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## **Electronic Supplementary Information**

## Effect of Copper Oxide on HF Reduction

Copper foil is the conventional current collector of choice for lithium metal batteries due to its stability at anode potentials and resistance to alloying with lithium. However, most researchers use copper foils which have been cleaned only with water and organic solvents if not purely as-received, leaving intact the native copper oxide layer. In contrast, reports in literature of columnar lithium metal result from work performed using acid cleaned working electrode substrates, with the effect of copper oxide on this growth mode being unclear. To investigate this, copper substrates with and without the native oxide layer were tested as shown in Figure S1. Both copper foil and evaporated copper films which have been acid cleaned to remove the native oxide layer and expose metallic copper exhibit a characteristic voltage plateau at ~2 V vs Li/Li+ when cycled at 0.5 mA/cm<sup>2</sup> in LP30 electrolyte (1 M LiPF<sub>6</sub> in EC/DMC=1/1 (wt/wt)) with 100 ppm HF added, indicative of the electrocatalytic reduction of HF. In contrast, as-received copper foil which has only been cleaned with water and ethanol to remove carbonaceous deposits does not have a high voltage HF reduction plateau and the charge passed while still at positive potentials is over twice that of the oxide-free copper substrates. The shape of the curve for the sample with a native oxide layer is qualitatively similar to that reported by Huang et al. for SEI formation on CuO nanowires in LiPF<sub>6</sub>/carbonate electrolytes.<sup>37</sup> However, subsequent plating through the initial SEIs show that all three working electrodes yield a columnar morphology as evidenced by optical images (Figure S2). This demonstrates that electrochemical characterization alone is insufficient for predicting lithium metal microstructure. All experiments in this study used acid cleaned evaporated copper films for consistency. It is also notable that LillCu cells assembled using oxide containing copper foils which have been cleaned only with DI water and ethanol exhibit a similar OCV to cells with acid cleaned working electrodes (~3.3 V vs  $Li/Li^+$ ), while uncleaned copper foil containing adventitious carbon exhibits a much lower OCV of less than 3 V, and this leads to macroscopically nonuniform lithium deposition. We believe that the precise role of the native copper oxide layer and other surface characteristics of current collectors in lithium metal batteries is deserving of additional studies to help inform more scalable surface treatments and cleaning procedures.



Figure S1: Copper substrates which have been acid cleaned to expose metallic copper (orange and blue) exhibit an HF reduction plateau at ~1.9 V vs  $Li/Li^+$ , while copper substrates with an intact native oxide layer (red) do not. Cells were cycled at 0.5 mA/cm<sup>2</sup> in LP30 electrolyte with 100 ppm added HF.



Figure S2: Columnar lithium metal can be observed optically as the highly monodisperse structure results in a blue-purple coloration. This occurs when lithium is electrodeposited at  $0.5 \text{ mA/cm}^2$  from electrolyte with 100 ppm added HF on copper working electrodes with (a) and without (b) acid cleaning to remove the native oxide layer.

Sample	%Li	%C	%0	%F
SEI on Cu (as-received)	33.42	6.29	2.43	57.86
SEI on Cu (+100 ppm HF)	41.39	4.31	2.11	52.19
SEI on Li (as-received)	43.67	6.26	4.85	45.22
SEI on Li (+100 ppm HF)	54.51	6.05	4.97	34.47

*Table S1: Atomic percentages from XPS of elements in the SEI of samples on Cu and electroplated Li formed in electrolytes with and without 100 ppm added HF.* 



Figure S3: XPS depth profiling data of the SEI formed on coper in (a) as-received and (b) 100 pm HF added electrolytes. The sputter rate, calibrated by SiO2, was  $\sim 2$  nm/min. The peak shift in the Li and F spectra is an artifact created by the Ar ion sputtering.



Figure S4:  $I(\chi)$  at the LiF (111) diffraction peak of SEI formed on copper by galvanostatically bringing the electrode down to 0 V vs Li/Li<sup>+</sup> at 0.5 mA/cm<sup>2</sup> in as-received LP30, showing no indication of crystallographic texturing.



Figure S5: Background subtracted 1D scattering patterns at different  $\chi$  angles showing the LiF (111) peak for SEI formed on copper by galvanostatic cycling at 0.5 mA/cm<sup>2</sup> down to 0 V vs Li/Li<sup>+</sup> in LP30 with 100 ppm added HF. The I(q) integration done at  $\chi$ =70±2.5° shows a peak at q=2.71Å<sup>-1</sup> while the integration at  $\chi$ =55±2.5° does not, indicative of (111) crystallographic texture.



Figure S6:  $I(\chi)$  at the Li (110) diffraction peak from the scattering pattern of SEI formed on lithium metal electroplated in as-received LP30 by galvanostatic cycling at 0.5 mA/cm2 to a capacity of 1 mAh/cm<sup>2</sup> showing no peaks, indicating a lack of crystallographic texturing for lithium metal.





Figure S7: XPS depth profiling data of the SEI formed on lithium metal in (a) as-received and (b) 100 pm HF added electrolytes. The sputter rate, calibrated by SiO2, was  $\sim 2$  nm/min.



Figure S8: Top-view SEM micrographs of lithium metal columns electroplated from LP30 electrolyte with 100 ppm added HF at (a)  $0.2 \text{ mA/cm}^2$ , (b)  $0.5 \text{ mA/cm}^2$ , and (c)  $1.0 \text{ mA/cm}^2$ . All scale bars are 500 nm. The average column diameter for each current density is (a) 153 nm, (b) 137 nm, and (c) 125 nm.



Figure S9: 1D GISAXS Intensity vs  $q_y$  profiles from a cell with 100 ppm added HF cycled from OCV (a), to a plated capacity of 1 mAh/cm<sup>2</sup> at 0.5 mA/cm<sup>2</sup> (b), stripped to 1 V vs Li/Li<sup>+</sup> (c), followed by a second plating half cycle to 1 mAh/cm<sup>2</sup> (d). Intensity oscillations show evidence for the presence of a columnar morphology. The absence of oscillations in (d) indicate the columnar morphology was not maintained after stripping to 1 V vs Li/Li<sup>+</sup>.