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Stimulating Cu-Zn Alloying for Compact Zinc Metal Growth towards High Energy Aqueous Batteries and Hybrid Supercapacitors

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Experimental details

Chemicals: Urea (> 99%), zinc sulfate (ZnSO₄, > 99.9%), and zinc oxide (ZnO, > 99.9%) were used as received (purchased from Sigma-Aldrich). In order to remove the water residue and trapped air, Choline chloride (ChCl, Tokyo Chemical Industry (TCl), 98%) and zinc triflate (Zn(OTF)₂, Sigma-Aldrich, > 98%) were dried under vacuum at 120 °C and 150 °C successively for 12 h before use. Before adding Zn salts into de-ionized (DI) water for preparing an aqueous electrolyte, DI water was bubbled with nitrogen gas for 10 min under ultrasonication to remove dissolved oxygen. Mn(CH₃COO)₂·4H₂O (> 99%), potassium permanganate (KMnO₄, Sigma-aldrich, > 99%), multi-walled CNTs (MWCNT, Carbon Nanomaterial tech. Co., Ltd.), phenazine (PNZ, Tokyo Chemical Industry Co., Ltd., > 99.0%), activated carbon (AC, Aladdin Co., Ltd.), Super P carbon black (Timcal), polyvinylidene fluoride (PVDF, Solvay), and polytetrafluoroethylene (PTFE) binder solution (60 wt% dispersion in H₂O, Sigma-Aldrich) were used as received for preparing cathodes.

Preparation of DES-Zn and Aq-Zn anodes: Zn foil (Alfa Aesar, 99.994%) was mechanically pressed to have a thickness of 80 μ m using a roll press. DES (denoted as 12CU) was prepared by mixing choline chloride (ChCl) and urea at a molar ratio of 1:2 at 70 °C until a transparent liquid was formed. The resulting solution was then added with the selected Zn salt and used as an electrolyte for Zn plating. To prepare a Zn anode with a finite capacity, we assembled a CR2032-type coin cell consisting of Cu (or Ti) foil and Zn foil as working and counter/reference electrodes, respectively, with a glass fiber separator (Whatman, GF/F). For the preparation of DES-Zn, Zn plating on Cu foil (working electrode) was conducted at current densities ranging from 0.1 to 1 mA cm⁻² at 60 °C using 150 μ L of DES-based electrolyte (mainly 0.6 M Zn(OTF)₂ unless otherwise noted). Cyclic voltammetry (CV) was conducted before the Zn plating to activate and stabilize Cu foil in a voltage range from -0.3 V to 0.6 V (versus Zn/Zn²⁺) at a scan rate of 5 mV s⁻¹. The Aq-Zn anodes were prepared following the same procedure with DES-Zn while using an aqueous electrolyte (mainly 2 M ZnSO₄ unless otherwise noted) at current densities ranging from 0.1 to 2 mA cm⁻² at 30 °C.

Preparation of PNZ, AC cathode: PNZ was ground with Super P, then added with the PTFE binder solution in a weight ratio of 6:3:1. Mixing the composite for 20 min resulted in a free-standing electrode which was then cut into 1 cm² and dried in a dry room for 24 h. The areal mass loading of PNZ was around 4.5 mg cm⁻². The AC cathode was prepared by mixing AC, Super P, and PTFE binder in the weight ratio of 8:1:1. The free-standing AC electrode was dried under vacuum at 30°C for 24h. The areal mass loading of AC was around 6.7 mg cm⁻².

