

Ultralow and Biodegradable Electrolyte Additives for Dendrite-Free Zn Anodes

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Experimental Section

Materials

Zinc sulfate heptahydrate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, purity 99.5%), sodium sulfate (Na_2SO_4 , purity 99.0%) and isopropyl alcohol (IPA, purity 99.7%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Capryhydroxamic acid (CHA, purity 99.0%), deuterated water (D_2O , purity 99.9%), polytetrafluoroethylene (PTFE, purity 60wt%), lithium iodide trihydrate ($\text{LiI} \cdot 3\text{H}_2\text{O}$, purity 98%) n-octanoic acid (n-OAA, purity 99.0%), n-octanol (n-OAL, purity 99.0%), acetyl hydroxamic acid (AHA, purity 98%) and iodine (I_2 , purity 99.8%) were purchased from Aladdin. Activated carbon (AC, XFP01) was purchased from Xianfeng Nano Company. All reagents were of analytical grade and could be used without further purification. Commercial zinc foil (Zn foil, purity 99.99%) and copper foil (Cu foil, purity 99%) were purchased from Cyber and Guangdong Kondxin New Energy Technology Co., Ltd., respectively. Before use, they were washed several times with deionized water and ethanol, then, cut into circular pieces with diameters of 12 mm and 14 mm, respectively for following test.

Electrolyte preparation

2 M ZnSO_4 electrolyte: Used an analytical balance (Mettler-Toledo, ME104E/02, Shanghai, China) to weigh out 143.7750 g $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ into a 250 mL volumetric bottle, added distilled water to the scale line, and shook well.

1 M Na_2SO_4 electrolyte: Used an analytical balance (Mettler-Toledo, ME104E/02, Shanghai, China) to weigh out 35.5100g Na_2SO_4 into a 250 mL volumetric bottle, added distilled water to the scale line, and shook well.

Other electrolytes: Added an electrolyte additive CHA at different mass fractions (0.001wt%, 0.005wt%, 0.01wt%) to 2 M ZnSO_4 electrolyte to prepare electrolytes containing CHA. Added 0.005wt% n-OAL, n-OAA, AHA to 2 M ZnSO_4 electrolyte to prepare electrolytes with different additives. Added 0.005wt% CHA to 1 M Na_2SO_4 electrolyte to prepare electrolytes containing CHA.

Iodide cathode solution (1 M LiI + 0.1 M I_2): Used an analytical balance (Mettler-Toledo, ME104E/02, Shanghai, China) to weigh out 0.6345 g I_2 and 4.6973 g

$\text{LiI}\cdot 3\text{H}_2\text{O}$. Dissolved completely in a small beaker, then transfer to a 25 mL volumetric flask, added distilled water up to the mark, and shook well.

Materials Characterization

X-ray diffraction (XRD) patterns were recorded using an XRD diffractometer (Rigaku, SmartLab 9KW, Japan) with monochromatic Cu α radiation ($\lambda = 1.5418 \text{ \AA}$). Scanning electron microscope (SEM) images, Energy Dispersive Spectrometer (EDS) and EDS Mapping were obtained using a field emission scanning electron microscope (FESEM, Zeiss Gemini 300, Germany) coupled with an X-ray energy dispersive spectrometer (Oxford Instruments INCAx, UK). 3D shape measurements were taken using a three-dimensional laser confocal microscope (3D-CLSM, VT6000, CHOTEST, China). In situ optical images were taken from an optical microscope (YM520R, Suzhou Yusheng, China). XPS spectra were measured using an X-ray photoelectron spectrometer (XPS, Thermo Scientific ESCALAB Xi+, USA). Fourier-transformed infrared spectra (FT-IR) were measured on an infrared spectrometer (Tensor 27, Bruker, Germany). ^1H NMR spectra were obtained on a 400MHz fully digital nuclear magnetic resonance spectrometer (AVANCE NEO 400, Bruker, Germany) using D_2O as the solvent. Raman spectra were characterized at room temperature using an in situ UV confocal Raman spectrometer (LabSpec6, Shuangxu, Shanghai, China) with a 532 nm excitation. The viscosity of the electrolyte was obtained using a high-temperature and high-pressure rheometer (MARS60, HAAKE, USA). The conductivity of the electrolyte was measured using a conductivity meter (DDSJ-308F, Leici, Shanghai, China). The pH chart was measured using a pH meter (FE28, Mettler-Toledo, Shanghai, China) and a pH plane electrode (LabSen 371, Sanxin, Shanghai, China). The surface wettability of the electrolyte was measured using a contact angle meter (DSA 100S, Kruss, Germany).

