Supporting Information

# Unraveling the Regulation of Polyhydroxy Electrolyte Additive for a Reversible, Dendrite-Free Zinc Anode

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**Supplemental Experimental Details**

***Materials***:

Zn foil (~0.1 mm) and Pt were purchased from Haoxuan Metal Material Co., Ltd. $ZnSO_4 \cdot 7H_2O$ (>99.0%), sucrose (TS, >99.9%), Ag/AgCl electrode, ammonium persulfate (APS, >99.99%) and $V_2O_5$ powder (>99.99%) were purchased from Sinopharm Chemical Reagent Co., Ltd. All other reagents were analytical grade and used directly without further purification. Deionized water was used to prepare all aqueous electrolytes.

***Materials Characterization*:**

The micromorphology of the samples was observed using scanning electron microscopy (SEM, FEI-Quanta 250, USA). The elemental analysis of the samples was characterized using a scanning electron microscope (FE-SEM, JSM-7500, Japan) equipped with corresponding energy-dispersive X-ray (EDX) elemental mapping. The crystal structure of the samples was characterized through the X-ray diffraction analysis (XRD, Smart Lab, Rigaku, Japan) with Cu-Kα (λ= 1.540598 Å, Smart Lab) source (scan rate of 4º $min^{-1}$) in the 2θ range of 5º~85º. The analysis of the electrolytes was carried out by H magnetic resonance imaging (NMR spectroscopy (Bruker advance III) and Fourier transform infrared spectrum (FTIR, NICOLET iS50, USA).

***Electrochemical Tests***:

Electrochemical characterization of symmetrical Zn//Zn cells with two different electrolytes was conducted using both transparent cells and 2032-type coin cells. Electrochemical impedance spectroscopy (EIS) of these cells was conducted on an electrochemical workstation (CHI660E, Shanghai, China) over the frequency range of 100 kHz to 1 Hz. The Zn//$V_2O_5$ coin and pouch cells were galvanostatically charged/discharged in the voltage range of 0.2–1.5 V vs. $Zn/Zn^{2+}$ at different current densities on a Land CT5001A battery tester, and specific capacities were calculated based on the active mass of $V_2O_5$ cathode. The mass of $V_2O_5$ and Zn foil are approximately 1.5 mg and 100 mg, respectively. The width of Zn, $V_2O_5$, and separator are 14 mm, 14 mm, and 18 mm, respectively. In addition, the amount of Suc-containing electrolyte used is 90 μL.

***Transparent Zn Cell and In Situ Dendrite Observation***:

A transparent Zn-Zn cell was designed to observe the Zn dendrite growth. Specifically, a transparent glass dish, two Zn ribbons (0.5 cm × 3 cm), and two plastic clamps form a pool for observing the Zn dendrites. The transparent glass dish is used to store the electrolyte. The Zn dendrites growth was in situ observed by an optical microscope equipped with a digital camera. Meanwhile, the transparent Zn cell was tested for Zn stripping/plating using an electrochemical workstation (CHI660E).

***Theoretical Calculations***:

The Vienna ab initio simulation package (VASP) was used to perform all the calculations.[1] The electronic exchange-correlation energy was implemented using the Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation (GGA), and the projector augmented wave (PAW) method describing electron-ion interactions.[2] In geometry optimization settings, the atomic positions were optimized until all components of the forces on each atom were less than -0.05 eV/Å and the total energy converge was set to below $10^{-5}$ eV. The DFT-D3 correction was used to describe van der Waals interactions.[3] A cutoff energy of 400 eV and a Monkhorst-Pack k-point grid of 2×2×1 were used, respectively. A vacuum of 15 Å was set to circumvent periodic interactions between the atoms.

The binding energy (Eb) is defined as

$$Eb=E_{A+B} – (E_A+E_B)$$

where $E_{A+B}$ is the total energy of a combined system of A and B, $E_B + E_A$ is the sum of the total energies of A and B before the combination. A and B refer to Suc, $Zn^{2+}$, $H_2O$, and Zn slab (002), respectively.

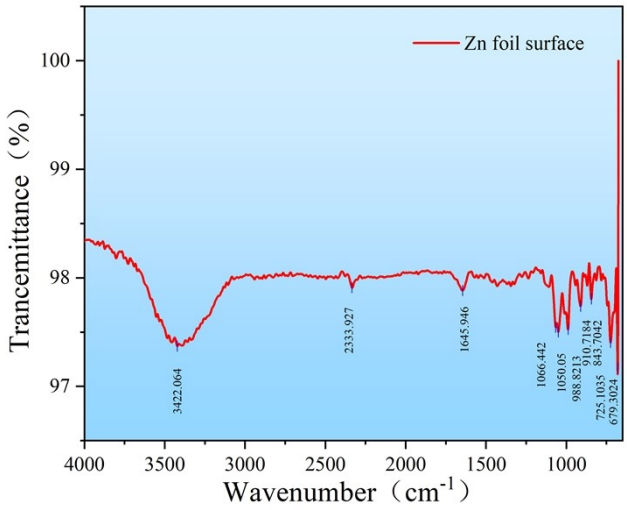



Fig. S1. FTIR spectrum of Zn foil soaked in 1 M $ZnSO_4$ with Suc after 1 day.

