Supporting information

In situ formation of zincophilic–hydrophobic layers *via* self-assembling additives for stabilizing zinc metal anodes

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1. Experimental section

***1.1 Synthesis of I_2 cathode*：** I_2 and supercapacitor activated carbon were mixed and ground in a ratio of 1:1, and the mixture was heated in an oven at 120°C for 5h to obtain the I_2 cathode material required for the experiment.

***1.2 Electrolyte Preparation*：** Zinc sulfate ($ZnSO_4$, Aladdin, > 99%) was added to deionized water (DI) to dissolve, and a 1 M $ZnSO_4$ (ZSO) solution was obtained. Different qualities of vinyl sulfate (ES, Dodochem,99.8%) were added to the ZSO electrolyte to give ZSO + 5 mM ES, ZSO + 10 mM ES, and ZSO + 15 mM ES electrolytes. The optimal concentration of ES was measured at 10 mM.

***1.3 Electrochemical measurements*：** A homogeneous material was prepared by mixing I_2, polyethylene difluoride (PVDF, Dodochem), and conductive carbon black (Super P, Fotochem) in an 8:1:1 ratio and by adding 1-methyl-2 pyrrolidone (NMP, Innochem, Innochem, 99.9%). Cover the mixed material with 20 μm thick Ti foil and place in an oven at 50°C for 8 h. The active material content of the cathode was 0.8 mg cm^{-2} and cut into sheets of Φ8 mm. Combining synthetic I_2 with PTFE emulsion (PTFE, Guangdong Canrd New Energy Technology Co., Ltd.) Mix in isopropanol (Adamas, 99.8%) in a ratio of 9:1 to prepare the cathode of the Zn-I_2 whole cell. It was coated onto a stainless steel mesh (Φ = 16 mm) with a mass of about 15.20 mg cm-2 of the coated active substance, and then placed in an oven at 50 °C. The Zn-I_2 battery is assembled from an I_2 cathode, Zn foil (Zn, 99.99% purity, Φ 14 mm, thickness 100 μm), glass fiber, and separator (Φ 19 mm). The Zn-Zn, Zn-Cu and Zn-I_2 cells are assembled in a CR2032 coin cell battery. Tafel curve analysis was performed on Zn-Zn cells using CHI660E with a voltage range of -0.5 V - 0.5 V and a sweep rate of 5 mV s^{-1}. The scan rate was kept constant at 1 mV s^{-1} and a linear scanning voltammetry (LSV) test was performed using a Zn-Cu half-cell. Zn-Zn symmetrical cells were tested by chronometric current method (CA) at a constant overpotential of -150 mV for a duration of 300 s. Electrochemical impedance spectroscopy (EIS) was performed using a Zn-I_2 cell with a scan rate fixed at 5 mV s^{-1}. Cyclic voltammetry (CV) was measured with a Zn-I_2 cell and the test scan rate was set at 0.1-1 mV s^{-1}. Electrochemical impedance spectroscopy (EIS) was performed using a Zn-I_2 cell, and the scan rate was fixed at 5 mV s^{-1}. All of these tests were performed using CHI660E potentiostats. Where R_{ct} is the interfacial resistance, A is the frequency factor, R is the gas constant, and T is the absolute temperature. The data about depth of discharge (DOD) were acquired by the equations[1]:

$$DOD_{(\%)} = \frac{C_{actual,\ area}}{C_{theoretical,\ area}} \times 100\% = \frac{C_{actual,\ area}}{l \times \rho \times C_{theoretical,\ mass}} \times 100\%$$

Where $C_{actual,\ area}$ (mAh cm^{-2}) is the actual areal capacity during the plating/stripping of Zn, $C_{theoretical,\ area}$ (mAh cm^{-2}) is the theoretical areal capacity of Zn foils, $C_{theoretical,\ mass}$ (mAh g^{-1}) is the theoretical mass capacity of Zn, l (cm) and ρ (g cm^{-3}) are the thickness and density of Zn foils, respectively.

