

Supportive information

Unraveling the Significance of Zinc Ratio in Water-in-Salt Electrolytes

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Experimental section

Preparation of materials and electrolytes

Zinc foil (100 μm thickness, 99%), titanium foil (100 μm thickness, 99%), and copper foil (10 μm thickness, 99%) were purchased from Goodfellow. Zinc chloride (ZnCl_2 , 100%) and lithium acetate (LiAc, 99%) were purchased from Sigma-Aldrich and Organics, respectively, and used without any further treatment. ZnCl_2 salt was stored and weighed inside the glove box. Precalculated amounts of ZnCl_2 and LiAc salts were put in vials. Water was added to each vial with gradual increments and the mixtures were stirred after each addition till a saturation point was obtained. The vials were kept for 24 hours at room temperature to confirm the dissolution of the salts. The titanium foil was prepared by punching with a 19 mm diameter electrode puncher machine and soaking in diluted 1 M HNO_3 solution and shaking for around 10 min, followed by rinsing with ultrapure water and acetone three times, respectively, and then drying under vacuum. Similar procedure was followed to prepare Copper foil electrode except it was soaked in 1 M HCl solution. Similarly, zinc-foil was prepared by punching with a 13 mm diameter electrode puncher machine followed by washing with ultrapure water and acetone three times each, and drying under vacuum.

Characterizations

Raman spectroscopy of the electrolytes was conducted on a Witec Alpha 300M+ instrument. 532 nm laser was used and operated at a power of 20 mW at the source. The spectra were collected in backscattering geometry in a confocal micro-Raman mode with a 20 \times objective. The solutions

were placed in a small Quartz cuvette of thickness of 2mm. Each spectrum was collected at an integration time of 2 seconds with 20 accumulations with a resolution of approximately 2 cm^{-1} . The spectra of the water region were fitted using the Gaussian function. To observe the morphology and byproducts on the zinc surface, the immersed and cycled Zn electrodes were washed with water and dried under vacuum. SEM pictures were performed on a LEO 1550 Gemini Zeiss microscope. Powder X-ray Diffraction (PXRD) measurements were performed on a Rigaku Smart Lab diffractometer, using Cu K α radiation at 1.5406 \AA , with steps of 0.1° and a scanning rate of $0.5^\circ\text{ min}^{-1}$. XPS measurements were performed using a Thermo Fisher Scientific K-Alpha, and data were treated with XPSpeak 4.1 software.

Electrochemical measurements

All electrochemical measurements were done using Biologic battery testing instrument at room temperature ($23 - 24\text{ }^\circ\text{C}$) and were tested 2 to 3 times. All the cyclic voltammetry, LSV and cycling stability experiments were performed after the electrolyte was purged with nitrogen gas. The Zn||Zn symmetrical batteries consisting of two Zn electrodes ($\Phi 13\text{ mm}$), a glass fiber separator ($\Phi 19\text{ mm}$), and $120\text{ }\mu\text{L}$ electrolyte were assembled in a coin cell in the air. The Zn||Ti and Zn||Cu cells for the reversibility test were assembled using Cu/Ti foil ($\Phi 19\text{ mm}$), Zn foil ($\Phi 13\text{ mm}$), and glass fiber separator ($\Phi 19\text{ mm}$) in 120 mL electrolyte. Galvanostatic charge-discharge cycling tests of Zn||Zn, Zn||Ti, and Zn||Cu cells were performed on a BioLogic instrument. Cyclic voltammetry (CV) dissolution/deposition was performed in a 3-electrode cell using titanium foil as a working electrode, platinum as a counter electrode, and Ag/AgCl as a reference electrode at $10\text{ mV}^{-\text{s}}$ in a potential window of -1.7 to 0 V . Chronoamperometry (CA) tests were measured using Zn||Zn symmetric cells under a polarization voltage of -150 mV and 10 mV for 900 s and 1800 s to determine the zinc ions transference number and the deposition process, respectively. Linear sweep voltammetry (LSV) curves were conducted using Zn||Ti half cells from OCV to -1.7 V at a scan rate of 10 mV s^{-1} similar to the CV protocols. Nucleation overpotentials were conducted using Zn||Ti cells at a current density of 1 mA cm^{-2} and capacity of 0.5 mAh cm^{-2} . The electrochemical impedance spectroscopy (EIS) measurements were performed in the range of 100 kHz to 100 mHz at a voltage amplitude of 10 mV .

The Zn^{2+} transference number ($t_{Zn^{2+}}$) of the electrolyte was measured using a Zn||Zn symmetric cell via EIS and CA measurements by applying constant polarization voltage. The $t_{Zn^{2+}}$ was calculated using the Bruce-Vincent-Evans equation as described below: ^{1, 2}

$$t_{Zn^{2+}} = \frac{I_s (V - I_0 R_0)}{I_0 (V - I_s R_s)}$$

Where ΔV is the applied polarization voltage (10 mV) across the cell, R_0 and R_s represent the interfacial resistances before and after polarization, respectively; I_0 and I_s are the initial current before the polarization and the stable current after the polarization, respectively.

Physicochemical properties

The density of the sample at 25°C was determined in a density oscillation tube (DMA 5000M, Anton Paar, Graz). The viscosity at 25°C was measured and evaluated with an Automated Microviscometer (AMVn, Anton Paar, Graz), a capillary with a diameter of 1.6 mm at 70° angle and repeated measurements. Ionic conductivity was tested using the impedance method via Biologic electrochemical testing instrument at 25°C.

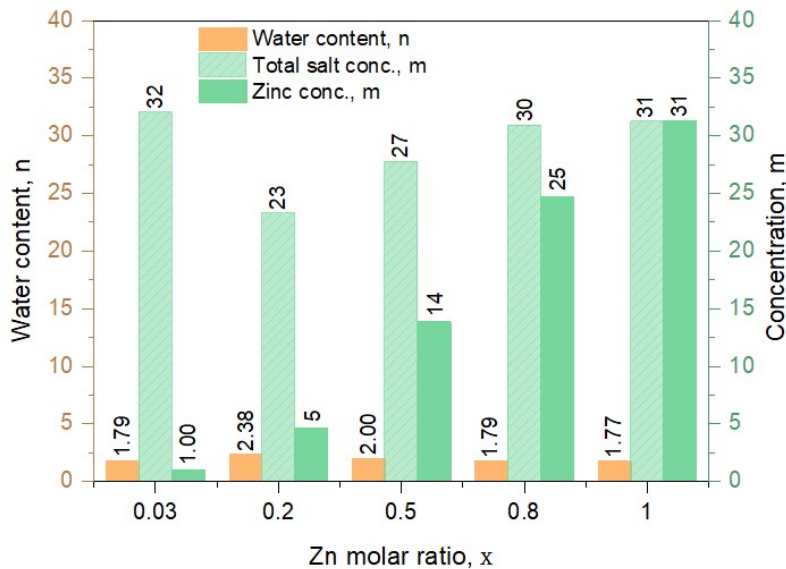


Figure S1: Zinc molar ratio versus water content, zinc concentration, and total salt concentration in various WISEs with different $ZnCl_2$ and LiAc molar ratios.

Table S1: Physicochemecal properties of different WISEs having different Zn molar ratios at 25 °C.