Electrochemical measurement

The electrochemical performances of the Zn anodes were evaluated at room temperature using the coin cells (Canrd Co., Ltd.). In the half cells, commercial Zn foils (thickness: 50 μm) and Cu foils (thickness: 9 μm) were used as the working electrode and the reference electrode respectively. Glass microfiber membranes

(Whatman series, GF/F) were used as the separator. The electrode/separator discs were cut from the Zn/Cu foils or the separator by the precision disc cutter (MTI KJ GROUP, MSK-T10, China). The diameters of the Zn disc, the Cu disc and the separator were 12, 14, and 19 mm. The electrolyte, ZnSO₄ or ZnSO₄-CHA, was added to wet the separator. The symmetric cells of Zn||Zn were assembled by two Zn discs and sealed by coin cell crimper (MTI KJ GROUP, MSK-110, China) to examine the electrochemical performance. The asymmetric cells of Zn||Cu were assembled by Zn and Cu discs into one 2025-type coin cell. In the half cells, constant current tests were conducted using a LAND battery test system (LAND CT-3002A, China) at various current densities and areal capacities. In the Zn||Cu half cells, Zn metal was deposited on the copper substrate during discharge and then charged back to the cut-off voltage of 0.5 V (relative to Zn²⁺/Zn) at the same current in each cycle.

In the full cells, iodine was taken as the cathode material. Typically, AC was mixed with polytetrafluoroethylene (PTFE) in a weight ratio of 9:1 in isopropyl alcohol (IPA) to form a paste. The paste was then rolled into a freestanding film. It was then pressed onto a titanium mesh and heated under vacuum at 60 °C for 12 hours. Subsequently, the titanium mesh loaded with the pressed film was punched into small discs with a diameter of 10 mm. The mass loading of AC in the cathode was about 3-4 mg·cm⁻². An iodine catholyte (3 mg/20 μL) was dripped onto the cathode, and fully absorbed by the AC in the cathode. This cathode was coupled with the Zn anode, the glass microfiber membrane and the electrolyte (100 μL) as the full cells.

Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), linear sweep voltammetry (LSV), linear polarization (LP) curves, and chronoamperometry (CA) diffusion curve measurements were conducted on an electrochemical workstation (CHI760E, China). All the Zn||I₂ full cells were measured in the range of 0.4~1.6 V. Specifically, CV measurements were performed in a two-electrode configuration at a scan rate of 0.1 mV s⁻¹, with Zn foil as the anode and I₂ as the cathode. EIS plots were carried out in the frequency range of 10⁻¹-10⁵ Hz. LP and LSV curves were measured in a three-electrode configuration at a scan rate of 1 mV s⁻¹, where Zn foil, Pt foil, Ag/AgCl was employed as working, counter and reference

electrode, respectively. CA curves were measured using an electrochemical workstation (Autolab PGSTAT 302N, Switzerland), where Zn||Zn cells were measured at a constant potential.

The data for Depth of Discharge (DOD) is obtained by the following equation:

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

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

Calculate method of adsorption energy

The adsorption energy calculations at the DFT level were performed by using the DMol3 program package in Materials Studio. The generalized gradient approximation (GGA) with the exchange-correlation functional Perdew-Burke-Ernzerh (PBE) was used. A cutoff energy of 400 eV was used for the plane-wave basis set. The geometry optimization convergences with forces on atoms and energy differences were smaller than 0.02 eV/Å and 10⁻⁵ eV, respectively.

The adsorption energy of CHA and H₂O adsorbed on Zn are defined as:

$$E_{\text{adsorption energy}} = E_{\text{Zn/CHA}} - E_{\text{Zn}} - E_{\text{CHA}}$$

$$E_{\text{adsorption energy}} = E_{\text{Zn/H}_2\text{O}} - E_{\text{Zn}} - E_{\text{H}_2\text{O}}$$

Where E_{Zn} , E_{CHA} and $E_{\text{H}_2\text{O}}$ were the total energy of the adsorbate and bare surface directly obtained from DFT calculations, respectively, while $E_{\text{Zn/CHA}}$ and $E_{\text{Zn/H}_2\text{O}}$ were the total energy of optimized adsorbate-surface.

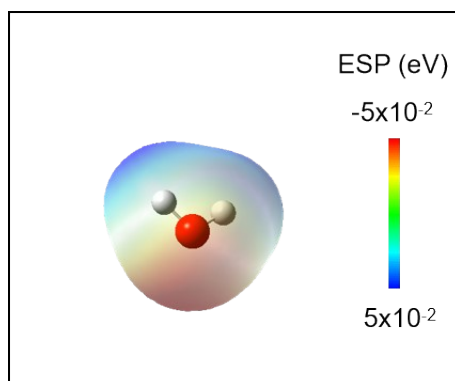


Fig. S1. ESP map of H₂O.

