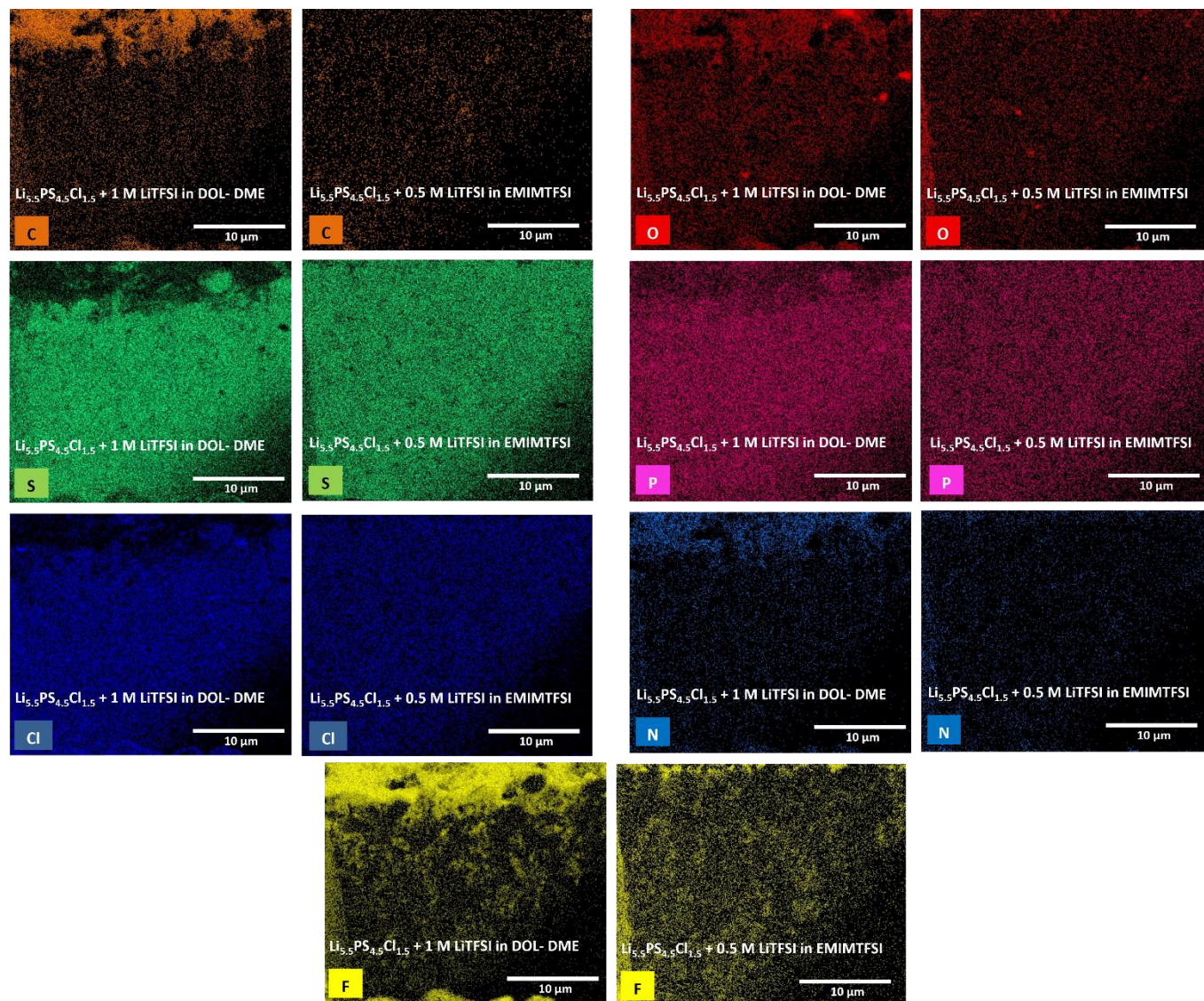