Zinc molar ratio	pH	Viscosity (mPa s)	Conductivity (mS cm⁻¹)	Density (g cm⁻³)
0.03Zn(Ac) ₂ 0.97KAc 1.79H ₂ O	10.9	48	29	1.471
0.2ZnCl ₂ 0.8LiAc 2.38H ₂ O	5.9	537	4	1.366
0.5ZnCl ₂ 0.5LiAc 2.00H ₂ O	2.3	265	8	1.629
0.8ZnCl ₂ 0.2LiAc 1.79H ₂ O	-0.9	317	5	1.951
1ZnCl ₂ 1.778H ₂ O	<-2	467	6	2.188

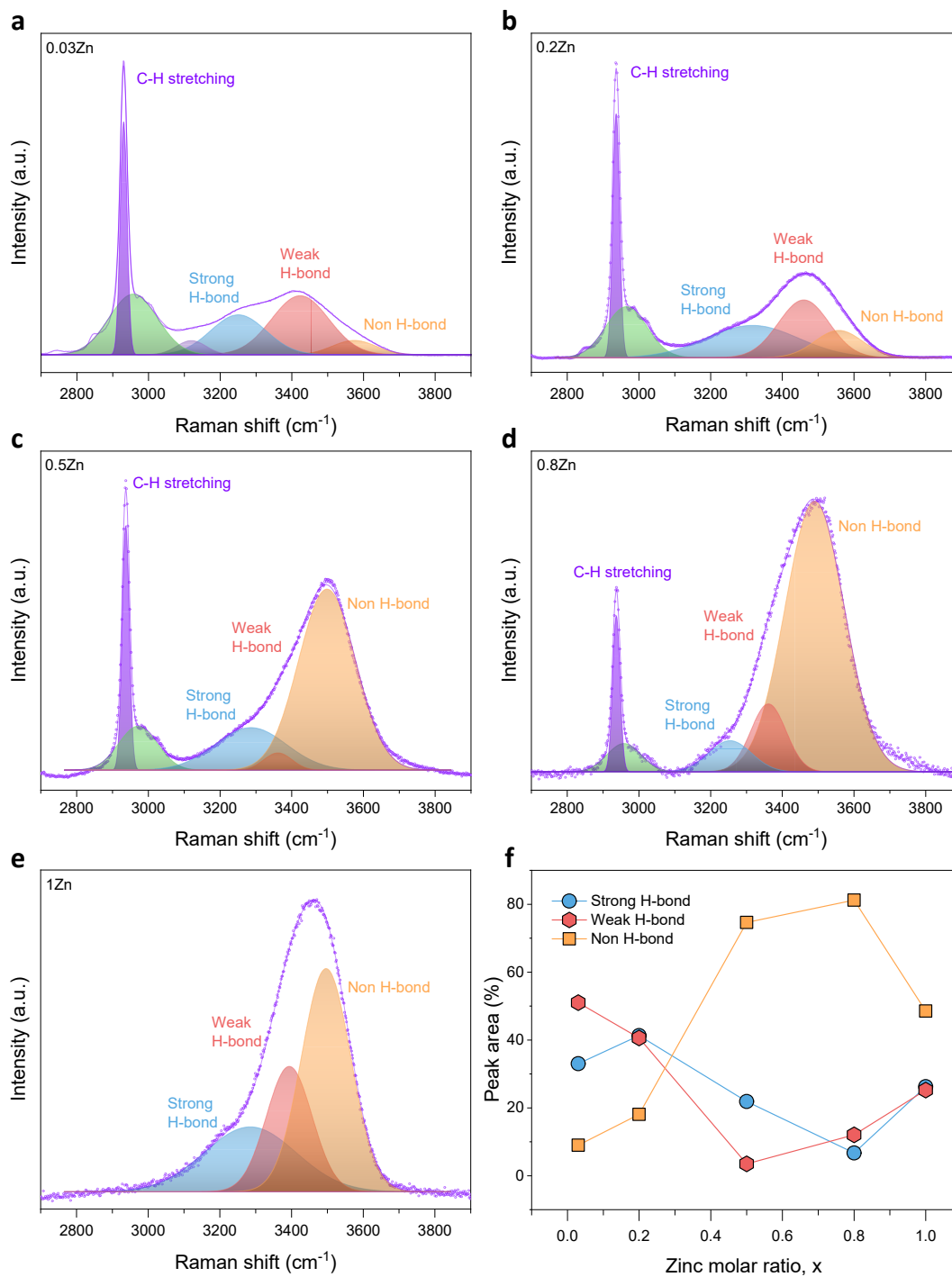


Figure S2: (a) Deconvolution of water molecules' O-H stretching Raman spectra of (a) 0.03Zn, (b) 0.2Zn, (c) 0.5Zn, (d) 0.8Zn, and (e) 1Zn WISEs. (f) The corresponding deconvoluted peak areas.

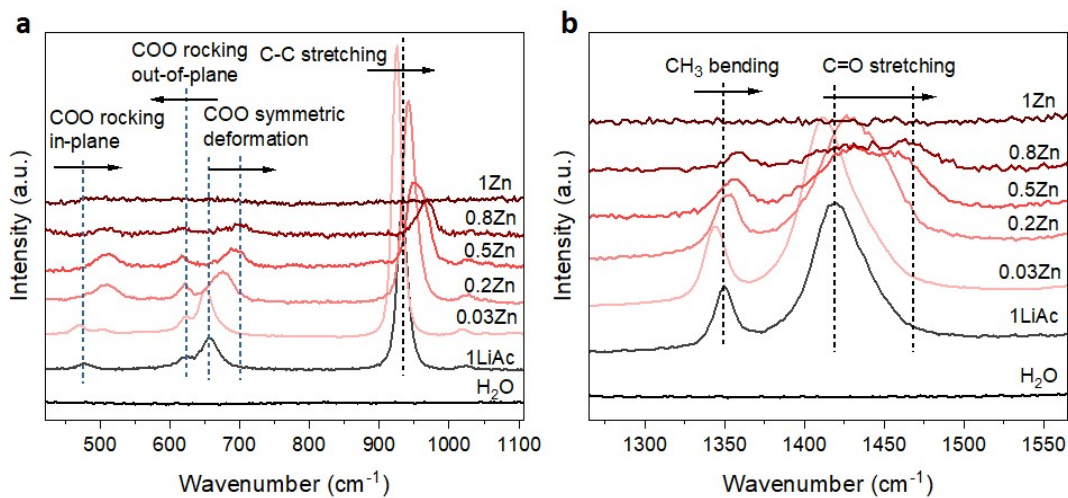


Figure S3: Raman spectra of acetate anions in different electrolytes at different region.

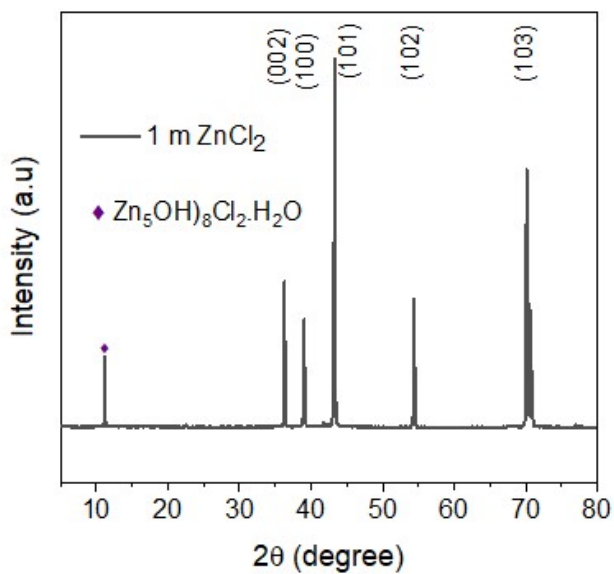


Figure S4: XRD patterns of Zn foil immersed in diluted 1 m ZnCl₂ electrolyte for 10 days.

