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Abstract

The instability of the zinc/electrolyte interface, caused by uncontrolled reactions involving water, protons, and anions, remains the primary obstacle for aqueous zinc-ion batteries (AZIBs). Herein, we report a novel strategy, via synergizing solvation reconstruction and interfacial kinetic screening, that fundamentally reprograms zinc nucleation and growth behavior. Methanol reconstructs the solvation sheath and reduces water activity; ascorbic acid contributes to interfacial regulation through preferential adsorption and coordination interactions with Zn species. This kinetic screening regulates Zn nucleation and facilitates preferential growth of (002)-oriented Zn deposition thermodynamically, promoting dendrite-free zinc anodes. Furthermore, ascorbic acid acts as an acid-base buffer to stabilize local pH and induces *in situ* formation of an organic-inorganic gradient solid electrolyte interphase (SEI). Consequently, symmetric cells cycle stably for ~2000 h, and Zn||V₂O₅ full cells achieve 96.8% capacity retention after 5000 cycles at 1 A g⁻¹. This work establishes interfacial kinetic screening as a general principle for stabilizing metal anodes.

Keywords: Zn anode, interfacial kinetics, electrolyte, self-assembly, pH regulation

Introduction

Aqueous zinc-ion batteries (AZIBs) have attracted significant attention as a safe and sustainable alternative to lithium-based battery systems for future stationary energy storage applications, owing to their intrinsic safety, economic feasibility, and favorable performance¹⁻⁴. As the anode material for AZIBs, zinc metal offers a high volumetric capacity of 5855 mAh cm⁻³, which is more than 2.5 times that of lithium metal (2061 mAh cm⁻³)⁵⁻⁷. Coupling non-flammable aqueous electrolytes with zinc metal anodes endows AZIBs with fast kinetics and high safety⁸⁻¹⁰. However, zinc metal anodes are thermodynamically unstable in aqueous electrolytes. Interfacial zinc corrosion (mainly attributed to attack by active water), hydrogen evolution reaction (HER), the formation of byproducts such as ZnO and Zn(OH)₄²⁻, and uncontrolled dendritic zinc growth are the major obstacles hindering the development of practical zinc anodes^{5, 11-13}.

To address these challenges, significant efforts have been made to stabilize zinc anodes via artificial interfacial coatings or electrolyte modification¹⁴⁻¹⁸. While pre-constructed solid layers can physically isolate zinc from water, they often suffer from mechanical mismatch and interfacial delamination during long-term cycling. Electrolyte-based strategies, particularly those focusing on solvation regulation or reducing water activity, have shown partial success in mitigating HER. However, these approaches are generally guided by the principle of minimizing interfacial resistance and accelerating ion transport, implicitly emphasizing accelerated interfacial kinetics as a desirable pathway

for improving Zn reversibility¹⁹⁻²². In contrast, zinc metal is thermodynamically unstable in aqueous environments, and excessively facile interfacial kinetics tend to amplify parasitic reactions and promote uncontrolled nucleation²³⁻²⁵. Low nucleation barriers allow zinc to deposit indiscriminately on high-energy facets, leading to porous morphologies and dendrites. These considerations suggest that the core challenge for zinc anodes is not insufficient reaction kinetics, but rather the lack of interfacial selectivity. The electrochemical behavior of zinc metal is primarily influenced by the characteristics of the electrode-electrolyte interface (EEI), including the electric double layer (EDL) structure^{26, 27}, the composition of the solid electrolyte interphase (SEI)²⁷⁻²⁹, and the local pH environment^{27, 30, 31}. Fortunately, these three factors can be effectively regulated within the microspace by introducing additives.

To date, researchers have developed various electrolyte modification strategies, including salt concentration regulation, co-solvents (e.g., methanol, ethylene glycol)^{19, 32, 33}, functional additives (e.g., citric acid)³⁴⁻³⁷, and quasi-solid-state electrolytes. The interfacial regulation mechanisms of these strategies can be mainly divided into three categories:

(I) additives adsorb on the electrode surface and enter the Zn^{2+} solvation sheath, undergoing reductive decomposition during electrodeposition to form SEI film;

(II) pH-buffering additives balance H^+/OH^- concentrations through neutralization reactions without electron transfer³⁸;

(III) co-solvents weaken the interaction between cation-anion pairs, reconstruct the hydrogen-bond network, and accelerate the transition of Zn^{2+} solvation/desolvation at the interface from a transient to a steady state^{39, 40}.

However, single electrolyte additives cannot reconcile the trade-off between fast ion transport and effective blocking of harmful species. Therefore, by designing multi-scale interfacial regulation layers with complementary functionalities, it is expected to effectively integrate the superior properties of different materials. Through complementary regulation and synergistic coupling across different molecular scales, such layers, it can simultaneously address multiple issues, including dendrite formation, parasitic reactions, and interfacial passivation, thereby greatly enhancing the cycling stability of zinc metal anodes and enabling higher capacity and longer cycle life in AZIBs.

In this work, we break through the limitations of single-component electrolyte regulation and propose a synergistic solvation-interfacial regulation strategy using methanol (MeOH, 40 vol%) as an economical co-solvent and ascorbic acid (H_2Asc , AA) as a functional additive. MeOH acts as a co-solvent to reconstruct the primary solvation sheath of Zn^{2+} , disrupt the strong hydrogen-bond network, and significantly reduce water activity⁴¹. H_2Asc interacts with Zn species through adsorption contributing to interfacial regulation and interphase stabilization. This layer also induces the formation of SEI, guiding uniform Zn deposition along the thermodynamically stable (002) plane, thereby achieving regulation from bulk solvation structure to interfacial kinetics. In addition, the inherent acid-base buffering capacity of ascorbic acid dynamically and statically regulates the local pH environment at the interface, suppressing HER and the formation of byproducts such as zinc hydroxide sulfate (ZSH). The optimized electrolyte delivers highly reversible, dendrite-free zinc anodes with an over 800 h at 5 mA cm^{-2} and 10 mAh cm^{-2} , and the $\text{Zn}||\text{V}_2\text{O}_5$ full cell achieves 96.8% capacity retention after 5000 cycles at 1 A g^{-1} .

