A Solid Solution Alloy Current Collector to Stabilize Zinc Metal Anode

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Experimental Section

Material Preparation

Fabrication of Cu–In current collector: Copper (Cu, 99.9999%) and indium (In, 99.95%) were combined at a mass ratio of 98:2 as raw materials to produce Cu alloy ingots using a vacuum induction melting furnace. The ingots were wire-cut into sheets, rolled to a thickness of 90~100 μm, and then cut to the desired sizes. Before testing, both Cu–In and Cu current collectors were polished with 3000-grit sandpaper to achieve a smooth, reflective surface.

Synthesis of MnO_2: A total of 14 mL hydrazine hydrate solution was added dropwise to 200 mL of 4 mmol L^{-1} $Mn(Ac)_2 \cdot 4H_2O$ solution and stirred for 5 minutes before undergoing hydrothermal treatment at 180 °C for 12 hours. The resulting $Mn(OH)_2$ was filtered, washed with water several times, and dried in a vacuum oven at 60 °C. Subsequently, 1 g of $Mn(OH)_2$ was dispersed in 250 mL of water and sonicated for 10 minutes to form a uniform suspension. Following this, 50 mL of 10 wt.% NaClO solution was added dropwise to the $Mn(OH)_2$ dispersion. The final layered δ-MnO_2 nanoplates were obtained after a 24-hour reaction with continuous stirring.

Characterization

Scanning electron microscopy (SEM, FEI Quanta 450 FEG SEM) was employed to examine the morphological evolution of the current collector during galvanic corrosion. X-ray diffraction (XRD) analysis was performed using a Bruker D2 Phaser with Cu Kα radiation ($\lambda = 0.15418$ nm), operated at 30 kV and 10 mA. Transmission electron microscope (TEM) was conducted using the JEOL/JEM-F200.

Electrochemical measurement

Asymmetrical cells were assembled using CR2032 coin cells with 100 μL of 2 M $ZnSO_4$ aqueous electrolyte, with the electrodes separated by Whatman glass fiber membranes. For full-cell assembly, Zn was pre-deposited in a two-electrode system at a constant current of 1 mA cm^{-2}, targeting a deposition capacity of 5 mAh, which corresponds to an areal capacity of 4.42 mAh cm^{-2} for a 1.2 cm diameter electrode. The actual Zn deposition thickness, mass, and other relevant parameters are detailed in Fig. S1. The cathode was prepared by coating a mixture of MnO_4, carbon black, and PVDF (mass ratio 7:2:1) onto carbon cloth, with an areal mass loading of 2–2.5 mg cm^{-2}. The electrolyte volume was fixed at 100 μL of 2 M $ZnSO_4$.

Cyclic voltammetry (CV) was performed on an electrochemical workstation (CHI 760E), with measurements conducted in a coin cell at a scan rate of 2 mV s^{-1}. The Tafel tests were conducted on an electrochemical workstation (CHI 760E) in a three-electrode system using 2 M $ZnSO_4$ as the electrolyte, with a scan rate of 5 mV s^{-1}. Galvanostatic charge/discharge tests were carried out using LAND and NEWARE testing systems.