***1.4 Theoretical calculations*：** The calculations are performed using the CASTEP module of Materials Studio for first-principles calculations. The ionic step convergence criterion is set to a total energy change of less than 10^{-5} eV, a maximum force of less than 0.1 eV/Å, a maximum pressure of less than 0.2 GPa, and a maximum displacement of less than 0.005 Å. The electronic step convergence standard is set to 10^{-5} eV. The plane wave truncation energy was set to 400 eV, and the TS method (Tkatchenko-Scheffler) was used to correct the DFTD dispersion. The Brillouin zone was sampled using a 1×1×1 grid of *k*-points.

***1.5 Characterizations*：** X-ray photoelectron spectroscopy (XPS) was used to analyze post-cycling Zn in Thermo Scientific K-Alpha. Fourier transform infrared spectroscopy (FTIR) analysis of cyclic Zn was performed using the Thermo Fisher Scientific Nicolet iS20. The MiniFlex 600 X-ray diffraction (XRD) measures Zn immersed in an electrolyte. The instrument uses a Zeiss Sigma 300 scanning electron microscope (SEM) to examine the morphology of Zn after cycling.

2. Supporting Figures

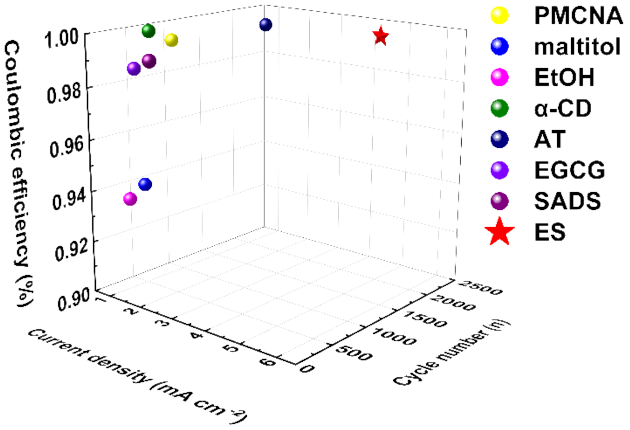

Fig. S1 Comparison of the cycling performance and CE of Zn-Cu half cells at different current densities using various electrolyte additives[1-8] (The areal capacity is 1 mAh cm^{-2}).

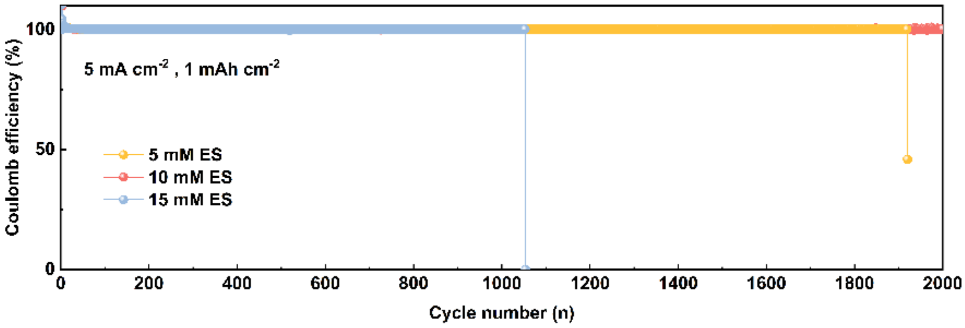

Fig. S2 Cycling performance comparison of Zn-Cu half-cells (5 mA cm^{-2}, 1 mAh cm^{-2}) using ZSO with different concentrations of ES.

