# **Supporting Information**

# Lithiophilic 3D Porous CuZn Current Collector for Stable Lithium-Metal Batteries

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## **EXPERIMENTAL METHODS**

### 1. Current collector preparation

3D CuZn and 3D Cu current collector preparation steps are depicted in Figure 3. First, a commercially purchased brass sheet (H62, 38 wt% Zn) with 100 µm thickness was sliced into 15 mm diameter discs (brass sheets). These brass sheets were then attached to glass sheets with glue and dried overnight. This sheet assembly was then placed in 10M hydrochloric acid at 60 °C and allotted 2, 4 and 8 h for dealloying. Corrosion perforation of the brass sheet occurred after 8 h. 3D CuZn current collectors, named 2h-3D CuZn, 4h-3D CuZn and 8h-3D Cu, were prepared in parallel. After corrosion perforation, dealloyed brass sheets were then rinsed using distilled water and ethanol for several times. Prior to experimental use, samples were placed in a 60°C tube furnace for 12 h with nitrogen gas and dried to obtain 3D porous Cu current collectors with different dealloying degrees.

#### 2. Material characterization

X-ray diffraction (XRD) analysis was conducted to investigate crystalline phases within the 20 range of 30~80 ° using a 10° per minute increment. Sample morphology and structure was observed via scanning electron microscopy (Hitachi S-4700, Hitachi, Japan, FESEM) at 10 kV and transmission electron microscopy (TEM, FEI, Tecnai G2 F30) with an energy dispersive X-ray (EDX) attachment. After cycling, batteries were carefully disassembled in an argon-filled glove box to obtain current collector/Li composite anodes and observe morphology. The anode composites were then rinsed with diethyl carbonate (DEC) three times to remove electrolytes and dried in glove box at room temperature before characterization.

# 3. Electrochemical characterizations

CR2025 coin cells were assembled in an argon-filled glove box for CE and performance testing. Planar Cu and 3D porous current collectors were used as working electrodes, Li metal as counter electrodes, and Polypropylene (PP) as separator. 80  $\mu$ L of an electrolyte composition with 1 M LiPF<sub>6</sub> mixture, 1:1 volume ethylene carbonate (EC) and diethyl carbonate (DEC) ratio, and 0.1M LiNO<sub>3</sub> additive was used. Cycling and rate performance was then conducted using LAND battery programs. Batteries were initially cycled for three cycles from 0.01 ~ 1.5 V at a current density of 0.05 mA cm<sup>-2</sup> to stabilize SEI and remove electrode impurities. Then, Li was plated a 1 mAh cm<sup>-2</sup> on the current collectors and removed at 1.5 V for each cycle. For symmetric tests, 4 mAh cm<sup>-2</sup> Li metal was initially plated at 0.5 mA cm<sup>-2</sup>. Testing was then performed at 0.5 mA cm<sup>-2</sup> and 1 mA cm<sup>-2</sup> with a plating/stripping 1 mAh cm<sup>-2</sup> Li capacity.

### 4. Computational Method

Density functional theory for total energy and geometric optimization calculations were performed using Vienna Ab-initio Simulation Packages (VASP).<sup>1-2</sup> Projected augmented wave (PAW)<sup>3</sup> formalisms were used for electron-ion interactions. Generalized gradient approximations formulated by Perdew, Burke, and Ernzerhof (PBE)<sup>4</sup> were employed for exchange-correlation functions. 400 eV energy cutoffs for plane-wave expansion of the wavefunctions were also applied. A supercell of Cu(111), Cu(200), CuZn(100), CuZn(110) surfaces with at least 6 layers of atoms (containing 24, 48, 24 and 24 substrate atoms, respectively) were constructed for Li atom adsorption calculations. A vacuum layer of 10 Å in the Z direction was also created to avoid the interactions between adjacent surfaces. In all calculations 3 layers of atoms at the bottom were fixed to mimic bulk structures, while only atoms in the top 3 layers were allowed to relax until the Hellmann-Feynman forces were less than 0.01 eV Å-1. Adsorption energies were calculated with the equation: Eads=Etotal-Esubstrate-ELi-atom, where Etotal is the total energy

of the system after Li atom adsorption, Esubstrate is the total energy of the clean substrate before adsorption, and ELi-atom is energy of a free Li atom.

# SUPPLEMENTARY DISCUSSION



Figure S1. Cu-Zn phase diagram.

**Table S1**. Single-atom Li adsorption energy at different positions on the stable surface (unit:eV)

Crystal planes Adsorption position	Cu-111	Cu-200	CuZn-100	CuZn-110
Α	-1.293	-1.119	-0.878	<b>A-Cu</b> -1.280 <b>A-Zn</b> -1.108
В	-1.392	-1.230	-1.186	-1.406
H	-1.392	-1.380	-1.42/	-1.244

A, B, and H represent Li atom adsorption sites on the stable surface. Specifically, A represents the atom-top site, B represents the bond-top site and H represents the hollow-top site. A-Cu and A-Zn represent Li atoms adsorbed on the top site of Cu and Zn, respectively.



