

Supplementary Information For

Fast-charging aqueous batteries enabled by a three-dimensional ordered Zn anode at deliberate concentration polarization

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Methods

Synthesis of the 3DZn@CP electrode

The 3DZn@CP electrode was prepared by an electrodeposition in two-electrode system, where two Zn foils were used as both counter and working electrodes, 1 M ZnSO₄ aqueous solution was employed as electrolyte. The distance between the two Zn electrodes was set as 1 mm. After applying a constant current density of -20 mA cm⁻² for 30 min, the 3DZn@CP electrode was fabricated, which should be washed with deionized water and dried in a vacuum oven before further use.

Structural Characterizations

The morphology of electrodes was analyzed by a HITACHI SU8010 SEM instrument. XRD measurement was conducted on a Bruker AXS D8 Advance X-ray diffractometer with Cu K α radiation (40 kV, 30 mA). The optical images were obtained by a Canon EOS 5D Mark III Digital SLR.

Electrochemical Measurements

The electrochemical performance of Zn and 3DZn@CP electrodes was evaluated on a Neware battery tester (BTS, CT-4008) or an electrochemical workstation (VMP3, Biologic). The symmetric cells were assembled using standard CR2025 coin cells, glass fiber separator (WHATMAN, GF/C) and 6 M KOH + 0.2 M Zn(acac)₂ electrolyte. The full cells were assembled using Zn/3DZn@CP anode, glass fiber separator, Ni(OH)₂ cathode, and 6 M KOH + 0.2 M Zn(acac)₂ electrolyte. The Zn electrodes was pre-scanned in 6 M KOH + 0.2 M Zn(acac)₂ for 100 cycles at 40 mV⁻¹ in order to be activated before full cell performance evaluation (**Figure S14**). The Ni(OH)₂ cathode was prepared using a hydrothermal method: Namely, a piece of Ni foam with a diameter of 9 mm was washed with 3 M HCl, deionized water, and ethanol before transfer to a 50 mL of Teflon-lined autoclave containing 2.5 mmol Ni(NO₃)₂·6H₂O, 25 mmol urea, and 40 mL distilled water. The autoclave was then sealed and heated at 120 °C for 10 h to prepare Ni(OH)₂ cathode. The mass-loading of Ni(OH)₂ on Ni foam was determined to be 2.1 mg cm⁻² by mass weighting before and after deposited procedure. Considering the theoretical capacity of β -Ni(OH)₂ material (**Figure S15**) is 289 mAh g⁻¹, the charge-discharge current density of the Ni-Zn batteries was set to be 30.3 mA cm⁻² to ensure the rate of 50 C. CV profiles of the full cells were obtained at a low sweep speed of 1

mV s⁻¹. EIS was recorded with frequency range 100 KHz to 0.1 Hz under open circuit voltage with an amplitude of 5 mV. The electrochemical surface area of the Zn and 3DZn@CP electrodes was evaluated by measuring the capacitance of the surface electrical double-layer using Nyquist plots fitted by an equivalent circuit. C_{dl} was calculated by the Hirschorn-Orazem formula: $C_{dl} = Q^{1/\alpha} (R_s^{-1} + R_{ct}^{-1})^{(\alpha-1)/\alpha}$, where R_s was the solution resistance, R_{ct} was the charge-transfer resistance, Q was the constant phase angle parameter, α was the constant phase angle parameter. CA measurements were conducted at an overpotential of -100 mV. LSV measurements were performed at a low sweep rate of 1 mV s⁻¹ in a three-electrode system with a saturated calomel electrode as reference electrode and a carbon rod as counter electrode.

Theoretical calculation

The limiting current density was calculated using the Sand's model under the condition that Zn²⁺ exhaustion happened at the anode: $i_L = 2c_b D F / (1 - \rho_+) L$, where c_b is the concentration of ZnSO₄ salt in the conducting phase, D is the diffusion coefficient of Zn ions, F is the Faraday's constant, L is the gap distance between the two Zn electrodes (i.e. 1 mm), and ρ_+ is the transference number of Zn²⁺ in ZnSO₄ electrolyte.