Results and Discussion

Since the equilibrium potential of Zn^{2+}/Zn (-0.76 V vs. SHE) is lower than H^+/H_2 (0 V vs. SHE), Zn is thermodynamically unstable in aqueous environments. As a result, spontaneous corrosion and interfacial HER are inevitable. The consumption of H^+ leads to a localized accumulation of OH^- , which drives Zn^{2+} to react with OH^- and SO_4^{2-} to form byproducts such as $\text{Zn}_4\text{SO}_4(\text{OH})_6 \cdot n\text{H}_2\text{O}$, leading to the aggravation of dendrite growth. Therefore, the electrolyte must effectively mitigate corrosion during both cycling and resting conditions. Herein, a new hybrid electrolyte is prepared by dissolving AA (0.02 M) in MeOH (40% vol) and 2 M ZnSO_4 aqueous solution (baseline, ZS), which is denoted as ZS-MA. The concentrations of MeOH and AA were optimized considering factors such as flammability,

solubility, and corrosion resistance (Figure S1-S3). In addition, the electrochemical stability window of this microemulsion electrolyte can reach 2.39 V (Figure S4). MeOH and AA exhibit complementary contributions to solvation and interfacial regulation. On one hand, MeOH acts as a co-solvent that reduces the freezing point and weakens Zn^{2+} - H_2O interactions, thereby lowering water activity and facilitating Zn^{2+} desolvation. On the other hand, AA functions as both a chelator and an adsorbate that preferentially adsorbs on the Zn anode surface, creating a molecular buffer layer. This adsorbed AA layer not only guides uniform Zn deposition along the (002) plane but also serves as an acid-base buffer. When local pH rises due to H^+ consumption during electrodeposition, the ionization equilibrium of AA dynamically supplies H^+ , blocking the pathway for side reactions such as hydrogen evolution and byproduct formation. Through this synergistic interplay, the ZS-MA electrolyte simultaneously optimizes solvation chemistry, interfacial kinetics, and pH stability, as summarized in Figure 1a.

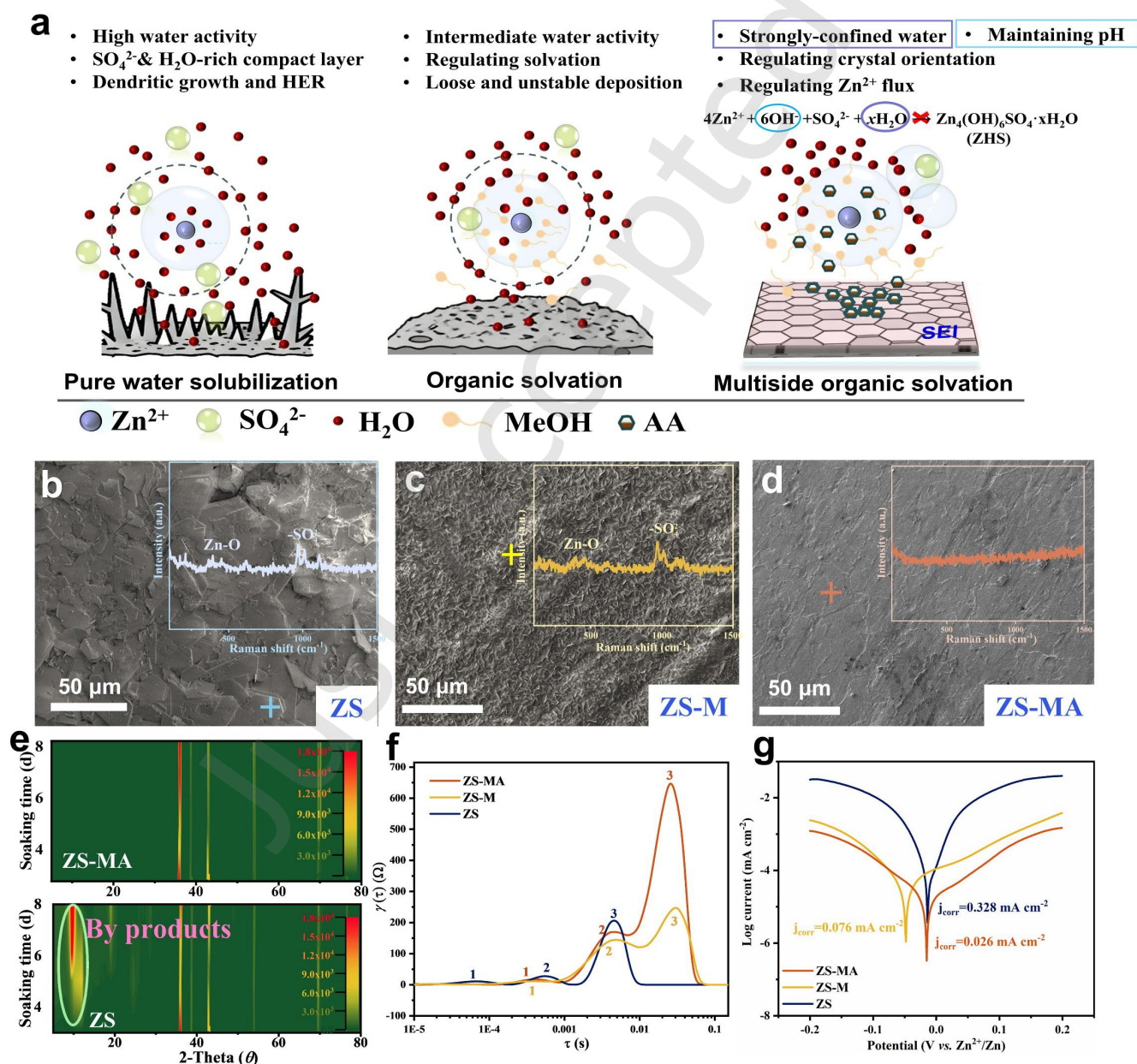


Figure 1. (a) Schematic of Zn^{2+} deposition in different electrolytes. SEM images of Zn foil after immersion in different electrolytes for 10 days, with insets showing the corresponding Raman spectra at the positions marked by crosses, (b) ZS electrolyte, (c) ZS-M electrolyte, (d) ZS-MA electrolyte. (e) XRD patterns of Zn foil after being immersed in the electrolyte for different time. (f) Distribution of relaxation times, and (g) Tafel plots for ZS, ZS-M and ZS-MA electrolyte.

We evaluated Zn anode interface stability in ZS, ZS-M, and ZS-MA electrolytes. After immersion, Raman spectra (Figure 1b-d) showed Zn-O (ZnO or ZSH) and SO_4^{2-} peaks in ZS and ZS-M, while ZS-MA exhibited only a flat baseline, confirming that AA effectively stabilizes the thermodynamic process at the interface. Scanning electron microscope (SEM) images after 3 and 30 days (Figure S5) further illustrated the corrosion behavior. In ZS, irregular hexagonal byproducts accumulated heavily; in ZS-M, byproducts were fragmented and vertically embedded, with localized large aggregates after 30 days; in ZS-A, severe cracking occurred. In contrast, ZS-MA maintained a flat, shiny surface after 3 days and even after 30 days showed no dendrites or corrosion products, confirming that the ternary electrolyte effectively suppresses interfacial side reactions. X-ray diffraction (XRD) showed a distinct ZSH peak at $2\theta \approx 10^\circ$ for ZS and ZS-M, but not for ZS-MA, confirming the unique role of AA in suppressing ZSH formation (Figure 1e, S6). Electrochemical impedance spectroscopy (EIS) revealed that adding AA to ZS-M increased charge transfer resistance (R_{ct}) fivefold relative to ZS, attributed to AA's hydroxyl groups forming an adsorbed molecular layer that kinetically impedes interfacial charge transfer, suppresses corrosion, and modulates deposition kinetics. (Figure S7). Specifically, the optimized electrolyte exhibits an increased R_{ct} , suggesting the synergistic interaction between methanol and AA induces a regulated interfacial kinetic environment, while the individual contribution of AA depends on the surrounding solvation structure. Distribution of relaxation times (DRT, Figure 1f) further revealed that ZS-MA exhibits longer relaxation times (τ) for peaks associated with H_2O adsorption (peak 1), water migration (peak 2), and water decomposition (peak 3), indicating effective blocking of water molecules from the Zn surface. Linear sweep voltammetry (LSV, Figure S8) showed that ZS-M and ZS-MA shift the hydrogen evolution reaction (HER) onset potential to more negative values (at -10 mA cm^{-2}), whereas AA alone slightly shifts it positively, confirming that methanol reduces water activity and weakens the hydrogen-bond network. Tafel plots (Figure 1g) demonstrated that ZS-MA has the lowest corrosion current (0.026 mA cm^{-2}) and the most positive corrosion potential.