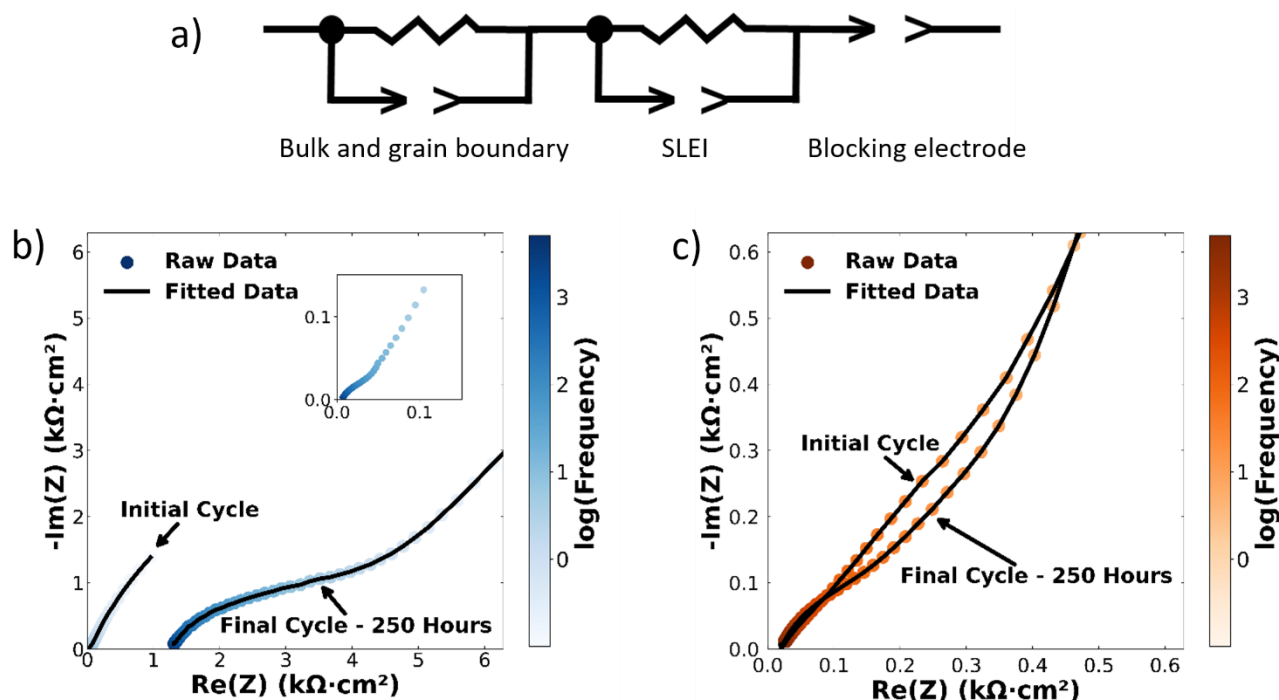