Preparation of α -MnO₂/carbon nanotube (CNT) cathode: The α -MnO₂/CNT nanocomposite was

prepared by using Mn(CH₃COO)₂·4H₂O, KMnO₄, and MWCNT as starting materials through a hydrothermal and coprecipitation method.^{1, 2} MWCNT (diameter: 5-15 nm, length: ~10 μ m) was first treated in nitric acid (60%) at 90 °C for 12 h under magnetic stirring and then washed with DI water for several times until the pH reached 7. After washing the acid-treated CNT (0.125 g), it was mixed with a solution made with 1.7 g Mn(CH₃COO)₂·4H₂O dissolved in 75 mL DI water under continuously stirring. Next, the mixture was added drop-wisely into an 80 mL aqueous solution containing 0.725 g KMnO₄ and continuously stirred for 0.5 h. Then, the obtained mixture was loaded into a 200 ml Teflon-lined autoclave and heated at 90 °C for 6 h. The product was washed several times with DI water and dried at 80°C for 12 h. The cathode was prepared by mixing α -MnO₂/CNT, Super P, and polyvinylidene fluoride (PVDF) in a weight ratio of 7:2:1 in N-methyl-2-pyrrolidone (NMP). The slurry was casted onto Ti foil and dried at 80 °C for 12 h. The active mass loading was around 0.5 mg cm⁻². To mitigate the capacity fade of MnO₂ caused by the loss of electrochemically active Mn²⁺ ions, we introduced a freestanding CNT film between the cathode and separator of full cells.³ CNT films were fabricated by filtration after tip sonication for 10 min. The CNT films were immersed in nitric acid (60%) at 80 °C for 8 hours and then rinsed with deionized water several times for neutralization. The obtained CNT films were dried in a vacuum oven at 80 °C for 3 hours. The thickness of CNT films was around 100 μm.

Characterization of Materials: Zn anodes for morphological characterizations were prepared by disassembling the coin cell after Zn plating, followed by rinsing the samples with N, Ndimethylformamide (DMF). The microstructures were examined using a field-emission scanning electron microscopy (FE-SEM, Regulus 8230, Hitachi, Japan) equipped with an Energy Dispersive X-ray Spectroscopy (EDS, Ultim Max, Oxford, UK) attachment. The samples to observe cross-sectional views were obtained by using an ion-milling system (Airblade 5000, IM5000CTC, Hitachi, Japan). The global surface topographies of the Zn anodes were analyzed with a NanoFocus MicroSurf 3D confocal white light microscope (NanoFocus AG, Germany). The confocal image covers an area of 640,000 μ m², and the amplitude parameters (S_a , S_q) were calculated based on the standard ISO 25178-2 (calculation details are denoted in Note S1). The grazing incidence X-ray diffraction (GIXRD) measurement was performed with a Bruker D8 ADVANCE diffractometer (Cu Ka X-ray source operated at 40 kV and 40 mA) at incidence angles of 0.5 and 1°. The X-ray photoelectron spectroscopy (XPS) measurement (NEXSA, ThermoFisher Scientific) was performed with a monochromatized Al Ka (1486.6 eV) as the Xray source. For the XPS analysis, Cu foil was immersed in DES for 12 h in an argon-filled glovebox and transferred with an airtight holder to protect the sample from contamination. The electron backscatter diffraction (EBSD, Symmetry, Oxford, UK) analysis was performed with a SEM (Amber X, TESCAN, Czech Republic). To analyze the Cu-Zn alloy interlayer with EBSD, consecutive Zn plating and stripping was

conducted on Cu foil in DES. The Zn deposits (0.5 mAh cm⁻²) formed by the galvanostatic intermittent titration technique (GITT, applying a periodical pulse current of 100 μ A cm⁻² for 15 min with intermittent 30-min breaks) were removed by applying a constant current of 20 μ A cm⁻² and voltage cut off of 0.05 V (versus Zn²⁺/Zn). The EBSD results were analyzed with an EBSD data reprocessing software (AZtecCrystal, Oxford, UK).