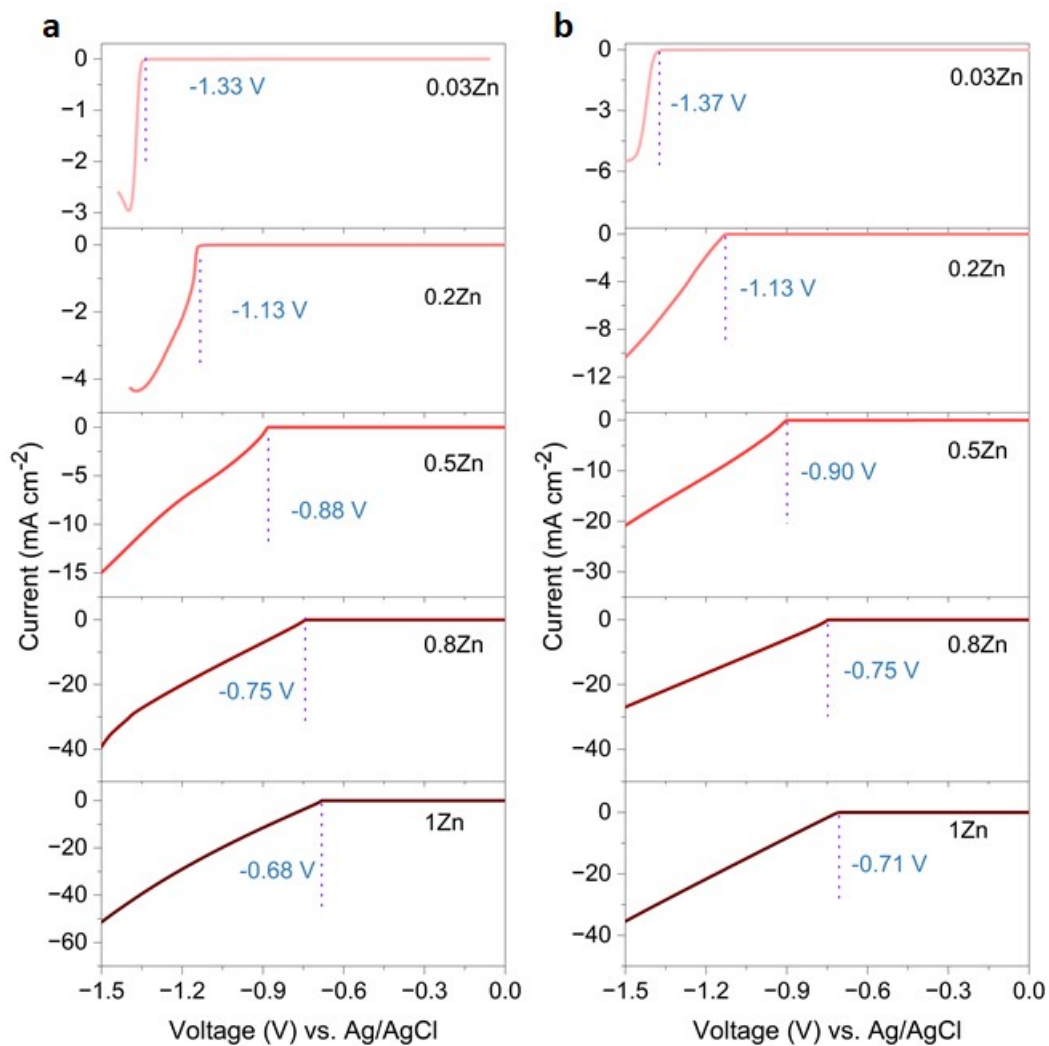


Figure S5: LSV profiles of different electrolytes on glassy carbon electrode using three electrode system at a scan rate of (a) 1 mV s⁻¹ and (b) 10 mV s⁻¹.

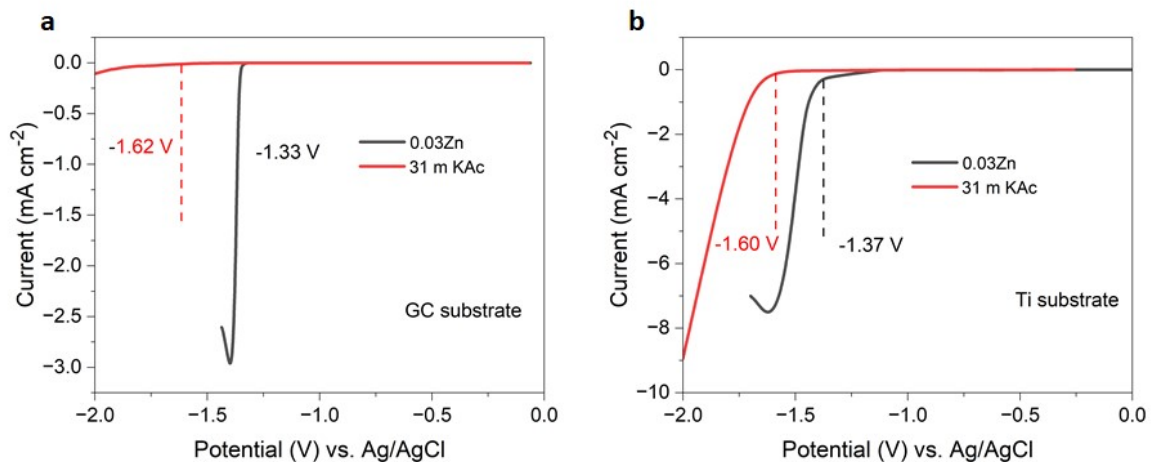


Figure S6: LSV profiles of (a) 0.03Zn and 31 m KAc electrolytes on GC substrate at 1 mV s^{-1} and (b) 0.03Zn and 31 m KAc electrolyte on Ti substrate at 10 mV s^{-1} .

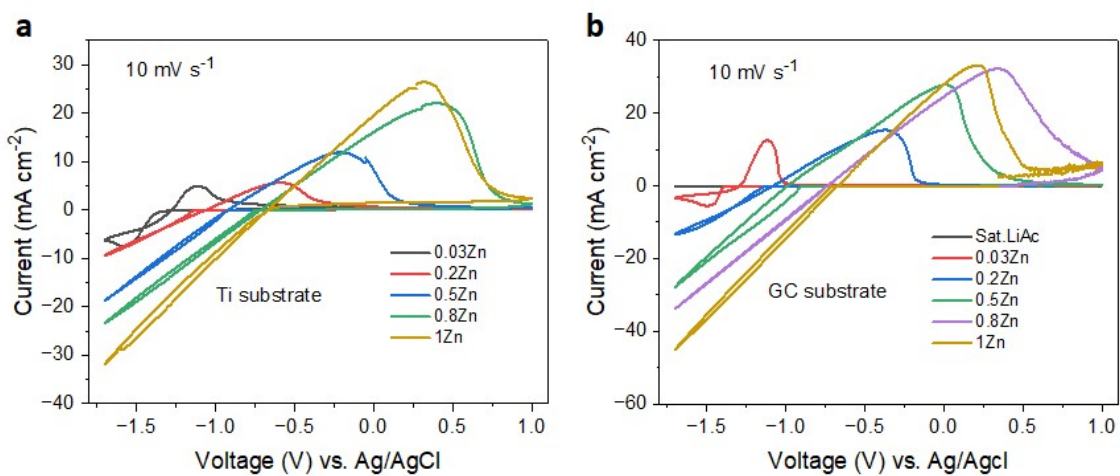


Fig. S7: CV profiles in different WISEs at 10 mV s^{-1} on (a) Ti substrate and (b) GC substrate

