

Supporting Information

Highly Reversible Zinc Metal Anodes Enabled by Protonated Melamine

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Experimental Procedures

Electrolyte preparation : 2 M ZnSO₄ electrolyte was prepared by dissolving Zn salts (ZnSO₄·7H₂O, Sinopharm, AR) in deionized water. The pH of 2 M ZnSO₄ electrolyte was measured to be 3.8. The control electrolytes were prepared by adding different concentration (0.1, 0.3, and 0.5 g L⁻¹, respectively) of melamine (C₃H₆N₆, Sinopharm) into 80 mL 2 M ZnSO₄ electrolyte. The optimized electrolyte was 2M ZnSO₄ with 0.3 g L⁻¹ melamine and denoted as Mel/ZnSO₄ electrolyte. The pH of Mel/ZnSO₄ electrolyte was measured to be 4.8. 0.5 M Na₂SO₄ electrolyte was first prepared by dissolving Na₂SO₄ (Sinopharm, AR) in deionized water. The pH of 0.5 M Na₂SO₄ electrolyte was then adjust to 4 by adding ultra-dilute sulfuric acid solution for hydrogen evolution reaction tests.

Materials Characterization : The Zn deposition morphology was acquired by the field-emission scanning electron microscopy (FESEM, Hitachi S-4800). Bruker Vertex 70 Fourier transform infrared (FTIR) spectrophotometer was employed to collect the FTIR spectra of as-prepared electrolyte. The Raman spectra of as-prepared electrolyte were recorded by HORIBA JY LabRAM HR Evolution. The surface compositions of Zn anodes were investigated by X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi) equipped with Al K α X-ray source (2 kV and 6 mA). The Zn anode was washed with deionized water before the XPS characterization. The SHIMADZU UV 2600 was adopted to collect the Uv-vis spectra of relevant electrolyte.

Electrochemical Characterization : The chronoamperometry curve was collected at a fixed potential of -1.4 V in the three-electrode system using Zn plate (1×1 cm) as working electrode, Pt plate (1×1 cm) as counter electrode, and Ag/AgCl as reference electrode. The electrochemical impedance spectroscopy (EIS) of the Zn-Zn cells was conducted on a CHI 660e electrochemical workstation over the frequency range of 100 kHz to 0.01 Hz. The differential capacitance curves are plotted based on the results from alternating current voltammetry tests (the amplitude is 5 mV, with a potential range extended from 1.0 to 0 V versus Zn²⁺/Zn). Tafel plots were measured by scanning

between -0.8 and -1.1 V at 1 mV s^{-1} with Zn plate as the working electrode and counter electrode, and Ag/AgCl as the reference electrode, respectively. The hydrogen evolution reaction potential was recorded using linear sweep voltammetry method with a scan rate of 5 mV s^{-1} in Na_2SO_4 and Mel/ Na_2SO_4 electrolyte. Zn symmetric cells (ZBs) were assembled by sandwiching the glass fiber (separators) between commercial Zn plates ($70 \text{ }\mu\text{m}$, 45 mAh cm^{-2}) in CR2032-type cell filled with Mel/ ZnSO_4 or ZnSO_4 electrolyte. Zn-Cu half cells were assembled using Zn plate ($70 \text{ }\mu\text{m}$, 45 mAh cm^{-2}) as anode, Cu foils ($20 \text{ }\mu\text{m}$) as cathode, and glass fiber as separator. Zn ions hybrid supercapacitors were assembled using Zn plate ($70 \text{ }\mu\text{m}$, 45 mAh cm^{-2}), activated carbon cloth, and hydrophilic mixed cellulose membrane as anode, cathode, and separator, respectively. The electrolyte volume for Zn ions hybrid supercapacitors is controlled to be $40 \text{ }\mu\text{L}$. The activated carbon cloth was prepared by a simple air calcination method at $400 \text{ }^\circ\text{C}$ for 2 hours according to the previous study^{S1, S2}.

