

Supporting Information

Transition-Metal Ions Intercalation Chemistry Enabled Manganese Oxides-Based Cathode with Enhanced Capacity and Cycle Life for High-Performance Aqueous Zinc-Ion Batteries

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1. The nominal valence states calculation

The nominal valence states of Mn of the different samples can be calculated based on the measured ΔE in Figure 2b, which can be determined quantitatively with the following equation.¹⁻²

$$\text{AOS} = 8.956 - 1.126 \Delta E$$

Where AOS denotes the calculated nominal valence states of Mn. The energy differences (ΔE) were measured with 4.63 eV, 4.98 eV, and 5.21 eV for the MnO₂, MnO₂-Na and MnO₂-Cu samples, respectively. Accordingly, the valence states of Mn in MnO₂, MnO₂-Na, and MnO₂-Cu are 3.74, 3.35, and 3.1, respectively.

2. Supplementary Figures

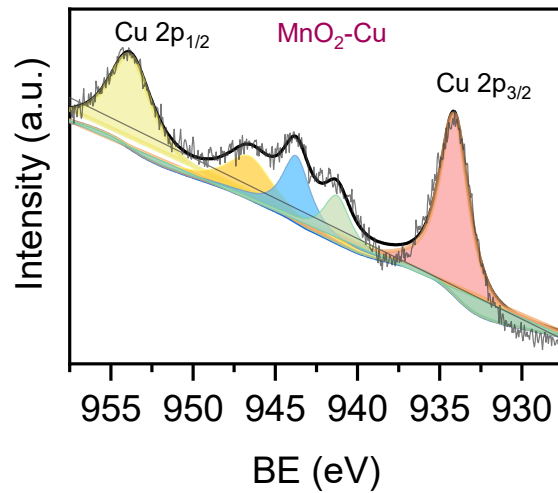


Figure S1. XPS core-level spectra of Cu 2p of the obtained MnO₂-Cu.

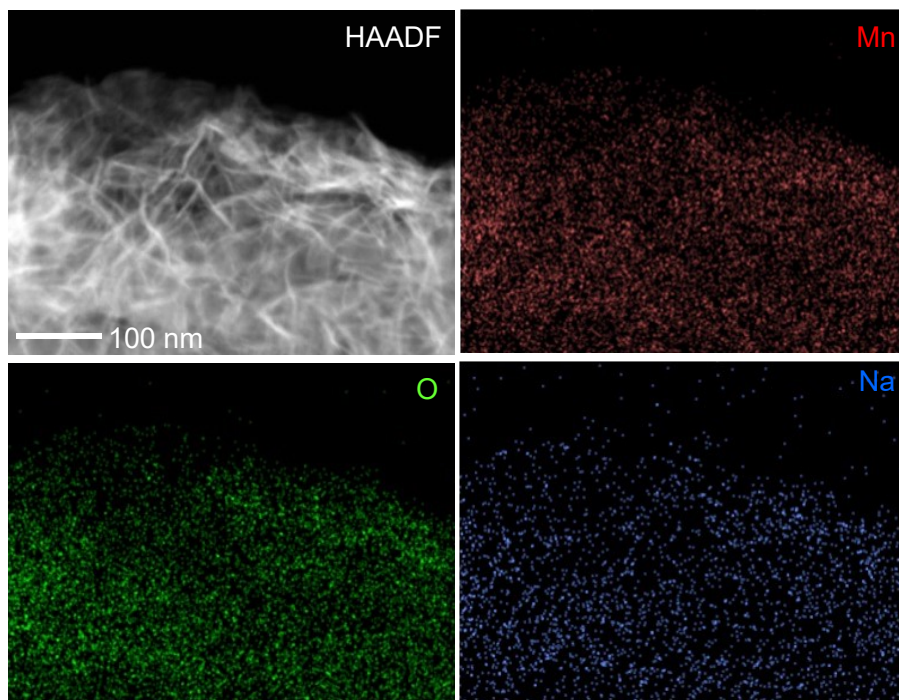


Figure S2. Elemental maps of the sample MnO₂-Na.