Raman spectroscopy shows a distinct C-O peak ($\sim 1030 \text{ cm}^{-1}$) appeared in ZS-M and ZS-MA but not in ZS-A, confirming methanol dominates Zn^{2+} solvation (Figure 2a-c). In ternary electrolytes, the concentration-dependent Raman evolution of the C-O stretching vibration indicates that AA can interact with Zn^{2+} and modulate the local solvation structure through its strong coordination capability, which is consistent with the DFT-calculated strong Zn^{2+} -AA interaction. SO_4^{2-} symmetric stretching peak ($\sim 980 \text{ cm}^{-1}$) remained unchanged in ZS-A (limited effect of AA) but decreased significantly in ZS-M (methanol weakens Zn^{2+} - SO_4^{2-} interaction). In ternary systems, this peak decreased linearly with AA concentration, confirming AA's role in solvation reconstruction. Peak fitting distinguished contact ion pairs (CIP) and solvent-separated ion pairs (SSIP). The CIP proportion decreased with increasing AA, indicating SO_4^{2-} is expelled from the solvation sheath, optimizing ion transport and stabilizing solvation structure (Figure 2b,c). Fourier transform infrared (FTIR) spectroscopy further revealed the evolution of molecular interactions (Figure 2d). The bending and stretching vibrations of O-H were observed at $\sim 1660.6 \text{ cm}^{-1}$ and $\sim 3530 \text{ cm}^{-1}$, respectively. Upon the introduction of methanol, both peak intensities weakened with a slight blue shift, indicating reduced hydrogen bonding and a decrease in free water. Moreover, carbonyl ($\text{C}=\text{O}$) vibration signal was detected at $\sim 1755 \text{ cm}^{-1}$, confirming the presence of $\text{C}_6\text{H}_7\text{O}_6^-/\text{C}_6\text{H}_5\text{O}_6^-$ redox couples in the electrolyte. This peak shifted slightly and showed much higher intensity in ZS-MA than in ZS-A, suggesting AA- Zn^{2+} coordination is enhanced. The $-\text{SO}_4^{2-}$ peak ($\sim 1100 \text{ cm}^{-1}$) decreased in intensity, red-shifted, and split, indicating weakened direct Zn^{2+} - SO_4^{2-} coordination and a tendency to form solvent-separated ion pairs (SSIP) in the outer solvation sheath. Additionally, nuclear magnetic resonance (NMR) spectra (Figure S9) showed signal shifts in the presence of MeOH and AA, providing further evidence of hydrogen-bond network reconstruction. Figure 2e compares the binding energies of H_2O - Zn^{2+} - $\text{CH}_3\text{OH}/\text{C}_6\text{H}_8\text{O}_6$ for different binding sites of ascorbic acid. Due to its high concentration (40 vol%), methanol predominantly regulates the overall solvent environment. Meanwhile, AA, owing to its strong Zn^{2+} affinity, participates in local solvation regulation that can reconstruct the hydrogen bonding network in the optimized electrolyte because of the electronegative carbonyl and hydroxyl groups, thereby dominating the interfacial regulation process. As depicted in the electrostatic potential (ESP) mapping (Figure 2f),

the oxygen atoms of the enediol group ($-\text{C}(\text{OH})=\text{C}(\text{OH})-$) in ascorbic acid possess lone-pair electrons with strong electron-donating capability, enabling strong Zn^{2+} attraction. This optimizes bulk solvation and reduces free water activity, suppressing interfacial side reactions. Figure 2g shows pH evolution during Zn^{2+} deposition; notably, AA acts as an acidic buffer, dynamically replenishing H^+ and stabilizing pH at 4.48, thereby preventing sustained corrosion of the Zn anode.