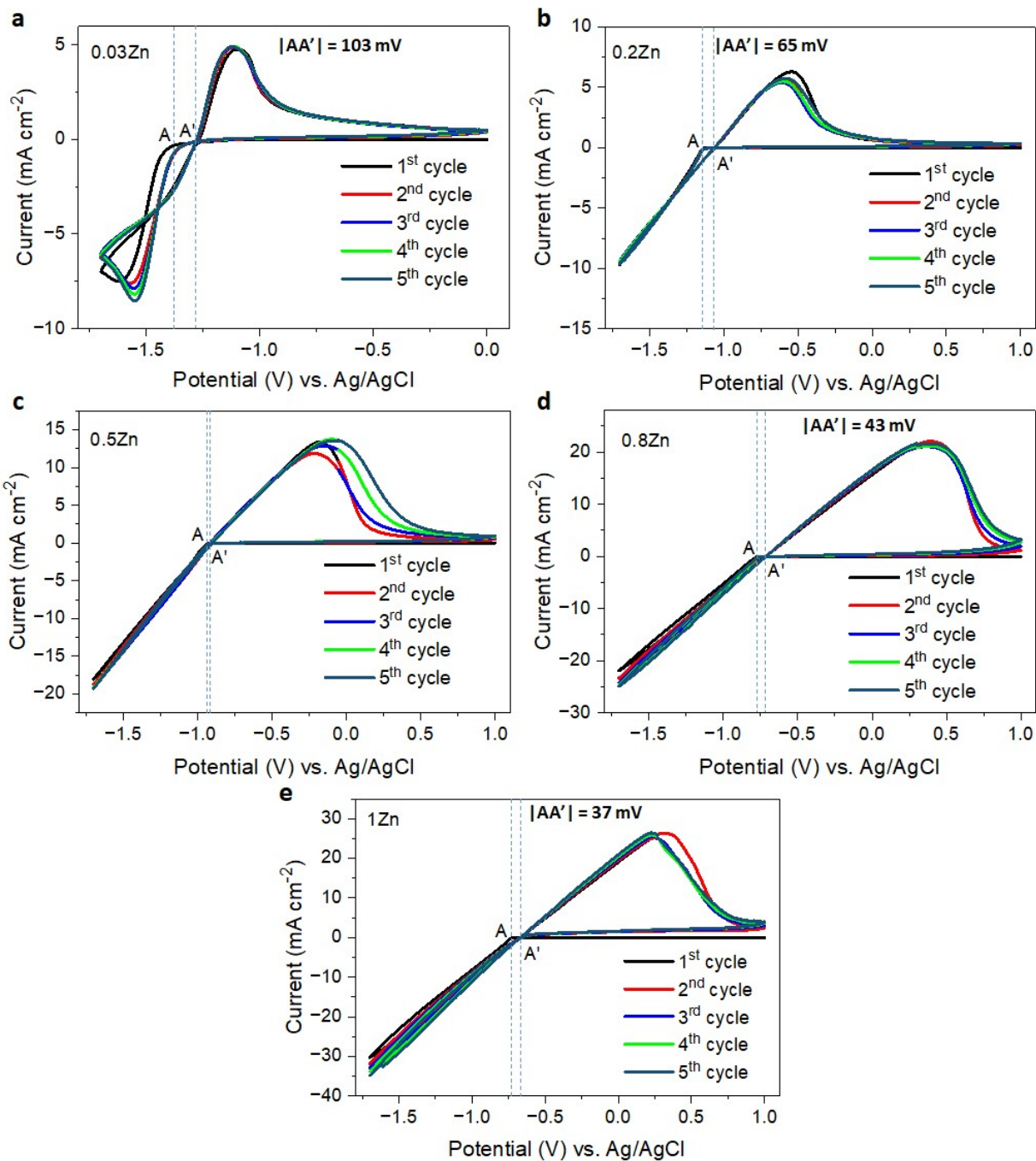


Figure S8: Cyclic voltammetry (CV) profiles using three electrode system at 10 mV s^{-1} in (a) 0.03, (b) 0.2, (c) 0.5 Zn, (d) 0.8, and (e) 1Zn WISEs.

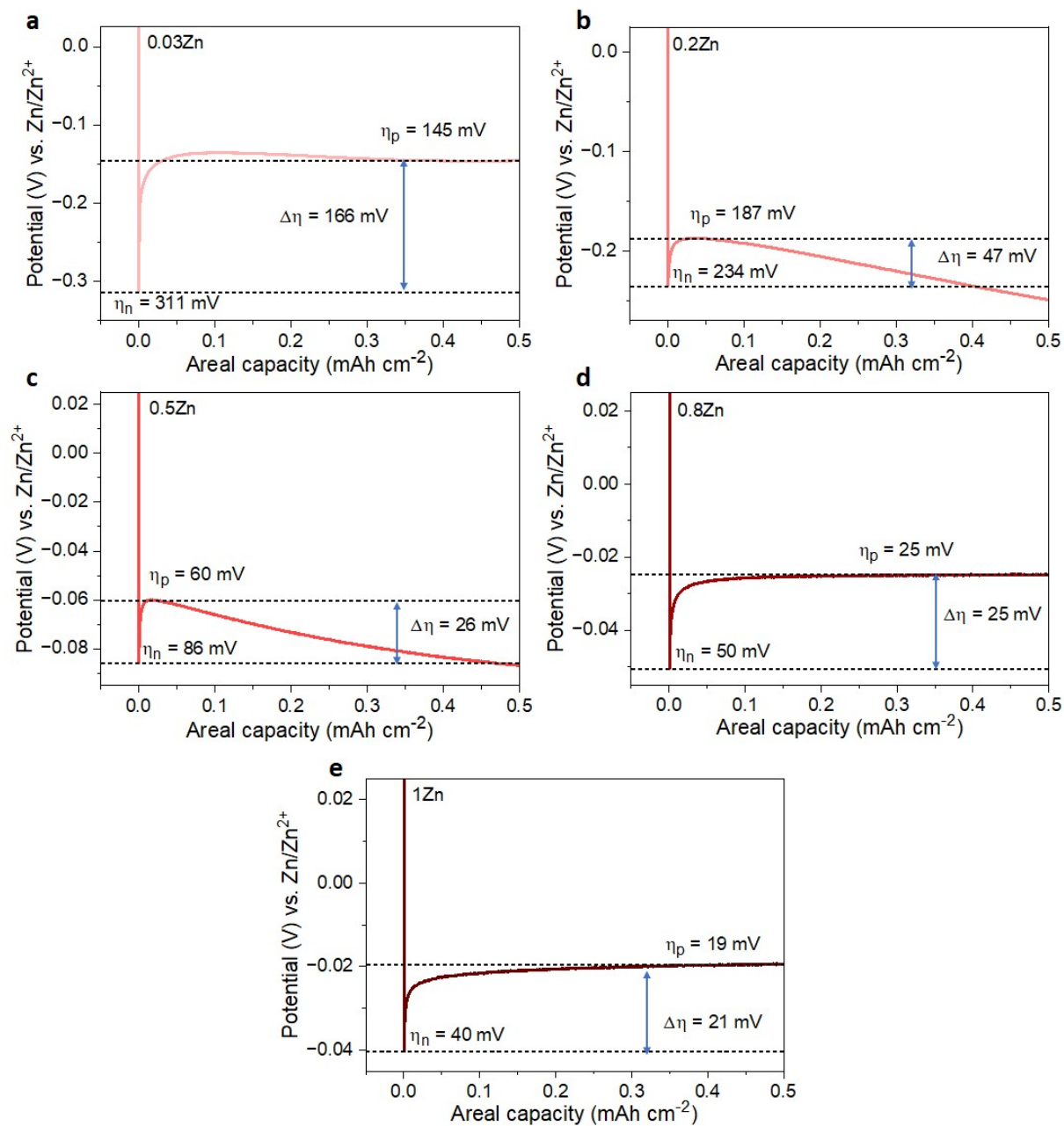


Figure S9: Initial Zn nucleation overpotentials of Zn||Ti half cells at 1 mA cm⁻² and 0.5 mAh cm⁻² (a) 0.03, (b) 0.2, (c) 0.5, (d) 0.8, and (e) 1Zn electrolytes.