DFT calculation method : The DFT calculation was performed by the Vienna Ab-initio Simulation Package (VASP), and the exchange-correlation energy was approximately described by the Perdew-Burke-Ernzerhof (PBE) functional based on the generalized gradient approximation (GGA). In all calculation, a cutoff energy with the value of 400 eV was used for the plane wave basis, and the convergence criteria for the ionic relaxation and the electronic self-consistent calculation were set to $0.02 \text{ eV } \text{\AA}^{-1}$ and 10^{-5} eV , respectively. The Zn (0001) surface is modeled by a five-layers 5×5 surface supercell (25 Zn atoms per layer) with only considering the Γ point for saving the computational resources. The long-range dispersion correction for the van der Waals interaction was implemented through the DFT-D2 method in all calculation.

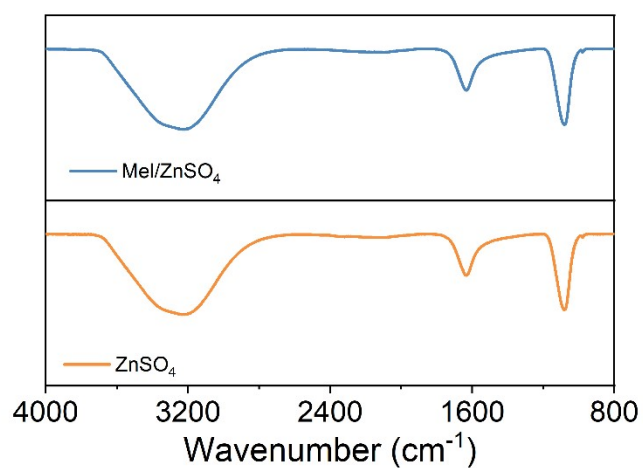


Fig. S1. The FTIR of Mel/ZnSO₄ and ZnSO₄ electrolyte.

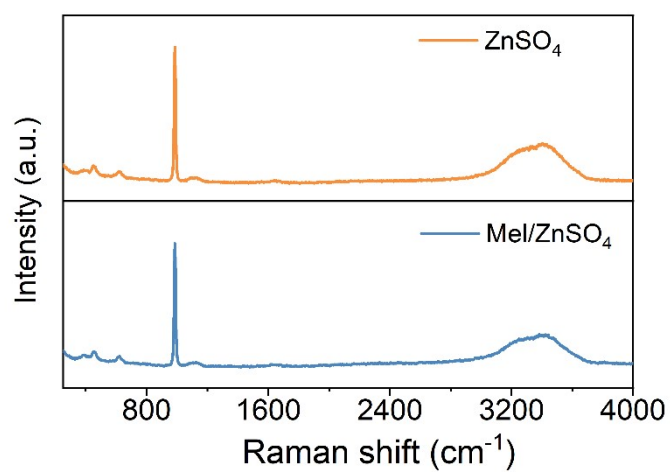


Fig. S2. The Raman spectrum of Mel/ZnSO₄ and ZnSO₄ electrolyte.

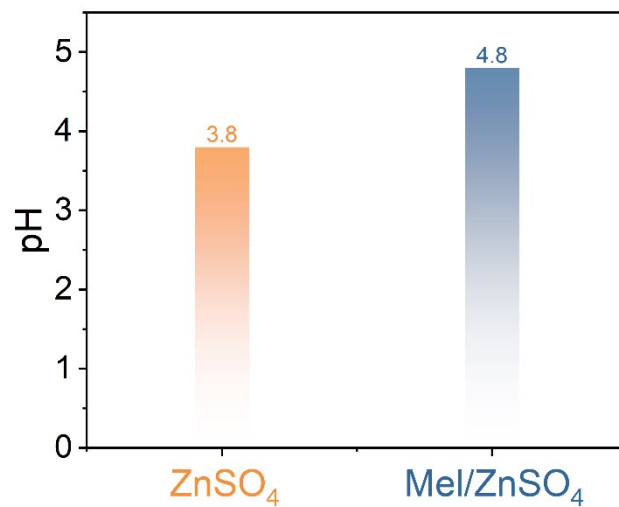


Fig. S3. The pH of Mel/ZnSO₄ and ZnSO₄ electrolyte.

