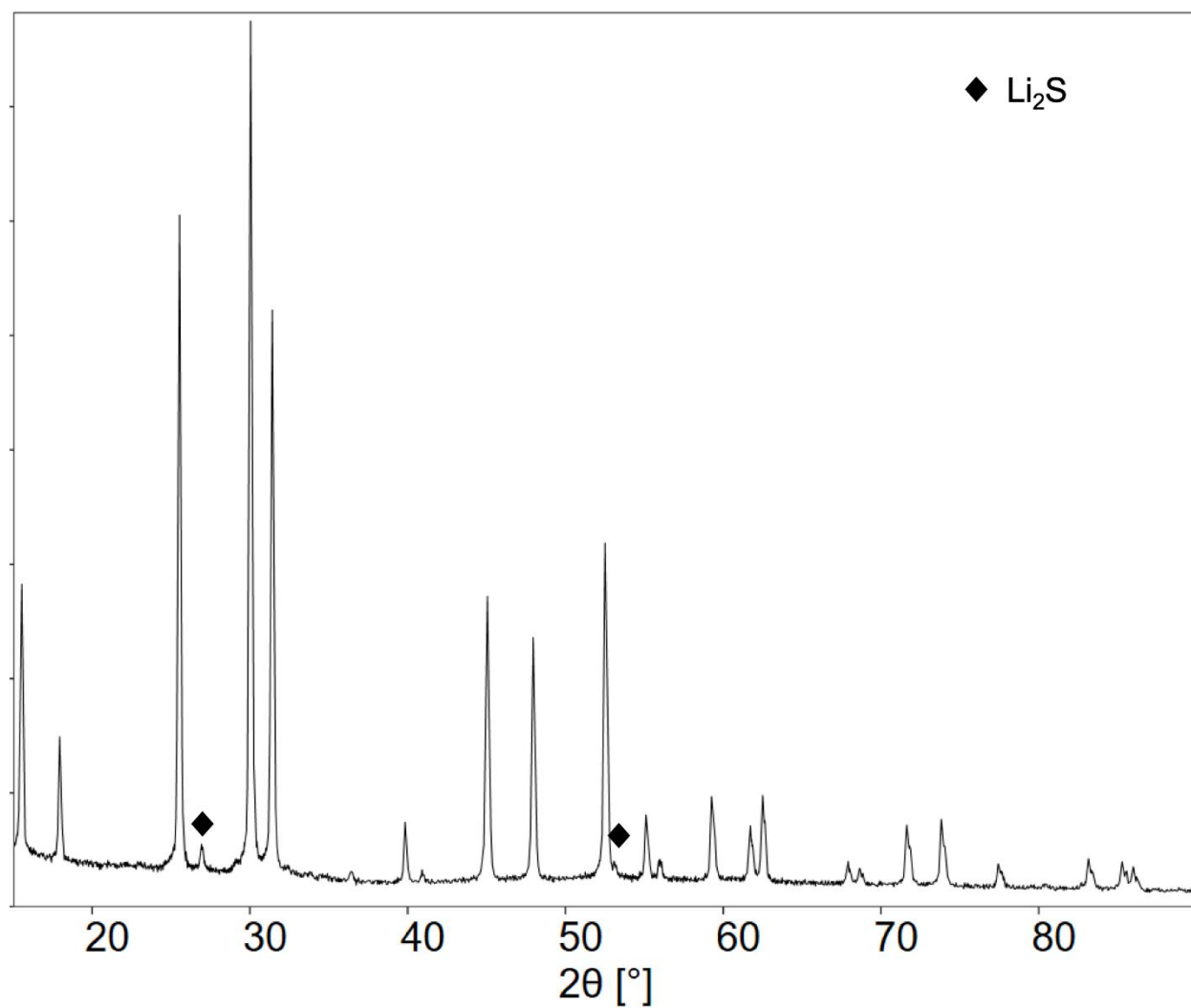


**Figure S7:** The pressure dependence of Bulk, grain boundary and SEI resistance of a Li/Li<sub>6</sub>PS<sub>5</sub>Cl/Li cell at a) -20 °C and b) 25 °C. Note that the error bars give the error in the least-squares fittings only.





**Figure S8:** 3-electrode cycling under 5 MPa pressure moving 1  $\text{mAh}\cdot\text{cm}^{-2}$  capacity at 25 °C a) full data and b) expanded, and at 80 °C c) full data and d) expanded.



**Figure S9:** Powder X-ray Diffraction (PXRD) of  $\text{Li}_6\text{PS}_5\text{Cl}$ . All peaks are assigned to the  $\text{Li}_6\text{PS}_5\text{Cl}$  cubic phase except those marked by ◆, which are assigned to  $\text{Li}_2\text{S}$  impurity.