Electrochemical characterizations: The electrochemical performances of Zn||Zn symmetric cells and full cells were analyzed with the WBCS-3000 battery cycler (Wonatech Co. Ltd., Korea) and VMP3 potentio/galvanostat (Bio-logic Scientific Instruments, France) by using coin-type and pouch-type cells. 100 μ L of 2 M ZnSO₄ aqueous electrolyte was used for the Zn||Zn symmetric cells. The same electrolyte condition was used for Zn||PNZ and Zn||AC full cells. An aqueous electrolyte having 3 M Zn(OTF)₂ and 0.1 M Mn(TFSI)₂ was used for Zn||MnO₂ full cells.

The pouch-type Zn|| α -MnO₂ cells were fabricated by pairing 2.2 × 2.2 cm² DES-Zn or Aq-Zn anode with 2 × 2 cm² α -MnO₂ cathode. The DES-Zn and Aq-Zn anodes were prepared by electrodeposition in pouch cells consisting of 2.2 × 2.2 cm² Zn foil, 2.5 × 3 cm² Cu foil, and 3.5 x 5 cm² glass fiber separator. The performances of pouch cells were evaluated in a voltage range of 0.9-1.7 V at 0.5 mA cm⁻² and 3.75 mA cm⁻². GITT measurements were conducted with coin cells using Zn metal as an anode and Cu (or Ti) foil as a cathode. 0.6 M Zn(OTF)₂ DES (12CU) solution and 2 M ZnSO₄ aqueous solution were used as the electrolyte, respectively. Linear polarization measurements were conducted in a three-electrode system using beaker cells. The Aq-Zn and DES-Zn (1 mAh cm⁻²) were used as the working electrode. Carbon fiber and saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. The extrapolation of cathodic and anodic Tafel lines was carried out in a potential range ±75 mV with respect to corrosion potential (*E*_{corr}) at a scan rate of 3 mV s⁻¹.



Fig. S1 SEM images of Zn deposits (1 mAh cm⁻²) after electrodeposition on Cu foil (a, b) using an aqueous electrolyte (2 M ZnSO₄) at 2 mA cm⁻², and (c, d) using a DES (12CU) electrolyte (0.1 M ZnSO₄) at 0.1 mA cm⁻².



Fig. S2 (a) A SEM image of Zn deposits (1 mAh cm⁻²) after electrodeposition on Cu foil using 0.1 M ZnO in 12CU at the current density of 0.1 mA cm⁻². (b) The enlarged view of (a) showing micron-sized Zn particles.



Fig. S3 SEM images of Zn deposits after electrodeposition at the current density of (a) 0.1 mA cm^{-2} , (b) 0.3 mA cm^{-2} , (c) 0.5 mA cm^{-2} , and (d) 1 mA cm^{-2} using $0.6 \text{ M Zn}(\text{OTF})_2$ in 12CU. The areal capacity was 1 mAh cm^{-2} .



Fig. S4 SEM images of Zn deposits after electrodeposition at the current density of (a) 0.1 mA cm^{-2} , (b) 0.5 mA cm^{-2} , and (c) 2 mA cm⁻² using 2 M ZnSO₄ aqueous electrolyte. The areal capacity was 1 mAh cm⁻².



Fig. S5 Cross-sectional SEM images of the Zn deposits (2 mAh cm⁻²) after electrodeposition on Cu foil (a) using 2 M ZnSO₄ aqueous electrolyte at 2 mA cm⁻², and (b) using 0.1 M ZnSO₄ in 12CU at 0.1 mA cm⁻².



Fig. S6 Height deviations along the x and y-axis of (a, b) DES-Zn and (c,d) Aq-Zn samples. Note that the height profiles of the x and y-axis were drawn across the center of the sample. S_a and S_q cover the entire area of 640,000 μ m².



Fig. S7 3D topographic images and the corresponding height profiles of (a-c) DES-Zn, (d-f) Aq-Zn plated at the areal capacity of 4 mAh cm⁻².