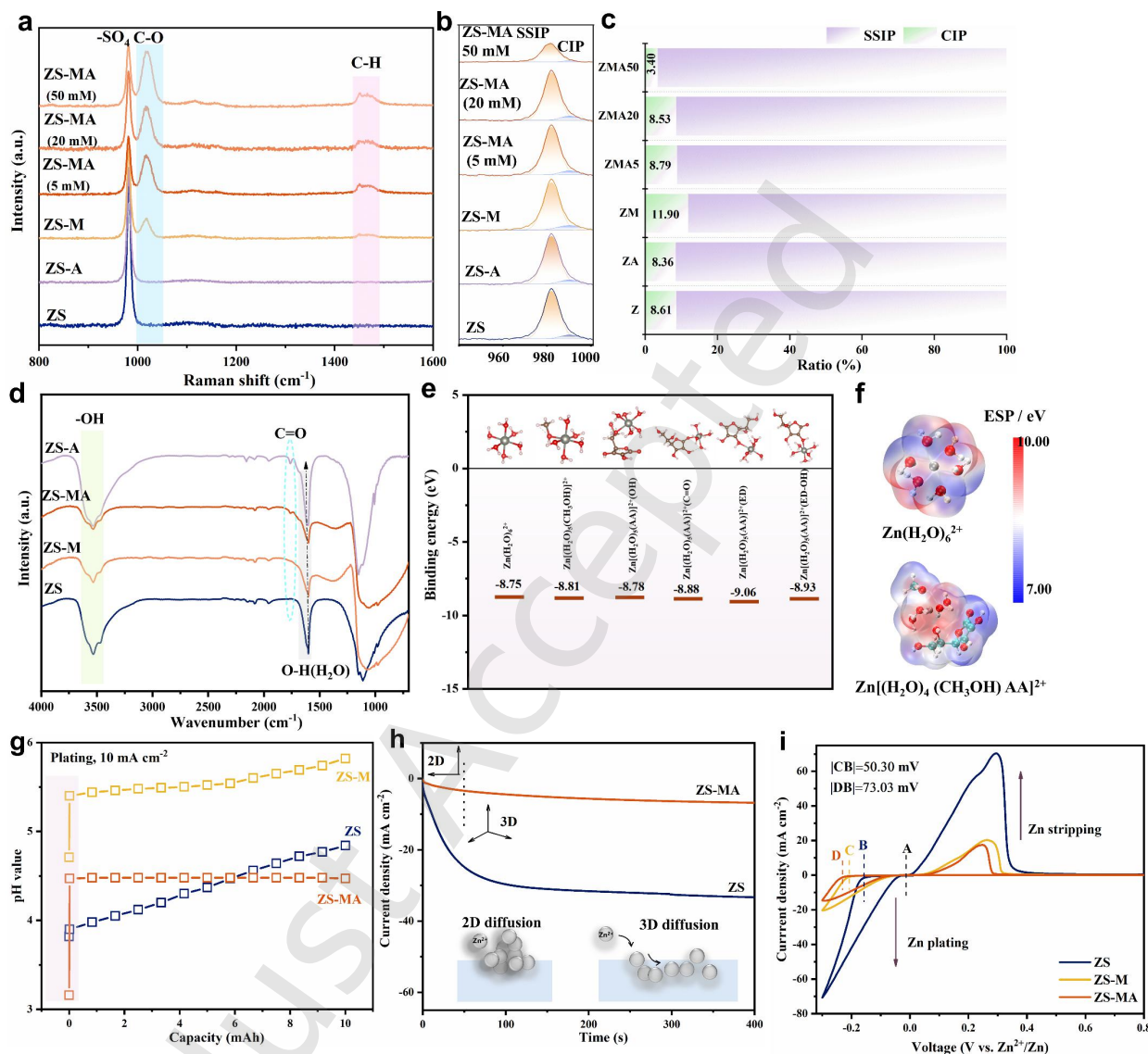


Figure 2. (a) Raman spectra of the different solvent. (b) The fitted peaks of Raman spectra in both anhydrous organic electrolytes. (d) FTIR spectra in the different electrolytes. (e) Binding energies between Zn^{2+} and various species; (f) Molecular electrostatic potential maps for different electrolyte systems. (g) *In situ* pH value of Zn^{2+} deposited process in the different electrolytes. (h) CA curves and (i) CV curves of the different electrolytes.

In chronoamperometry (CA) tests at a constant overpotential of -150 mV, the ZS electrolyte exhibited a continuously increasing current density, indicating uncontrolled 2D diffusion and persistent dendrite growth. In contrast, the hybrid electrolyte enabled a brief 2D diffusion followed by a stable 3D diffusion, suggesting that AA-mediated interfacial regulation restricts uncontrolled lateral Zn^{2+} migration and promotes oriented deposition along the Zn(002) plane (Figure 2h). Cyclic voltammetry (CV) shows that methanol increases the nucleation overpotential by 50.3 mV, and ascorbic acid (AA) further raises it by 22.73 mV, forcing nucleation at energy-favorable sites and suppressing random nucleation on high- surface- energy planes (Figure 2i). At 8 mA cm^{-2} , the ZS- MA electrolyte exhibits the highest polarization voltage (0.52 V) across all current densities, effectively regulating Zn^{2+} redox kinetics (Figure S10a,b). ZS- MA also shows a higher activation energy ($47.61 \text{ kJ mol}^{-1}$) than ZS

(34.04 kJ mol⁻¹) and ZS- M (45.37 kJ mol⁻¹), demonstrating that AA increases the desolvation energy barrier (Figure S11a-d). The contact angle further confirms the adsorption behavior of AA molecules on the Zn anode surface, which is beneficial for uniform distribution of Zn²⁺ flux (Figure S12a-c). The nucleation behavior follows the Scharifker-Hills 3D instantaneous nucleation model. ZS- MA exhibits a longer time to reach peak current, indicating a larger electrochemically active surface area (Figure S13a). Differential capacitance curves (Figure S13b) show significantly lower capacitance for ZS- MA, attributed to the formation of a low dielectric- constant molecular layer by adsorbed AA, which reconstructs the EDL, raises the nucleation overpotential, and fundamentally suppresses dendrite formation.

For Zn metal, zinc adopts a hexagonal close-packed (HCP) structure with a *c/a* ratio of approximately 1.85, exceeding the ideal HCP value of about 1.63, leading to randomly oriented, loose, and porous structures. Therefore, promoting epitaxial growth along the (002) plane is an effective strategy to suppress dendrites. XRD was performed on Zn electrodes after different deposition capacities to evaluate the influence of the ZS-MA electrolyte. The ZS-MA electrolyte not only induced preferred (002) growth but also completely suppressed ZSH byproducts. The relative texture coefficients (RTCs) of the (002), (100), and (101) planes (Figure 3a, S14) show that in ZS-MA, the (002) plane gradually dominates with increasing deposition time, its RTC rising from 73.1% to 86.5%. Adsorption energy calculations reveal that AA molecules have much more negative adsorption energies on all Zn facets than water or methanol. AA preferentially adsorbs on the (100) and (101) planes, exposing the (002) plane as the preferred deposition site (Figure 3b). X-ray photoelectron spectroscopy (XPS) with Ar⁺ sputtering depth profiling was carried out to investigate the SEI layer in the various types of electrolytes. As exhibited in Figure 3c, for the ZS-MA electrolyte, S2p and C1s profiles reveal an increasing presence of inorganic components, including ZnS and ZnCO₃, which were detected in the inner SEI region. The formation of ZnS is attributed to the interfacial conversion of sulfate-related species from ZnSO₄ electrolyte under the highly reducing Zn deposition environment, which has been reported as one of the inorganic components in Zn-based SEI layers⁴². These electrolyte-derived inorganic species contribute to the formation of a compact interphase and suppress direct contact between Zn and reactive electrolyte components. ZnS is also detected in ZnSO₄ electrolyte without MeOH/AA (Figure S15a). Furthermore, the significant C=O signal is attributed to the chemisorption of C₆H₇O₆⁻ and the decomposition of anions. Its intensity decreases with increasing etching depth, indicating that the outer layer of the SEI is enriched with organic components, thereby forming an organic-inorganic hybrid gradient SEI structure. In contrast, for the ZS and ZS-M electrolytes, the characteristic ZnCO₃ signal on the Zn anode surface drops sharply after Ar⁺ sputtering (Figure S15b,c). White light interferometry shows a deposited layer height difference of 33.74 μm in ZS (Figure 3d) versus 25.11 μm in ZS-MA (Figure 3e), demonstrating uniform deposition induced by AA. TOF-SIMS further confirmed that ZS-MA suppresses ZSH byproducts, evidenced by the SO₃⁻ signal. In ZS, SO₃⁻ is intense and deep, indicating abundant ZSH and poor stability. In ZS-M, the signal is somewhat reduced, showing limited suppression. In ZS-MA, the C₄H₅O₄⁻ fragments confirm organic components in the stable SEI, ensuring high reversibility (Figure 3f). SEM examined surface and cross-sectional morphologies under the same deposition capacity (Figure 3g). In ZS, epitaxially grown whiskers intertwine into a highly uneven surface, causing local electric field concentration; further deposition leads to preferential dendrite growth and rapid separator piercing. In ZS-M, low-dielectric methanol provides a uniform Zn²⁺ flux, refining grains, but lattice mismatch between Zn (002) and the polycrystalline substrate results in randomly oriented, rough, flake-like deposits. After introducing AA, dendrites are suppressed, and the Zn anode maintains a smooth, compact surface across all deposition capacities. FIB cross-sections confirm dense deposition in ZS-MA. The high-energy-barrier interface constructed by the ternary synergistic electrolyte strongly suppresses deposition on high surface-energy planes. Consequently, only the thermodynamically most stable (002) plane (lowest surface energy) becomes the preferred growth orientation, ensuring long-term cycling stability. The relaxation time (τ) values for different kinetic processes differ significantly between the two electrolytes. In the ZS-MA electrolyte, the relaxation peaks corresponding to surface migration of Zn²⁺ (R_{mig}), charge transfer (R_{ct}),

and diffusion (R_{diff}) remain consistently stable with low τ values, indicating a shortened 2D diffusion process and well-regulated ion transport (Figure 3h). In contrast, the bare ZS electrolyte exhibits progressively increasing τ values during cycling, reflecting disrupted ion flux and unstable interfacial kinetics (Figure 3i). These results demonstrate that the ZS-MA electrolyte establishes an efficient and reversible ion transport pathway, fundamentally suppressing dendrite growth from the kinetic perspective.