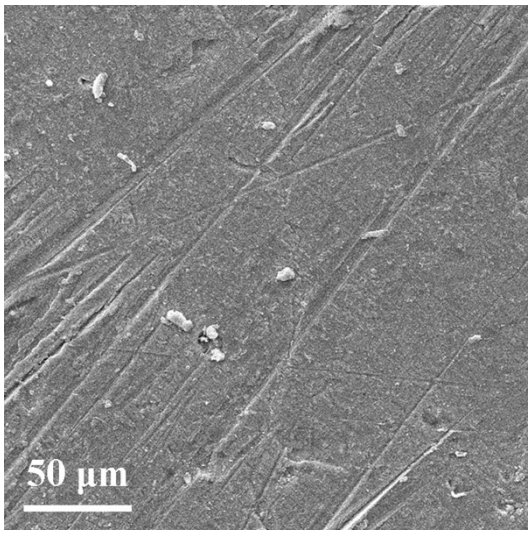



**Fig. S2.** SEM image of the pure Zn foil.

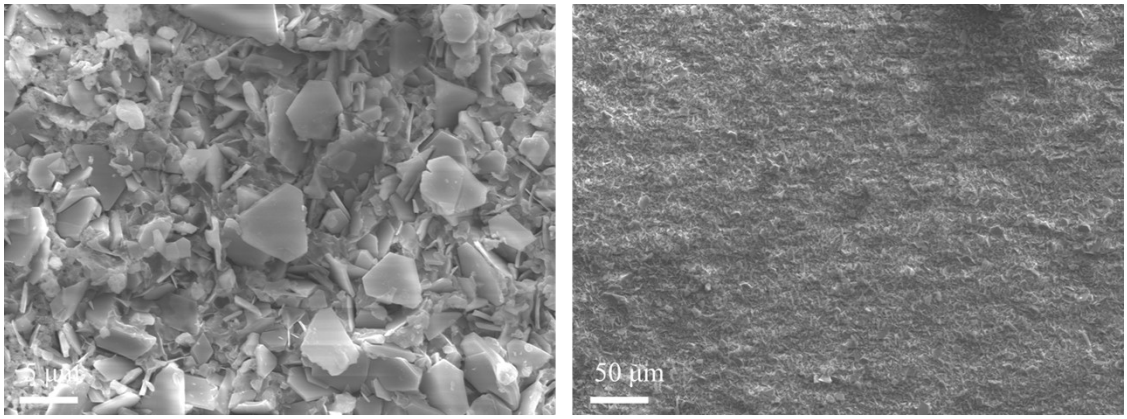



**Fig. S3.** SEM images at different magnifications for the Zn foil soaked in 1 M $ZnSO_4$ after 7 days.

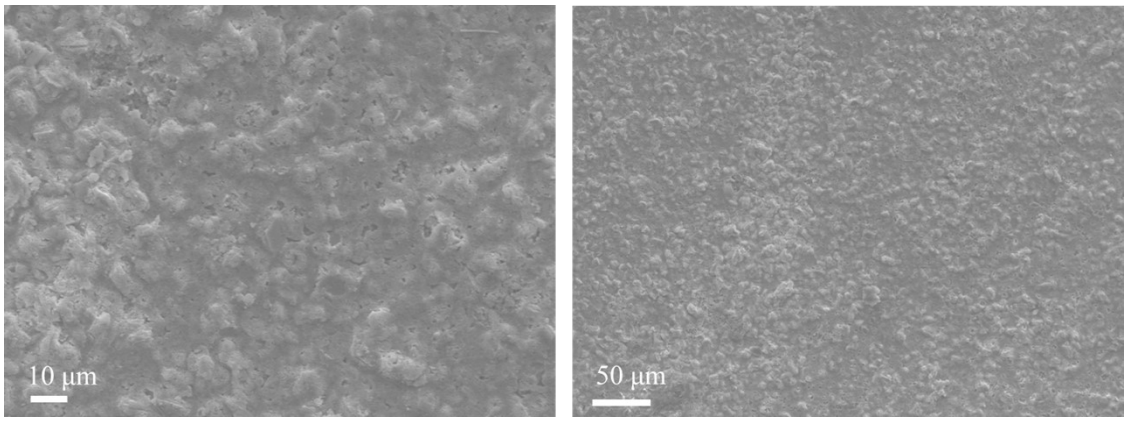
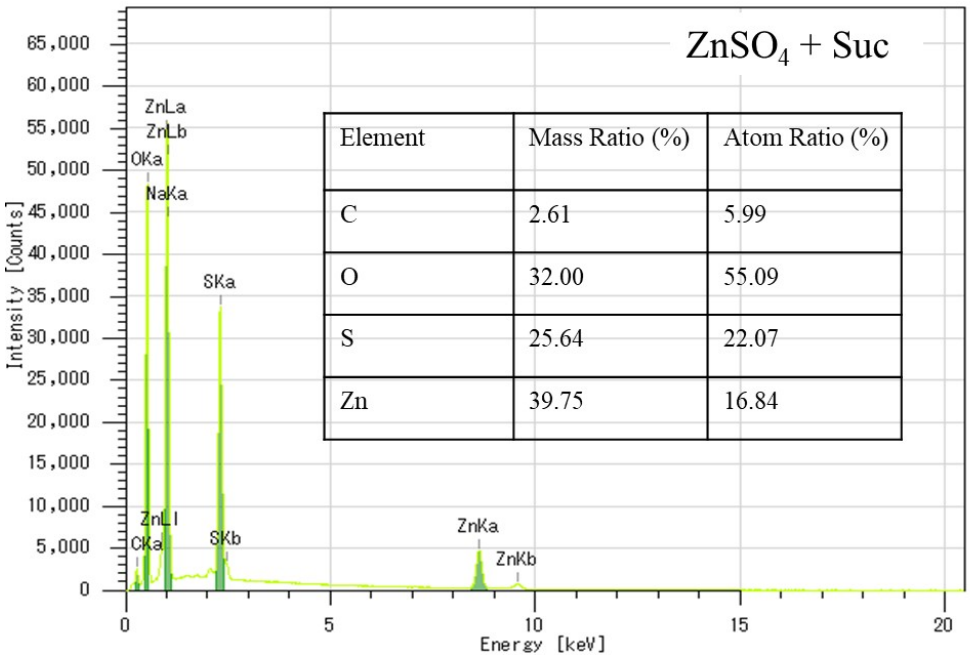