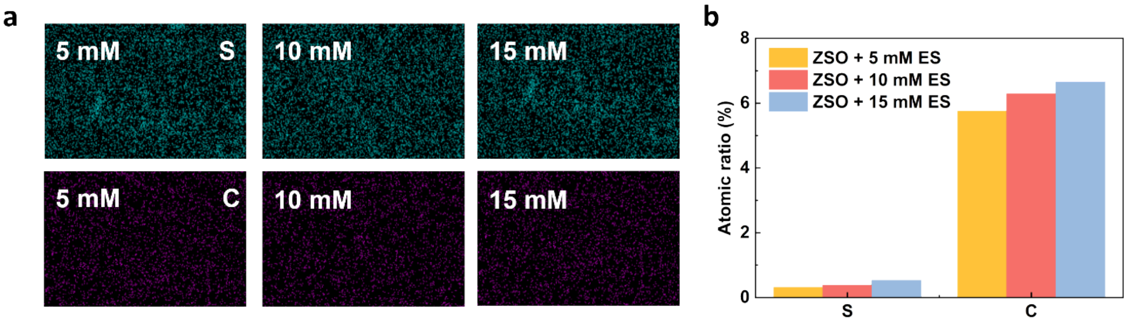

Fig. S3 EDS mapping and corresponding EDS elemental content distribution of cycling for 50 h with Zn foil (test conditions 1 mA cm^{-2}, 1 mAh cm^{-2}) using different concentrations of ES.

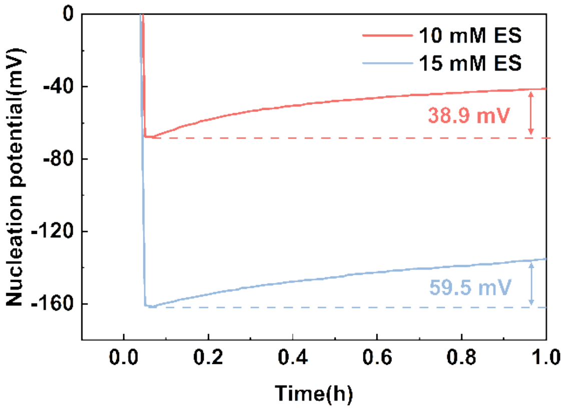

Fig. S4 Nucleation overpotentials of Zn-Cu half-cells using different electrolytes at 1 mA cm^{-2} and 1 mAh cm^{-2}.

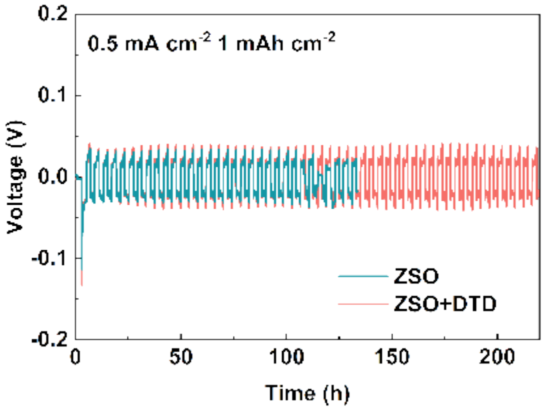

Fig. S5 Cycling performance comparison of Zn-Zn symmetric cells (0.5 mA cm^{-2}, 1 mAh cm^{-2}) using different electrolytes.

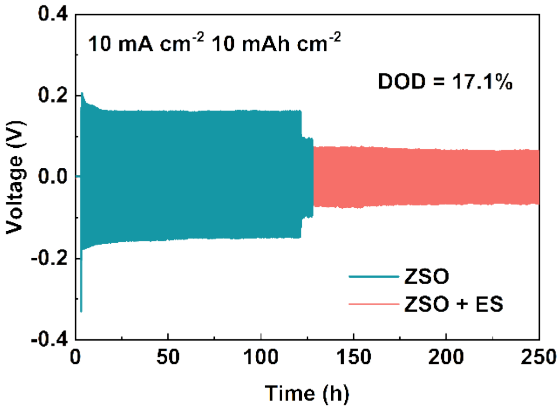

Fig. S6 Cycling performance comparison of Zn-Zn symmetric cells (10 mA cm^{-2}, 10 mAh cm^{-2}) using different electrolytes.