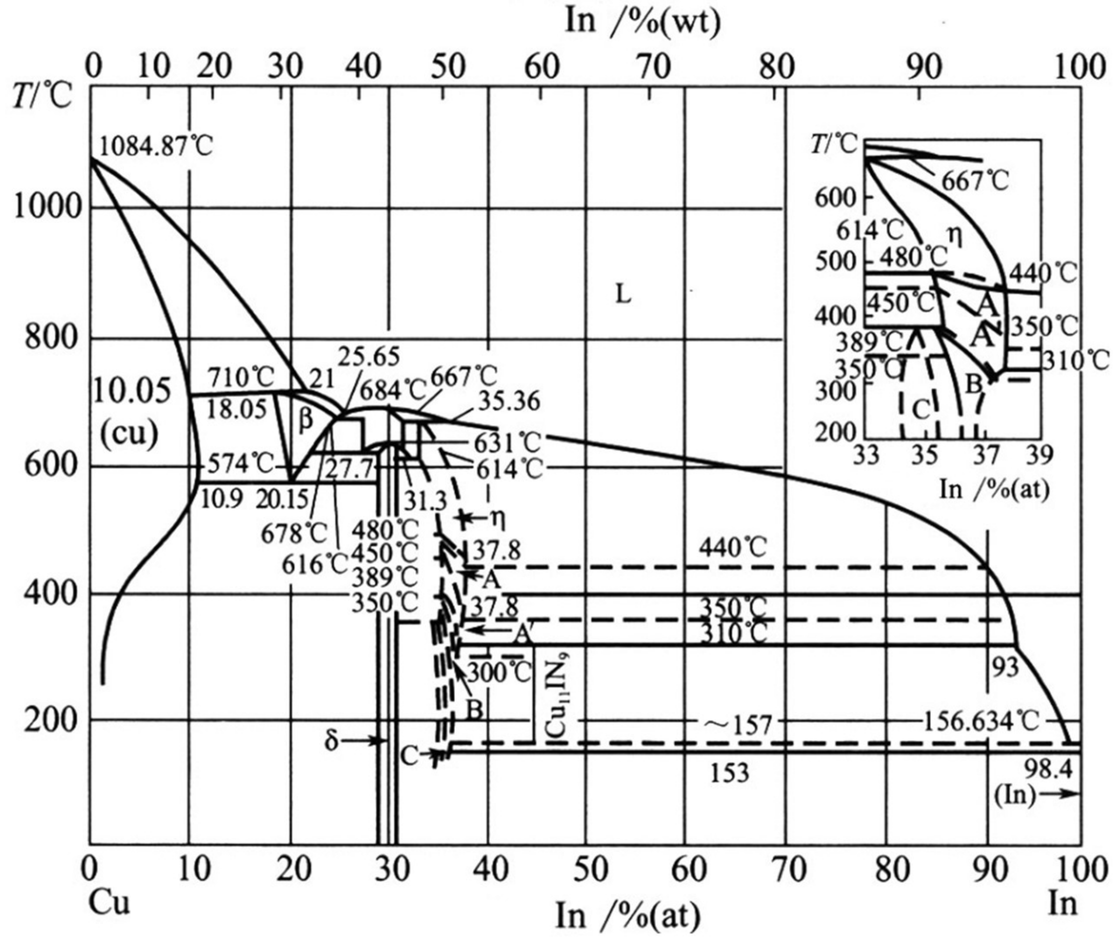

Fig. S1 Cu–In phase diagram[1].