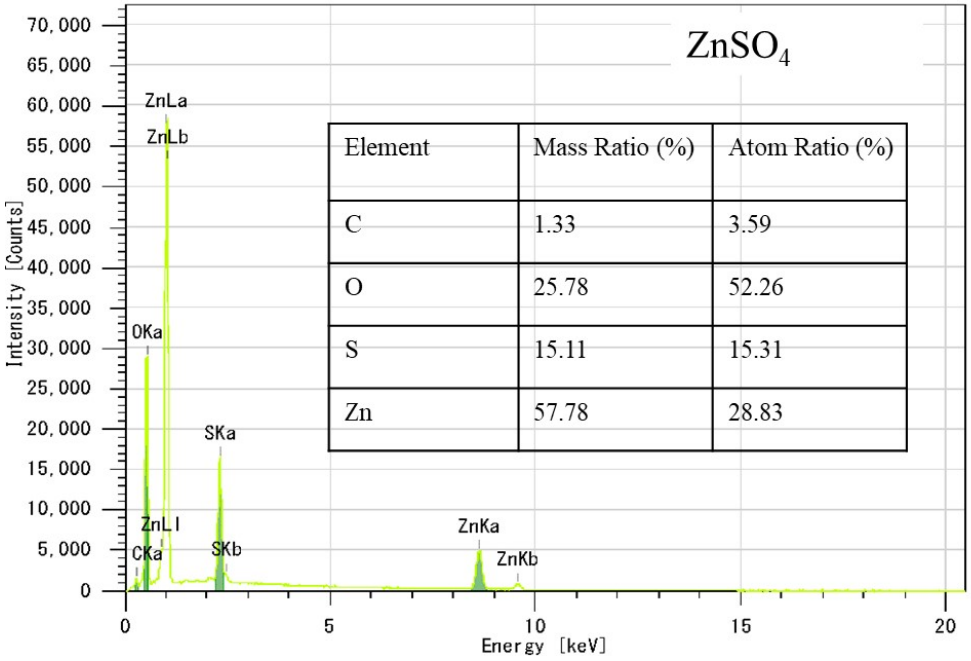



**Fig. S4.** SEM images at different magnifications for Zn foil soaked in 1 M $ZnSO_4$ with Suc after 7 days.




| Element | Mass Ratio (%) | Atom Ratio (%) |
|---|---|---|
| C | 2.61 | 5.99 |
| O | 32.00 | 55.09 |
| S | 25.64 | 22.07 |
| Zn | 39.75 | 16.84 |