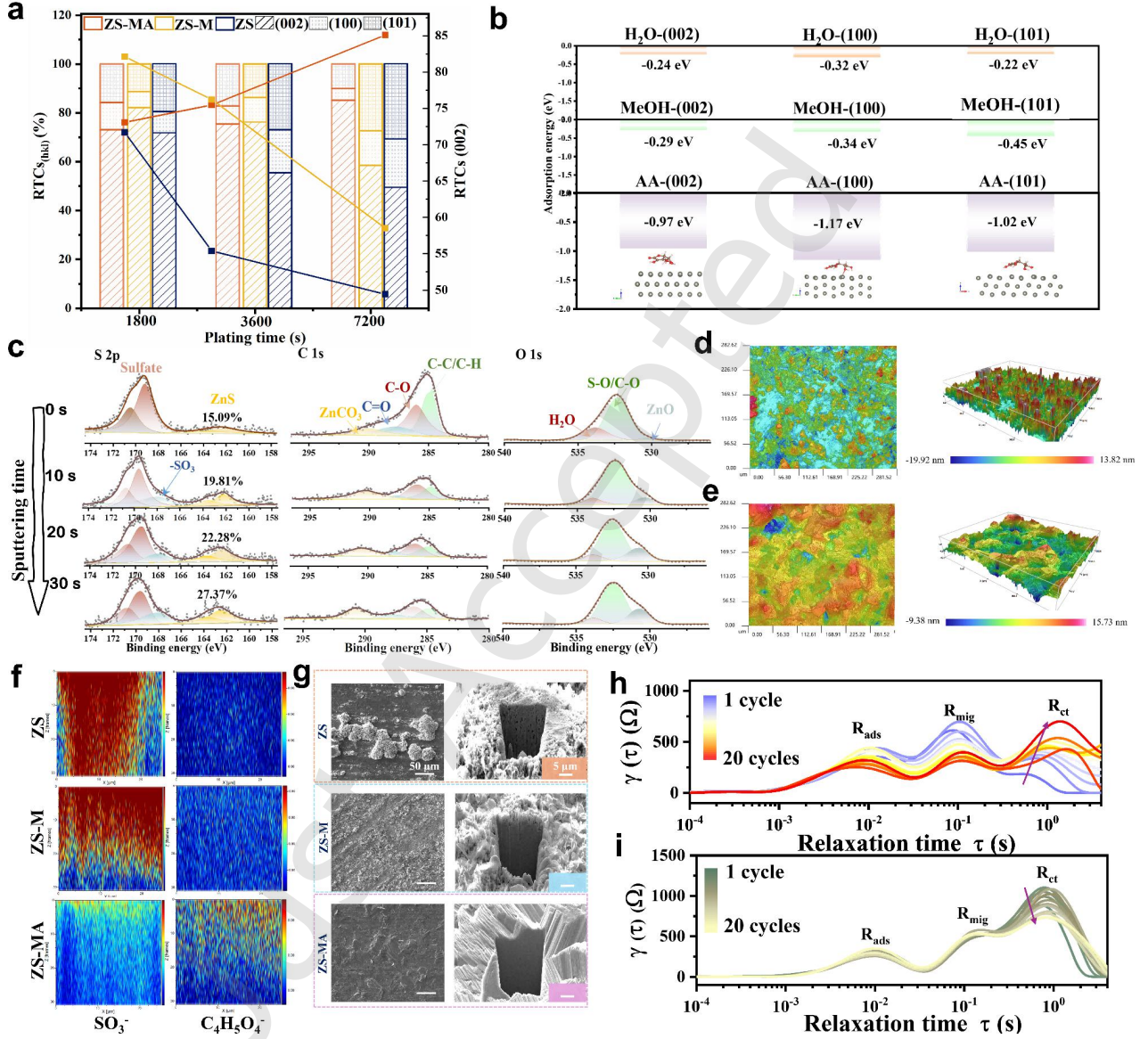


Figure 3. (a) RTCs values of different Zn crystal planes ((002), (100), (101)) on Zn anodes after Zn deposition with different capacities in ZS, ZS-M, and ZS-MA electrolytes, along with the evolution of RTCs for the (002) plane as a function of plating time. (b) Adsorption energies of H₂O, MeOH, and AA molecules on different Zn facets. (c) Depth profiles of the S 2p, C 1s and O 1s spectra after 10 cycles at a current density of 5 mA cm⁻² with ZS-MA electrolyte. White light interference spectra of the Zn anode after cycling in (d) ZS and (e) ZS-MA electrolyte. (f) TOF-SIMS of the Zn anode cycled in ZS, ZS-M and ZS-MA electrolytes. (g) Top-view and cross-sectional (right) SEM images of Zn deposition process on Zn foil at 1 mA cm⁻² for 1 mA h cm⁻² in ZS, ZS-M, and ZS-MA electrolytes. DRT curves of Zn anodes from 1 to 20 cycles in (h) ZS electrolyte and (i) ZS-MA electrolyte.

