

## Supplementary Information

### Mediation of the Electrochemical Polarization for Durable Zinc Anode

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## Experimental Section

### Electrolyte preparation

All electrolytes in this work were prepared using deionized water (DI water) as the solvent. To prepare the ZSO, 2 mol  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  (ACS, 99%, purchased from Aladdin) dissolved in water to obtain a 1 L solution. To prepare the  $x\text{-KSeCN/ZSO}$  ( $x=1,2.5,5,10$ ), 1, 2.5, 5, 10 mol KSeCN (ACS, 99%, purchased from Aladdin) along with 2 mol  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  dissolved in water to obtain 1 L solutions, respectively.

### Cathode preparation

After mixing  $\text{V}_2\text{O}_5$  (98%), super P Li, and polyvinylidene difluoride (PVDF) in a mass ratio of 7:3:1, the cathode slurry was prepared by adding it to NMP. The prepared slurry was coated onto stainless steel foils with a thickness of 150  $\mu\text{m}$ , then dried at 80  $^\circ\text{C}$  for 12 hours and cut into slices with a diameter of 15 mm to obtain cathode electrodes (with an loading of  $\sim 1.5\text{mg cm}^{-2}$ ).

### Materials Characterization

XRD patterns were collected on a powder diffractometer (X'Pert3 powder, PANalytical) with Cu  $\text{K}\alpha$  radiation ( $\lambda=1.5418 \text{ \AA}$ ). The morphology and corresponding energy-dispersive spectrometer (EDS) mapping of the samples were characterized by SEM (GeminiSEM 300, ZEISS). Raman spectra were obtained with an excitation line at 532 nm (LabRAM HR800). The chemical state and composition were evaluated by an ESCALAB 250 photoelectron spectroscopy (Thermo Fisher Scientific) at  $1.2 \times 10^{-9}$  mbar using Al  $\text{K}\alpha$  X-ray beam (1486.6 eV). All XPS spectra were calibrated by shifting the detected adventitious carbon C 1s peak to 284.4 eV.

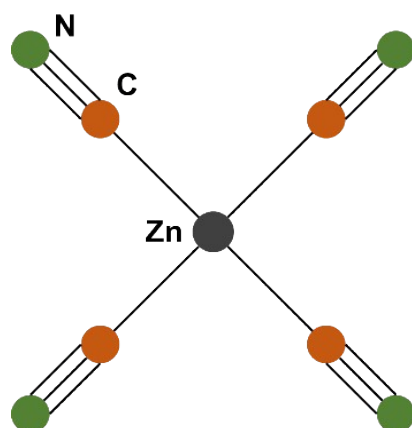
### Electrochemical Characterization

The electrochemical performance of Zn anodes was characterized with an electrochemical workstation (EC-lab). ZSO or 2.5-KSeCN/ZSO was utilized as the electrolyte, Zn foils (thickness:  $\sim 50 \mu\text{m}$ ; Alfa Aesar; purity: 99.99+%) employed as the working electrode, Pt foils served as the counter electrode, and Ag/AgCl (saturated KCl) was used as the reference electrode. The polarization curves of Zn anodes were measured using a three-electrode system in different electrolytes. Linear sweep voltammetry (LSV) was employed with a scan rate of 1  $\text{mV s}^{-1}$ . A comparison of the polarizability of two electrolytes was conducted. Electrochemical impedance spectroscopy (EIS) tests were conducted on assembled Zn|Zn cells (Zn foil thickness:  $\sim 20 \mu\text{m}$ ; Zn foil diameter:  $\sim 15\text{mm}$ ) over the frequency range of 500 kHz to 10 mHz at different temperatures. The test was performed in an incubator with an amplitude of 10 mV, and all Zn|Zn symmetric cells were tested after 12 hours. Cyclic voltammetry (CV) curves of