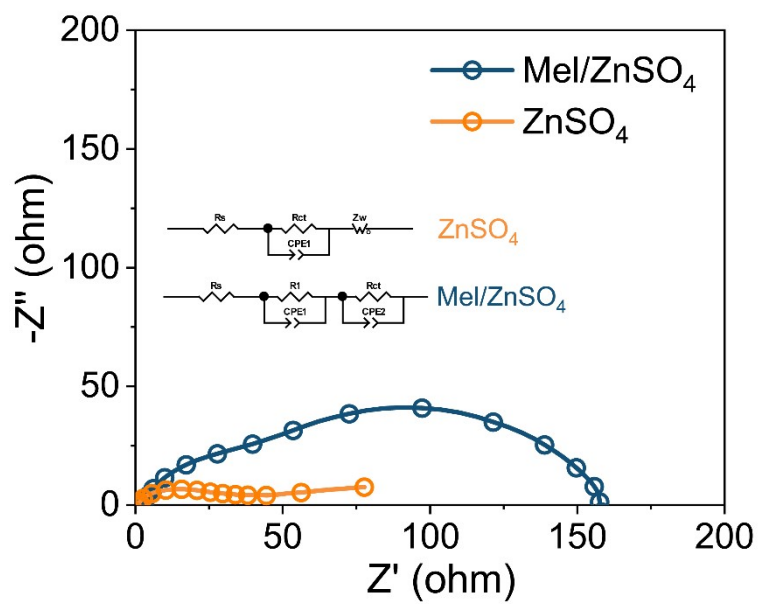


Fig. S4. The EIS curves of Zn|Zn symmetric cells tested in Mel/ZnSO₄ and ZnSO₄ electrolyte.

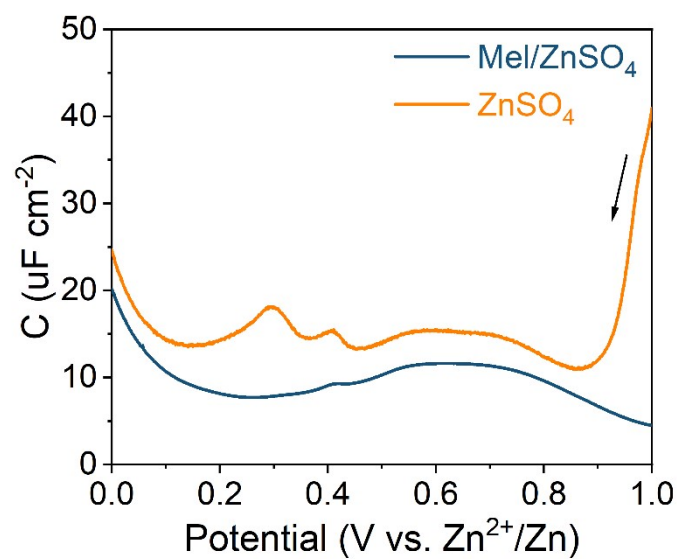


Fig. S5. The differential capacitance curves of Zn|Cu half cells tested in Mel/ ZnSO_4 and ZnSO_4 electrolyte.

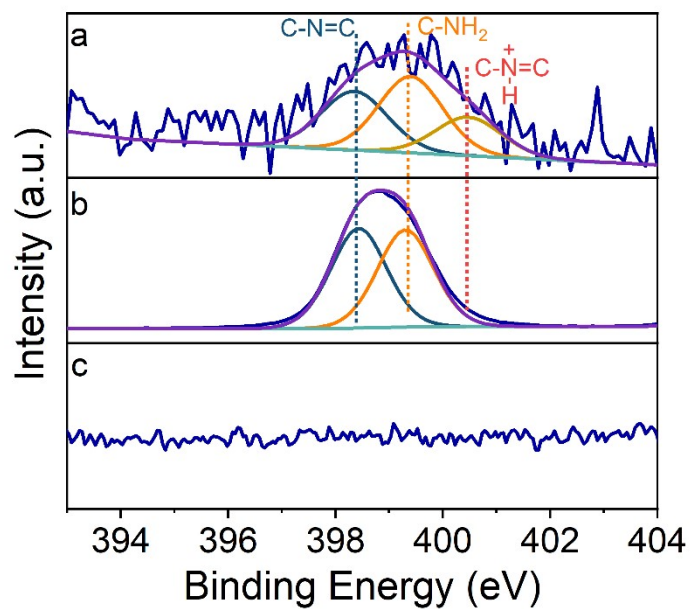


Fig. S6. The N1s spectrum of a) Zn anode immersed in Mel/ ZnSO_4 , b) melamine powder, and c) Zn anode immersed in ZnSO_4 electrolyte.