Faraday Discussions

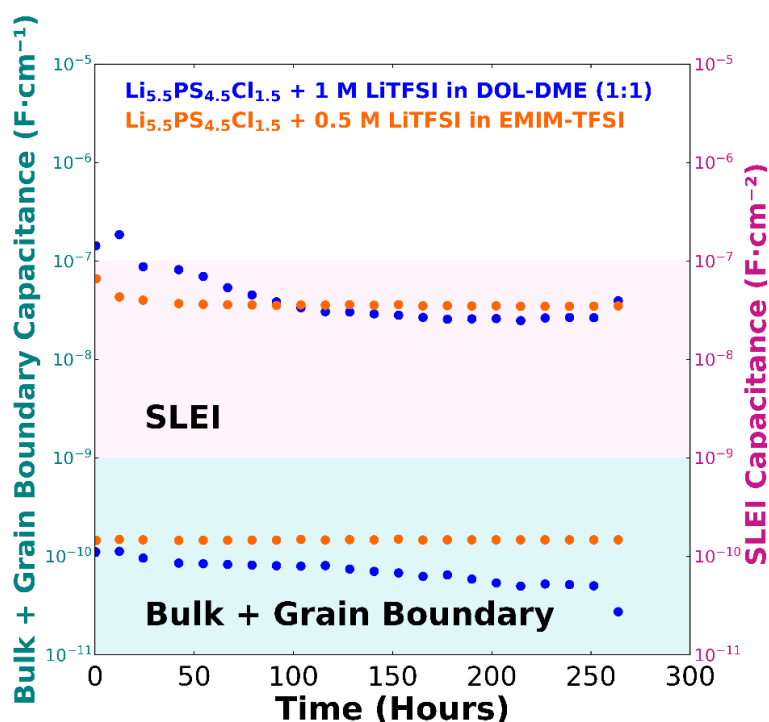
SUPPLEMENTARY INFORMATION



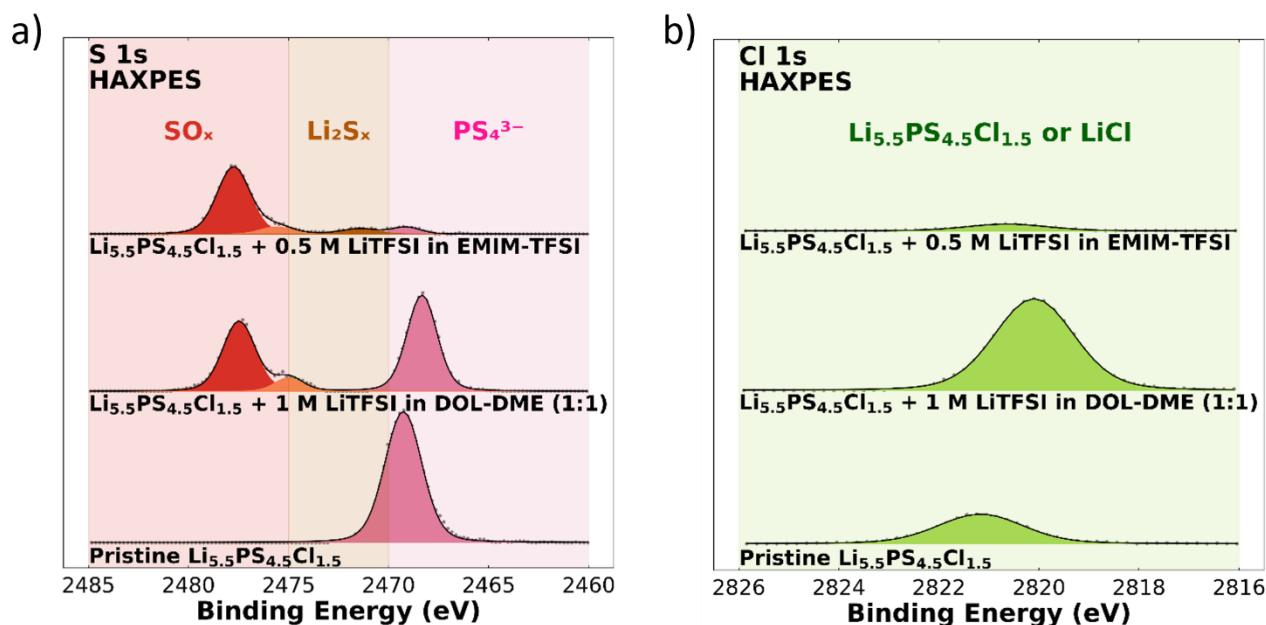
Supplementary Figure 1: EDX elemental distribution mapping corresponding with secondary electron imaging shown in Figure 1. The left image in each pair shows elemental mapping of a $\text{Li}_{5.5}\text{PS}_{4.5}\text{Cl}_{1.5}$ disk after immersion for 250 hours in 1 M LiTFSI in DOL-DME (1:1). The right image in each pair shows elemental mapping of a $\text{Li}_{5.5}\text{PS}_{4.5}\text{Cl}_{1.5}$ disk after immersion for 250 hours in 0.5 M LiTFSI in EMIMTFSI. The maps show the elemental distributions of carbon (orange), oxygen (red), sulfur (green), phosphorous (pink), chlorine (blue), nitrogen (light blue), and fluorine (yellow).