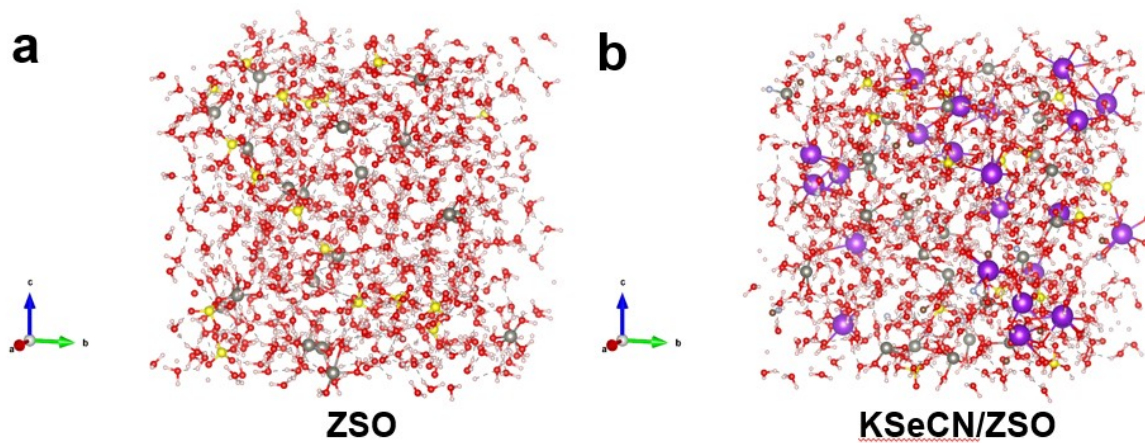
Zn|Zn symmetric cells in different electrolytes were measured within the voltage range of  $-0.2$  to  $0.6$  V using a three-electrode system at a scan rate of  $1 \text{ mV s}^{-1}$ . Chronoamperometry (CA) measurements of Zn foils with different electrolytes were carried out at a constant potential of  $-150$  mV. LSV curves were tested with a three-electrode system to compare the corrosion potential and corrosion current of Zn foils in different electrolytes (with a scan rate of  $1 \text{ mV s}^{-1}$ ). Hydrogen evolution reaction (HER) curves were measured at room temperature with a three-electrode system. Coulombic efficiency (CE) and nucleation overpotential (NOP) measurements were conducted on the LAND battery testing system (M340A, LANHE). Cu|Zn batteries were assembled in CR2025 coin cells using Cu foil (working electrode), Zn foil (counter electrode), glass fiber separator, and ZSO or 2.5-KSeCN/ZSO electrolyte ( $\sim 150 \mu\text{L}$ ). Testing was carried out under conditions of  $2 \text{ mA cm}^{-2}$  and  $1 \text{ mAh cm}^{-2}$ . Long-term galvanostatic cycling tests were conducted with the LAND battery testing system (M340A, LANHE). Zn|Zn symmetric cells (Zn foil thickness:  $\sim 20 \mu\text{m}$ ; Zn foil diameter:  $\sim 15 \text{ mm}$ ) were assembled using CR2025 coin cells. For the Zn|V<sub>2</sub>O<sub>5</sub> full cells, a glass fiber separator was used to separate the V<sub>2</sub>O<sub>5</sub> cathode and Zn anode, with ZSO or 2.5-KSeCN/ZSO serving as the electrolyte (Zn foil thickness:  $\sim 20 \mu\text{m}$ ; Alfa Aesar; purity: 99.99+%, Cu foil thickness:  $\sim 20 \mu\text{m}$ ; Alfa Aesar; purity: 99.99+% and glass fiber separator thickness:  $0.29 \pm 0.01 \text{ mm}$ ; Ologytech; aperture:  $1.63 \mu\text{m}$ ; weight:  $66 \text{ g m}^{-2}$ ). Long-term constant current cycling measurements were performed on the LAND battery testing system (M340A, LANHE). CV curves of the Zn|V<sub>2</sub>O<sub>5</sub> full cells was conducted with an electrochemical workstation (EC-lab).

### Theoretical Calculations

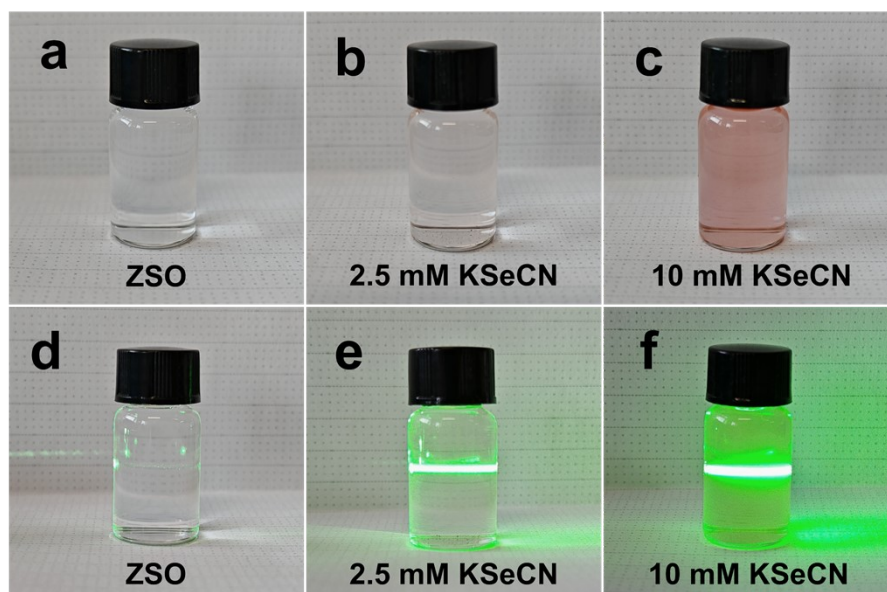
All DFT calculations were conducted using the Cambridge Sequential Total Energy Package (CASTEP) module within the Materials Studio software package. The interactions between electrons were described using the Perdew–Burke–Ernzerhof (PBE) interaction correlation functional in the generalized gradient approximation (GGA) considering spin polarization. Considering van der Waals forces, the dispersion function in all calculations used Grimme. The energy cutoff of the plane wave basis was set to  $400 \text{ eV}$ . The Gamma center used a Monkhorst–Pack  $2 \times 2 \times 1$  k-point grid to sample the First Brillouin–zone, and optimized the geometric structure. Gibbs free energy of Zn ion were calculated using Gaussian 09 software at B3LYP level with LAN2DZ. Molecular dynamics simulations were carried out under the microcanonical (NVE) ensemble by Forcite software at  $298 \text{ K}$ , for  $20 \text{ ps}$  with the time step of  $1 \text{ fs}$  with Universal forcefield.



