

Supporting Information for

**Insights on the work function of the current collector
surface in anode-free lithium metal batteries**

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Supporting Figures

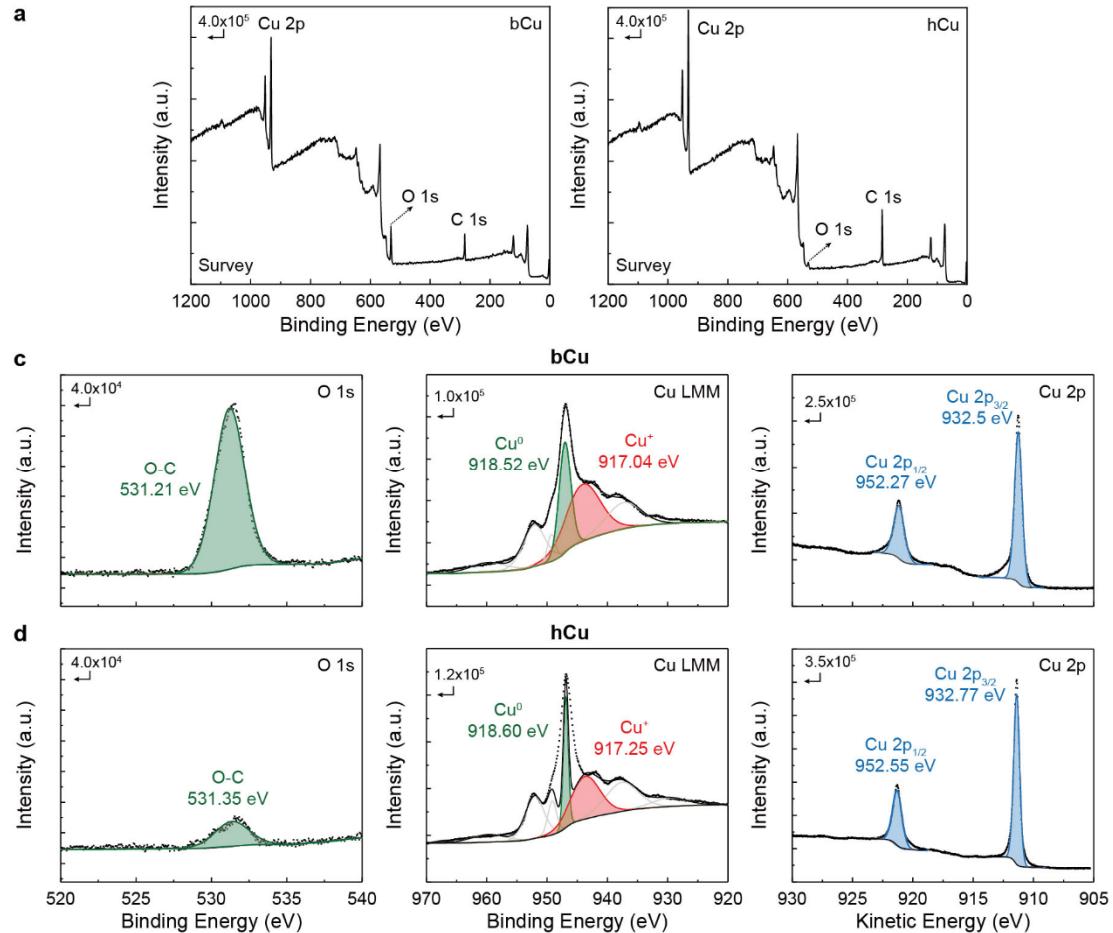


Fig. S1 Surface composition analysis using X-ray photoelectron spectroscopy (XPS). (a) Survey peak analysis for bCu and hCu. (b) O 1s, Cu LMM, and Cu 2p XPS spectra for bCu (top) and hCu (bottom).

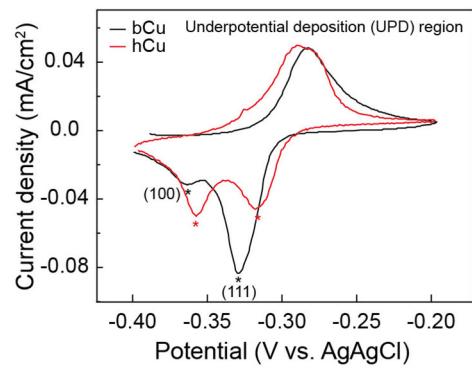


Fig. S2 Cyclic voltammograms for hCu and bCu film in $0.1 \text{ M HClO}_4 + 1 \text{ mM Pb(Cl)}_2$ at a scan rate of 10 mV/s in a voltage range from -0.2 V to -0.4 V (vs. Ag/AgCl).

	bCu	hCu
Conductivity [S cm ⁻¹]	9.68×10^5	1.26×10^6
R [ohm sq ⁻¹]	1.2×10^{-4}	7×10^{-5}

Table. S1 Electrical surface conductivity and resistance of bCu and hCu measured using 4-point probe method.