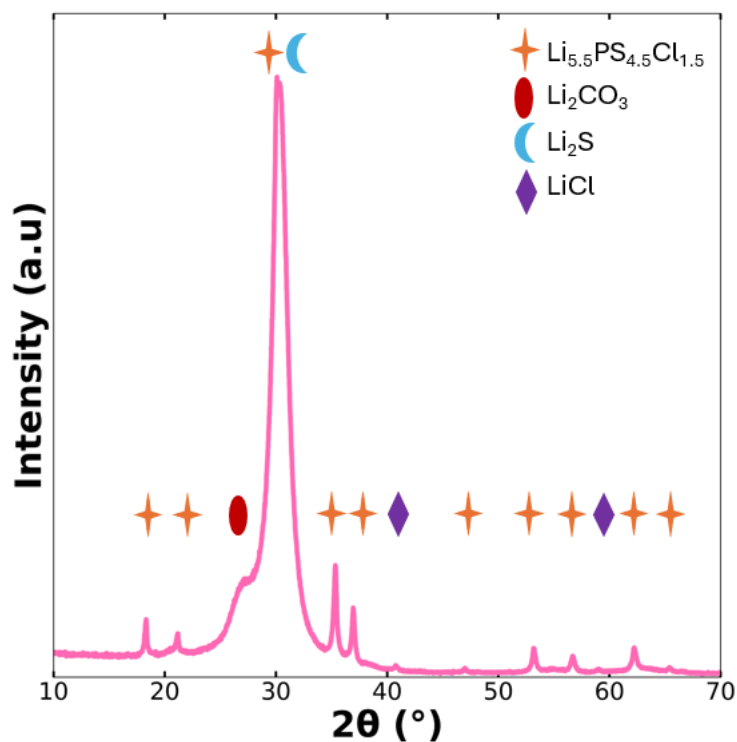
Supplementary Figure 2: Fitting of the time-resolved electrochemical impedance spectroscopy shown in Figure 2. a) The equivalent circuit model used to fit the data: $(R_{\text{bulk+gb}}C_{\text{bulk+gb}})(R_{\text{SLEI}}C_{\text{SLEI}})CPE$. Individual fittings of the first and final Nyquist plots for symmetric cells using the liquid electrolytes: b) 1 M LiTFSI in DOL-DME (1:1) (blue), and c) 0.5 M LiTFSI in EMIMTFSI (orange).



Supplementary Figure 3. Graph showing the normalised capacitances of bulk + grain boundary transport processes (green), and transport through the solid-liquid electrolyte interphase (pink) with time. Capacitances remain largely stable with time. Blue points show capacitances of transport processes in the symmetric cell with 1 M LiTFSI in DOL-DME (1:1) liquid electrolyte, and orange points show capacitances of transport processes in the symmetric cell with 0.5 M LiTFSI in EMIMTFSI liquid electrolyte.



Supplementary Figure 4: HAXPES of (a) the S 1s region, and (b) the Cl 1s region for: Pristine Li_{5.5}PS_{4.5}Cl_{1.5} (bottom), Li_{5.5}PS_{4.5}Cl_{1.5} immersed in 1 M LiTFSI in DOL-DME (1:1) for 250 h (middle), and Li_{5.5}PS_{4.5}Cl_{1.5} in 0.5 M LiTFSI in EMIMTFSI for 250 h (top). Fittings show the presence of SO₄²⁻ species (red), SO₃²⁻ species (orange), Li₂S_x species (brown) and PS₄³⁻ species (pink), and Li_{5.5}PS_{4.5}Cl_{1.5}/LiCl (light green).



Supplementary Figure 5: Powder X-ray diffraction of pristine Li_{5.5}PS_{4.5}Cl_{1.5}. Symbols indicate reference PXRD patterns: Li_{5.5}PS_{4.5}Cl_{1.5} (orange star) and common impurity phases of Li₂CO₃ (red oval), Li₂S (blue crescent) and LiCl (purple diamond). It is possible that some of the impurities are observed due to side reactions from moisture sensitivity.