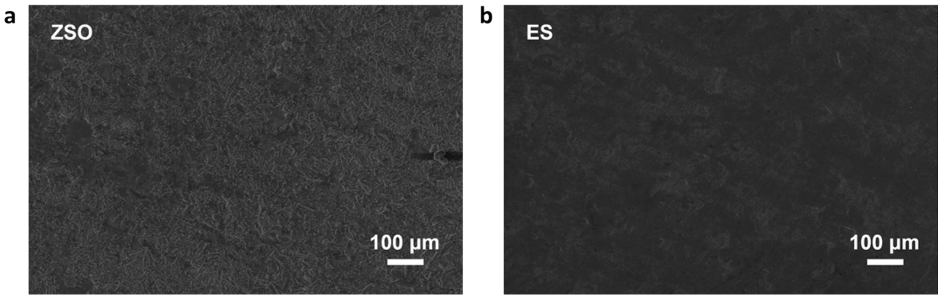

Fig. S7 SEM images of cycling for 50 h with Zn foil (test conditions 1 mA cm^{-2}, 1 mAh cm^{-2}) using (a) ZSO and (b) ZSO + ES.

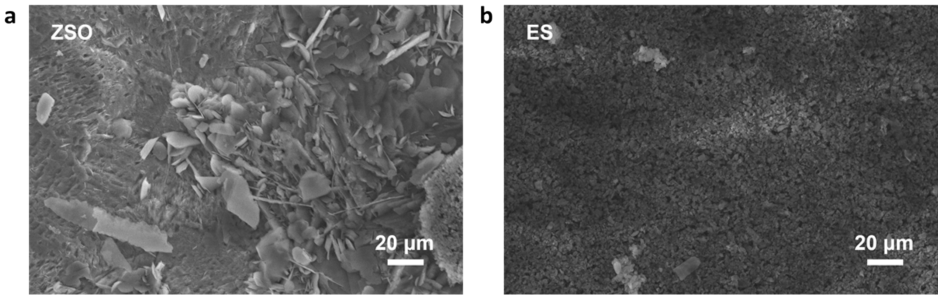

Fig. S8 SEM images of cycling for 200 h with Zn foil (test conditions 5 mA cm^{-2}, 1 mAh cm^{-2}) using (a) ZSO and (b) ZSO + ES.

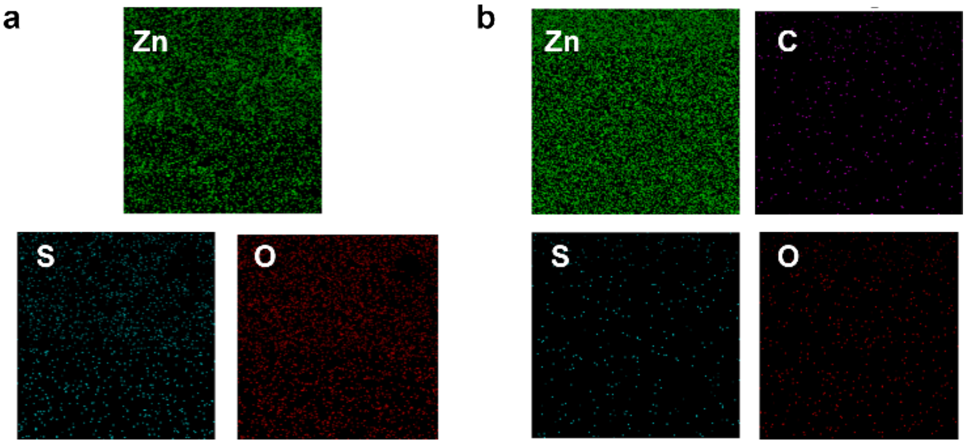

Fig. S9 EDS mapping of cycling for 50 h with Zn foil (test conditions 1 mA cm^{-2}, 1 mAh cm^{-2}) using (a) ZSO and (b) ZSO + ES.