Supplementary Figures

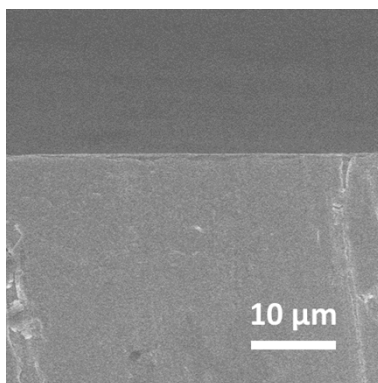


Figure S1 Cross-section SEM image of commercial Zn foil electrode.

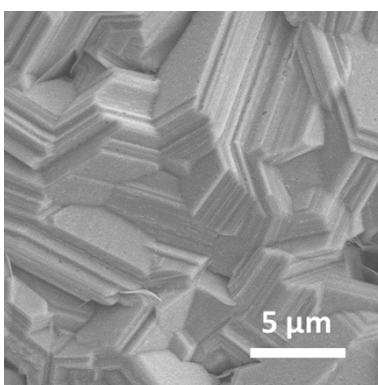


Figure S2 Top-view SEM image of as-prepared 3DZn@CP electrode.

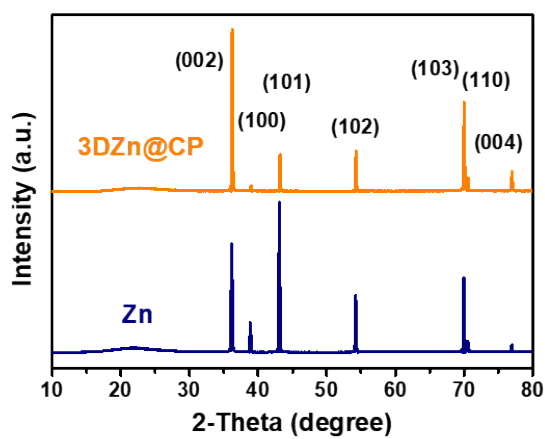


Figure S3 XRD patterns of commercial Zn and 3DZn@CP electrodes.

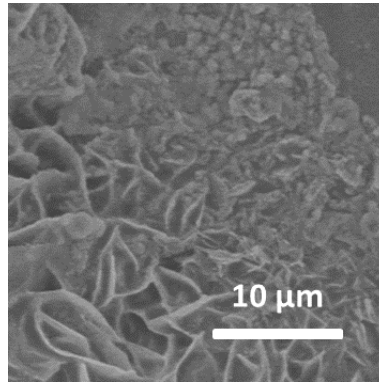


Figure S4 Top-view SEM image of electrodeposited Zn electrode at 50 mA cm^{-2} in 1 M ZnSO_4 electrolyte.

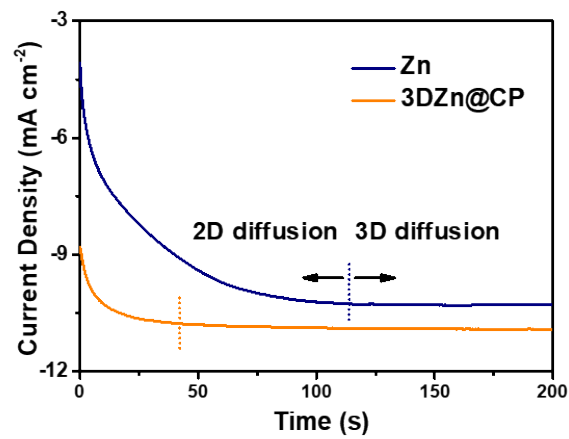


Figure S5 Chronoamperograms of commercial Zn and 3DZn@CP electrodes.