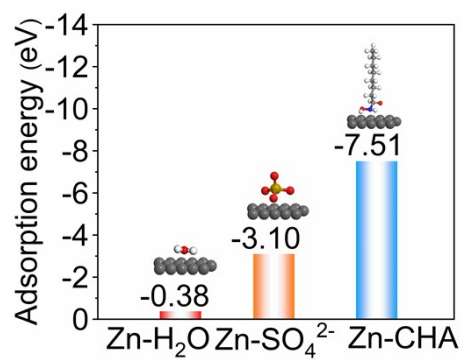


Fig. S2. The adsorption energies of H₂O, SO₄²⁻, CHA on the Zn(002) facet.

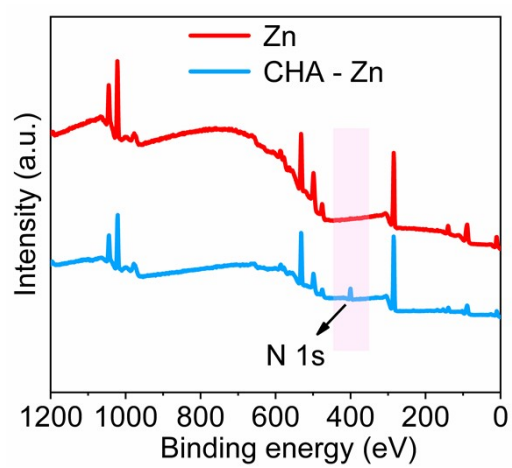


Fig. S3. XPS spectra of the Zn foils before and after the immersion into CHA.

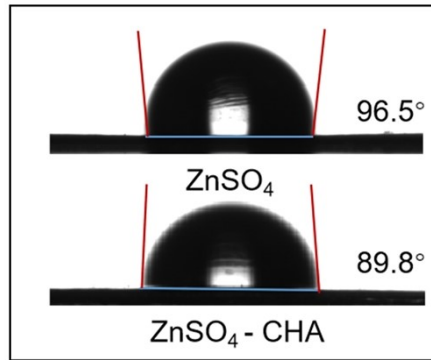


Fig. S4. Contact angles of ZnSO₄ and ZnSO₄-CHA on Zn foils.

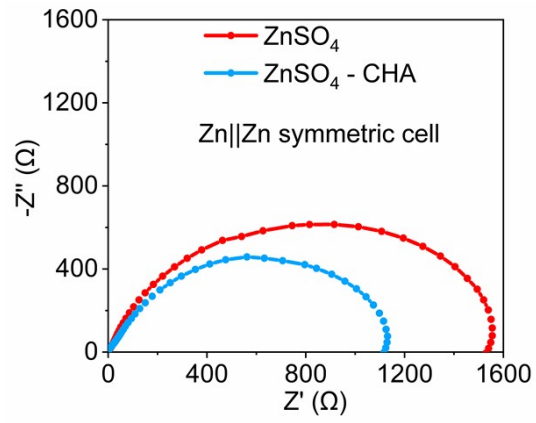


Fig. S5. Nyquist plots of the Zn||Zn symmetric cells in ZnSO_4 and $\text{ZnSO}_4\text{-CHA}$.

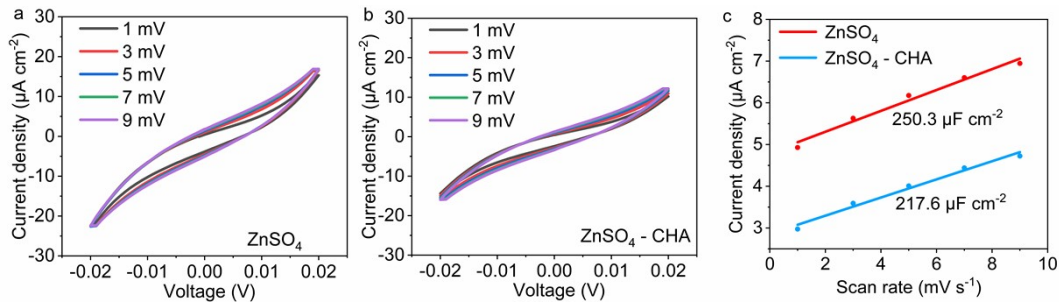


Fig. S6. Electric double layer capacitance (EDLC) measurements for Zn anode in Zn||Zn symmetric cells using ZnSO₄ or ZnSO₄-CHA as the electrolyte. CV curves of (a) ZnSO₄ and (b) ZnSO₄-CHA electrolytes at a voltage range from -20 mV to 20 mV under various scan rates. (c) The plots of capacitive currents versus scan rates for the cell cycled in ZnSO₄ and ZnSO₄-CHA electrolytes.

EDLC was calculated through $C = i_c/v$ equations. In CV scans, double layer current $i_c = dq/dt = d(C\phi)/dt = C(d\phi/dt) + \phi(dC/dt)$, $dC/dt = 0$, $d\phi/dt = \text{scan rate (v)}$. So $i_c = Cv$. The linear dependence of the capacitive current (i_c) on scan rate (v) can be used to determine the capacity. Capacity (C) is obtained from the slope of the i_c versus v graphs. Here, we choose $i_c = (i_{0v^+} - i_{0v^-}) / 2$. It is half value of current difference during forward scan and negative scan at 0 V.