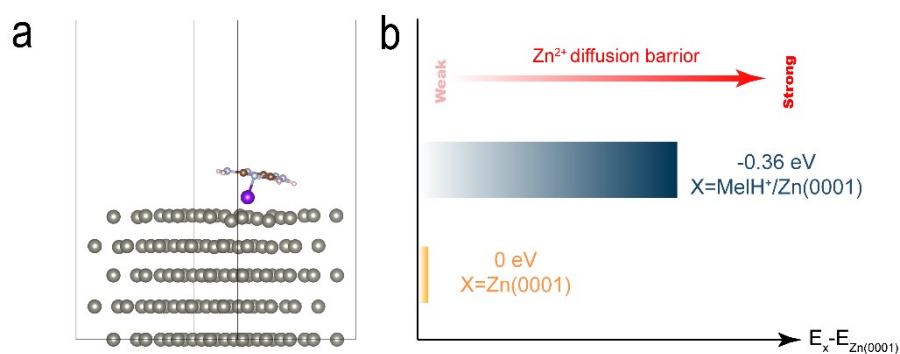


Fig. S7. a) The adsorption behaviour of Zn²⁺ on Zn (0001) modified by MelH⁺. b) The comparison of Zn²⁺ adsorption energy on the Zn (0001), and MelH⁺/Zn (0001).

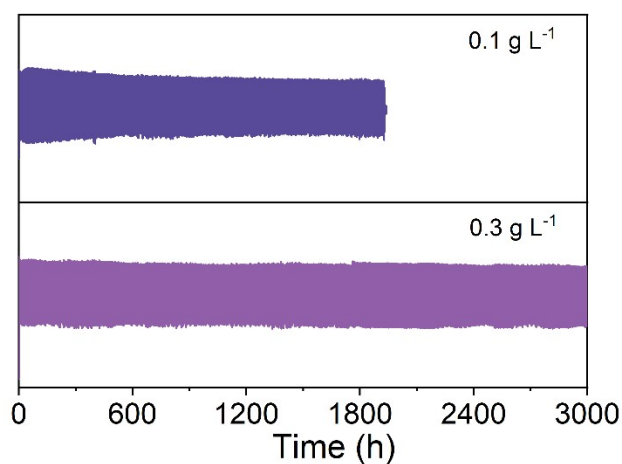


Fig. S8. Voltage profiles of Zn|Zn symmetric cells cycled in ZnSO₄ based electrolyte with different concentration of Mel additives.

As presented in Fig. S8, Zn|Zn symmetric cells cycled in ZnSO₄ electrolyte with 0.3 g L⁻¹ Mel additives delivers a longer cycle life of 3000 h than that in ZnSO₄ electrolyte with 0.1 g L⁻¹ Mel additives. When the Mel concentration further increased to 0.5 g L⁻¹, the as-prepared electrolyte exhibits white precipitation, which may be attributed to the

formation of $\text{Zn}_4\text{SO}_4(\text{OH})_6 \cdot x\text{H}_2\text{O}$ under the pH of 5.2, which is similar to the recently reported work^[S3]. Therefore, it is concluded that the optimized concentration of Mel additive is 0.3 g L^{-1} .

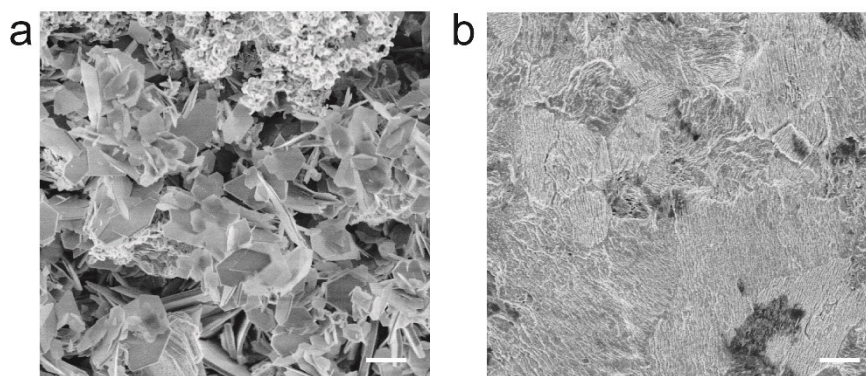


Fig. S9. The top-view SEM image of Zn|Zn symmetric cells using (a) ZnSO_4 and (b) Mel/ ZnSO_4 electrolyte at 40th cycle (scale bar: $4 \mu\text{m}$).