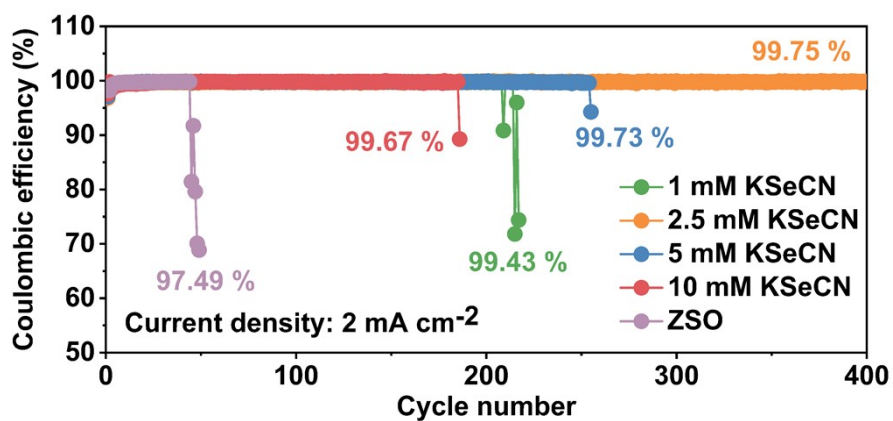
**Fig. S1.** Structure simulation diagram of  $\text{Zn}(\text{CN})_4^{2-}$ .



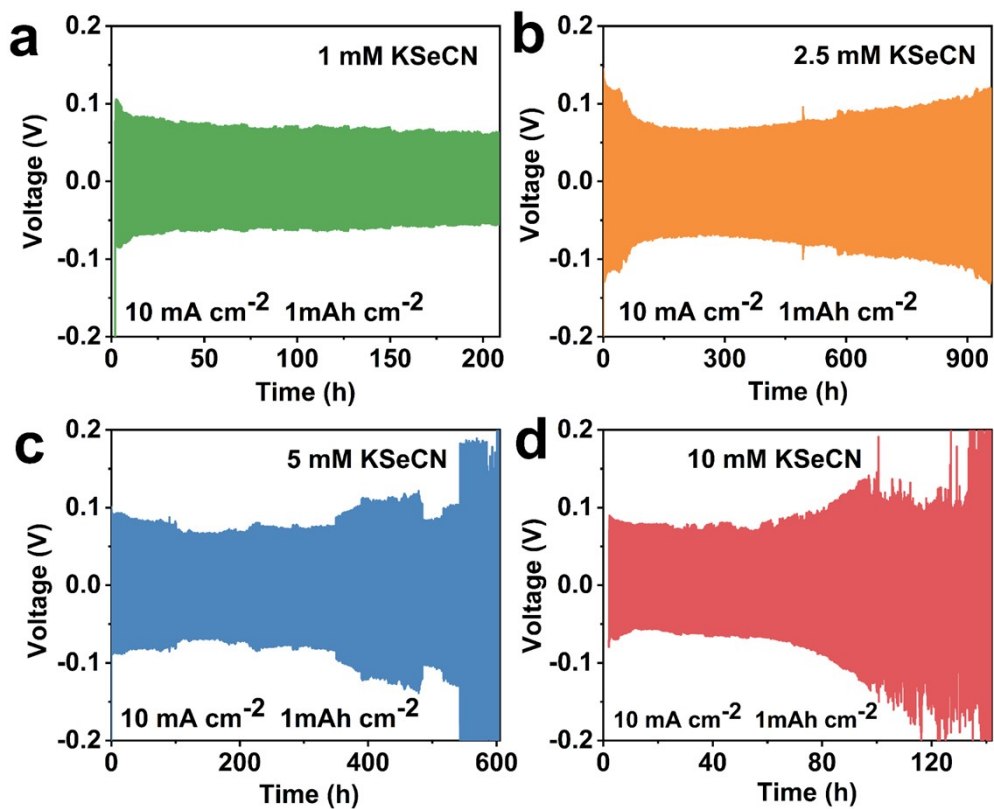
**Fig. S2.** The structural evolution of (a) ZSO electrolyte and (b) KSeCN/ZSO electrolyte by experiment and theoretical calculation.