Figure S2. Cu and brass H62 XRD patterns

XRD measurements were carried out to analyze the phase compositions of Cu and brass H62, as shown in Figure S2. Diffraction peaks of planar Cu at  $2\theta$ =43.34°, 50.47° and 74.17° correspond to (111), (200), and (220) planes of Cu (PDF#70-3039). Brass was composed of Cu0.64Zn0.36 and CuZn, which consisted of a solid solution and intermetallic compound composed of Zn and Cu, respectively.<sup>1</sup> Corresponding indices of diffraction peaks at  $2\theta$ =42.32°, 49.27° and 72.24° are (111), (200), (220) of Cu0.64Zn0.36 (PDF#50-1333), while diffraction peaks at  $2\theta$ =43.47°, 63.01°, and 79.62° correspond to (110), (200), and (211) planes of CuZn (PDF#02-1231).



**Figure S3**.TEM images of Planar Cu a) and brass H62 b),c). d-f) EDX mapping images of brass H62.

Figure S3a-c presents the TEM images of planar Cu and brass H62. (111) and (200) crystal planes of Cu correspond with 0.1806 and 0.2086 nm lattice spaces, while 0.2950 and 0.2080 nm lattice spaces correspond to (100) and (110) CuZn phase crystal planes (intermetallic compound) respectively. At Cu0.64Zn0.34 , the  $\alpha$  phase of solid solution, the (111) and (200) crystal planes appear. EDX mapping images of brass H62 (Figure S3d-f) show uniform distribution of Cu and Zn elements in the alloy.



Figure S4. XRD patterns of brass H62 after different dealloying durations.

Brass H62 XRD pattern evolutions after different dealloying time are shown in **Figure S4**. With increases in dealloying time, alloy gradually weaken and disappear, while Cu peaks begin to appear and gradually strengthen. This indicates a gradual reduction in CuZn alloy phases within the porous structure. At 8h, the brass had completely converted into pure 3D porous Cu.



**Figure S5**. a,b) Symmetric cell cycles with 2h-3D CuZn and 8h-3D Cu current collectors at 1.0 mA cm<sup>-2</sup> and 0.5 mA cm<sup>-2</sup>. c) Voltage profiles for the first three cycles and between d) 300~312 h in 2h-3D CuZn and 8h-3D symmetric cell Cu current collectors at 0.5 mA cm<sup>-2</sup>.

2h-3D CuZn and 8h-3D Cu current collectors were selected to assemble cells with Li metal to test long-term cycling performance, as shown in Figure S5a and b. 2h-3D CuZn exhibited superior cycle life over 1000 and 450 h with small polarization at 0.5 and 1 mA cm<sup>-2</sup>. However, 8h-3D Cu suffered significant polarization and voltage oscillation at approximately 320 and 160 h at 0.5 and 1 mA cm<sup>-2</sup>. This random voltage oscillation was attributed to disordered growth of Li dendrites and the formation of "dead Li". Voltage profiles during the first three cycles and 300~312 h at 0.5 mA cm<sup>-2</sup> are shown in Figure S5c and d. During the initial cycles,

2h-3D CuZn current collector exhibited a small overpotential of about 18 mV, while 8h-3D Cu exhibited an overpotential greater than 40mV. When time increased to 300~312 h (Figure S5d) the curve of 8h-3D Cu fluctuated sharply while 2h-3D CuZn remained stable, which indicates uneven Li dendrite growth. It illuminates that the lithiophilic residual CuZn alloy in the frameworks is favorable to the enhancement of cycling stability.



**Figure S6**. Cross-sectional morphology of different current collectors after total Li deposition at 3mAh cm<sup>-2</sup> and 2 mA cm<sup>-2</sup>: a) Planar Cu, b) 2h-3D CuZn, c) 4h-3D CuZn, d) 8h-3D Cu. Distance between white and yellow dotted lines represent thickness of ordinary current collector and Li layer grown outside.

As shown in Figure S5. For planar Cu, the Li layer is grown on the Cu sheet surface with a thickness of 48.2  $\mu$ m (Figure S5a). As for 4h-3D CuZn and 8h-3D Cu current collector, thickness of surface Li layers were 8.2 and 13.7  $\mu$ m, respectively (Figure S5b, c). This thickness difference resulted from lithiophilicity of CuZn phases in 4h-3D CuZn, which induced Li growth in the inner pores and improved the 3D porous structure efficiency. Moreover, total thickness of 2h-3D

CuZn after deposition was about 100  $\mu$ m, which was quite similar to the Cu sheet alone (Figure S5d). This illustrates excellent lithiophilicity and almost complete inner pore Li deposition, which contributes to superior electrochemical performance.

# REFERENCES

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