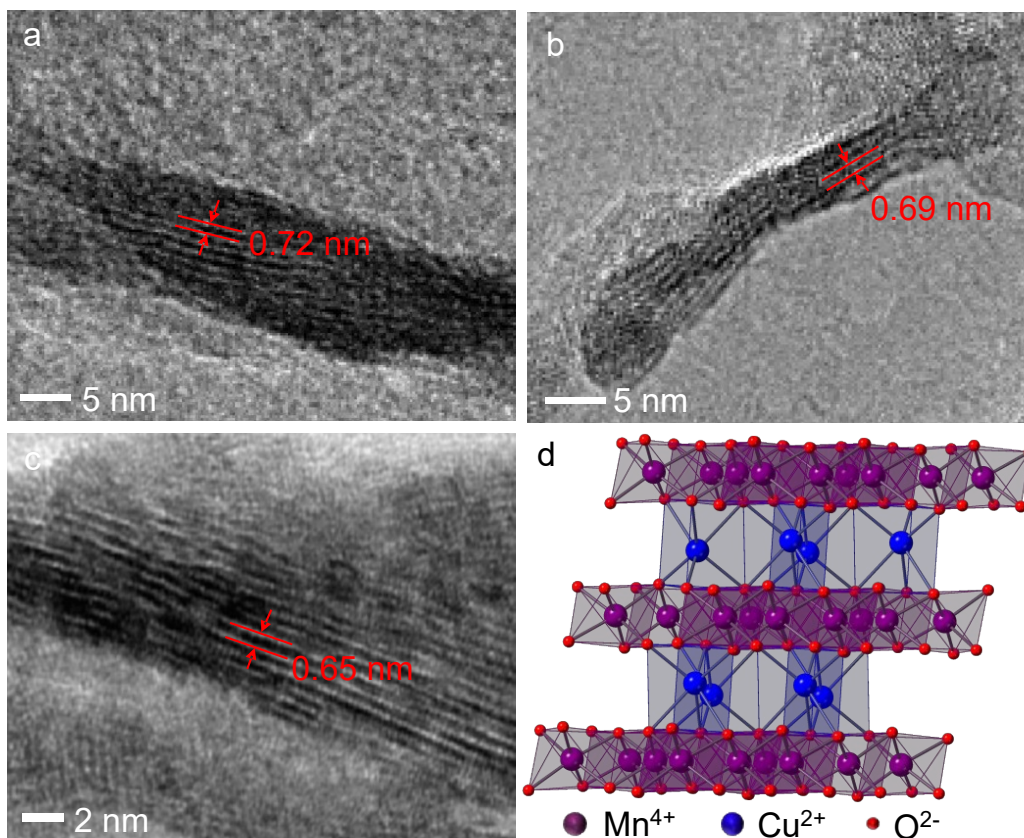


Figure S3. Representative TEM images with the lattice stripe view of the obtained MnO₂, MnO₂-Na, and MnO₂-Cu. (a) MnO₂ with the interlayer spacing of 0.72 nm; (b) MnO₂-Na with the interlayer spacing of 0.69 nm; (c) MnO₂-Cu with the interlayer spacing of 0.65 nm; (d) schematic illustrating the crystal structure of MnO₂-Cu with the interlay intercalated Cu²⁺.

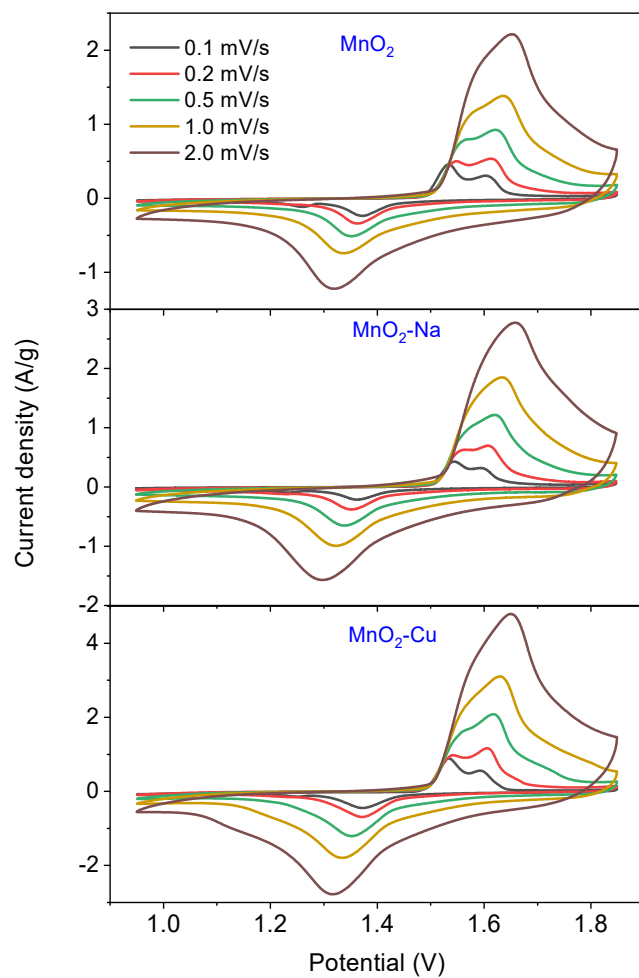


Figure S4. CV curves of the obtained MnO_2 , $\text{MnO}_2\text{-Na}$, and $\text{MnO}_2\text{-Cu}$ electrodes were recorded at the scan rate ranging from 0.1 mV/s to 2.0 mV/s.