**Fig. S5.** EDS spectrum of Zn foil soaked in 1 M $ZnSO_4$ after 7 days.




| Element | Mass Ratio (%) | Atom Ratio (%) |
|---|---|---|
| C | 1.33 | 3.59 |
| O | 25.78 | 52.26 |
| S | 15.11 | 15.31 |
| Zn | 57.78 | 28.83 |

**Fig. S6.** EDS spectrum of Zn foil soaked in 1 M $ZnSO_4$ with Suc after 7 days.

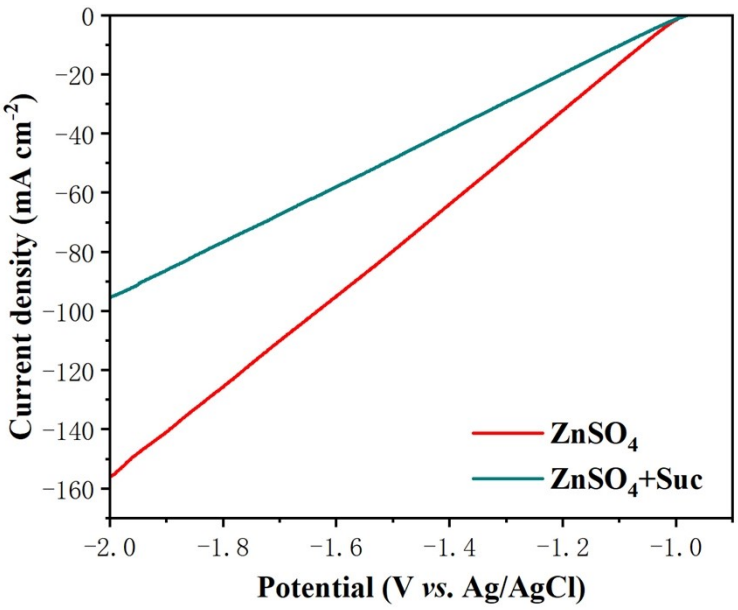



**Fig. S7.** Comparison of HER performance under $ZnSO_4$ and $ZnSO_4$ + Suc electrolyte systems.

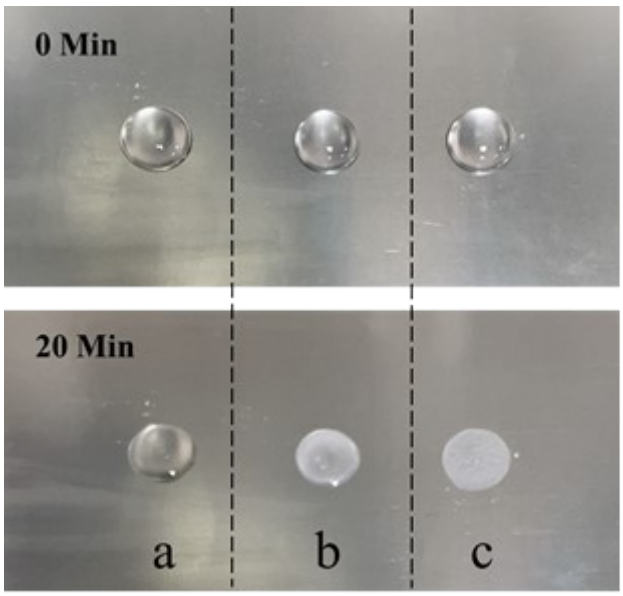



**Fig. S8.** Comparison of volatility among (a) 1 M Suc, (b) 1 M $ZnSO_4$ with 10 mM Suc, and (c) 1 M $ZnSO_4$ at room temperature.

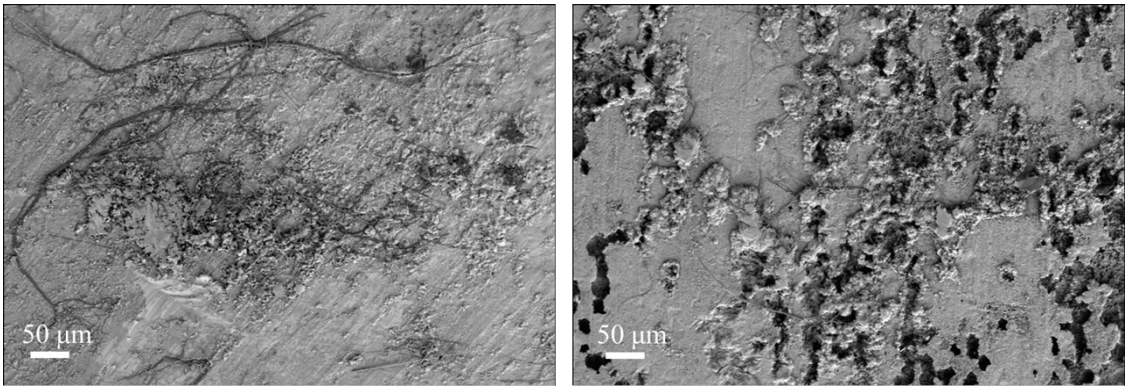



**Fig. S9.** SEM images of Zn electrodes that are cycled out of the cells in $ZnSO_4$ electrolyte after the 30$^{th}$ plating.