Fig. S8 GIXRD patterns of DES-Zn and Aq-Zn anodes with the areal capacity of (a) 1 mAh cm⁻², (b) 5 mAh cm⁻², respectively. To calculate the intensity ratio of $(002)_{Zn}$ to $(100)_{Zn}$ (i.e. I_{002}/I_{100}), we used the integrated peak area from 36.0 to 36.6° for $(002)_{Zn}$ and that from 38.6 to 39.2° for $(100)_{Zn}$.



Fig. S9 The voltage profiles upon stripping the electrodeposited Zn with areal capacities of (a) 5 mAh cm^{-2} and (b) 7 mAh cm^{-2} . Zn plating was first conducted in the DES electrolyte at 0.3 mA cm^{-2} , and the stripping was conducted in 2 M ZnSO₄ aqueous electrolyte at 2 mA cm^{-2} . The insets indicate the calculated capacities for de-alloying for each condition.



Fig. S10 (a) SEM image and (b) the corresponding EDS map of the Zn deposits (1 mAh cm⁻²) after electrodeposition at 0.1 mA cm⁻² on Ti foil using a DES electrolyte.



Fig. S11 SEM images of (a) bare Cu foil and (b) and the Cu foil treated with 12CU for 12 h at 25°C.



Fig. S12 SEM images of Zn deposits (1 mAh cm⁻²) grown on the Zn-rich alloy layer in an aqueous electrolyte. The alloy layer was formed in a DES electrolyte by plating Zn by the GITT method and subsequently removing Zn deposit by galvanostatic striping to 0.05 V. Then, 1 mAh cm⁻² of Zn was electrodeposited in 2M ZnSO₄ aqueous electrolyte.



Fig. S13 SEM images of (a-c) DES-Zn and (d-f) Aq-Zn electrodes retrieved from the symmetric cell after 1^{st} , 10^{th} , and 50^{th} cycles in an aqueous electrolyte. The Zn electrodes were galvanostatically cycled at 1 mA cm⁻² while using a reversible capacity of 0.5 mAh cm⁻² per cycle (DOD_{zn} = 25 %).



Fig. S14 Height deviations along the x and y-axis of the Aq-Zn electrode obtained from the symmetric cell after the (a, b) 1^{st} , (c, d) 10^{th} , and (e, f) 50^{th} cycles. The Zn electrodes were collected after galvanostatic charging and discharging at 1 mA cm⁻² while reversibly using a capacity of 0.5 mAh cm⁻² per cycle (DOD_{Zn} = 25%).



Fig. S15 Height deviations along the x and y-axis of cycled DES-Zn electrodes collected from symmetric cells after the (a, b) 1^{st} , (c, d) 10^{th} , and (e, f) 50^{th} cycles. The cycled Zn electrodes were obtained after galvanostatic charging and discharging at 1 mA cm⁻² for 0.5 h per each step (DOD_{Zn} = 25%).



Fig. S16 (a) Coulombic efficiency (CE) of DES-Zn||Zn and Aq-Zn||Zn cells cycled at 2 mA cm⁻² in 2 M ZnSO₄ aqueous electrolyte. (The original areal capacity of the prepared DES-Zn and Aq-Zn electrodes was 1 mAh cm⁻².) The voltage cut-off was set to 0.07 V for stripping to preserve the alloy interlayer during Zn plating/stripping consistently. The corresponding voltage profiles of different cycles for the (b) DES-Zn and (c) Aq-Zn cells. The magnified charge profiles of the selected cycles before the 10th and after the 37th cycles for the (d, f) DES-Zn and (e, g) Aq-Zn cells. The Aq-Zn cells exhibit lower CEs during the early cycles than the DES-Zn cells. Notably, after an 18-hour rest (38th cycle), the CE of Aq-Zn dropped significantly, as opposed to that of DES-Zn, which retained the original value after the break. The result indicates that the compact morphology of the DES-Zn anode effectively prevents side reactions.