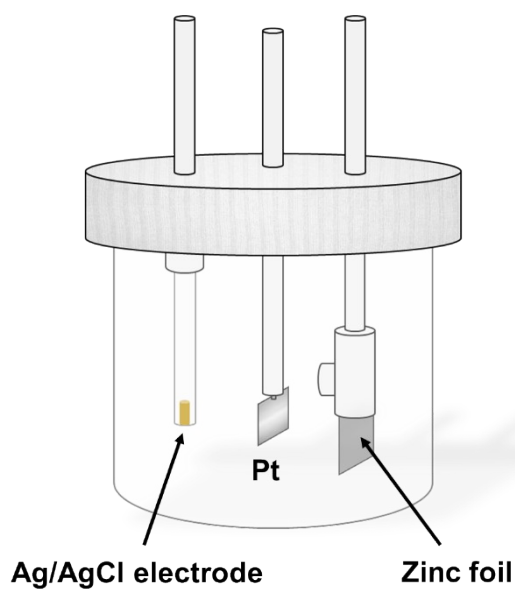
**Fig. S3** (a–c) Optical images of KSeCN/ZSO electrolytes with different KSeCN concentrations. (d–f) Optical images of KSeCN/ZSO electrolytes with different KSeCN concentrations under laser pointer illumination.



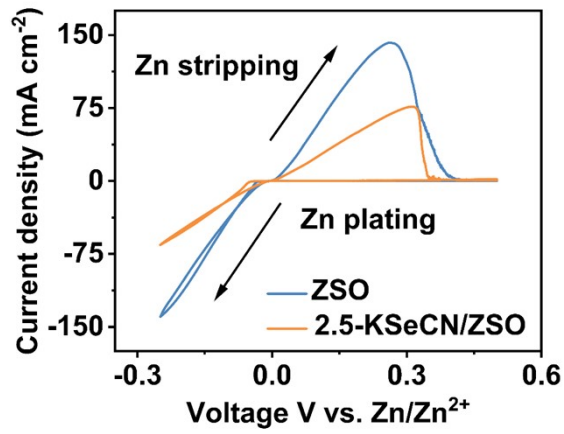
**Fig. S4** Coulombic efficiency of Cu|Zn cells with different electrolyte additive ratios.



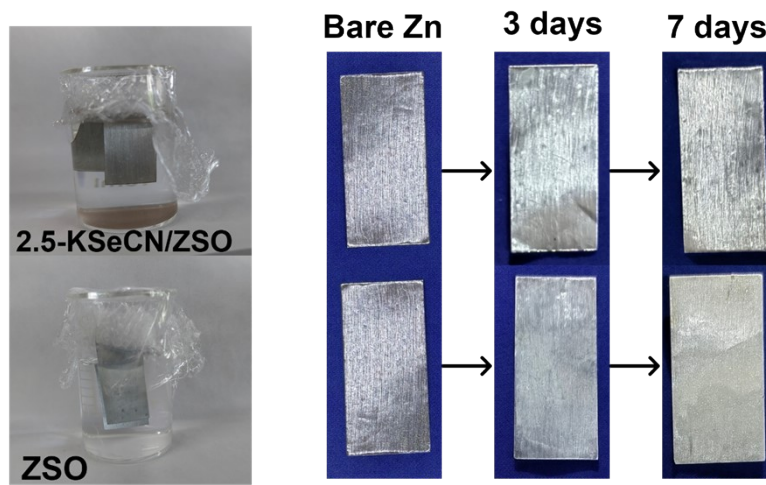
**Fig. S5** Long-term galvanostatic cycling performance of Zn|Zn cells using electrolytes with varying concentrations of KSeCN additive.



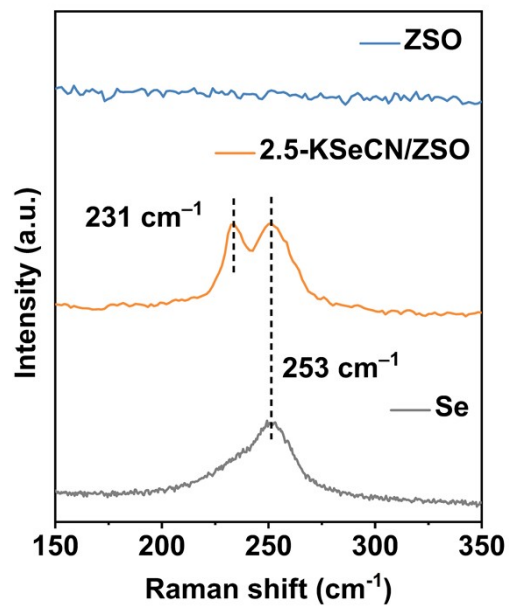
**Fig. S6.** Schematic of the three-electrode system.