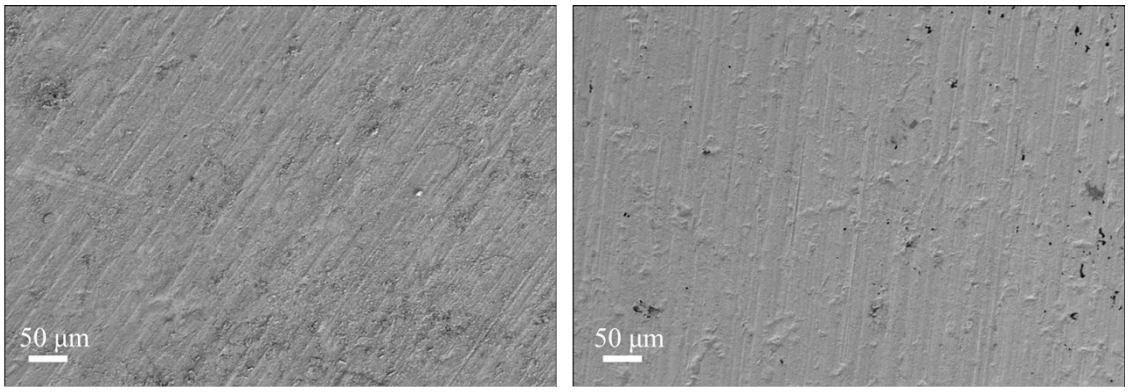



**Fig. S10.** SEM images of Zn electrodes cycled out of the cells in $ZnSO_4$ electrolyte with Suc after the 30$^{th}$ plating.

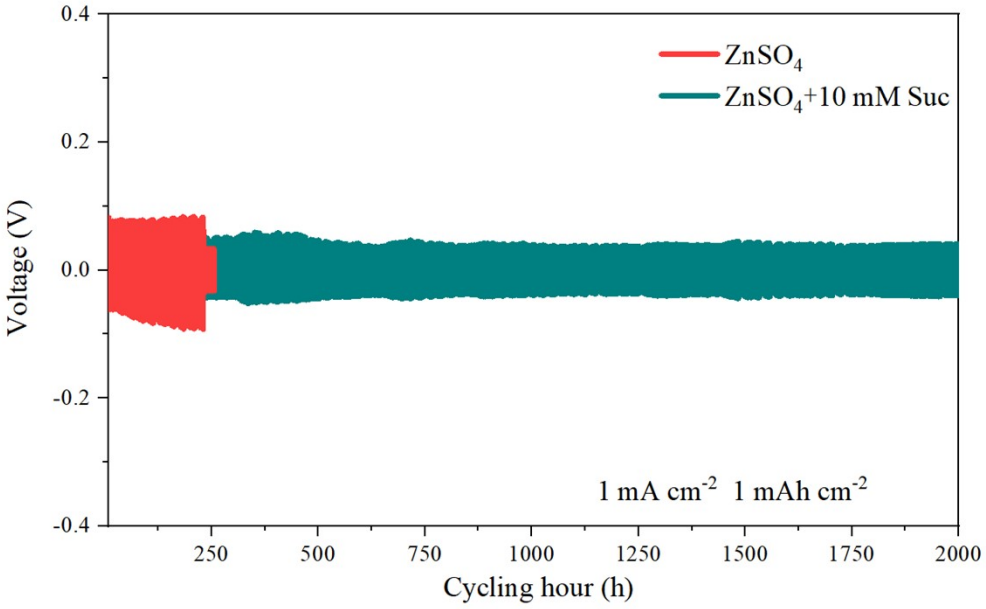



**Fig. S11.** Comparison of long-term galvanostatic charging/discharging of Zn//Zn symmetric cell between 1 M $ZnSO_4$ and 1 M $ZnSO_4$ with 10 mM Suc addition under a current density and deposition capacity of 1 mA $cm^{-2}$ and 1 mAh $cm^{-2}$, respectively.