Fig. S17 (a) The voltage profiles of DES-Zn||Zn and Aq-Zn||Zn cells obtained during the initial stripping process in 2 M ZnSO₄ aqueous electrolyte. (The original areal capacity of the prepared DES-Zn and Aq-Zn electrodes was 3 mAh cm⁻².) The current density and voltage cut-off for cycling were 0.5 mA cm⁻² and 0.6 V, respectively. The voltage profiles of the DES-Zn||Zn and Aq-Zn||Zn cells for the (b) 1st, (c) 2nd, and (d) 3rd cycles after the initial stripping. The DES-Zn electrode undergoes de-alloying reactions following the stripping of metallic zinc, exhibiting two additional voltage plateaus at 0.08 and 0.35 V. The de-alloying capacity remains nearly constant besides the initial stripping, which indicates that the alloying reaction barely progresses further during the repeated cycling in the aqueous electrolyte.



Fig. S18 (a) The voltage profiles and (b) magnified charge profiles of an Aq-Zn||Zn cell cycled at 0.5 mA cm⁻² with 0.6 V voltage cut-off for stripping. (The original areal capacity of the prepared Aq-Zn electrodes was 3 mAh cm⁻².) While a slight dealloying feature at 0.1 V appears after the initial stripping, the dealloying capacity (<0.05 mAh cm⁻²) was insignificant compared to that of DES-Zn.



Fig. S19 SEM images of the dense and compact Zn deposits (5 mAh cm⁻²) after electrodeposition at 0.3 mA cm⁻² on Cu foil using a DES electrolyte.



Fig. S20 Voltage profiles of (a) DES-Zn, and (b) Aq-Zn symmetric cells cycled at 1 mA cm⁻². The initial areal capacity loading of the prepared Zn electrodes was 5 mAh cm⁻² and a reversible capacity of 0.5 mAh cm⁻² was galvanostatically cycled (DOD_{Zn} = 10%),



Fig. S21 (a) Cycling performance of DES-Zn and Aq-Zn in symmetric cells. The cells were cycled at 3 mA cm⁻² for 1 h for each step. The initial loading of the prepared Zn electrodes was 7.5 mAh cm⁻² and thus the DOD_{Zn} for cycling was 40%. (b) After the 51th cycle, the enlarge voltage profile of the Aq-Zn cell indicates that the cell was shorted.



Fig. S22 Comparison of the DOD_{zn} and cumulative capacity from AZIB full cells in the recent reports with our work. The left side (white area) represents the previous demonstrations with a DOD_{zn} less than 5% (equal to n/p > 20), and the right side (yellow area) shows the AZIB examples with a DOD_{zn} greater than 20% (equal to n/p < 5). The detailed values are listed in **Table S3**.



Fig. S23 Cycling performances of the multiple DES-Zn, Aq-Zn, and Zn foil full cells paired with AC cathodes at a current density of 4 A g⁻¹. The sample name indicates the respective DOD_{Zn} for each cell, and the value on the right side represents the capacity retention for each cell after 3000 cycles. The initial loading of the DES-Zn and Aq-Zn anodes was identical (2.1 mAh cm⁻²). The DOD_{Zn} of the Zn foil was calculated based on the thickness of the foil (80 μ m).



Fig. S24 (a) Cycling performances of DES-Zn and Aq-Zn full cells paired with PNZ cathodes and the corresponding CEs (CE = charge capacity × 100 / discharge capacity). Voltage profiles of the (b) DES-Zn ||PNZ and (c) Aq-Zn ||PNZ full cells for the initial two cycles obtained at 0.1 C (1 C = 298 mAh g⁻¹_{PNZ}). Voltage profiles of (d) DES-Zn and (e) Aq-Zn ||PNZ full cells cycled at a current density of 0.5 C.



Fig. S25 The XRD pattern of the synthesized α -MnO₂/CNT composite powder.



Fig. S26 (a) A SEM image and (b-e) the corresponding EDS maps of the synthesized α -MnO₂/CNT composite electrode showing that α -MnO₂ nano-rods are embedded in the MWCNT matrix.