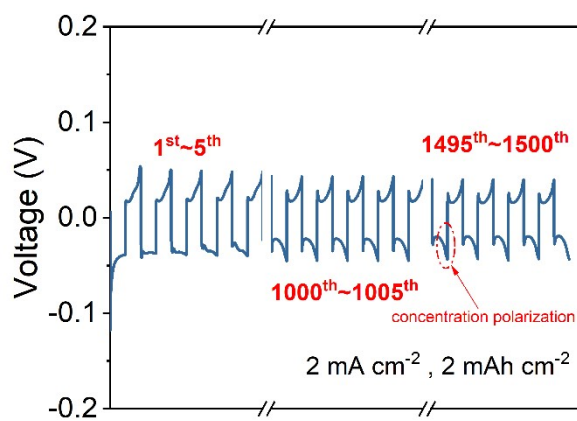


Fig. S10. Voltage profiles of Zn|Zn symmetric cells in Mel/ ZnSO_4 electrolyte at the selected cycles.

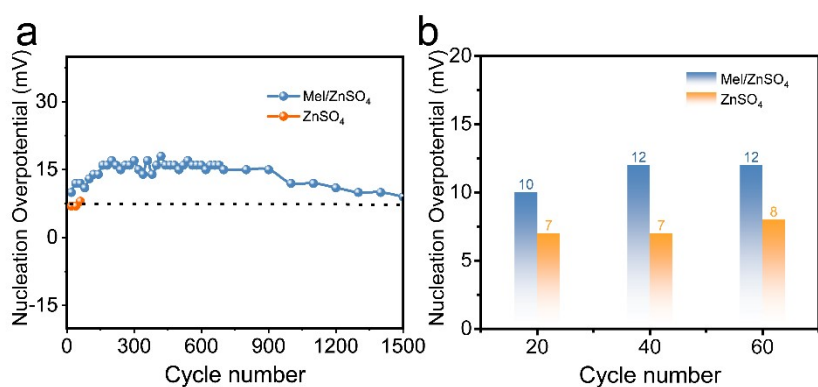


Fig. S11. (a) The nucleation overpotential evolution of Zn|Zn symmetric cells using ZnSO₄ and Mel/ZnSO₄ electrolyte. (b) The nucleation overpotential of Zn|Zn symmetric cells at the selected cycle.

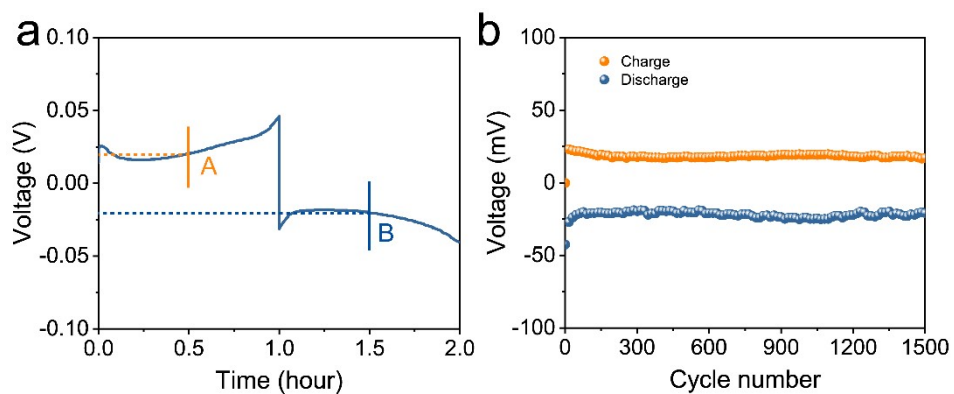


Fig. S12. (a) The illustration of mid-point voltage collected at discharge/charge capacity of 1 mAh cm⁻². (b) The mid-point voltage evolution of Zn|Zn symmetric cells using Mel/ZnSO₄ electrolytes.