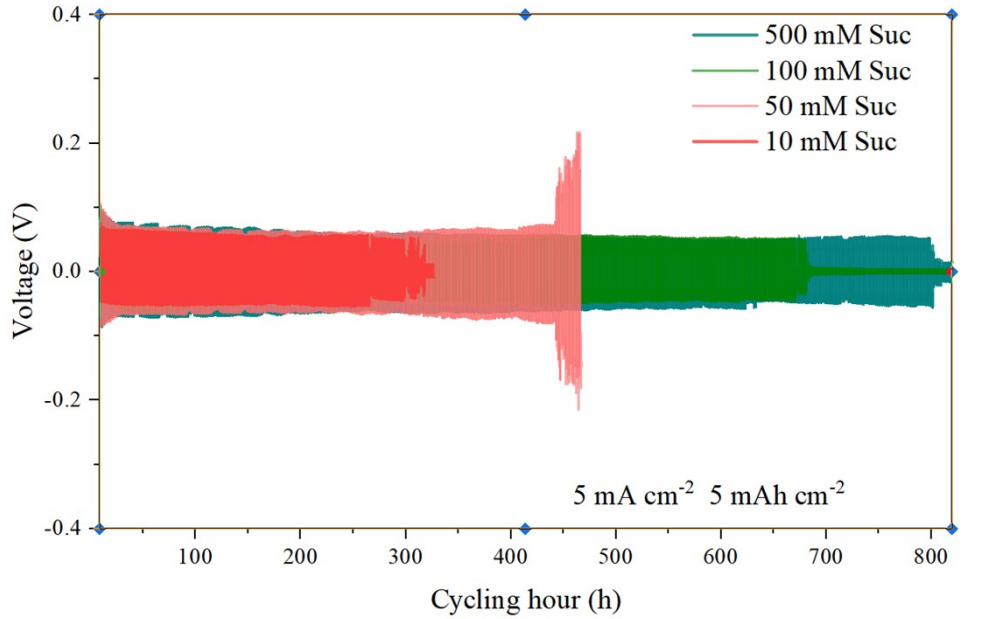



**Fig. S12.** Comparison of long-term galvanostatic charging/discharging of Zn//Zn symmetric cell with different Suc concentration addition under a current density and deposition capacity of 5 mA $cm^{-2}$ and 5 mAh $cm^{-2}$, respectively.

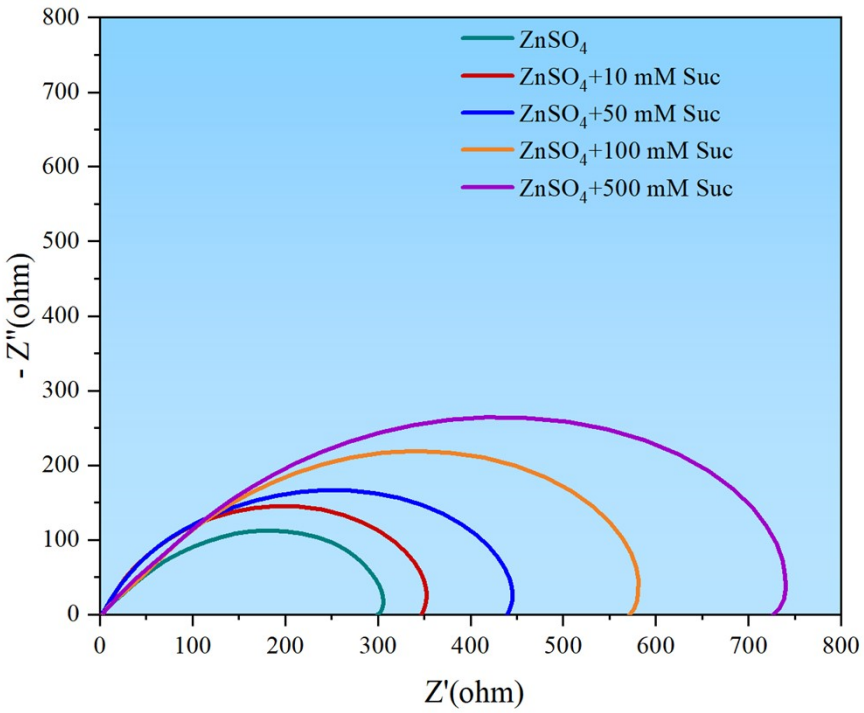



**Fig. S13.** Comparison of the electrochemical impedance of Zn//Zn symmetric cell in $ZnSO_4$ and $ZnSO_4$ with 10, 50, 100 and 500 mM electrolytes.