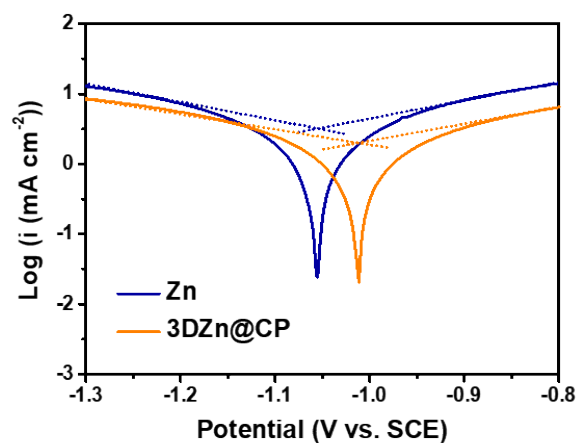


Figure S6 Corrosion linear polarization curves of commercial Zn and 3DZn@CP electrodes.

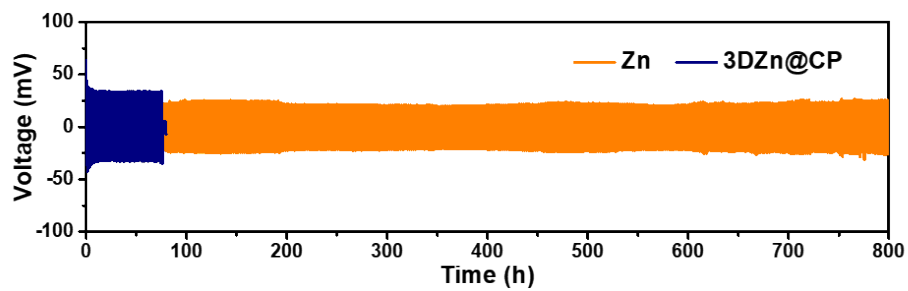


Figure S7 Voltage profiles of Zn||Zn and 3DZn@CP||3DZn@CP symmetrical cells at 1 mA cm⁻² and 0.5 mAh cm⁻².

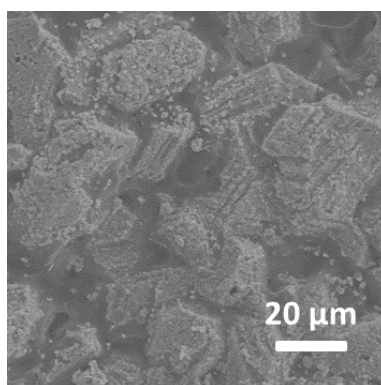


Figure S8 Top-view SEM image of the 3DZn@CP electrode after plating 10 mAh cm⁻² of metallic Zn at 20 mA cm⁻².

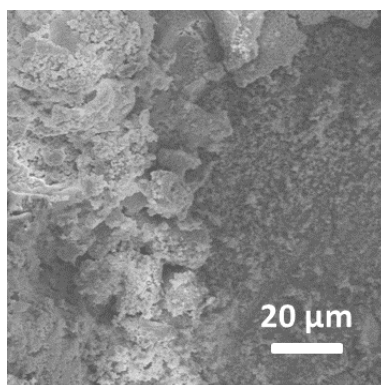


Figure S9 Top-view SEM image of the commercial Zn electrode after plating 10 mAh cm⁻² of metallic Zn at 20 mA cm⁻².

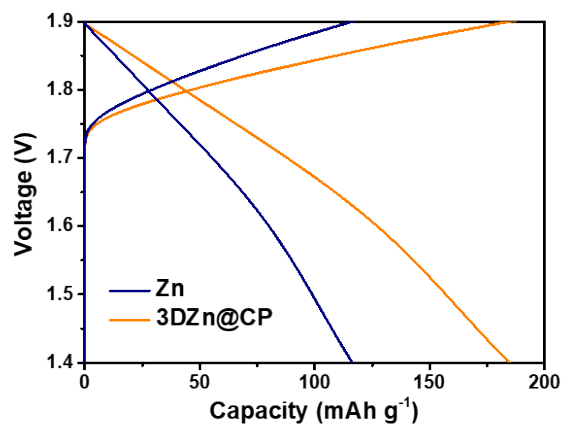


Figure S10 Charge/discharge curves of the Ni-Zn-based and Ni-3DZn@CP coin cells for the 1st cycle.