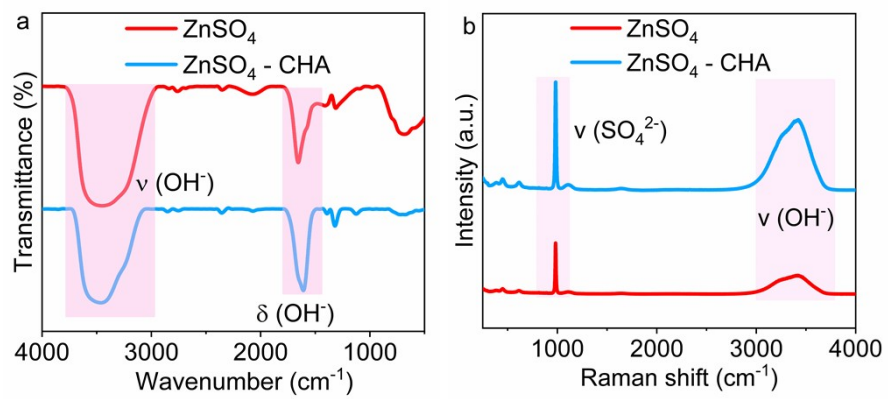


Fig. S7. (a) FT-IR and (b) Raman spectra of ZnSO₄ and ZnSO₄-CHA.

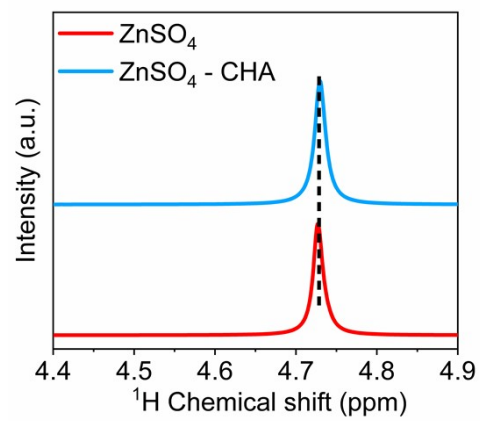


Fig. S8. ^1H NMR spectra of ZnSO_4 and $\text{ZnSO}_4\text{-CHA}$.

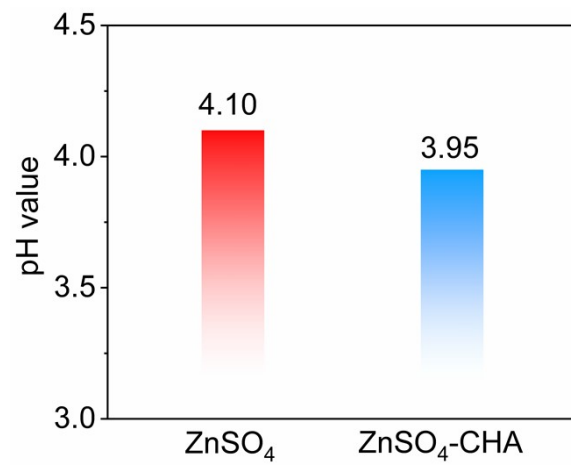


Fig. S9. pH charts of ZnSO₄ and ZnSO₄-CHA.

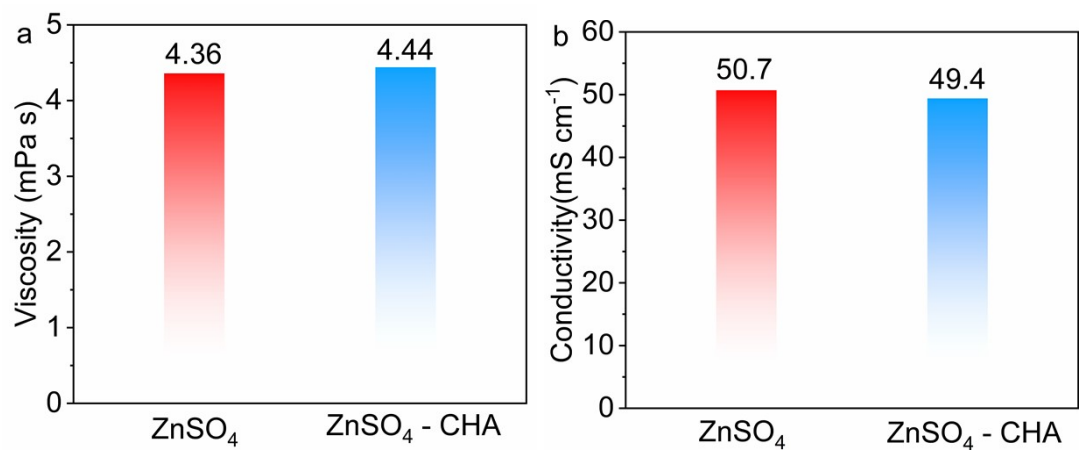


Fig. S10. (a) Viscosities and (b) ion conductivities of ZnSO₄ and ZnSO₄-CHA.