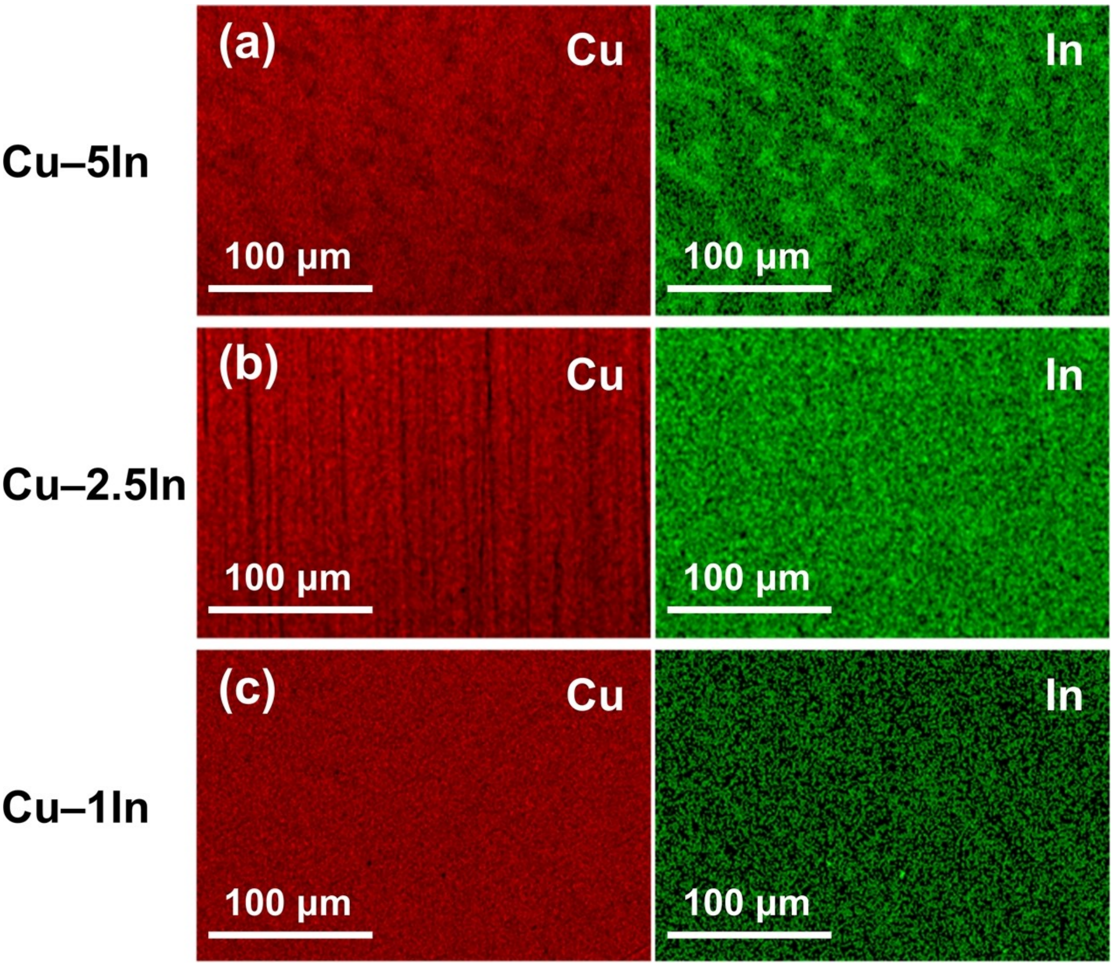

Fig. S2 EDS mapping of three Cu–In alloy and pure Cu.

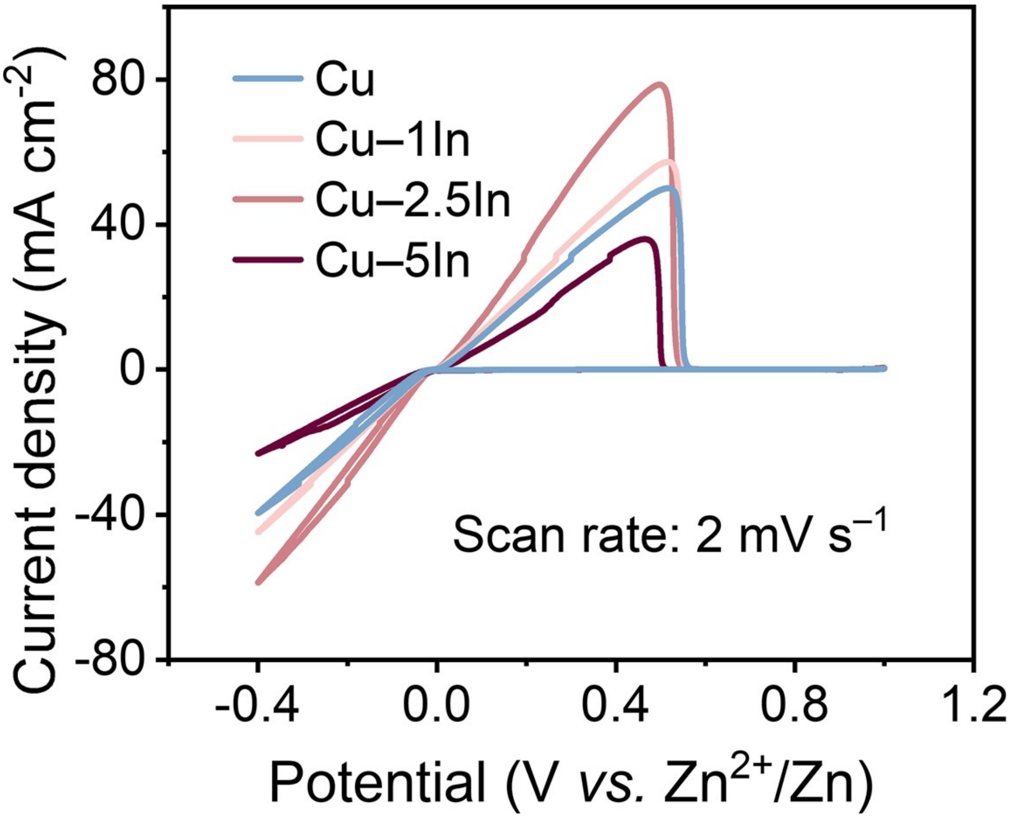

Fig. S3 CV curves of asymmetric cells.