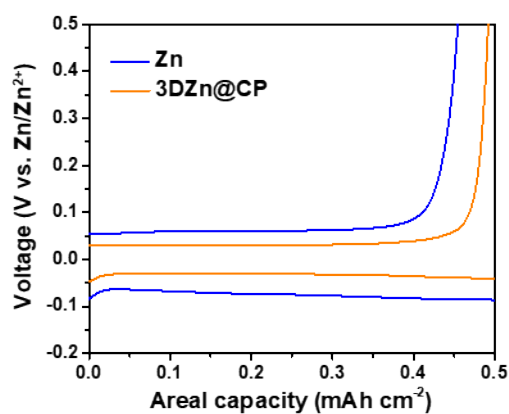


Figure S11 Electrochemical plating/stripping curves of Zn||Ti and 3DZn@CP||Ti cells at 2 mA cm⁻² and 0.5 mAh cm⁻².

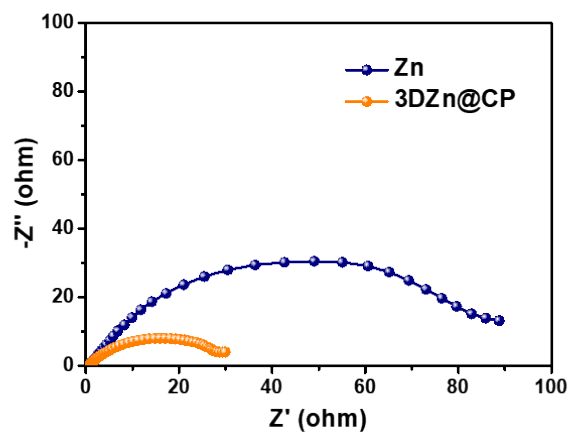


Figure S12 EIS plots of as-assembled Ni-Zn and Ni-3DZn@CP coin cells.

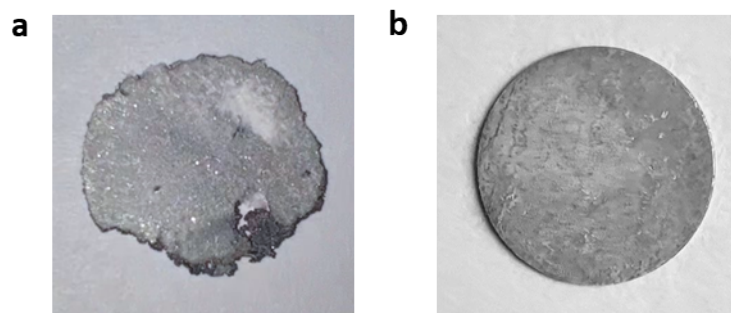


Figure S13 Digital images of (a) Zn and (b) 3DZn@CP electrodes after Ni-Zn coin cell cycling for 200 cycles at 50 C.

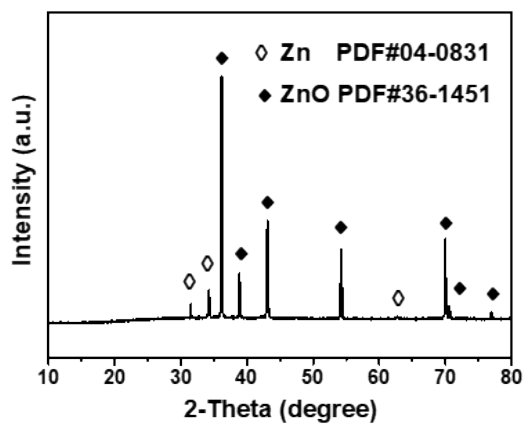


Figure S14 XRD analysis of the 3DZn@CP electrode after electrochemical activation.