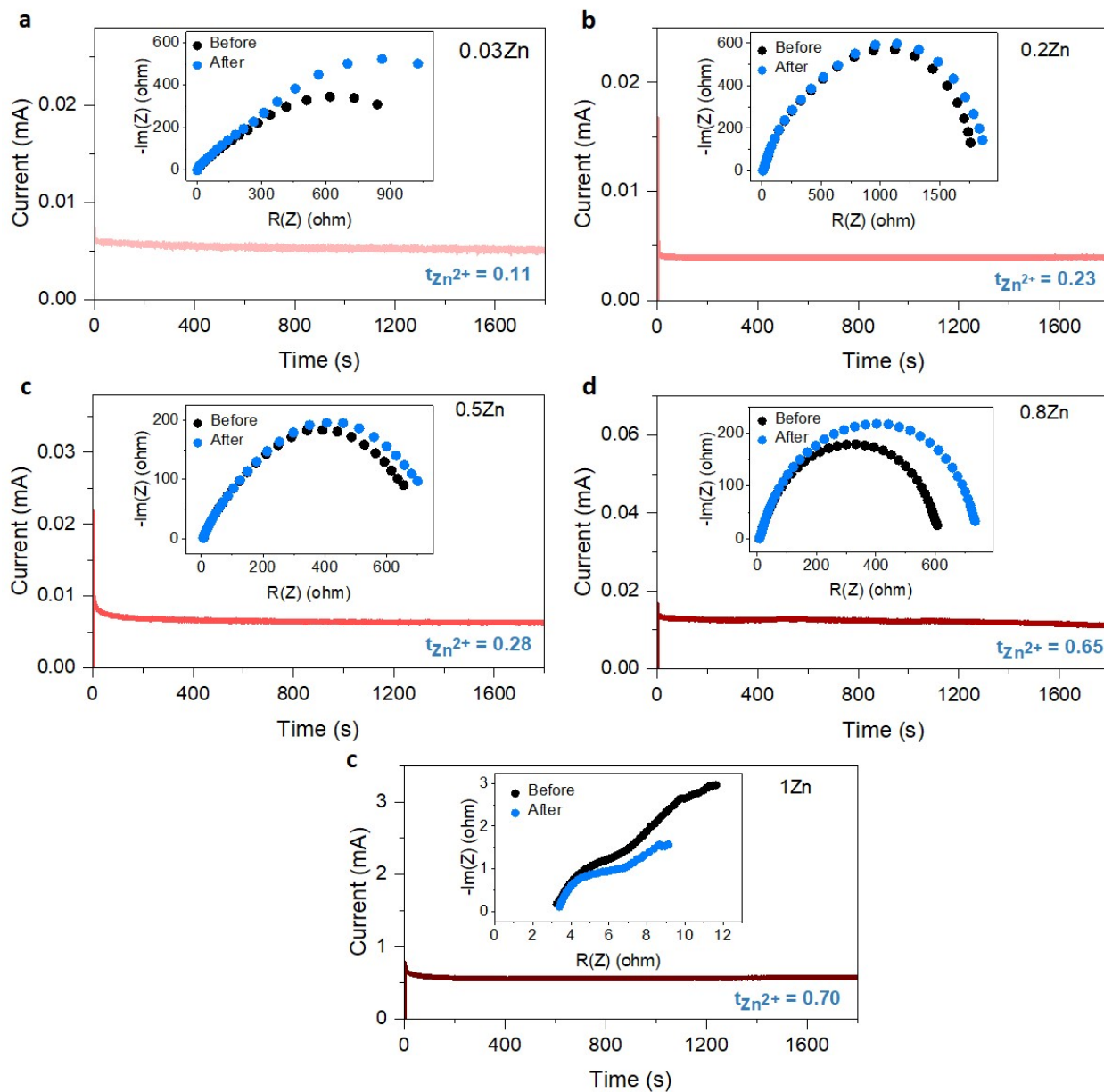


Figure S10: Current-time curves of Zn||Zn symmetric cells at polarization potential of 10 mV for 1,800 s using (a) 0.03, (b) 0.2, (c) 0.5, (d) 0.8, and (e) 1Zn electrolytes. Insets are the corresponding EIS graphs before and after polarization.

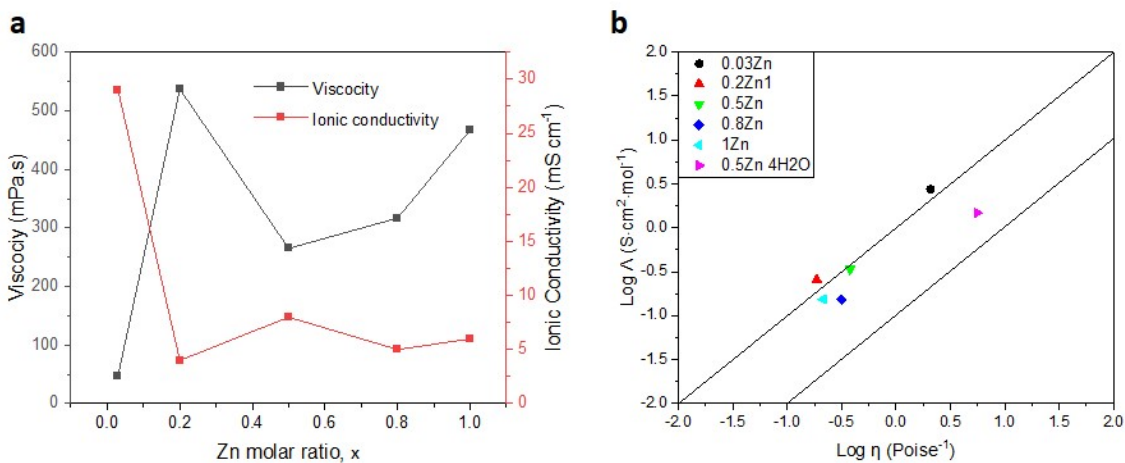


Figure S11: (a) Ionic conductivity and viscosity at various Zn molar ratios. (b) Walden plot in the at 25°C.

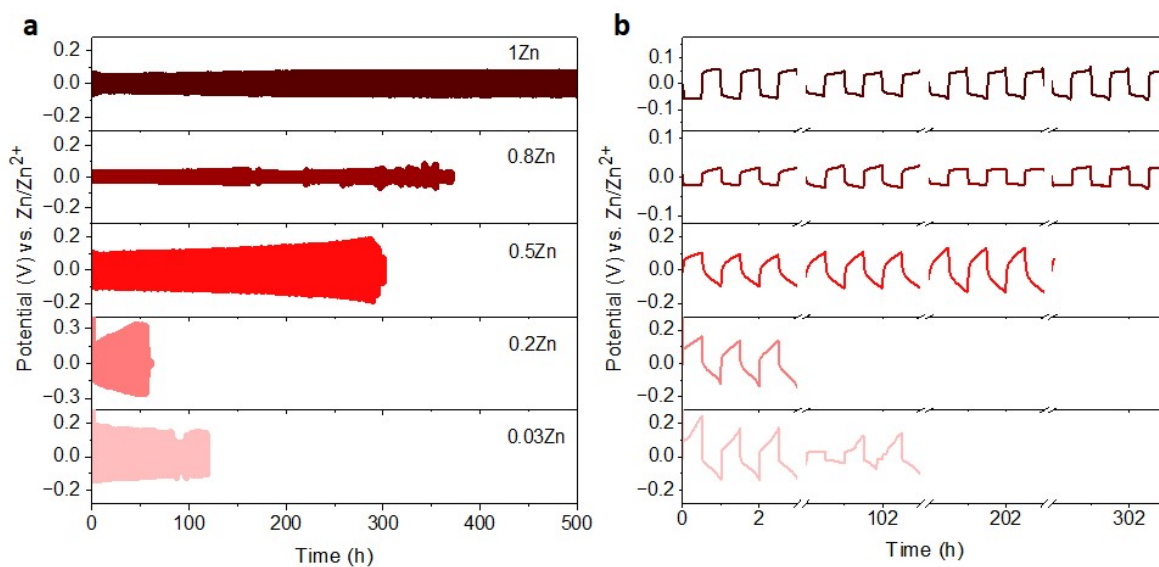


Figure S12: (a) Voltage profiles for Zn||Zn cells conducted in 0.03, 0.2, 0.5, 0.8, and 1Zn WISEs at current density of 1 mA cm⁻² with a capacity of 0.5 mAh cm⁻². (b) the corresponding polarization overpotentials profile

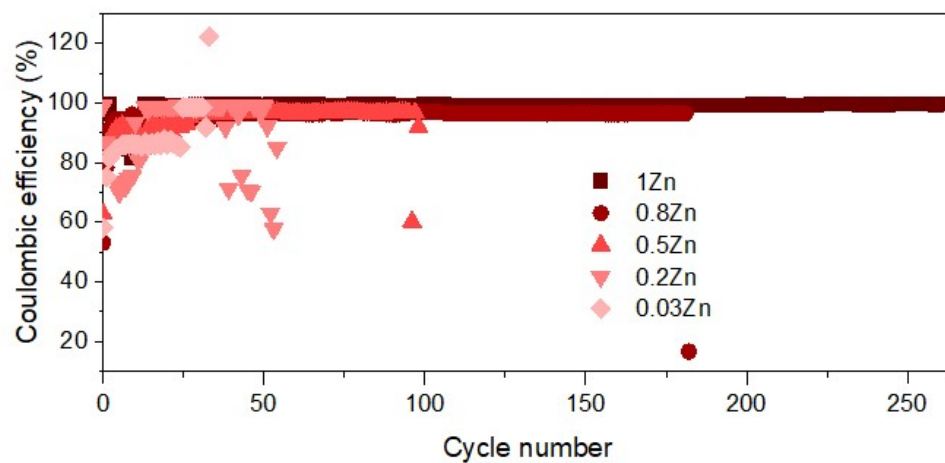


Figure S13: CE measurements of Zn||Ti cells using different WISEs at a current density of 1 mA cm^{-2} and a capacity of 0.5 mAh cm^{-2} .