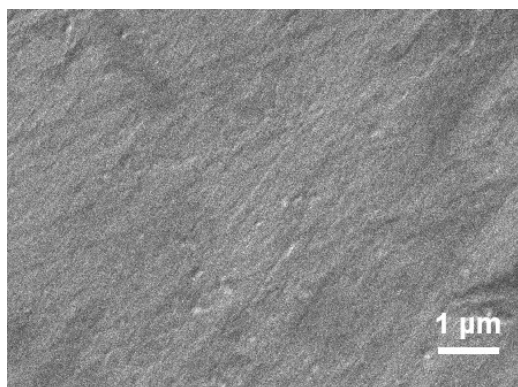


Fig. S11. SEM image of the pristine Zn foil.

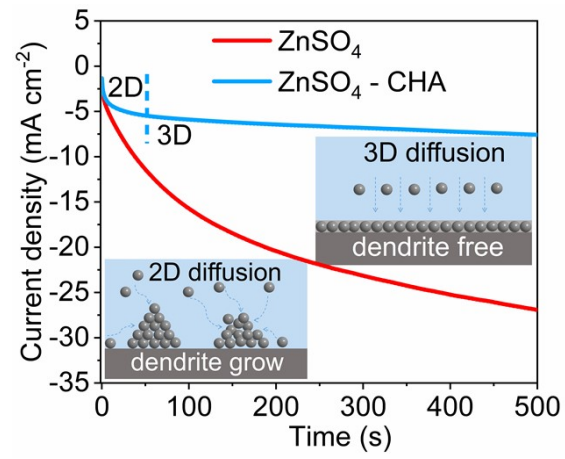


Fig. S12. CA curves of Zn||Zn symmetric cells in ZnSO₄ and ZnSO₄-CHA at a fixed potential of -150 mV.

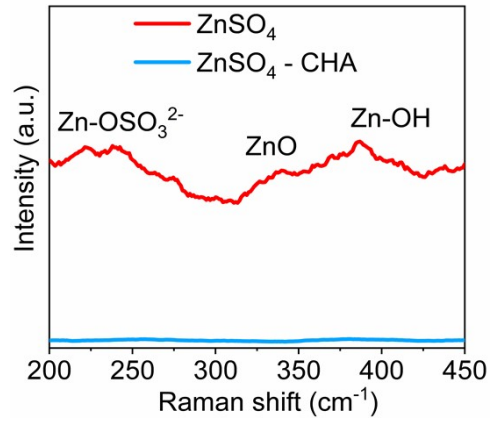


Fig. S13. Raman spectra of the Zn foils after 50 cycles in ZnSO₄ and ZnSO₄-CHA at 1 mA cm⁻² and 0.5 mAh cm⁻².

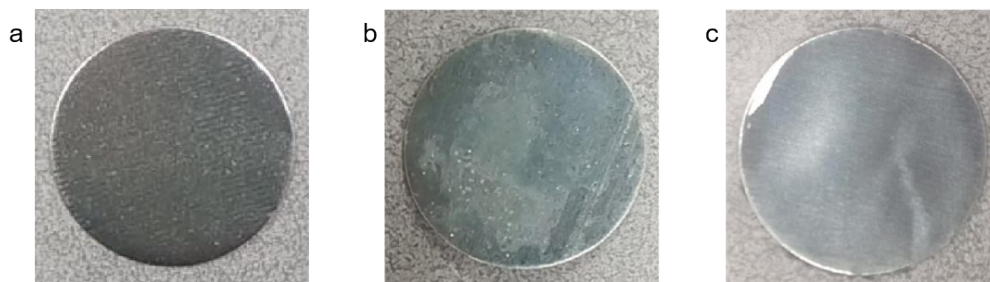


Fig. S14. Optical photos of (a) the pristine Zn foil, (b,c) the Zn foils after immersing into (b) ZnSO_4 and (c) ZnSO_4 -CHA for 7 days.