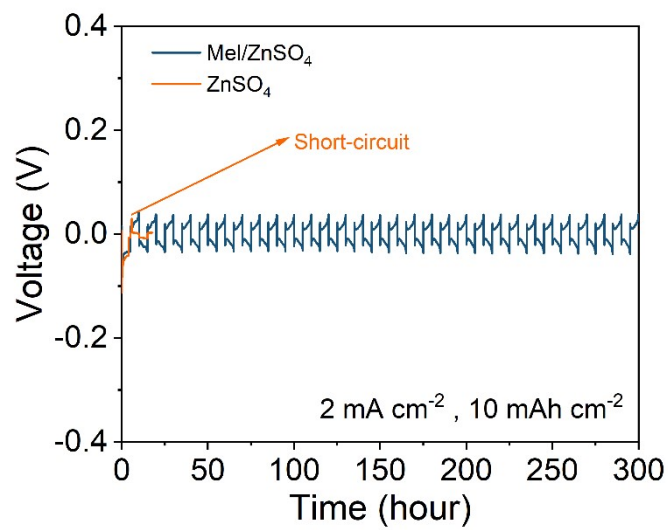


Fig. S13. Cycle stability of Zn|Zn symmetric cells using ZnSO₄ and Mel/ZnSO₄ electrolyte.

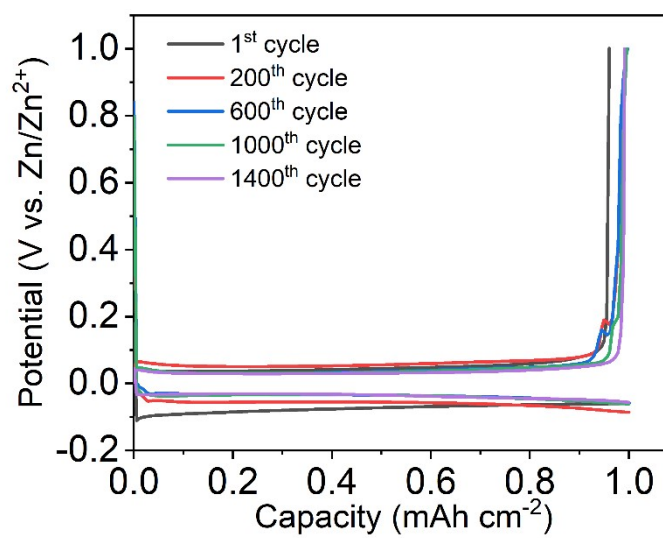


Fig. S14. Voltage profiles of Zn|Cu half cells using Mel/ZnSO₄ electrolytes at the selected cycles.

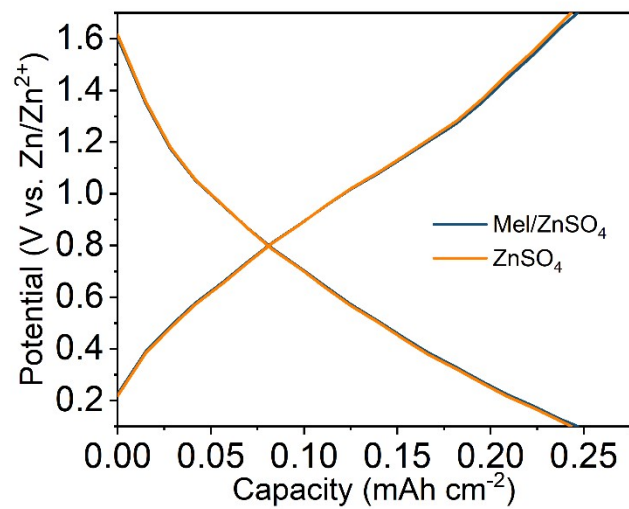


Fig. S15. The charge-discharge curves of ZHS using Mel/ZnSO₄ and ZnSO₄ electrolytes.

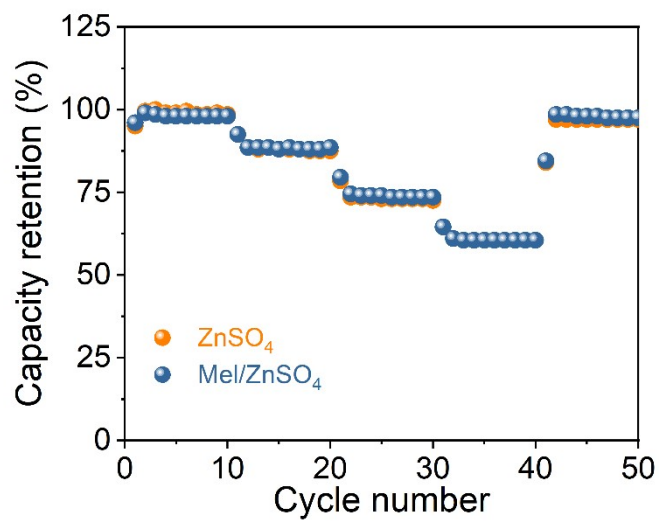


Fig. S16. The rate performance of ZHS tested in ZnSO₄ and Mel/ZnSO₄ electrolyte.