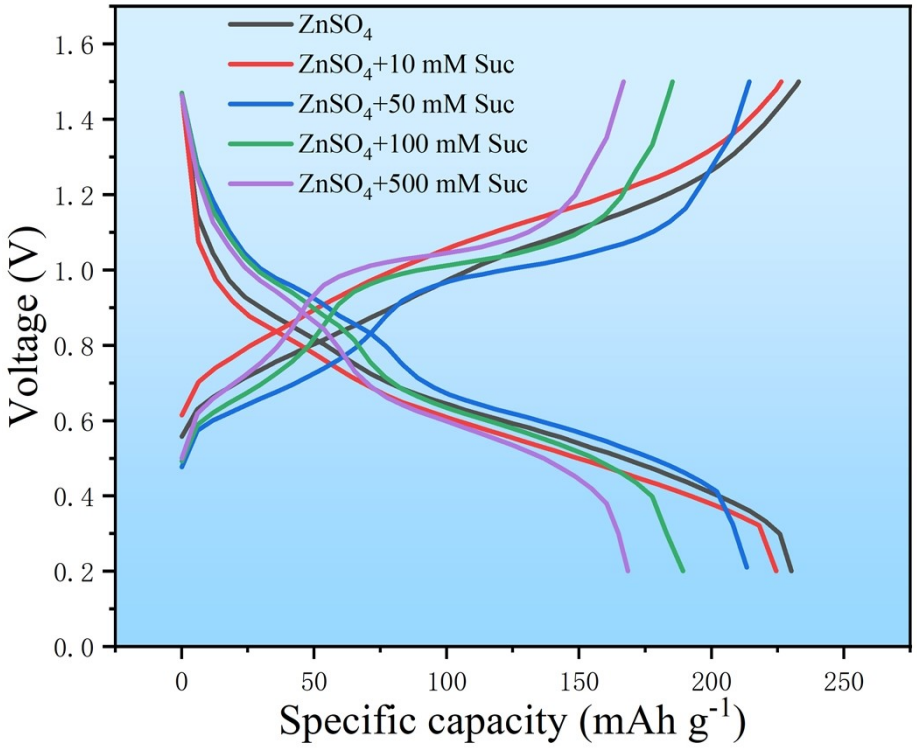



**Fig. S14.** Comparison of the specific capacity of Zn//$V_2O_5$ cells at a current density of 1 A $g^{-1}$ using $ZnSO_4$, and $ZnSO_4$ with 10, 50, 100 and 500 mM Suc electrolytes.

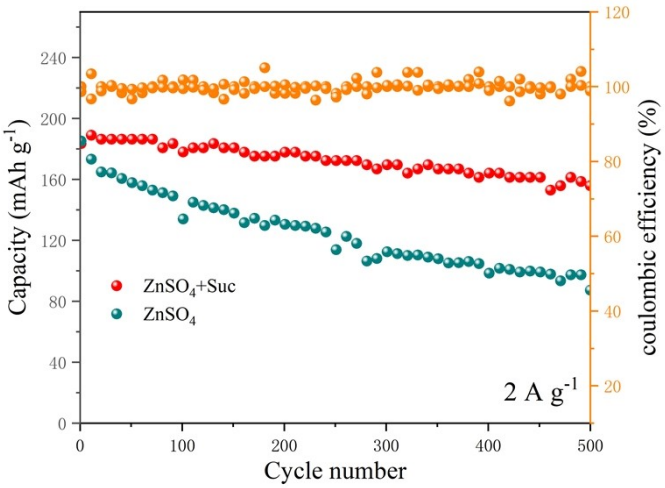



**Fig. S15.** Cycling performance of two Zn//$MnO_2$ coin cells at a current density of 2 A $g^{-1}$.

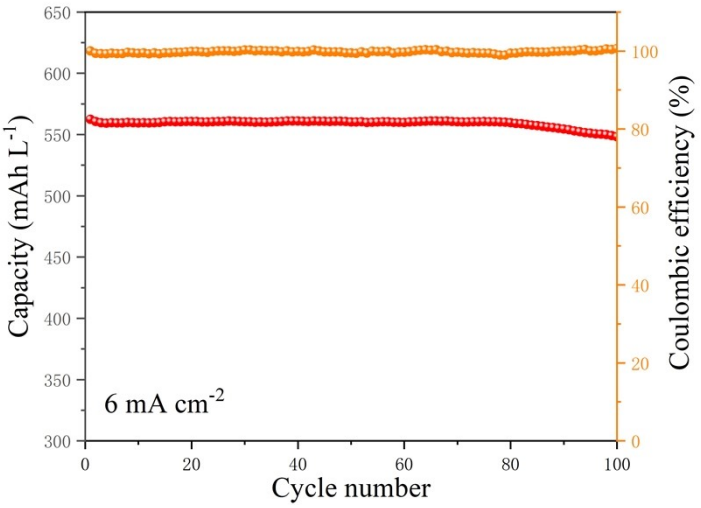



**Fig. S16.** Cycling performance of the Zn//$V_2O_5$ pouch battery under the current density of 6 mA $cm^{-2}$.

**Table S1.** Chemical cost estimation of reported electrolyte systems in ZIBs. (The cost is counted based on the price referred to Shanghai Aladdin Biochemical Technology Co., Ltd with all purity above 98%.)