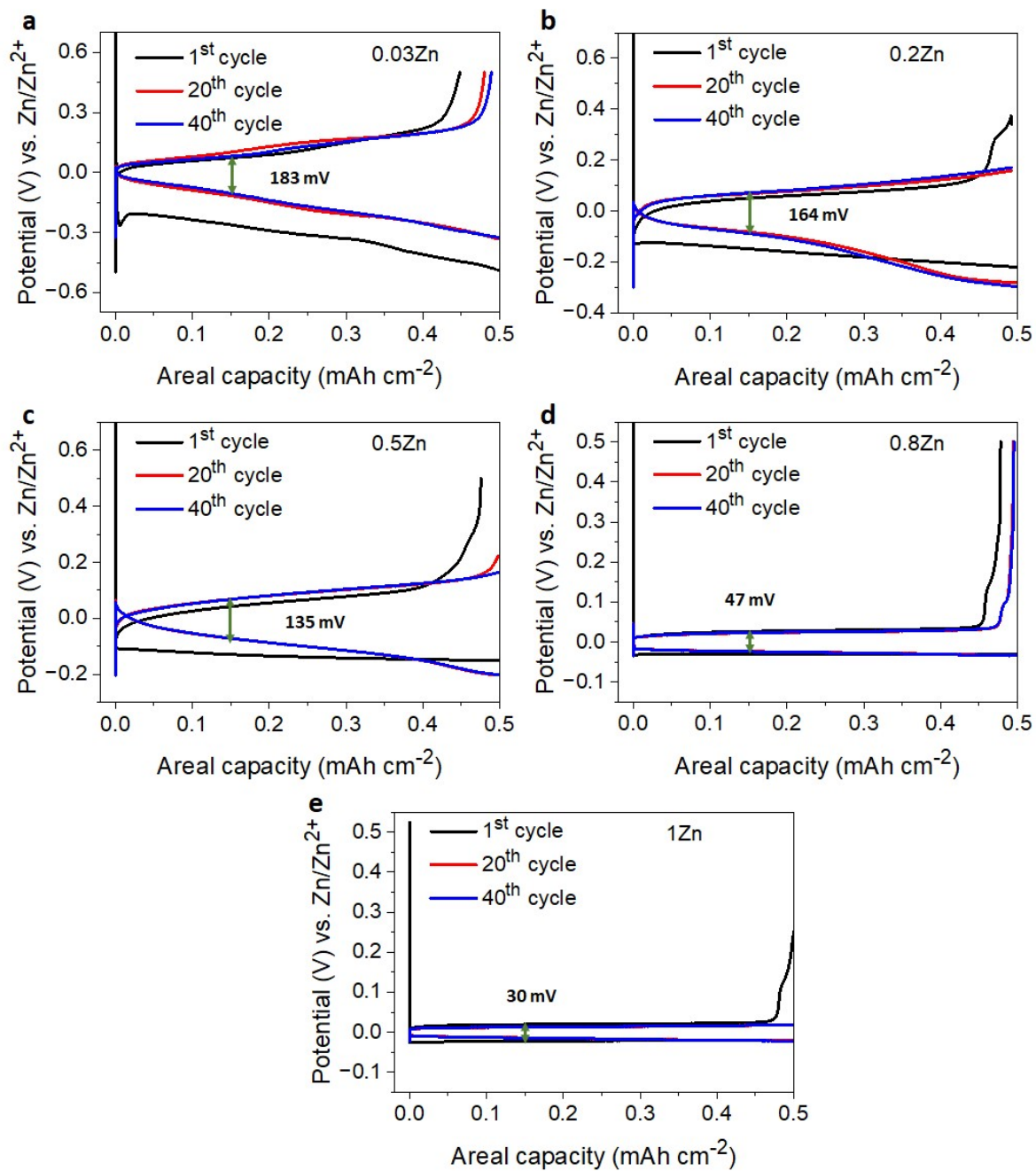


Figure S14: Galvanostatic voltage profiles of Zn||Cu cells in (a) 0.03, (b) 0.2, (c) 0.5, (d) 0.8, and (e) 1Zn electrolytes at a current density of 1 mA cm⁻² with a capacity of 0.5 mAh cm⁻².

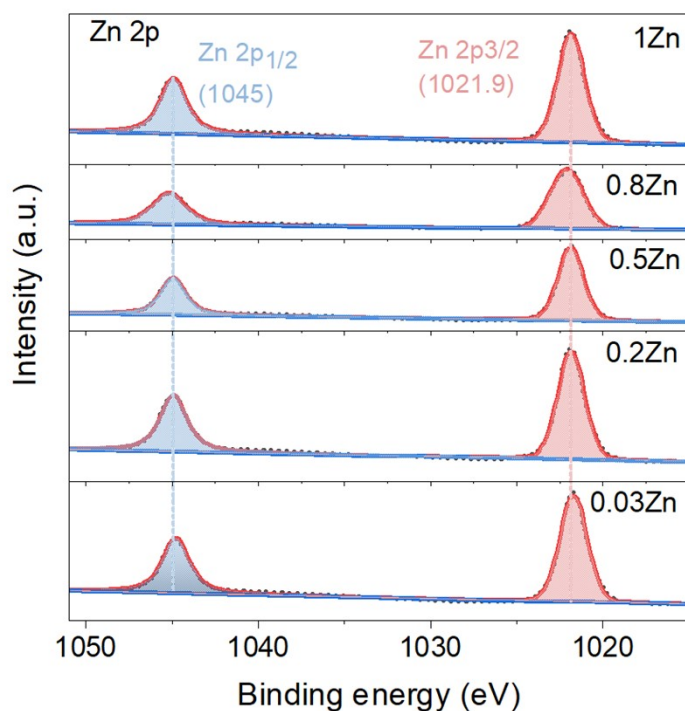


Figure S15: Zn 2p XPS spectra of cycled Zn anode surface in 0.03, 0.2, 0.5, 0.8, and 1Zn WISEs at current density 1 mA cm⁻² and a capacity of 0.5 mAh cm⁻² after 20 cycles.

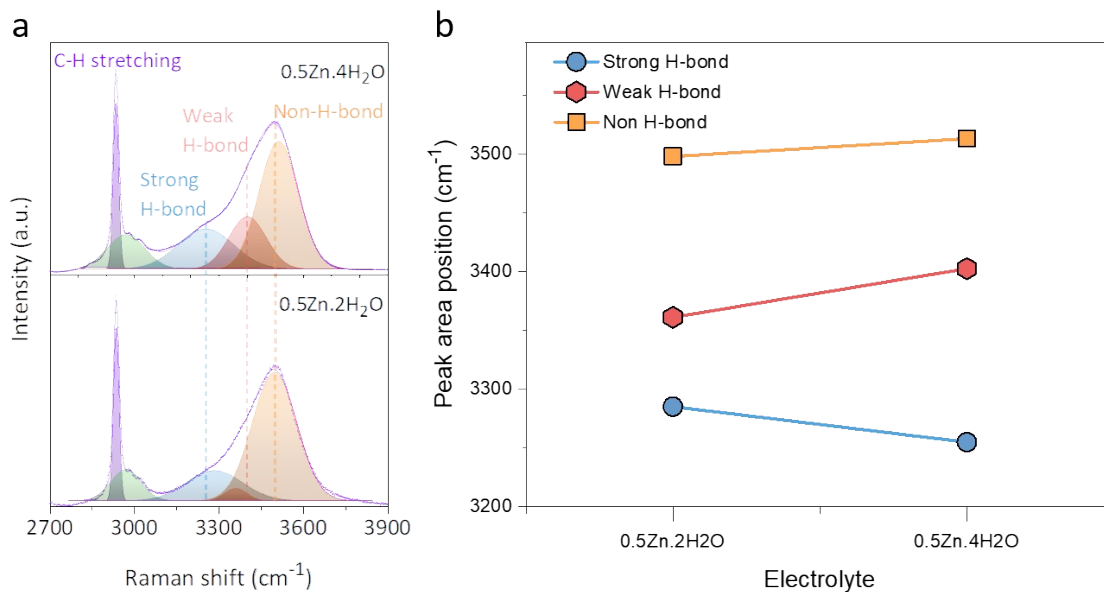


Figure 16: (a) Water region Raman spectra of 0.5Zn.4H₂O and 0.5Zn.2H₂O electrolytes. (b) The corresponding peak positions.