Fig. S27 Photograph of a fabricated DES-Zn $||\alpha$ -MnO₂ pouch cell.



Fig. S28 (a) Long-term cycling performances of pouch cells assembled with DES-Zn and Aq-Zn anodes coupled with α -MnO₂ cathodes. The current density and the voltage range were 3.75 mA cm⁻² and 0.9– 1.7 V. The corresponding voltage profiles of the pouch cells using the (b) DES-Zn and (c) Aq-Zn anodes for selected cycles. The capacity retentions of the DES-Zn and Aq-Zn cells were 83.8% and 69.0%, respectively, after 1000 cycles.



Fig. S29 (a) Cycling performances of pouch-type full cells using DES-Zn and Aq-Zn anodes coupled with α -MnO₂ cathodes. The current density and the voltage range were 0.5 mA cm⁻² and 0.9–1.7 V. The corresponding voltage profiles of the full cells using the (b) DES-Zn and (c) Aq-Zn anodes. In contrast to the DES-Zn full cell, the Aq-Zn cell suffered a rapid capacity decay in the early cycles.



Fig. S30 Voltage profiles of the (a, b) DES-Zn | α -MnO₂ and (c, d) Aq-Zn | α -MnO₂ full cells (coin-type cells) cycled at 0.3 C after the formation cycles at 0.1 C (1 C = 308 mAh g⁻¹ $_{\alpha$ -MnO₂). The DES-Zn cell operates stably, preserving the typical voltage plateaus and capacity over multiple cycles. However, the Aq-Zn cell suffers an abrupt capacity loss after the 3rd cycle, accompanied by the suddenly discontinued discharge, which indicates Zn depletion on the anode side.



Fig. S31 The voltage profiles of Zn || α -MnO₂ full cells at the 10th, 11th, 12th cycles at 0.2A g⁻¹. After the 10th cycle, the fully-charged Zn || α -MnO₂ cell went through a rest period for 48 h to conduct a self-discharge test and resumed cycling. (a) The DES-Zn || α -MnO₂ cell exhibited a discharge capacity of 130.94 mAh g⁻¹ in the 11th cycle after 48 h rest. In the 12th cycle, the cell exhibited 228.14 mAh g⁻¹, close to the 10th discharge capacity (230.61 mAh g⁻¹) before the rest step, indicating that the active Zn metal was still sufficient in the anode. (b) The Aq-Zn cell, however, exhibited almost zero and 34 mAh g⁻¹ of discharge capacity in the 11th and 12th cycles, respectively, indicating the depletion of Zn metal in the anode due to accelerated corrosion.

Table S1-S3

		Cathode					
	Practical specific capacity (mAh g ⁻¹)	Volumetric capacity (mAh cm ⁻³)	Thickness (μm)	Practical specific capacity (mAh g ⁻¹)	Volumetric capacity (mAh cm ⁻³)	Thickness (μm)	V _{nominal} (V)
Zn PNZ	200	250	40.0	820	5854	1.71	0.8
Zn MnO ₂	200	1006	9.94	820	5854	1.71	1.4
Graphite NMC811	190	903	11.08	360	814	12.29	3.6
Graphite LFP	161	765	13.08	360	814	12.29	3.3
HC NVPF	120	361	27.69	300	450	22.22	3.5
HC NVP	92	274	36.48	300	450	22.22	3.0

Table S1. A list of the original values for several battery systems used to calculate the energy density and the relative thickness in Fig. 1a-c. Detailed descriptions of the values are as follows.

(1) Energy density calculations are based on the total mass of the anode and the cathode active materials; separator, current collector, etc., are excluded from these calculations.