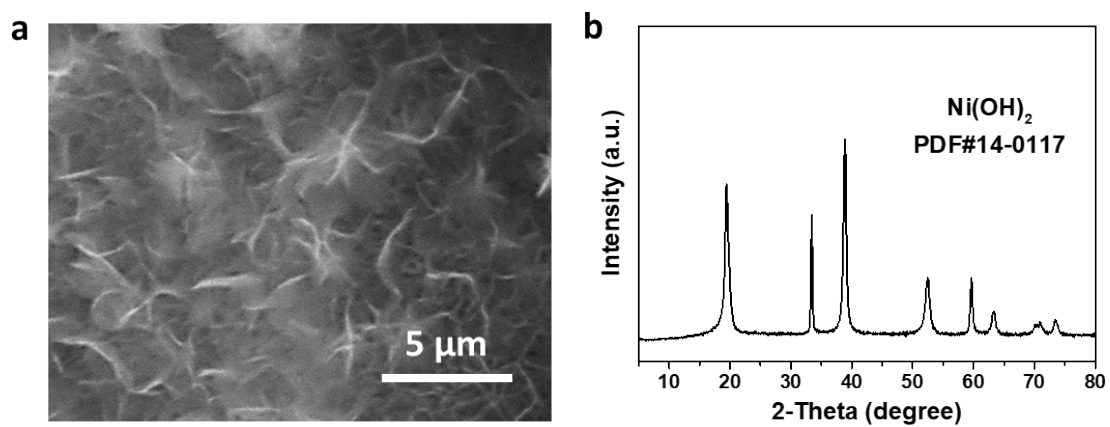


Figure S15 (a) SEM image and (b) XRD pattern of the as-prepared Ni(OH)₂ cathode materials.

Supplementary Table

Table S1 Performance comparison of Ni-3DZn@CP coin cells with those fast-charging aqueous Zn batteries in recent publications.

Batteries	Rates	Cycle-life	Capacity Retention	Reference
3DZn@CP Ni(OH) ₂	50 C	2000	97.7%	This work
PA-Zn MnO ₂	2 C	1000	88.0 %	Energy Environ. Sci. 2019, 12, 1938-1949.
(CS/CA) ₄ -Zn H ₂ V ₃ O ₈	13.2 C	14000	83.6%	Adv. Mater. 2024, 36, 2306734.
MPS-Zn NH ₄ V ₄ O ₁₀	7.2 C	1000	85.2%	Adv. Funct. Mater., 2024, 2315716.
MXene-Zn ZnI ₂	4.7 C	1500	99.6%	Adv. Energy Mater. 2024, 2400318.
Cu ₅ Zn ₈ @NC V ₂ O ₅	16.9 C	10000	89.2%	Adv. Energy Mater. 2024, 2400276.
Zn ₃ (PO ₄) ₂ -Zn MnO ₂	3.3 C	1000	86.2%	Small, 2024, 2310497.
Zn Na ₂ V ₆ O ₁₆ ·1.63 H ₂ O	1 C	2000	70%	Angew. Chem. Int. Ed. 2021, 133, 12546-12553.
3D MXene@Zn VO ₂	8.5 C	2000	77.2%	J. Mater. Chem. A 2023, 11, 13742-13753.
ZCYSM@Zn CVO	8.5 C	5000	80.4%	Adv. Mater. 2023, 35, 2303336.
Zn NaV ₆ O ₁₅ /V ₂ O ₅	8.5 C	3000	92.3%	J. Energy Chem. 2021, 55, 25-33.
Zn NaKVOH	3.4 C	1200	98.1%	eScience, 2022, 2, 209-218.