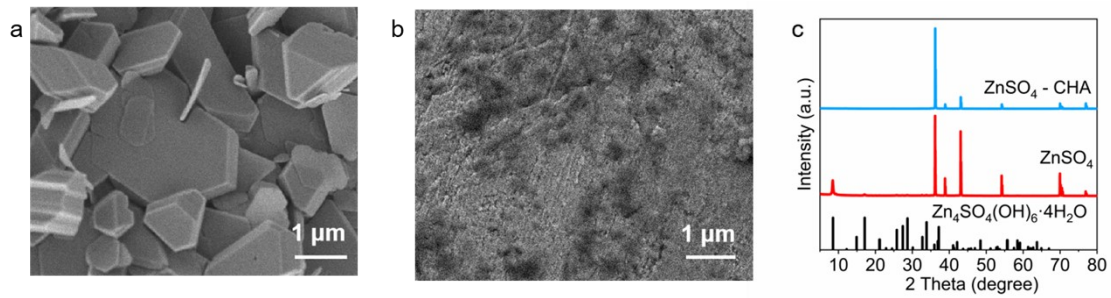


Fig. S15. SEM images of the Zn foils after immersing into (a) ZnSO₄ and (b) ZnSO₄-CHA electrolytes for 7 days. (c) XRD patterns of the Zn foils after immersing into ZnSO₄ and ZnSO₄-CHA electrolytes.

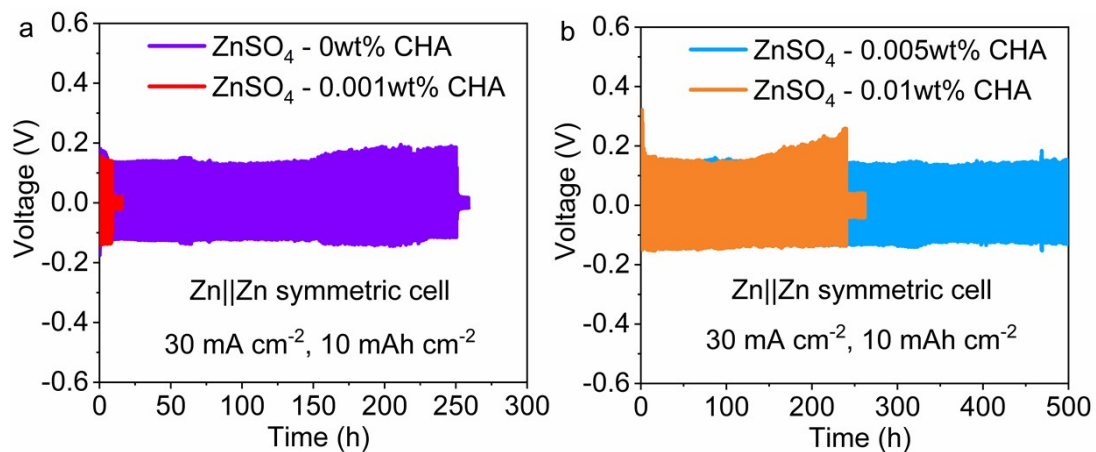


Fig. S16. Cycling performance of the symmetric cells in the electrolytes containing different concentrations of CHA at 30 mA cm⁻² and 10 mAh cm⁻², (a) 0wt% CHA and 0.001wt% CHA, (b) 0.005wt% CHA and 0.01wt% CHA.

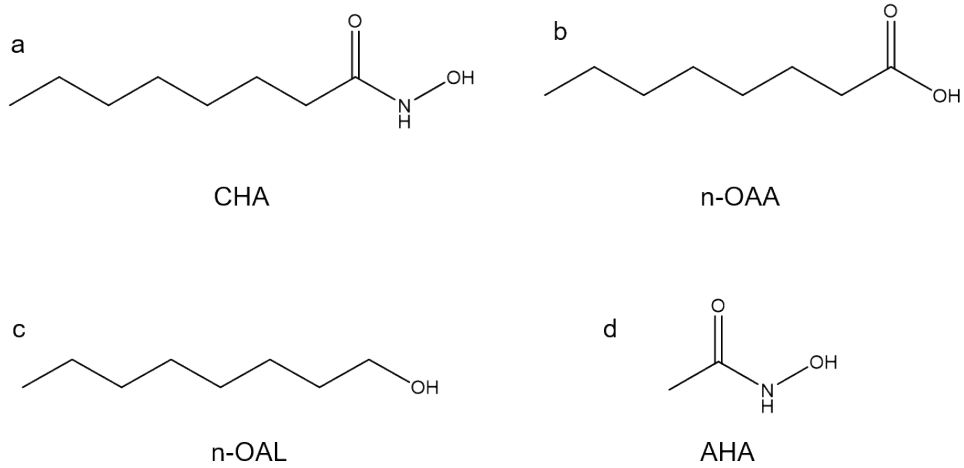


Fig. S17. The structure of (a) CHA, (b) n-OAA, (c) n-OAL and (d) AHA.