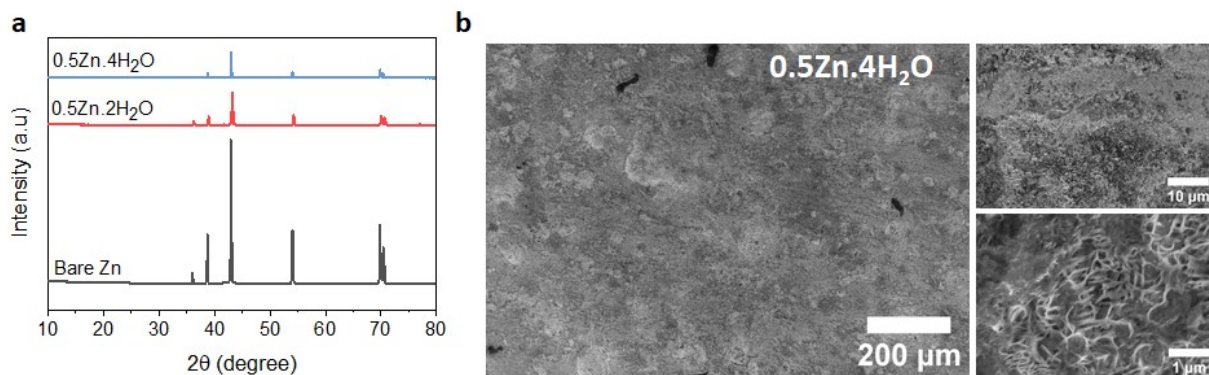


Figure S17: Soaking measurements of the Zn metal anode in 0.5 Zn.4H₂O electrolyte for 10 days at room temperature. (a) XRD patterns of the soaked Zn metal anode. (b) The corresponding SEM images at different magnification.

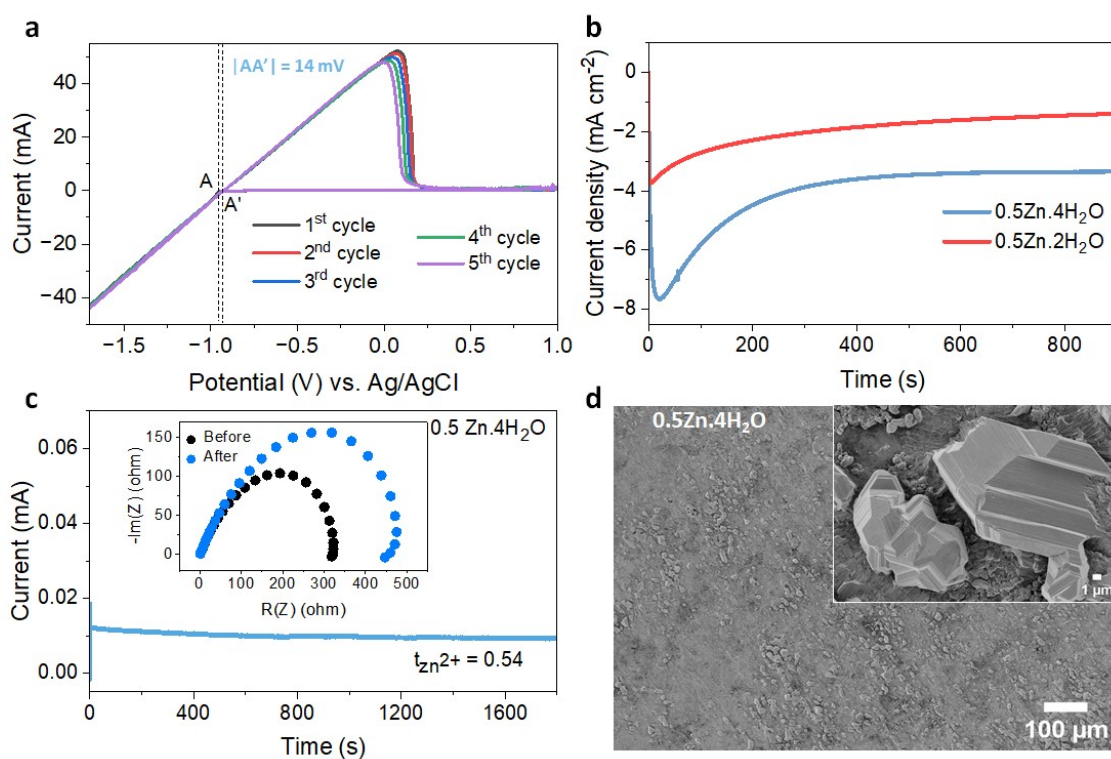


Figure S18: (a) CV of 0.5Zn.4H₂O electrolyte using three electrode system at 10 mV s⁻¹. (b) CA curves using Zn||Zn symmetric cell at polarization voltage of -150 mV in 0.5Zn.2H₂O and 0.5Zn.4H₂O electrolytes. (c) CA curves using Zn||Zn symmetric cell at polarization voltage of 10 mV for 1800 s in 0.5Zn.4H₂O electrolytes. The Inset is the corresponding EIS graphs before and after polarization. (d) The SEM images of deposited Zn in 0.5Zn.4H₂O electrolyte on Zn foil substrate.