(2) The practical specific capacity (C _{cathode}, C_{anode}) and average operating voltage ($V_{nominal}$) are taken as reported by the authors. ⁴⁻⁶

(3) The volumetric capacity (V _{cathode}, V_{anode}) is calculated by multiplying practical specific capacity by density. ^{6, 7}

(4) The thickness was calculated for each electrode with an areal capacity of 1 mAh cm⁻².

(5) The thickness of the full cell in Fig. 1c was calculated based on the sum of the thicknesses of the anode and cathode per unit energy density.

(6) The n/p ratio for calculating the energy density was used according to the previous study.⁸⁻¹⁰ Also, in the formulas, n denotes the value of n in the n/p ratio.

Gravimetric Energy Density (Wh kg⁻¹) =
$$\frac{C_{\text{cathode}} \times C_{\text{anode}}}{n \times C_{\text{cathode}} + C_{\text{anode}}} (V_{\text{nominal}})$$

Volumetric Energy Density (Wh L^{-1}) = $\frac{V_{cathode} \times V_{anode}}{n \times V_{cathode} + V_{anode}}(V_{nominal})$

Thickness of electrode (μ m) = $\frac{\text{Capacity (1 mAh) \times 10,000 } \mu\text{m cm}^{-1}}{\text{area (1 cm}^2) \times \text{Volumetric capacity (mAh cm}^{-3})}$ Thickness of full cell (μ m mWh⁻¹) = $\frac{\text{Cathode thickness (} \mu\text{m}) + n \times \text{Anode thickness (} \mu\text{m})}{1\text{mAh} \times \text{V}_{\text{nominal}}}$

No.	Concept	DOD _{Zn} (%)	Cumulative capacity (Ah cm ⁻²)	Areal capacity per cycle (mAh cm ⁻²)	Current density (mA cm ⁻²)	Reference
[1]	PA-Zn	2.13	2.00	0.25	0.5	Energy Environ. Sci., 2019 , 12, 1938-1949
[2]	KL-Zn	1.87	1.76	1.1	4.4	Adv. Funct. Mater., 2020 , 30, 2000599
[3]	Zn (002)	1.13	0.25	1	1	Adv. Mater., 2021 , 33, 2100187
[4]	Zn(OTF) ₂ based electrolyte	0.57	0.13	0.17	1	Angew. Chem. Int. Ed., 2021 , 60, 7213–7219
[5]	Mxene-Zn	3.41	0.25	1	5	Angew. Chem. Int. Ed., 2021 , 60, 2861–2865
[6]	hybrid electrolyte (H ₂ O-EG)	3.41	0.15	1	2	Energy Environ. Sci., 2020 , 13, 3527-3535
[7]	PVB-Zn	8.50	0.55	0.5	0.5	Adv. Funct. Mater., 2020 , 30, 2001263
[8]	TiO ₂ -Zn	12.20	0.28	2	2	Nat. Commun., 2020 , 11, 3961
[9]	VG separator	17.03	0.13	1	1	Adv. Mater., 2020 , 32, 2003425
[10]	SLM-Zn	25.32	0.25	2	1	Adv. Funct. Mater., 2021 , 31, 2107397
[11]	ZCS-Zn	50	0.38	3	3	Energy Environ. Sci., 2021 , 14, 3609-3620
	DES-Zn	40	0.60	2	3	Our work

 Table S2.
 Symmetric cell cycling performances reported in recent studies compared to our work.

Table S3. Full cell cycling performances and their cycling conditions in recent studies in comparison with our work. The DOD_{Zn} is calculated by dividing the cathode capacity by the anode capacity based on the denoted value in a literature, and the cumulative capacity is multiplied the average capacity per cycle by cycle life.