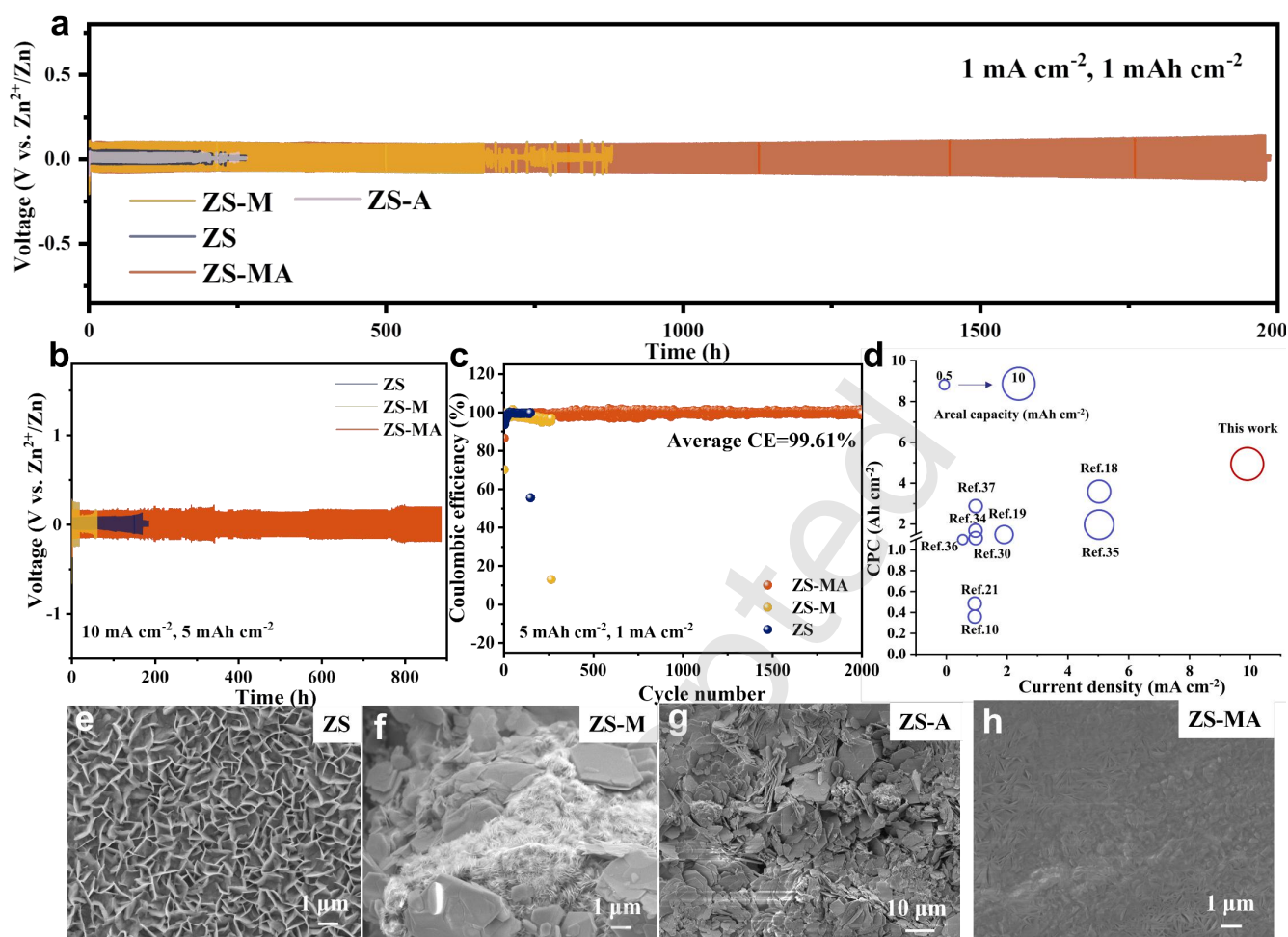


Figure 4. Long-term galvanostatic Zn plating/stripping of Zn||Zn symmetric batteries in different electrolytes (a) 1 mA cm^{-2} with a capacity of 1 mAh cm^{-2} . (b) 10 mA cm^{-2} with a specific capacity of 5 mAh cm^{-2} . (c) CE of Zn||Cu asymmetric cell using various electrolytes at 5 mA cm^{-2} . (d) Comparison of the cumulative plated capacity (CPC) in previous reports. SEM images after 100 cycles in (e) ZS electrolyte, (f) ZS-M electrolyte, (g) ZS-A electrolyte, and (h) ZS-MA electrolyte.

To evaluate the ZS- MA electrolyte for AZIBs, Zn||Zn symmetric cells were tested by galvanostatic charge-discharge (GCD). At 1 mA cm^{-2} and 1 mAh cm^{-2} , the ZS and the ZS- A electrolyte both failed within 200 h, accompanied by obvious voltage fluctuations (Figure 4a). In comparison, the ZS- M electrolyte cycled stably for over 600 h, and the ternary electrolyte ZS- MA exhibited a remarkably prolonged lifespan of nearly 2000 h. Even at 10 mA cm^{-2} and 5 mAh cm^{-2} , ZS- MA maintained stable over 800 h without voltage anomalies, far exceeding other electrolytes (Figure 4b). Zn||Cu asymmetric cells were used to examine coulombic efficiency (CE). The cell with ZS- MA electrolyte sustained stable Zn plating/stripping for ~2000 cycles, whereas ZS and ZS- M cells failed at 264 and 148 cycles due to dendrite growth (Figure 4c). Our work achieves a CPC of 4.5 Ah cm^{-2} at 10 mA cm^{-2} for symmetric cells, which is significantly higher than those reported in previous studies, demonstrating the outstanding cycling stability of our electrode (Figure 4d). In contrast, ZS and ZS- M cells showed severe voltage fluctuations after 150 and 360 cycles, respectively, indicating deteriorated reversibility and short circuit. Voltage-capacity profiles (Figure S16a-c) confirmed a stable cycling performance with ZS- MA, reaching 99.7% for 600 cycles, accompanied by relatively high polarization consistent with earlier analysis. After 100 cycles, in the ZS (Figure 4e), vertical, sharp and irregular flakes covered the Zn anode. Similarly, in the ZS-M and ZS-A electrolyte, numerous fibrous, moss-like dendrites and highly heterogeneous scattered flake-like deposits are observed in Figures 4f, 4g. While the surface of the Zn anode in ZS-MA remains relatively smooth (Figure 4h) with no prominent dendrites or large corrosion products, demonstrating effective

suppression of dendrite growth and side reactions. The performance arises from interfacial regulation by the $[\text{Zn}(\text{AA})(\text{MeOH})_x]^+$ complex, which suppresses dendrite nucleation and raises the kinetic barrier for side reactions. Moderate interfacial kinetics favors long-term reversibility, enabling highly reversible Zn plating/stripping through synergistic thermodynamic and kinetic control.