| Electrolyte type | Chemical | Aladdin catalog number (purity) | Mass required ($g \cdot L^{-1}$ electrolyte) | Unit Price ($\$ \cdot g^{-1}$) | Total price ($\$ \cdot L^{-1}$) | Reference |
|---|---|---|---|---|---|---|
| 3 m $ZnAc_2$ + 3 m LiAc + 30 m KAc | $ZnAc_2$ | Z110779 (99.99%) | 550.44 | 0.455 | 1271.7 | [4] |
| | LiAc | L118858 (99.99%) | 197.97 | 0.697 | | |
| | KAc | P108329 (99%) | 2944.2 | 0.300 | | |
| 1 M $Zn(TFSI)_2$ + 20 M LiTFSI | $Zn(TFSI)_2$ | Z299992 (98%) | 625.65 | 3.962 | 16287.37 | [5] |
| | LiTFSI | B398978 (99.9%) | 5741.6 | 2.405 | | |
| 30 m $ZnCl_2$ | $ZnCl_2$ | Z292534 (99.99%) | 4089 | 6.724 | 27494.44 | [6] |
| 4.2 M $ZnSO_4$ + 0.1 M $MnSO_4$ | $ZnSO_4$ | Z111855 (99%) | 1207.71 | 0.036 | 47.32 | [7] |
| | $MnSO_4$ | M111711 (99.99%) | 16.91 | 0.227 | | |
| 13 m $ZnCl_2$ + 0.8 m $H_3PO_4$ | $ZnCl_2$ | Z292534 (99.99%) | 1771.9 | 6.724 | 12094.34 | [8] |
| | $H_3PO_4$ | P120547 (99%) | 78.4 | 2.297 | | |
| 67% Maltose + 2 M $ZnSO_4$ | Maltose | M104816 (98%) | 670 | 0.102 | 75.17 | [9] |
| | $ZnSO_4$ | Z111855 (99%) | 189.78 | 0.036 | | |
| 32 vol% 3 M $ZnSO_4$ + 68 vol% EG | Ethylene glycol | E119700 （99.8%） | 756.84 | 0.163 | 133.30 | [10] |
| | $ZnSO_4$ | Z111855 (99%) | 276.06 | 0.036 | | |
| 10 m M Sucrose + 1 M $ZnSO_4$ | Sucrose | S112226 (99.9%) | 3.42 | 0.063 | 10.57 | This work |
| | $ZnSO_4$ | Z111855 (99%) | 287.56 | 0.036 | | |

**Table S2.** Comparison of high current stability performance of ZIBs from previous reports and our work.

| Cathode | Electrolyte | Cycling condition | | Capacity retention | Reference |
|---|---|---|---|---|---|
| | | Current ($A \cdot g^{-1}$) | Cycle number | | |
| $HfO_2$-coated ZVO | 1 M $ZnSO_4$ | 10 | 1000 | 84% | [11] |
| $V_2O_5$ | 1 M $Zn(CF_3SO_3)_2$ | 5 | 1000 | 99.3% | [12] |
| $NaCa_{0.6}V_6O_{16} \cdot 3H_2O$ | 3 M $Zn(CF_3SO_3)_2$ | 2 | 2000 | 94% | [13] |
| $VO_2$ | 1 M $ZnSO_4$ | 3 | 945 | 75.5% | [14] |
| $H_2V_3O_8$ | 3 M $Zn(CF_3SO_3)_2$ | 20 | 2000 | 87% | [15] |
| $Fe_5V_{15}O_{39}(OH)_9 \cdot 9H_2O$ | 1 M $ZnSO_4$ | 5 | 300 | 80% | [16] |
| α-$MnO_2$ | 1 M $ZnSO_4$ | 2.5 | 100 | 100% | [17] |
| $V_2O_5$ | 3 M $ZnSO_4$ | 2 | 400 | 93.4% | [18] |
| $MnO_2$ | 10 m M Glucose + 1 M $ZnSO_4$ | 3.08 | 1000 | 80% | [19] |
| $MnO_2$ | 2 M $ZnSO_4$ | 1 | 900 | 83.1% | [20] |
| $V_2O_5$ | 10 m M Sucrose + 1 M $ZnSO_4$ | 10 $A \cdot g^{-1}$ | 2000 | 96.2% | This work |

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