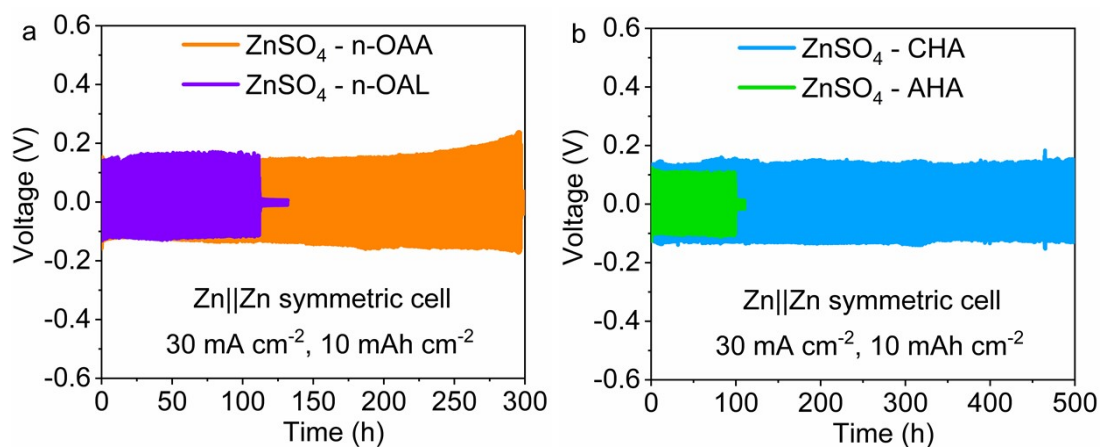


Fig. S18. Cycling performance of Zn||Zn symmetric cells in different electrolytes with 0.005wt% mass fractions at 30 mA cm⁻² and 10 mAh cm⁻², (a) ZnSO₄-n-OAA and ZnSO₄-n-OAL, (b) ZnSO₄-CHA and ZnSO₄-AHA.

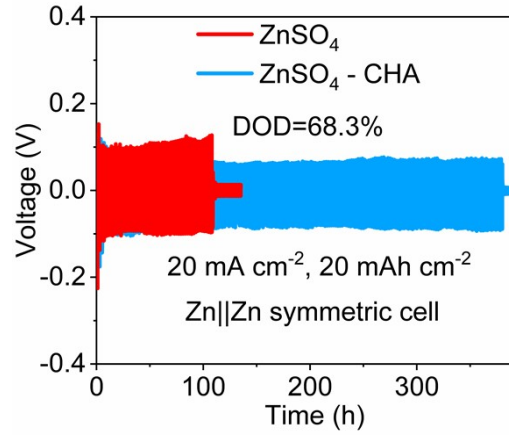


Fig. S19. Cycling performance of Zn||Zn symmetric cells at 20 mA cm⁻² and 20 mAh cm⁻² in ZnSO₄ and ZnSO₄-CHA.

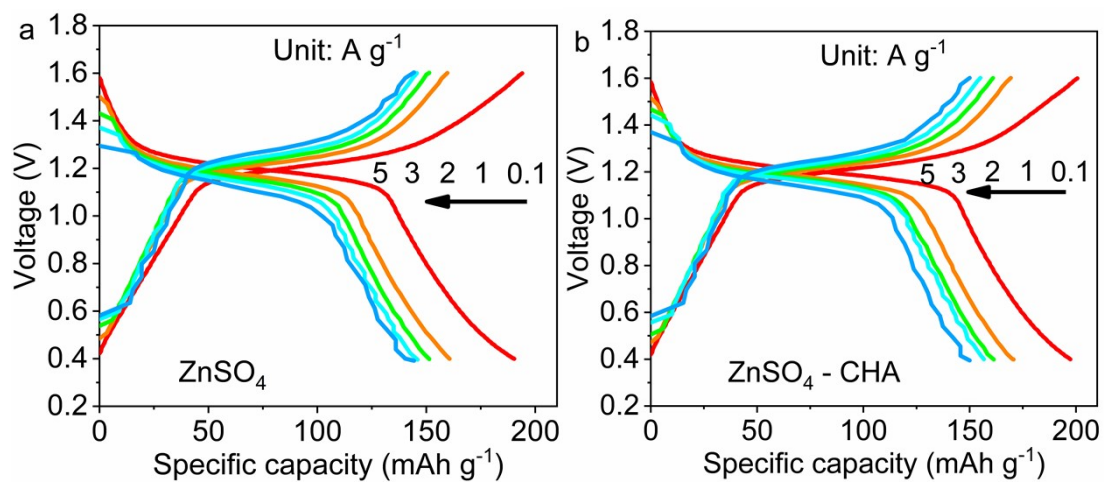


Fig. S20. The voltage profiles of the Zn||I₂ full cells in (a) ZnSO₄ and (b) ZnSO₄-CHA.

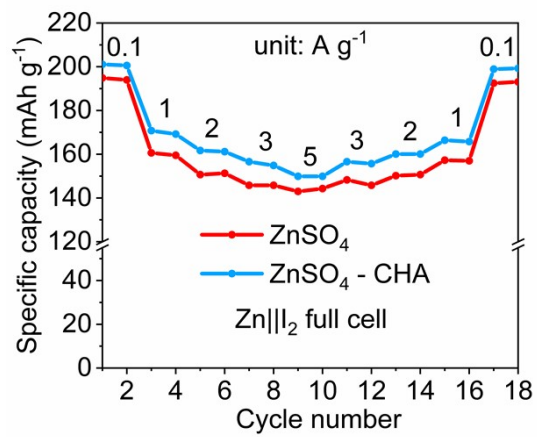


Fig. S21. Rate performance of the Zn||I₂ full cells using different electrolytes.