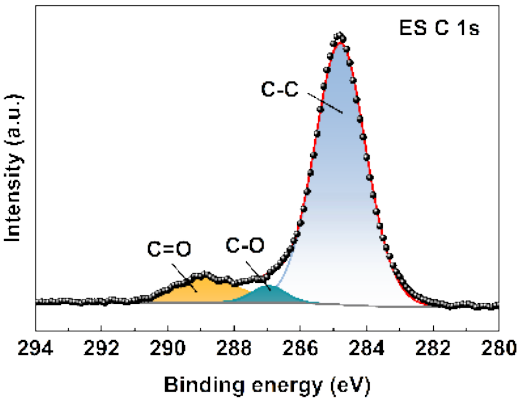

Fig. S10 XPS C 1s spectra of cycled Zn foil using ZSO + ES (1 mA cm^{-2}, 1 mAh cm^{-2}, 50 h).

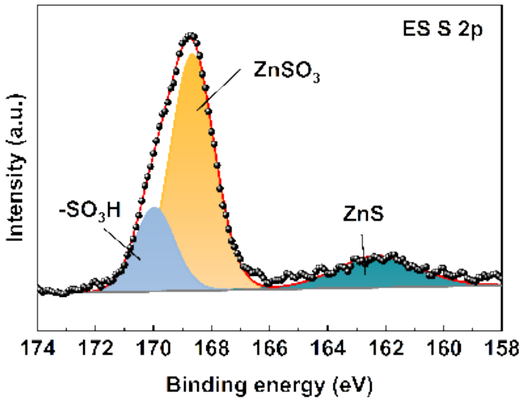

Fig. S11 XPS S 2p spectra of cycled Zn foil using ZSO + ES (1 mA cm^{-2}, 1 mAh cm^{-2}, 50 h).

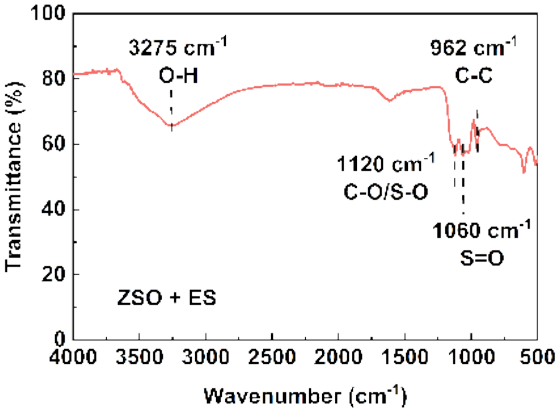

Fig. S12 FTIR spectra comparison of the cycled Zn anode using ZSO + ES.

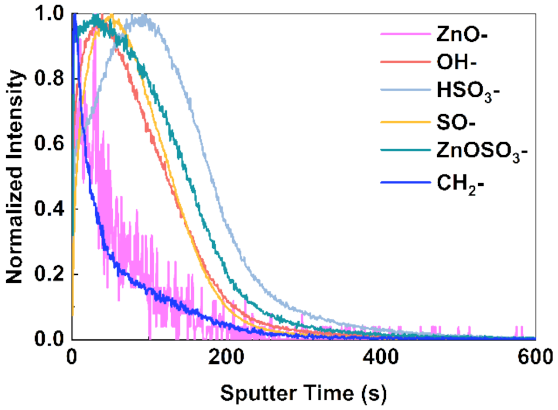

Fig. S13 Secondary ion intensity distribution map after 50 hours of cycling with Zn foil using ZSO + ES.

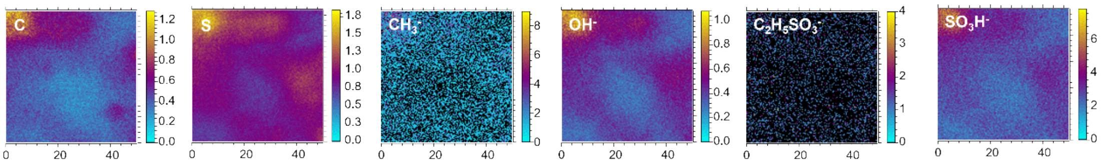

Fig. S14 TOF-SIMS content diagram of different components after 50 hours of cycling with Zn foil using ZSO + ES.