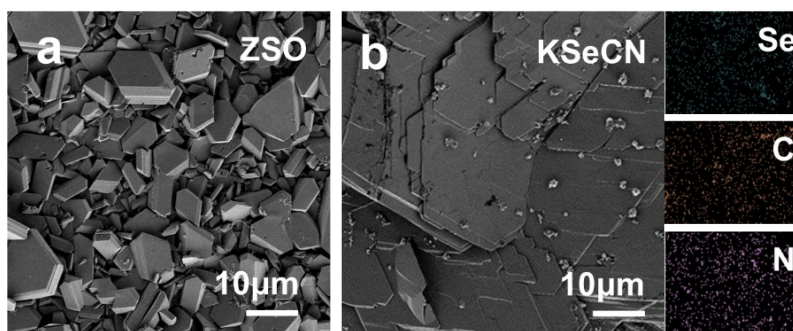
**Fig. S7.** CV curves of Zn|Zn symmetric cells using different electrolytes.



**Fig. S8.** Optical image of Zn foils after 7 days of immersion in different electrolytes.

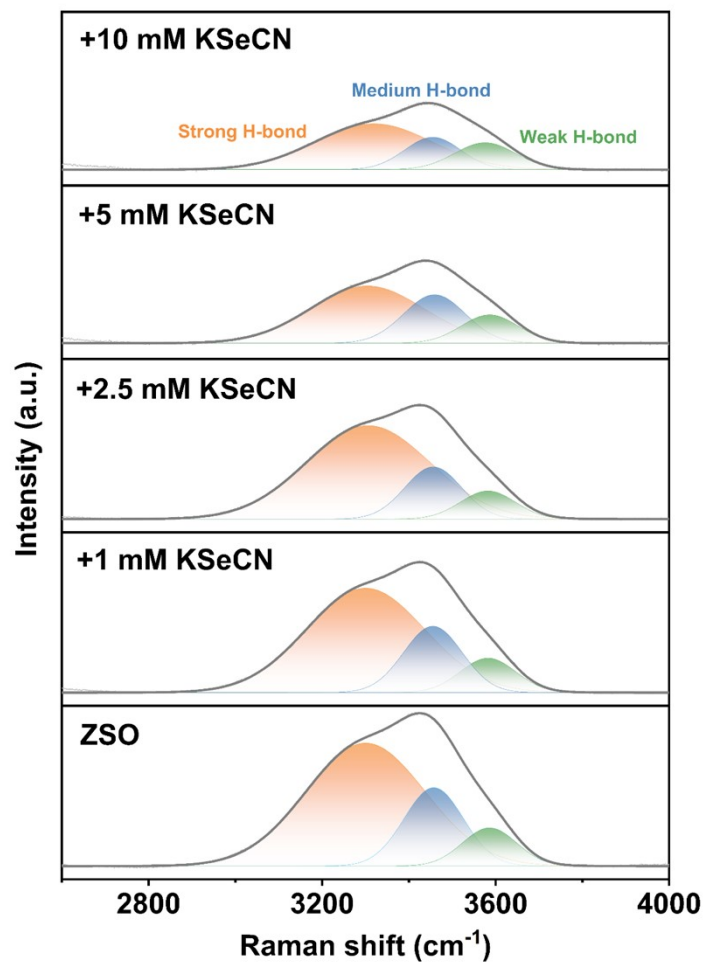


**Fig. S9.** Raman spectra of the Zn foils after immersing in different electrolytes for 14 days.

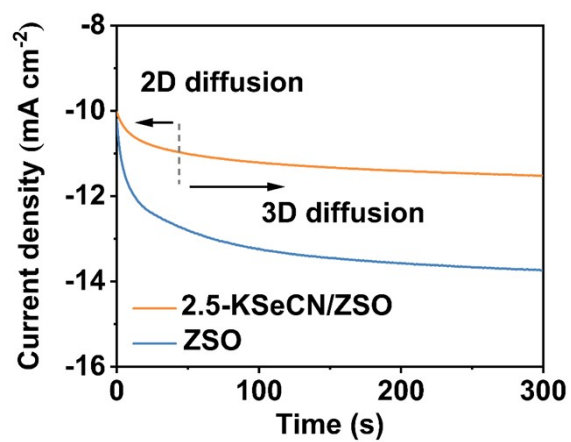


**Fig. S10.** SEM images and EDS mapping of the Zn foil surfaces after immersion in (a) ZSO or (b) 2.5-KSeCN/ZSO for 14 days.

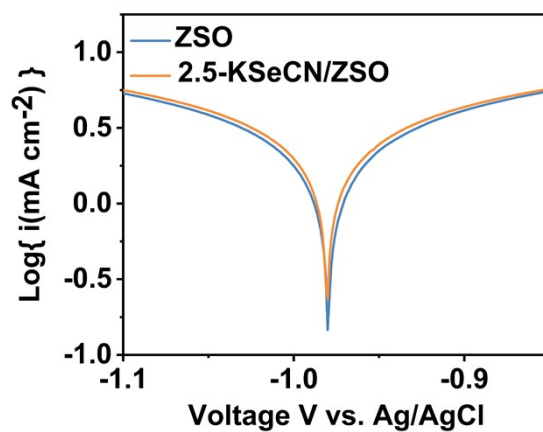




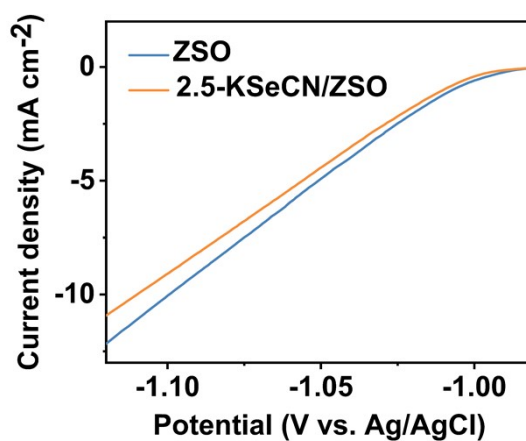
**Fig. S11.** Fitted raman spectra of ZSO electrolytes with different KSeCN concentrations.