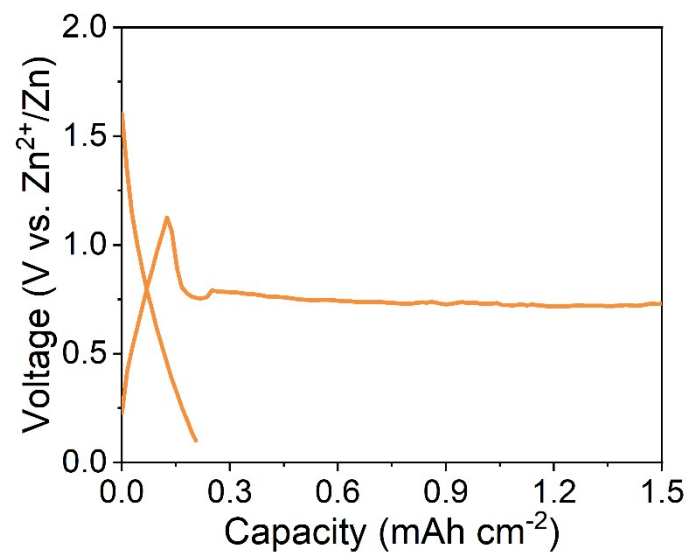


Fig. S17. The charge-discharge curves of ZHS in ZnSO₄ electrolytes at 133th cycle.

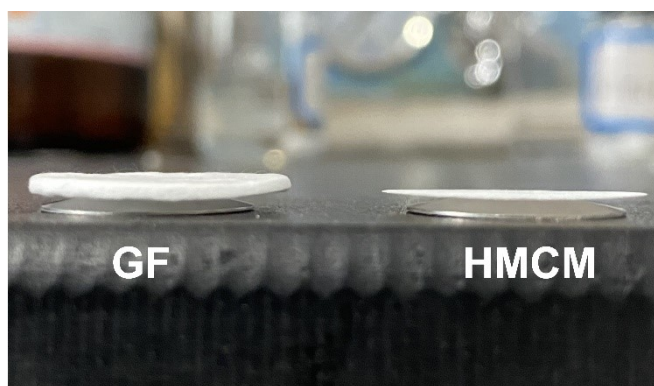


Fig. S18. The digital photo of glass fiber (GF) and hydrophilic mixed cellulose membrane (HMCM).

Table S1. The CPC comparison of Zn symmetric cells in Mel/ZnSO₄ electrolyte with previous literatures using other strategies.

strategy	Test condition	Cycle time (hour)	Cycle number	CPC (mAh cm ⁻²)	Reference
piZn	4 mA cm ⁻² ; 2 mAh cm ⁻²	300	300	600	S4
Zn (002)	1 mA cm ⁻² ; 1 mAh cm ⁻²	500	250	250	S5
cellulose-graphene coated Zn	0.25 mA cm ⁻² ; 0.5 mAh cm ⁻²	5500	1375	687.5	S6
Zn@ZnF ₂	1 mA cm ⁻² ; 1 mAh cm ⁻²	800	400	400	S7
Zn/Sn(200)	1 mA cm ⁻² ; 1 mAh cm ⁻²	500	500	500	S8
ZCS-Zn	2 mA cm ⁻² ; 4 mAh cm ⁻²	1200	300	1200	S9
ZF@F-TiO ₂	1 mA cm ⁻² ; 1 mAh cm ⁻²	460	230	230	S10
MXene coated Zn	0.2 mA cm ⁻² ; 0.2 mAh cm ⁻²	800	400	80	S11
Mel additive	2 mA cm⁻²; 2 mAh cm⁻²	3000	1500	3000	This work

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