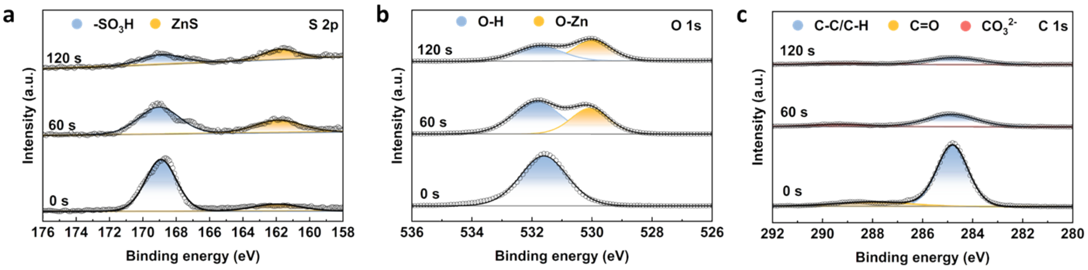

Fig. S15 Depth-profiling XPS with etching of cycling for 50 h with Zn foil (test conditions 1 mA cm^{-2}, 1 mAh cm^{-2}): (a) S 2p, (b) O 1s, (c) C 1s.

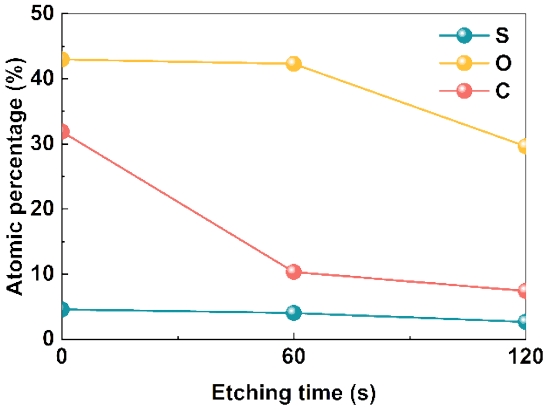

Fig. S16 Depth-profiling XPS atomic percentage plot of cycling for 50 h with Zn foil.

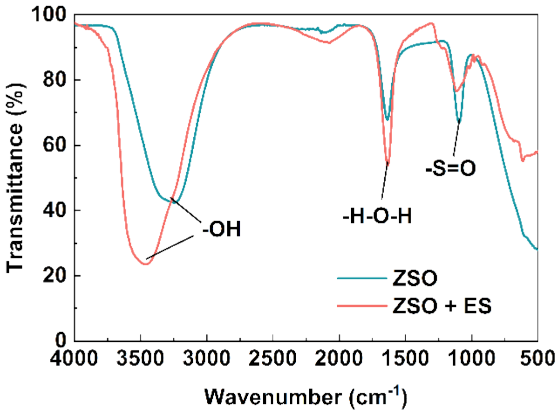

Fig. S17 FTIR spectra comparison of ZSO and ZSO + ES.

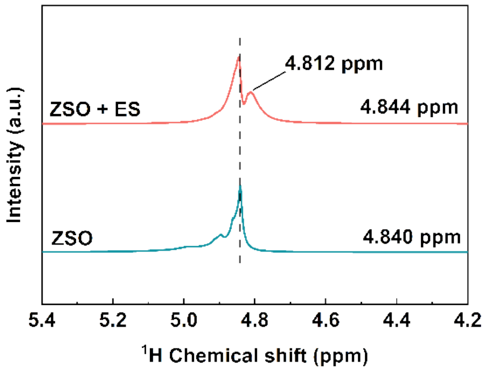

Fig. S18 ^{1}H NMR spectra of ZSO and ZSO + ES.