	Cu-In	Cu
Mass of deposited Zn	29 µm	35 µm
Thickness of deposited Zn	5.5 mg	6.3 mg

Fig. S4 Details on the current collector before and after Zn pre-deposition.

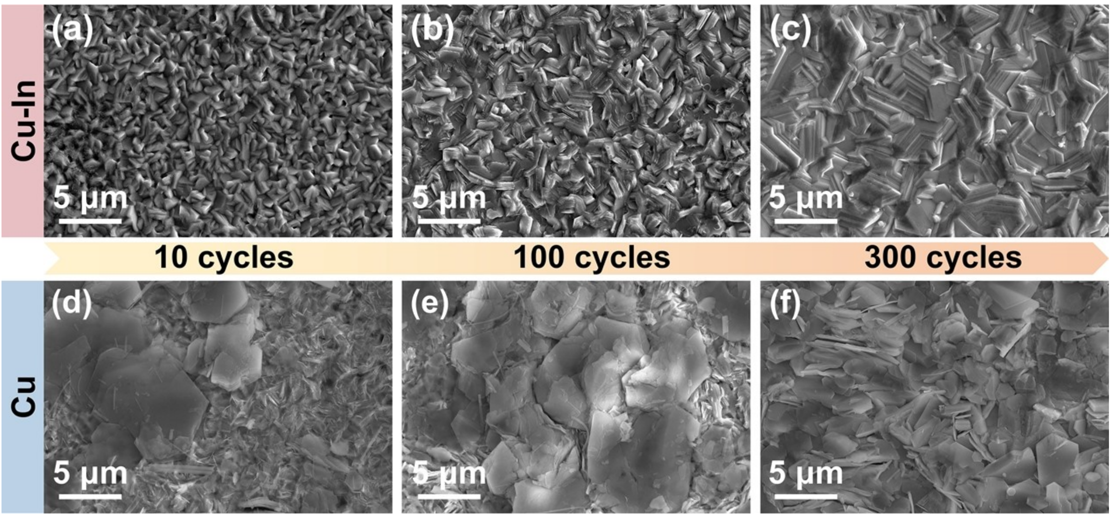

Fig. S5 SEM images of the deposited Cu–In (a–c) and Cu (d–f) electrodes after cycling 10, 100, and 300 times in the asymmetric battery.

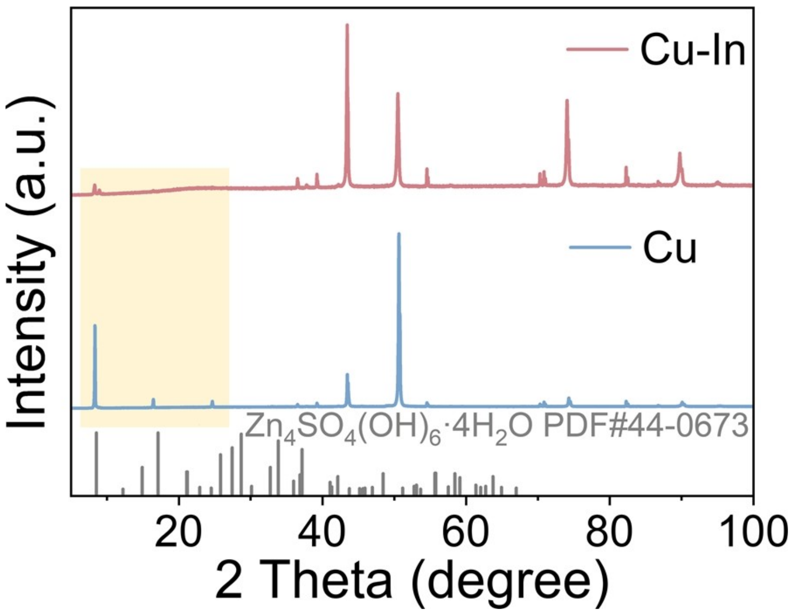

Fig. S6 XRD patterns after cycling 10 cycles in the asymmetric battery.

Notes and references

1 P. R. Subramanian and D. E. Laughlin, *Bulletin of Alloy Phase Diagrams*, 1989, **10**, 554-568.