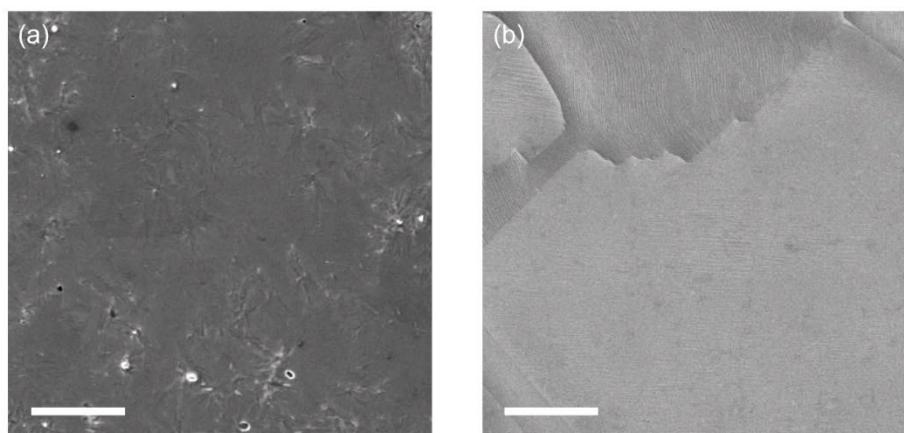


Fig. S3 Surface morphology of the Cu current collector surfaces. SEM images of (a) bCu and (b) hCu surface. Scale bars; 5 μm .

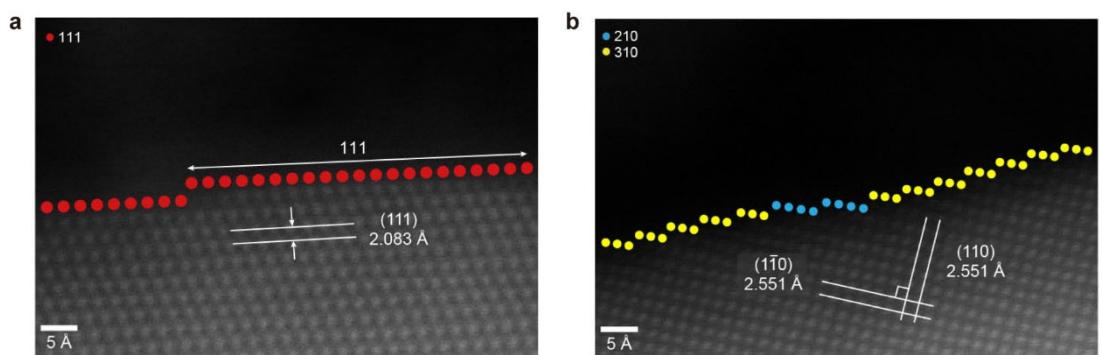


Fig. S4 Surface structure of Cu current collector after 10 cycles operation. TEM analysis for (a) bCu and (b) hCu after the repeated Li plating/stripping under 1 mA cm^{-2} / 1 mAh cm^{-2} condition for 10 cycles.

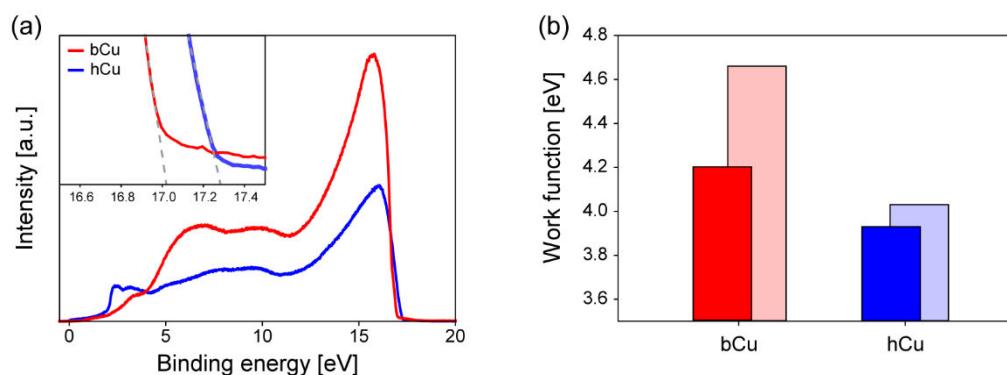


Fig. S5 Work function analysis for the Cu current collectors. (a) UPS analysis results for the bCu and hCu current collectors. (Inset: UPS spectra of the cut-off region) (b) Work functions of bCu and hCu current collectors investigated by UPS analysis and DFT simulation. Dark color and pale color indicate the work function obtained by each UPS analysis and DFT simulation.