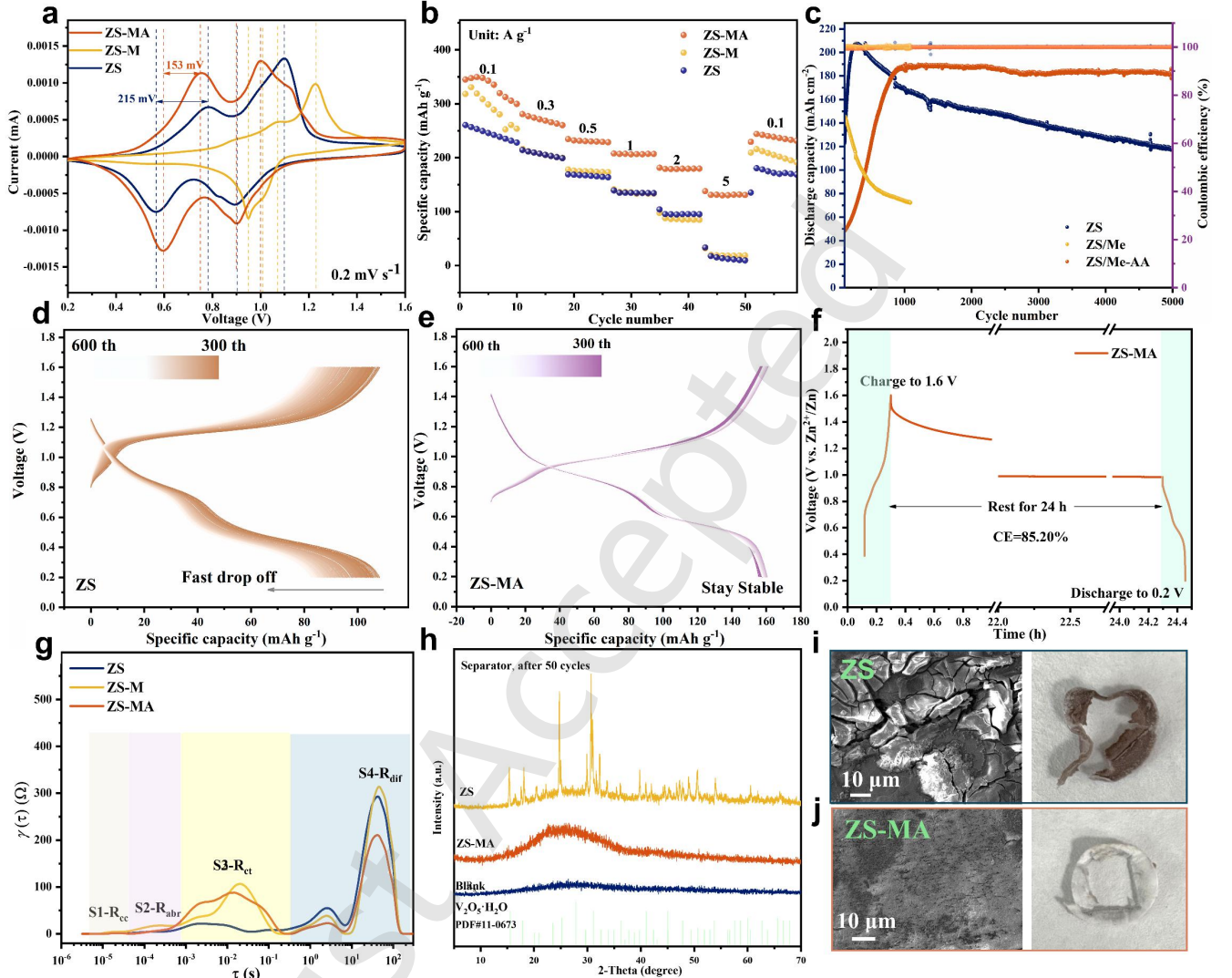


Figure 5. (a) CV curves. (b) Rate performance. (c) Long-term cycling performance of bare Zn||V₂O₅ full cells at 1 A g⁻¹. Charge-discharge curves from 300 to 600 cycles of (d) ZS electrolyte and (e) ZS-MA electrolyte. (f) Self-discharge test. (g) DRT plots derived from EIS spectra of different electrolytes. (h) XRD patterns of glass fiber separators after 50 cycles of the full cells with ZS and ZS-MA electrolytes. SEM image after cycling in (i) ZS electrolyte (left) and optical photograph of the separator (right), (j) ZS-MA electrolyte (left) and optical photograph of the separator (right).

When assembled with commercial V₂O₅ cathode, CV curves with the ZS-MA show the identical redox behavior compared to the ZS, implying the cathode reaction mechanism remains unchanged (Figure 5a). Furthermore, the ZS-MA exhibits superior rate capability (Figure 5b). It delivers 349.3 mAh g⁻¹ at 0.1 A g⁻¹ and retains 131.1 mAh g⁻¹ at 5 A g⁻¹ (37.5% retention). In contrast, ZS and ZS-M retain only 3.2% and 5.4%, respectively, due to severe interfacial polarization and sluggish kinetics at high rates. The GCD profiles of ZS-MA (Figure S17a) show stable voltage plateaus between 0.35-0.75 V across all current densities, confirming efficient Zn²⁺ transport and intercalation even at 5 A g⁻¹. Long-term cycling at 1 A g⁻¹ (Figure 5c) further demonstrates the superiority of ZS-MA. While ZS and ZS-M cells retain only 57.6% (after 5000 cycles) and 49.5% (after 1000 cycles) of their initial capacities, respectively. The ZS-MA cell maintains 96.8% capacity retention over 5000 cycles. Furthermore, the GCD profiles of ZS and ZS-MA electrolytes at 5 A g⁻¹ from the 300th to 600th cycles are shown in Figures 5d and 5e. The ZS-MA cell exhibits nearly overlapped profiles with negligible

polarization upon cycling. In contrast, the ZS cell undergoes rapid capacity decay under the same conditions. The thermodynamic instability of Zn in aqueous electrolytes is the primary cause of self-discharge. EIS was used to analyze the charge-transfer kinetics at the electrode/electrolyte interface. All Nyquist plots (Figure S17b) consist of a semicircle and a sloped line. As shown in Figure 5f and S17c, d, the self-discharge behavior was evaluated at 0.2 A g⁻¹. After rest for 24 h, the capacity retention is 82.5%, 82.76%, and 85.2% for ZS, ZS-M, and ZS-MA, respectively. The improved self-discharge resistance in ZS-MA is attributed to the stable interfacial layer formed on the Zn anode, which thermodynamically inhibits corrosion and hydrogen evolution, thereby minimizing Zn²⁺ loss. To investigate the cathode kinetics in the optimized electrolyte, CV tests were performed at scan rates of 0.4, 0.5, 0.6, 0.8, and 1 mV s⁻¹ (Figure S18a). The b-values for peaks 1-4 are as 0.53, 0.65, 0.71, and 0.53, indicating a diffusion-dominated battery behavior (Figure S18b). DRT analysis identified larger R_{ct}, likely due to a favorable adsorbed interface layer that suppresses side reactions. Meanwhile, the diffusion impedance (R_{diff}) in ZS- MA was much lower than in ZS, revealing faster Zn²⁺ bulk diffusion (Figure 5g). Galvanostatic intermittent titration technique (GITT) confirmed that Zn²⁺ diffusion coefficients (D_{Zn²⁺}) for ZS- MA were 10⁻⁷-10⁻⁸ cm² s⁻¹, about 1-2 orders of magnitude higher than that of ZS (10⁻⁹-10⁻¹⁰ cm² s⁻¹), confirming faster Zn²⁺ migration in the electrode bulk (Figure S18c, d). After 50 cycles, XRD of the separators in ZS- MA electrolyte was identical to the pristine separator, with no extra peaks. In contrast, numerous vanadium-based phases appeared on the separator cycled in ZS electrolyte (Figure 5h). SEM images revealed the obvious cracks on the V₂O₅ cathode surface after cycling in ZS electrolyte, optical images of the separators further confirm that the ZS-MA electrolyte suppresses the dissolution of V⁵⁺ (Figure 5i, j). After 100 cycles, the C 1s spectrum of the Zn anode collected from the ZS-MA electrolyte still exhibits characteristic C-O and C=O components, indicating the retention of organic species within the interphase, which are attributed to AA-derived components and their derivatives (Figure S19). Aqueous electrolytes freeze below 0 °C, limiting low-temperature use, while at -10 °C, the ZS-MA electrolyte enables stable cycling with a discharge capacity of 155 mAh g⁻¹ (Figure S20a). It remains clear, liquid, and free of precipitation or phase separation, confirming uniform liquid structure and excellent anti-freezing performance (Figure S20b,c). These results demonstrate the practical applicability of interfacial kinetic screening in full cell configurations.

