Supporting Information for “Resolving Nanoscopic and Mesoscopic Heterogeneity of Fluorinated Species in Battery Solid-Electrolyte Interphases by Cryogenic Electron Microscopy”

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Methods

Electrochemistry

Type 2032 coin cells were assembled in an argon glovebox with a polymer separator (Celgard 2325), Li metal foil (Alfa Aesar) as the counter/reference electrode, and a Cu foil was used as the working electrode for cyclability and XPS characterizations. For TEM characterizations, a Cu TEM grid was used as the working electrode for Li plating, and a Cu TEM grid with an amorphous carbon film was used as the working electrode for SEI formation experiments. The electrolyte used was 1.0 M LiPF$_6$ in 1:1 v/v ethylene carbonate/diethyl carbonate for SEI formation in FEC-free systems. In studies with FEC electrolyte additive, 1.0M LiPF$_6$ in 90 vol.% 1:1 v/v ethylene carbonate/diethyl carbonate and 10 vol.% fluoroethylene carbonate was used for XPS, Cryo-TEM of Li, and cycling. For Cryo-STEM of the SEI, the electrolyte was 1.0M LiClO$_4$ in 90 vol.% 1:1 v/v ethylene
carbonate/diethyl carbonate and 10 vol.% fluoroethylene carbonate. In all cases, cells were assembled with 75 μL of electrolyte.

Pre-formed Cu SEIs were deposited by assembling Li/Cu half cells in EC/DEC + 10 vol. % FEC 1.0 M LiPF₆ electrolyte, short-circuiting the cell for 24 hours, then disassembling the cell in an argon-filled glovebox. The electrode was rinsed thoroughly with diethyl carbonate (DEC) to remove residual electrolyte, the Li counter electrode replaced, and a new cell assembled with EC/DEC 1.0 M LiPF₆ electrolyte. Control cells were also short-circuited for 24 hours before testing.

Battery cycling was conducted at a current density of 1 mA cm⁻² and a capacity of 1 mAh cm⁻² (Arbin). Li plating on the TEM grid was conducted at a current density of 1 mA cm⁻² and a capacity of 0.2 mAh cm⁻². SEI formation on the carbon film TEM grid was conducted using linear sweep voltammetry with a sweep rate of 0.5 mV s⁻¹ from open circuit to 10 mV, and potentiostatically held at 10 mV for 8 hours (Biologic VMP3).

**Cryo-TEM preparation**

The batteries were disassembled in an argon-filled glovebox and rinsed with DEC to remove Li salts. Our rinsing procedure attempts to minimize artifacts by using minimal force and solvent volume; approximately 50 μL was carefully dropped onto the TEM grid after the battery is disassembled. Immediately after rinsing, the sample was sealed in an air-tight container, submerged in liquid nitrogen, and the container crushed to rapidly
expose the sample to cryogen without any air exposure. While immersed in liquid nitrogen, the sample was loaded into the cryo-EM holder (Gatan 626) and inserted into the TEM column. The cryo-EM holder uses a specialized shutter to prevent air exposure and condensation onto the sample, which preserves the specimen in its native state. Once inside the TEM column, the temperature was maintained at ~ -178 °C.

**Electron microscopy**

All cryo-(S)TEM characterizations were carried out using an FEI Titan 80-300 environmental (scanning) transmission electron microscope operated at an accelerating voltage of 300 kV with an energy resolution of 1 eV. The instrument is equipped with an aberration corrector in the image-forming lens, which was tuned before each sample analysis. The dose rate for HRTEM imaging was 1000 e⁻ Å² s⁻¹ with an exposure of 0.15 – 0.3 s using a Gatan OneView CMOS camera. The beam was blanked between images to minimize total e⁻ dose. Cryo-STEM EELS characterization was performed with a C2 aperture of 50 μm, a beam current of 75 pA, a camera length of 48 mm, and a pixel dwell time of 10 ms. These settings give a convergence angle of 9.3 mrad and an acceptor
angle of 27.8 mrad. EELS spectra were acquired on a GIF Quantum 966 with a dispersion of 0.25 eV/channel in Dual EELS mode, with the low-loss centered on the zero-loss peak and the core-loss centered on the O K edge. Thus, the Li K, O K, and F K edges can be simultaneously acquired. Energy drift during spectrum imaging was corrected by centering the zero-loss peak to 0 eV at each pixel. Maps were computed through a two-window method, with a pre-edge window fitted to a power-law background and a post-edge window of 20 – 40 eV on the core-loss signal. Some maps were spatially re-binned to increase signal to noise.

**XPS characterization**

Cu foil working electrodes after 5 Li plating and stripping cycles were prepared in an Ar glove box and rinsed with approximately 0.5 mL DEC to remove Li salts, then transferred to the XPS chamber using a vacuum transfer holder. XPS analysis was obtained on a PHI VersaProbe 1 scanning XPS microprobe with an Al Kα source. The XPS depth profiles were obtained by sputtering, with a sputter rate of 4 nm min⁻¹ calibrated by SiO₂.
Figure S1. XPS depth profiling at the Li and C binding energy.

Figure S2. EELS of the F K-edge from the Li SEI.
Figure S3. Cryo-STEM EELS mapping of the Cu L-edge from Figure 2b.

Figure S4. Linear sweep voltammetry of a C film TEM grid to 10 mV at 0.5 mV s⁻¹.

Figure S5. Comparison of F K-edge EELS in F-rich particles to LiF.
Figure S6. Bright field TEM image of LiF@Li$_2$O nanoparticle.
Figure S7. Effect of LiF on the current collector on Li metal cyclability.