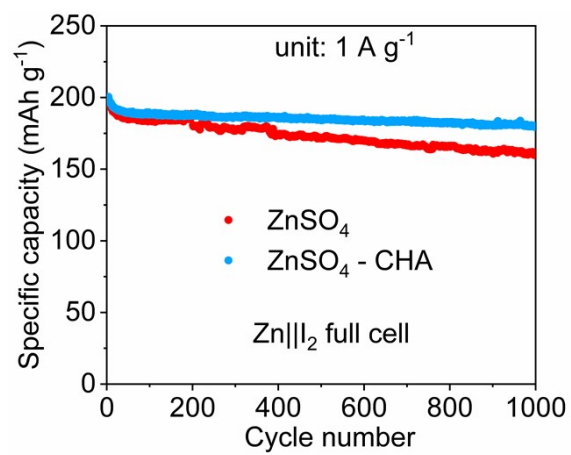


Fig. S22. Cycling performance of Zn||I₂ full cells using different electrolytes at 1 A g⁻¹.

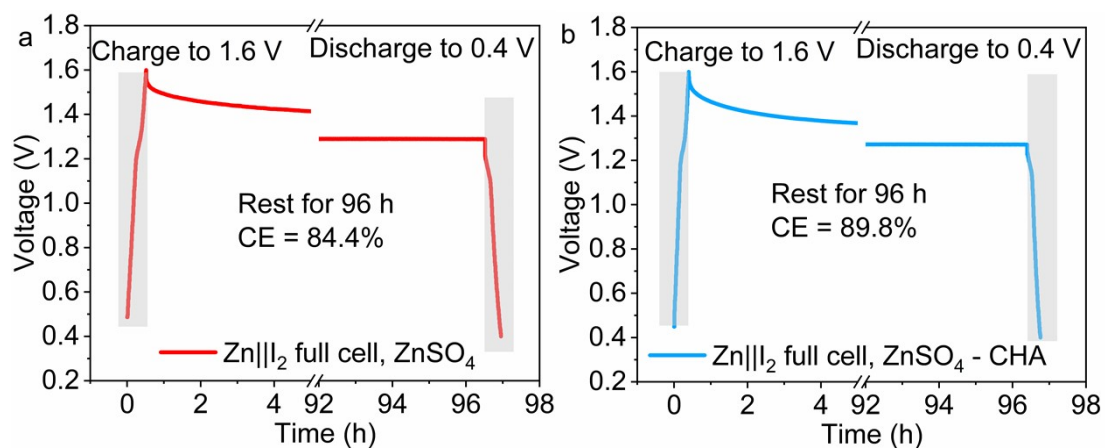


Fig. S23. Self-discharge behaviors of the Zn||I₂ full cells in (a) ZnSO₄ and (b) ZnSO₄-CHA electrolytes.

Table S1. Comparison of current density, areal capacity, and cycle life of Zn||Zn symmetric cells with various modified Zn-based aqueous electrolytes.

| Electrolyte | Current density (mA cm ⁻²) | Areal capacity (mAh cm ⁻²) | Cycling life (h) | Reference |
|-------------------------------|--|--|------------------|-----------|
| | 2 | 1 | >2900 | |
| 2M ZnSO ₄ /CHA | 30 | 10 | 500 | This work |
| | 20 | 20 | 380 | |
| 1M ZnSO ₄ /PA | 2 | 1 | 1000 | 1 |
| 2M ZnSO ₄ /NTA | 5 | 0.5 | 2100 | 2 |
| | 10 | 2 | 500 | |
| 1M ZnSO ₄ /SF | 1 | 1 | 1550 | 3 |
| 2M ZnSO ₄ /Gly | 20 | 20 | 80 | 4 |
| | 10 | 10 | 470 | |
| 2M ZnSO ₄ /xylitol | 1 | 1 | 1080 | 5 |
| 2M ZnSO ₄ /EDA | 1 | 1 | 2940 | 6 |
| 2M ZnSO ₄ /AZ | 5 | 20 | 260 | 7 |
| 2M ZnSO ₄ /DTAC | 1 | 1 | 2000 | 8 |
| 2M ZnSO ₄ /DA | 2 | 1 | 1000 | 9 |
| 2M ZnSO ₄ /Gln | 1 | 1 | 700 | 10 |
| 2M ZnSO ₄ /CTAB | 2 | 1 | 2000 | 11 |
| 1M ZnSO ₄ /DT | 2 | 1 | 650 | 12 |

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