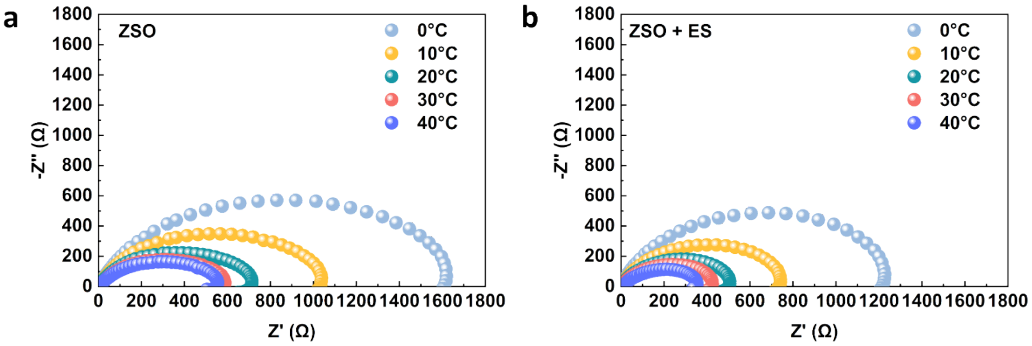

Fig. S19 EIS plots of Zn-Zn symmetric batteries at different temperatures using (a) ZSO and (b) ZSO + ES.

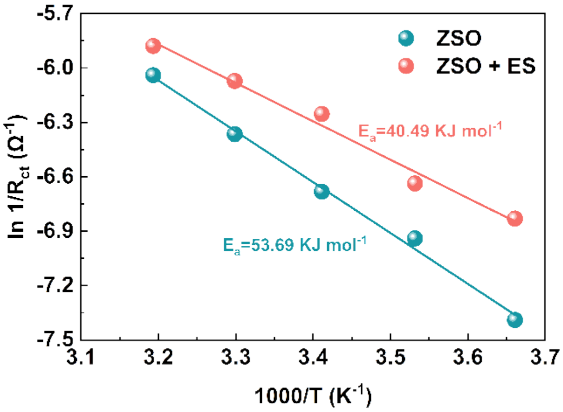

Fig. S20 The activation energies of the de-solvation process of hydrated Zn^{2+} in ZSO and ZSO + ES.

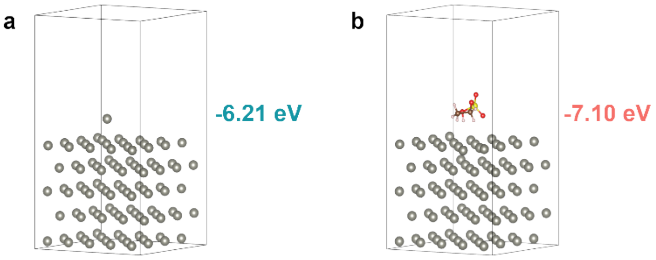

Fig. S21 Comparison of adsorption energies of Zn (002) with (e) Zn^{2+} and (f) C_2H_5-SO_3-OH.

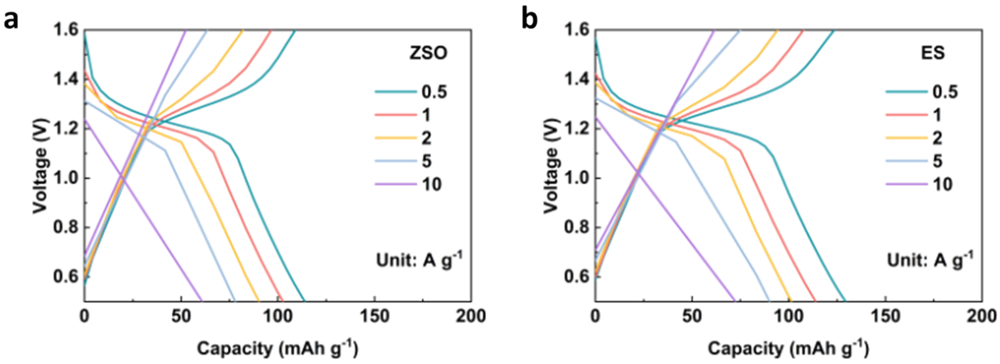

Fig. S22 The voltage profile of Zn-I_2 cells for rate testing using (a) ZSO and (b) ZSO + ES.