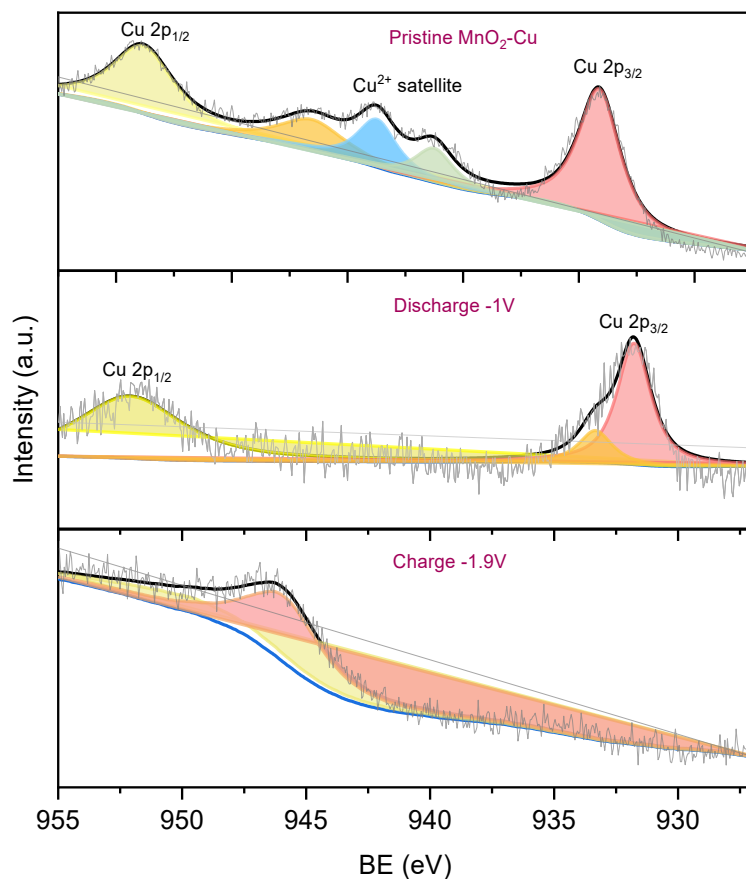


Figure S5. Valence states evolution of Mn in the $\text{MnO}_2\text{-Cu}$ electrode during different charge-discharge stages.

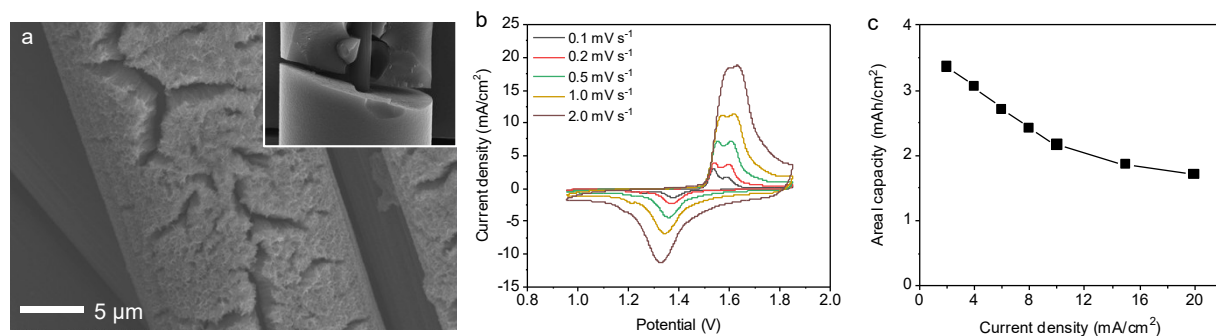


Figure S6. Electrochemical performance of $\text{MnO}_2\text{-Cu}$ electrodes with high mass loading up to $9.6 \text{ mg}/\text{cm}^2$. (a) Typical SEM image of the $\text{MnO}_2\text{-Cu}$ electrodes revealing the significantly thicker $\text{MnO}_2\text{-Cu}$ materials electrodeposited on the current collector carbon cloth; (b) CV curves recorded at different scan rates ranging from $0.1 \text{ mV}/\text{s}$ to $2.0 \text{ mV}/\text{s}$; (c) Rate capability at different charge-discharge current densities.

Reference

- 1 X. Tan, R. Liu, C. Xie and Q. Shen, *J. Power Sources*, 2018, **374**, 134-141.
- 2 A. Manceau, M. A. Marcus and S. Grangeon, *Am. Mineral.*, 2012, **97**, 816-827.