No.	Cell configuration	DOD _{Zn} (%)	Aver. capacity per cycle (mAh cm ⁻²)	Cycle	Cumulative capacity (Ah cm ⁻²)	Reference
[1]	Zn@MOF AC	4.80	0.31	20,000	6.19	Joule, 2019 , 3, 1289–1300
[2]	$Zn@ZnF_2\\ MnO_2$	2.73	3.10	1,000	3.10	Adv. Mater., 2021 , 33, 2007406
[3]	ZCS-Zn AC	0.27	0.13	6,000	0.76	Energy Environ. Sci., 2021 , 14, 3609-3620
[4]	$Cu\text{-}Zn \ MnO_2$	0.28	0.17	500	0.08	Chem. Eng. J., 2021 , 416 128062
[5]	$\frac{Zn(002)}{NH_4V_4O_{10}}$	0.43	0.19	2,000	0.38	Adv. Mater., 2021 , 33, 2100187
[6]	Mxene-Zn MnO ₂	1.02	0.22	500	0.11	Angew. Chem. Int. Ed., 2021 , 60, 2861
[7]	MMT-Zn MnO ₂	4.34	1.80	400	0.72	Adv. Energy Mater., 2021 , 11, 2100186
[8]	Zn-MOF MnO ₂	1.63	0.44	5,000	2.20	Adv. Energy Mater., 2020 , 10, 1904215
[9]	PVB-Zn MnO ₂	4.08	0.10	1,500	0.14	Adv. Funct. Mater., 2020 , 30, 2001263
[10]	Zn-Cu skeleton MnO ₂	4.33	0.23	300	0.07	ACS Sustainable Chem. Eng. 2019 , 7, 3, 3364– 3371
[11]	Zn-CNT MnO ₂	20	0.77	1,000	0.77	Adv. Mater., 2019 , 31, 1903675
[12]	SLM-Zn AC	25.51	1.43	750	1.07	Adv. Funct. Mater., 2021 , 31, 2107397
[13]	NGO-Zn∥ LMO	36	1.84	178	0.33	Adv. Mater., 2021 , 33, 2101649

[14]	$PA\text{-}Zn \ MnO_2$	38.46	2.42	600	1.45	Energy Environ. Sci., 2019 , 12, 1938-1949
[15]	$Zn\ V_2O_5$	42.86	0.88	500	0.44	Adv. Mater., 2021 , 33, 2007416
[16]	Zn-graphene MnO ₂	50	0.65	1,000	0.65	Science, 2019 , 366, 645– 648
	DES-Zn AC	25.75	0.45	7,000	3.17	Our work

Note S1-S2

Note S1. Method for calculating S_a, S_q values.

The amplitude parameters (S_a , S_q) were calculated according to the standard ISO 25178-2. S_a and S_q are defined as the mean height of the scale limited surface. The confocal image covers an area of 640,000 μm^2 .

S_a: Arithmetic mean of the absolute of the ordinate values within a definition area

$$S_a = \frac{1}{A} \iint_A |z(x, y)| dxdy$$

Sq: Root mean square value of the ordinate values within a definition area

$$S_q = \sqrt{\frac{1}{A} \iint_A |z^2(x, y)| dx dy}$$

Note S2. Calculation details about the areal capacity of Zn in alloy layer

(1) Calculation for the $wt_{Zn}\%$ in CuZn₄

$$wt_{Zn}\% = \frac{AW_{Zn} \times 0.8}{AW_{Cu} \times 0.2 + AW_{Zn} \times 0.8} \times 100 = 80.20\%$$

where AW_{Zn} =65.37^{11}, AW_{Cu} =64.54^{12}

(2) Calculation for the areal density of Zn in alloy layer

Areal density of Zn = $\rho_{CuZn4} \times \frac{wt_{Zn}\%}{100} \times alloy height (= 0.8 \ \mu m) = 0.4940 \ mg \ cm^{-2}$ where $\rho_{CuZn_4} = 7.7 \ g \ cm^{-3}.^{13}$

(3) Calculation for the areal capacity of Zn in alloy layer

Theoretical capacity of Zn (mAh g⁻¹) × areal density of Zn = $0.405 \text{ mAh cm}^{-2}$

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