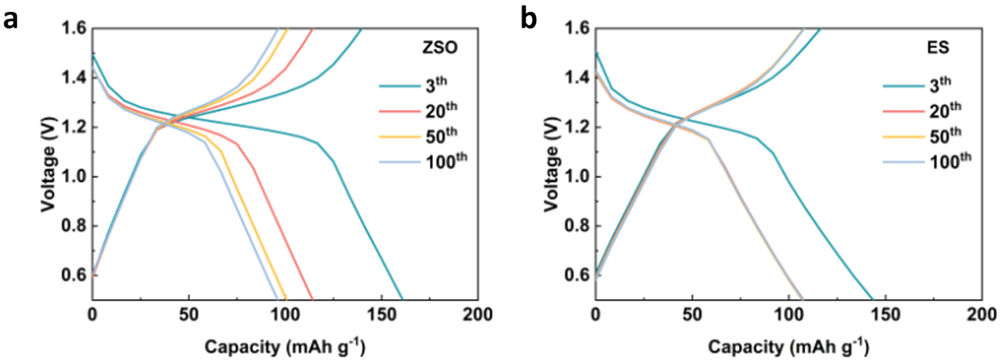

Fig. S23 The voltage profile of Zn-I_2 cells for cycling performance at 1 A g^{-1} using (a) ZSO and (b) ZSO + ES.

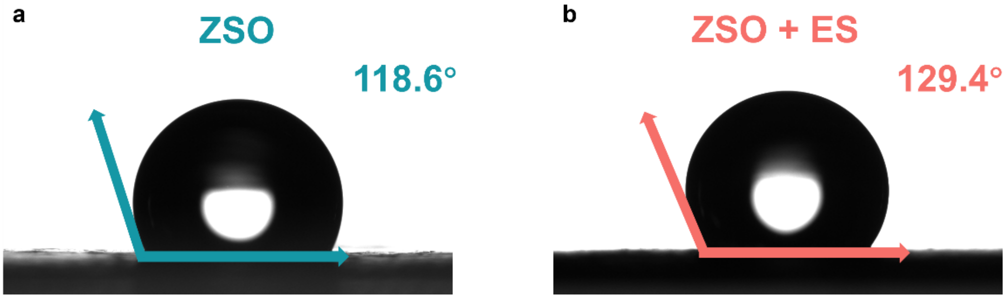

Fig. S24 Contact angles with I_2 cathode of (a) ZSO and (b) ZSO + ES.

Reference

1. D. Feng, Y. Jiao and P. Wu, *Angew. Chem. Int. Ed.*, 2023, **62**, e202314456.
2. J. Liu, S. Hu, H. Guo, G. Zhang, W. Liu, J. Zhao, S. Song, C. Han and B. Li, *Energy Chem.*, 2024, **95**, 57-67.
3. Z. Tian, H. Liu, M. Cheng, L. Cui, R. Zhang, X. Yang, D. Wu, D. Wang and J. Xia, *ACS Appl. Mater. Interfaces*., 2024, **16**, 21857−21867.
4. K. Zhao, G. Fan, J. Liu, F. Liu, J. L, X. Zhou, Y. Ni, M. Yu, Y. Zhang, H. Su, Q. Liu and F. Cheng, *J.Am.Chem.Soc.*, 2022, **144**, 11129-11137.
5. H. Cao, X. Zhang, B. Xie, X. Huang, F. Xie, Y. Huo, Q. Zheng, R. Zhao, Q. Hu, L. Kang, S. Liu and D. Lin, *Adv. Funct. Mate*r., 2023, **33**, 2305683.
6. L. Zhou, W. Zhou, H. Wang, Q. Deng, X. Ai, X. Zeng, X. Wu, C. Zhou and W. Ling, *Chem. Eng. J.*, 2024, **492**, 152324.
7. Y. Ding, L. Yin, T. Du, Y. Wang, Z. He, Jodie. Y, G. Li, J. Liu, S. Zhang, T. Yang and Z. Guo, *Adv. Funct. Mater.*, 2024, **34**, 2314388.