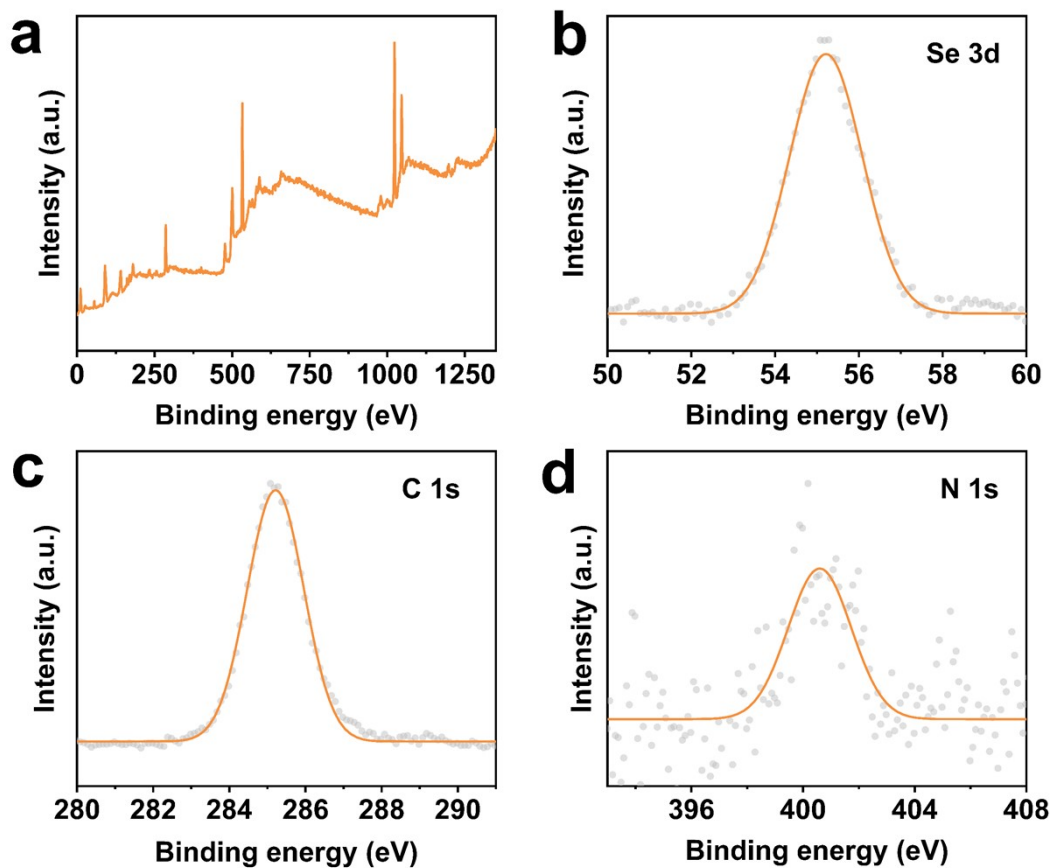
**Fig. S12.** CA curves of Zn anodes in different electrolytes at a  $-150$  mV overpotential.



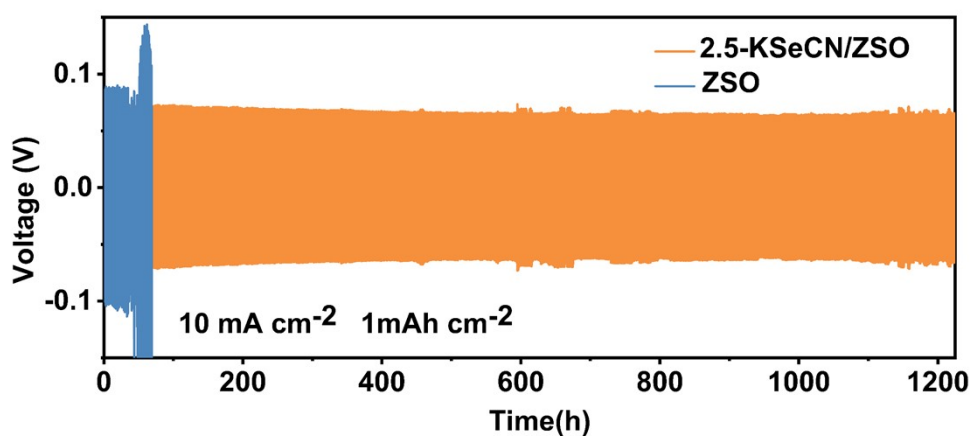
**Fig. S13.** Linear polarization curves presenting the corrosion on Zn anodes in different electrolytes at  $1 \text{ mV s}^{-1}$ .