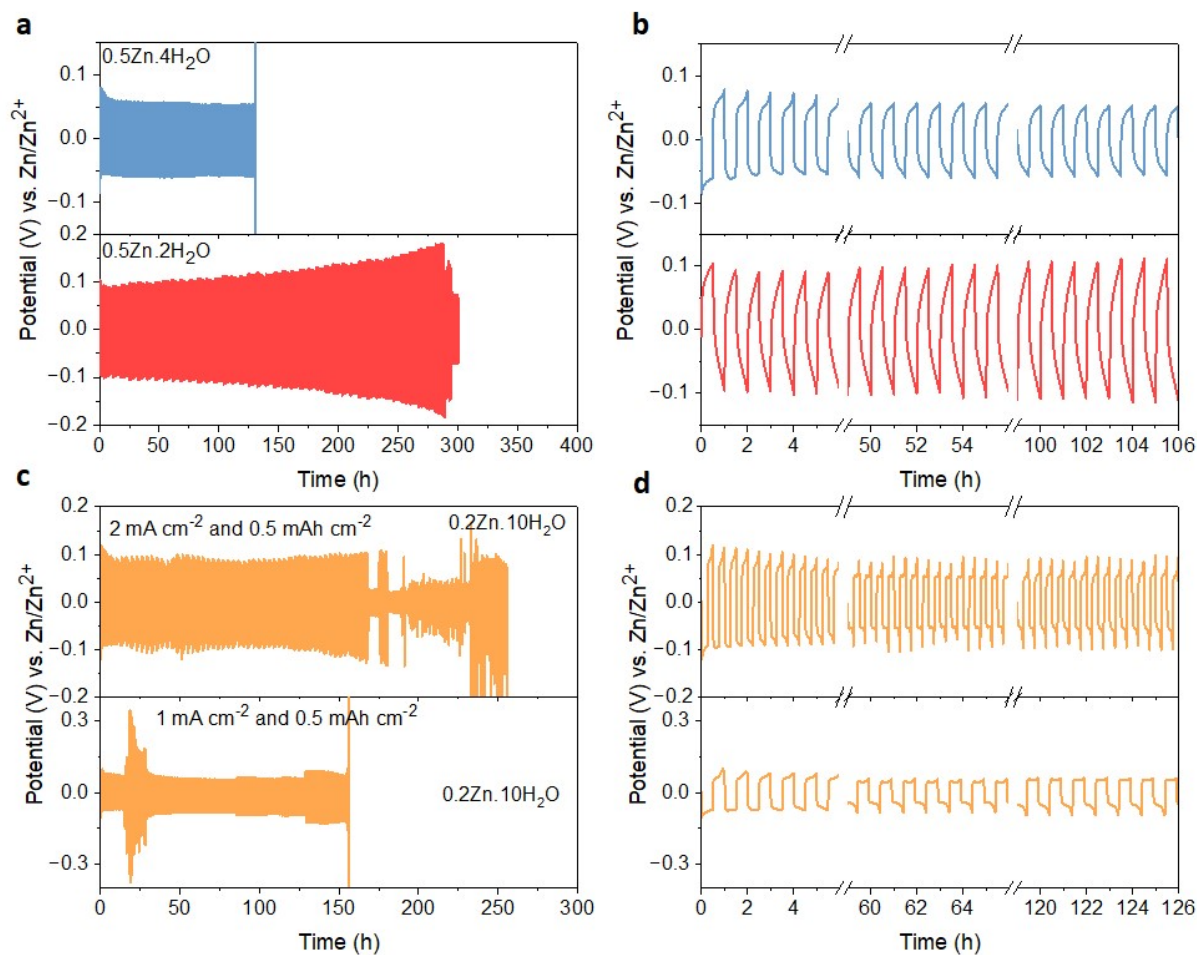


Figure S19: Cycling stability of Zn metal anode in (a) 0.5Zn.2H₂O and 0.5Zn.4H₂O electrolytes at a current density of 1 mA cm⁻² and with a capacity of 0.5 mAh cm⁻² (b) The corresponding overpotentials profiles. (c) Cycling stability of Zn anode in 0.2Zn.10H₂O at 1 mA cm⁻² and 2 mA cm⁻² with a capacity of 0.5 mAh cm⁻². (d) The corresponding overpotentials profiles.

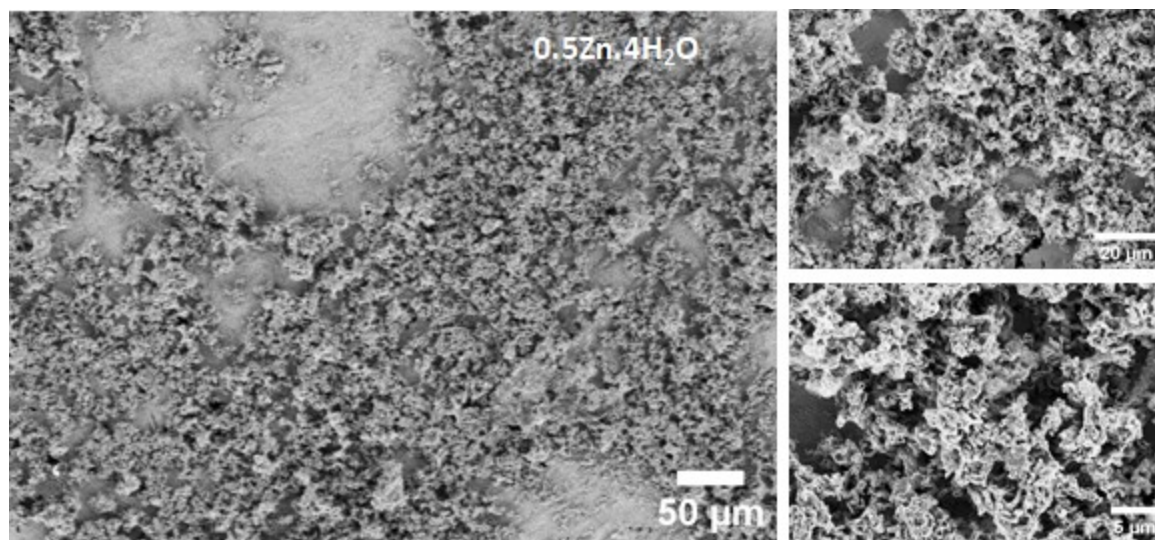


Figure S20: XRD and SEM images of Zn electrode in 0.5Zn.4H₂O after 20 cycles at 1mA cm⁻² and 0.5 mAh cm⁻² after 20 cycles.

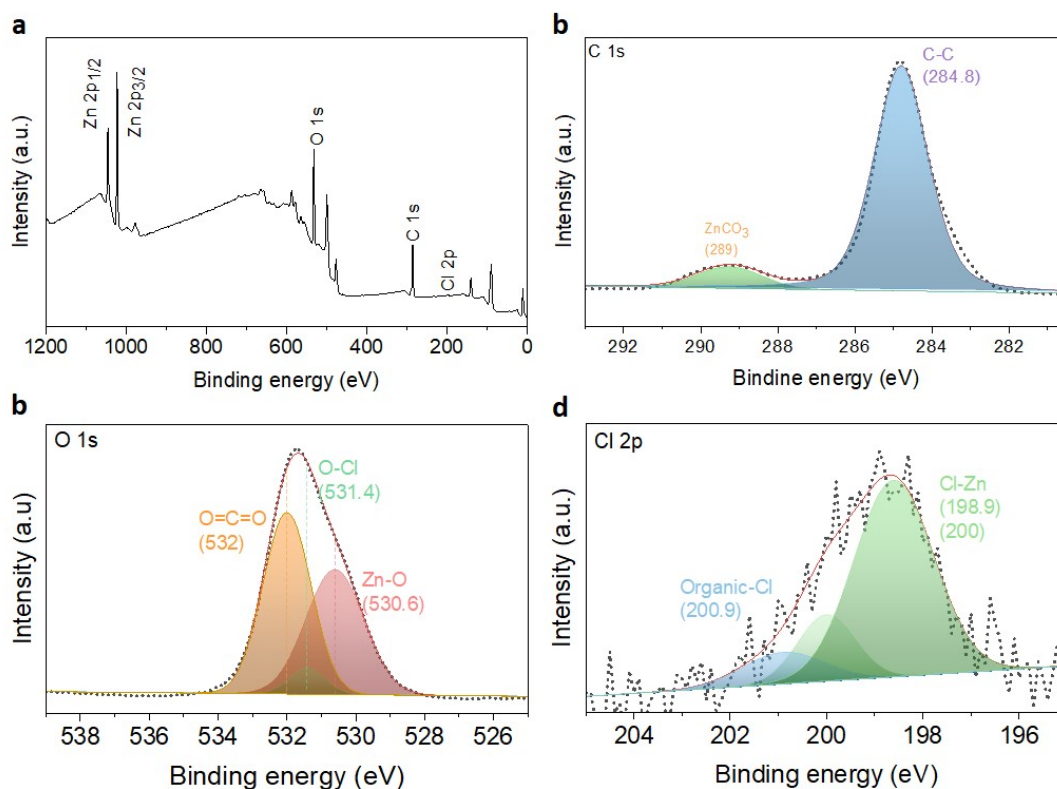


Figure S21: XPS spectra of 0.5Zn.4H₂O electrolytes at a current density of 1 mA cm⁻² with a capacity of 0.5 mAh cm⁻² after 20 cycles. (a) survey spectra, (b) C 1s, (c) O 1s, and (d) Cl 2p.

References

1. L. Cao, D. Li, T. Pollard, T. Deng, B. Zhang, C. Yang, L. Chen, J. Vatamanu, E. Hu, M. J. Hourwitz, L. Ma, M. Ding, Q. Li, S. Hou, K. Gaskell, J. T. Fourkas, X. Q. Yang, K. Xu, O. Borodin and C. Wang, *Nat. Nanotechnol.*, 2021, **16**, 902-910.
2. D. Han, C. Cui, K. Zhang, Z. Wang, J. Gao, Y. Guo, Z. Zhang, S. Wu, L. Yin, Z. Weng, F. Kang and Q.-H. Yang, *Nat. Sustain.*, 2021, **5**, 205-213.