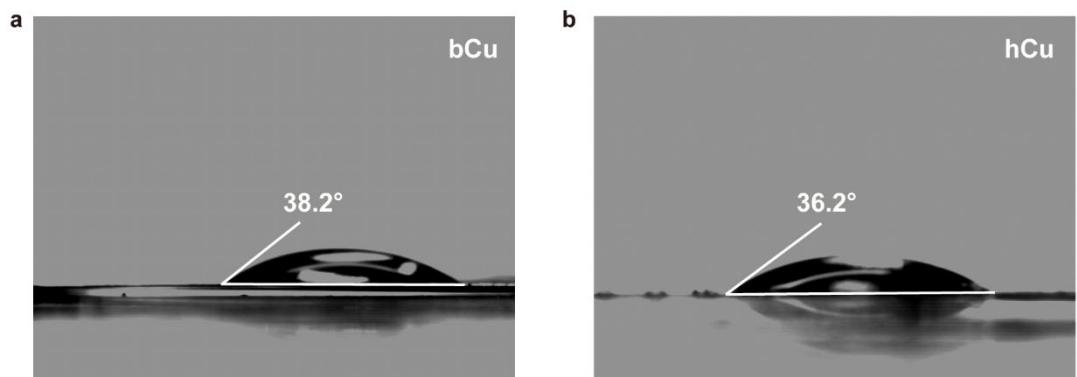


Fig. S6 Electrolyte wetting ability of bCu and hCu. Contact angle of the electrolyte drop (1 M LiFSI DME) on (a) bCu and (b) hCu.

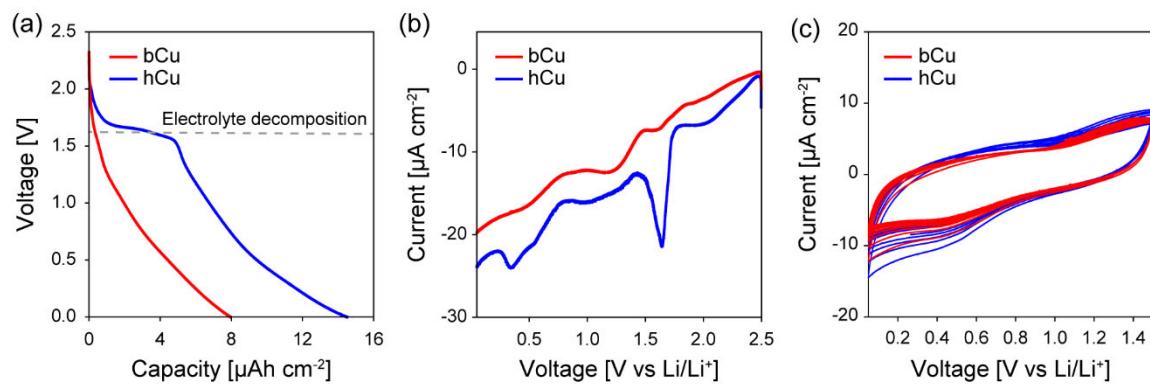


Fig. S7 Electrochemical analysis of the electrolyte decomposition on the current collector surface. (a) Galvanostatic reduction at 0.05 mA cm^{-2} , (b) linear sweep voltammetry analysis at a sweep rate of 1 mV s^{-1} , and (c) 10 cycles of cyclic voltammetry at a scan rate of 1 mV s^{-1} in the range of 0.05 to 1.5 V voltage range for bCu and hCu current collector.

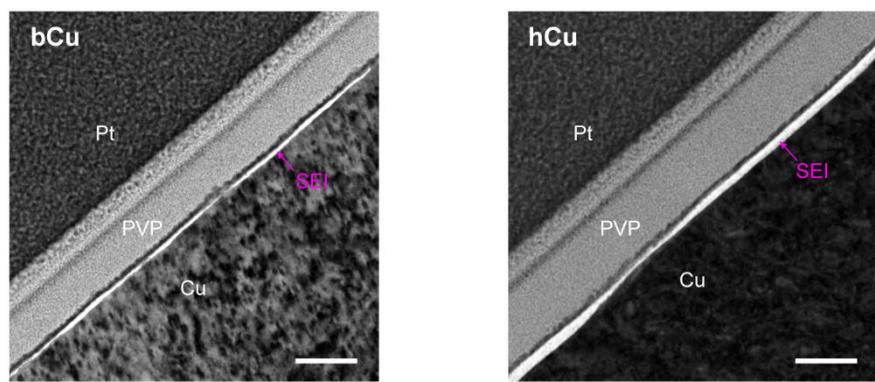


Fig. S8 Low magnification TEM images of the cross-section of bCu and hCu after the CV cycling (Fig. S7). Scale bars; 100 nm.