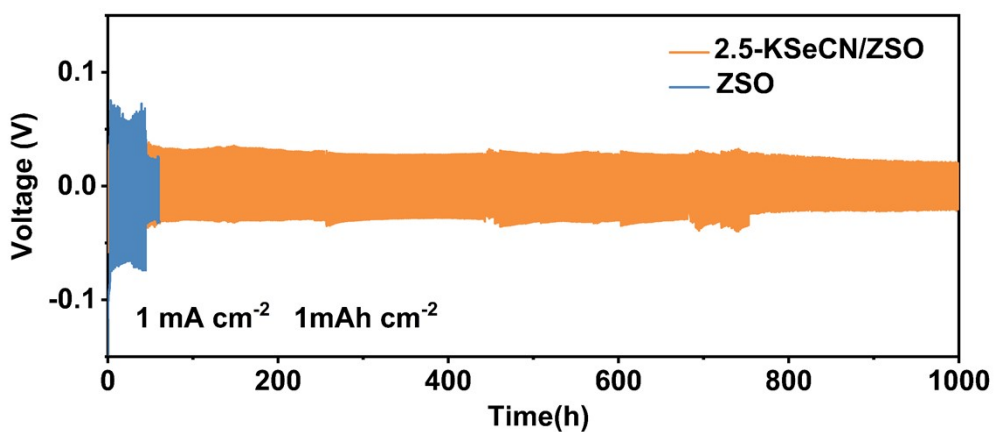
**Fig. S14.** HER curves in different electrolytes at  $1 \text{ mV s}^{-1}$ .



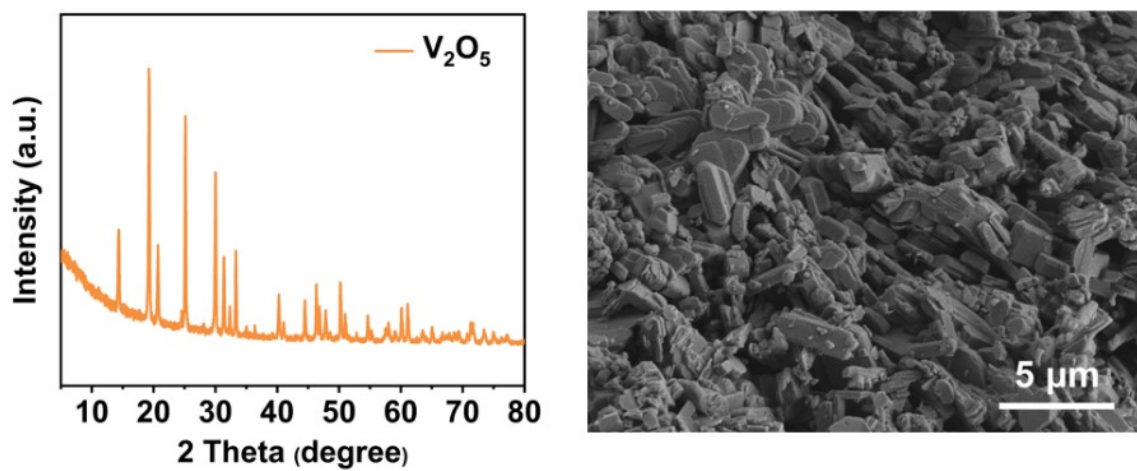
**Fig. S15.** XPS spectra of the Zn anode after 300 cycles in 2.5-KSeCN/ZSO at  $10 \text{ mA cm}^{-2}$  and  $1 \text{ mAh cm}^{-2}$ .



**Fig. S16.** Long-term galvanostatic cycling performance of Zn|Zn symmetric cells using different electrolytes at  $10 \text{ mA cm}^{-2}$  and  $1 \text{ mAh cm}^{-2}$ .



**Fig. S17.** Long-term galvanostatic cycling performance of Zn|Zn symmetric cells using different electrolytes at  $1 \text{ mA cm}^{-2}$  and  $1 \text{ mAh cm}^{-2}$ .



**Fig. S18.** XRD spectrum and SEM image of  $\text{V}_2\text{O}_5$ .

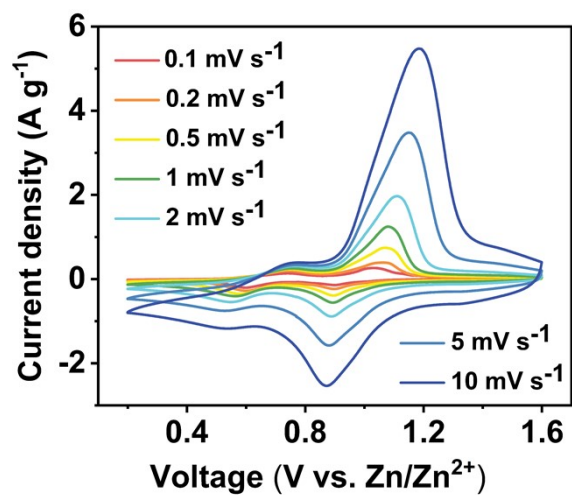


Fig. S19. CV curves of the full cells using 2.5-KSeCN/ZSO electrolyte at different scan rates.

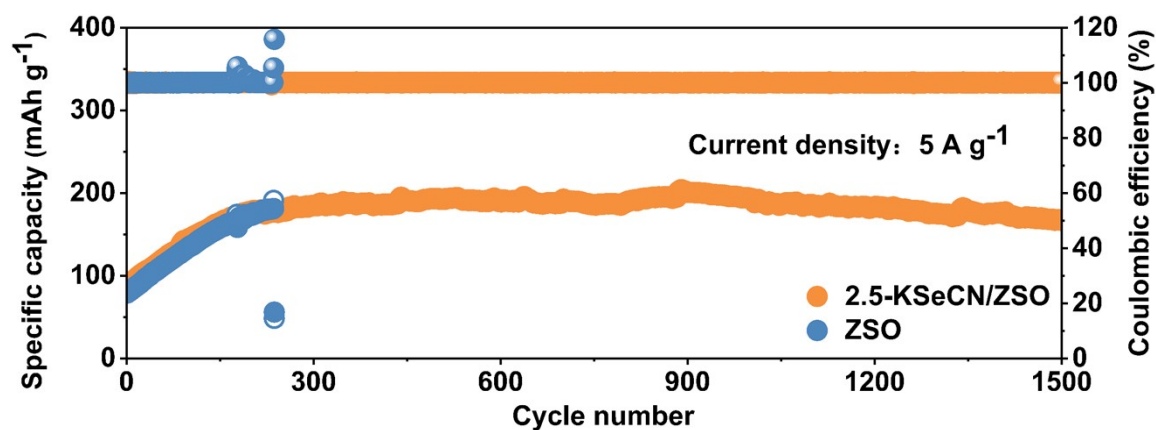
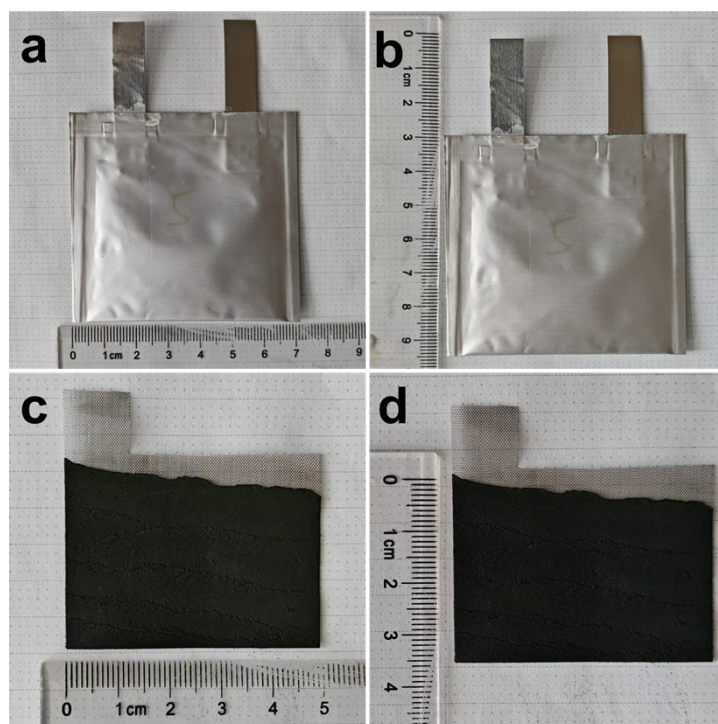


Fig. S20. Long-term galvanostatic cycling performance of Zn|V<sub>2</sub>O<sub>5</sub> full cells using different electrolytes at a current density of 5 A g<sup>-1</sup>.



**Fig. S21** Schematic images of (a,b) the pouch cell dimensions and (c,d) the cathode electrode sheet dimensions.

**Table S1.** The standard stability constants of  $Zn^{2+}$  complexes.

| Coordination complex | $K_f$                |
|----------------------|----------------------|
| $Zn(CN)^{2-}$        | $1.0 \times 10^{18}$ |
| $Zn(EDTA)^{2-}$      | $3.0 \times 10^{16}$ |
| $Zn(en)^{2+}$        | $1.3 \times 10^{14}$ |
| $Zn(NH_3)^{2-}$      | $4.1 \times 10^8$    |
| $Zn(OH)^{2-}$        | $4.6 \times 10^{17}$ |
| $Zn(ox)^{4-}$        | $1.4 \times 10^8$    |

ox: oxalate; en: ethylenediamine