Conclusions

In summary, we have developed a synergistic electrolyte strategy that stabilizes the Zn/electrolyte interface in aqueous Zn²⁺ ion batteries. By coupling methanol-dominated solvation reconstruction with AA-mediated interfacial kinetic regulation, and dynamic pH self-buffering, the ZS- MA electrolyte elevates the Zn nucleation overpotential and constructs a robust organic-inorganic gradient SEI. This kinetically selective interphase effectively suppresses hydrogen evolution, corrosion, and byproduct formation while enforcing texture- guided Zn deposition along the (002) plane. The resulting dense, smooth, and dendrite- free Zn anode enables an exceptionally long cycle life (~2000 h in symmetric cells) and high reversibility (99.43% CE in asymmetric cells). Moreover, the electrolyte simultaneously protects the V₂O₅ cathode by inhibiting vanadium dissolution, leading to 5000 stable cycles with 96.8% capacity retention. Beyond the Zn anodes, this work revises the conventional view that faster interfacial kinetics are always beneficial, and underscores kinetic screening, manifested as elevated nucleation overpotential, as a powerful and generalizable design principle for stabilizing reactive metal/electrolyte interfaces in dynamic electrochemical environments.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon reasonable request.

Acknowledgements

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Electronic Supplementary Material

Kinetic-screening electrolyte interface enables solvation reconstruction and interfacial regulation for dendrite-free zinc anodes

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This file includes:

- 1. Supplementary Experimental Procedures**
- 2. Supplementary Figures. 1-20**

1. Experimental Procedures

Preparation of electrolytes and electrodes

Ultra-pure water was performed to prepare aqueous electrolytes. For comparison, the pure 2 M $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (Aladdin Biochemical Technology Co., 99%) is labeled as baseline electrolyte (ZS), 2 M ZnSO_4 with 30%, 40%, 50% volumes of methanol (MeOH, Sinopharm Chemical Reagent Co., 99.8 %) were prepared and labeled as ZS-M. In this work, the optimal volume ratio of MeOH to H_2O is 4:6. Dissolving 20 mM L-ascorbic acid (AA) were added into the ZS-M mixed solvent n to achieve the modified electrolytes at different molar ratios, The optimal addition ratio was set at a trace amount of $20 \text{ mM} \cdot \text{L}^{-1}$. The ternary electrolytes are designated as ZS-MA.

Zn anode: The purchased Zn foil was repeatedly cleaned with deionized water and ethanol to remove the remaining stains, then punched into $\Phi 12 \text{ } \mu\text{m}$ discs to serve as the metal anode part. Thickness: $30 \text{ } \mu\text{m}$.

Cathode: Commercial vanadium pentoxide (V_2O_5) is directly used as the cathode material without any modification. Firstly, V_2O_5 , acetylene black, and polyvinylidene fluoride (PVDF) were stirred into a slurry with the ratio of 7:2:1, and then uniformly coated on the carbon paper. Then the carbon paper dried in an oven at $60 \text{ } ^\circ\text{C}$. for 12 h. The loading of the active material was between $2\text{-}3 \text{ mg cm}^{-2}$.

Material Characterization:

The attenuated total-reflectance Fourier transform infrared spectroscopy (ATR-FTIR, Thermo Fisher, Nicolet 6700) were used to characterize the spectra shifts of specific groups in the electrolytes and additives. Raman spectroscopy was supplied via TESCAN RISE S9000G. The time-of-flight secondary ion mass spectrometry (TOF-SIMS) and focused ion beam (FIB) system were collected by TESCAN S9000G equipped with a TESCAN C-TOF and TESCAN SOLARI, respectively. The SEM images were obtained using a field emission scanning electron microscope (SEM, Hitachi SU8010). The crystalline phases were identified through X-ray diffraction (XRD) analysis performed on a Bruker D8A A25X. Surface roughness

data were obtained by white light interference microscopy (sneox, sensofa). X-ray photoelectron spectroscopy (XPS) analysis was carried out with an ESCALAB 250XI (Thermo Scientific) spectrometer to investigate the chemical states of the elements. The contact angle was measured with the Krüss DSA 30. Distribution relaxation times (DRT) analysis was computed from EIS data by using an open-source Matlab toolbox of DRT tools, which was developed by Professor Francesco Ciucci's research group^[1-3]. DRT tools is freely available from the following site, <https://github.com/ciuccislab/DRTtools>.

Electrochemical measurements

The CR2032 type cells were assembled for electrochemical characterization including asymmetric, symmetric, and full cells in an ambient air environment. The electrolyte was designing solution, and the amount of electrolyte added in a single device was about 150 μL . The diameter of the cathode and anode electrodes was set at 12 mm, and Glass fiber (GF/D, Whatman) filter membrane was used as the diaphragm, and it was cut into a circle with a diameter of 19 mm. Linear sweep voltammetry (LSV), cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and tafel curve (Tafel) were conducted on the CHI770E (Shanghai, China) instrument. All galvanostatic cycling tests were conducted using a Neware system (CT2302A). The coulombic efficiency (CE) of Zn^{2+} plating/stripping for the $\text{Zn}||\text{Cu}$ half batteries, the discharge time was fixed at 5 mAh cm^{-2} , with a cut-off voltage of 0.6 V and a current density of 1 mA cm^{-2} . LSV in a three-electrode system (Zn foil electrodes as the working electrode, Ag/AgCl electrode as the reference electrode and carbon rod as the counter electrode) was scanned from the open circuit potential to the positive/negative polarization limits at a scan rate of 1 mV s^{-1} . The test range of EIS was set to 0.1 Hz-100 kHz.

Computational details

Adsorption energies on Zn(002), (100), and (101) surfaces were calculated using the CP2K package. The PBE exchange-correlation functional with Grimme's DFT-D3(BJ) dispersion correction was employed. Geometry optimizations were performed using the DZVP-MOLOPT-SR-GTH basis set, a plane-wave cutoff of 400 Ry, and a relative cutoff of 55 Ry. A slab model with four Zn layers was used; the bottom two layers were fixed. The Martyna-Tuckerman (MT) Poisson solver was applied under periodic boundary conditions in the XY plane. Adsorption energies were computed as $E_{ads} = E_{total} - (E_{slab} + E_{molecule})$ with counterpoise correction for basis set superposition error. SCF convergence criteria were set to EPS_SCF= 1.0×10^{-6} , EPS_DEFAULT= 1.0×10^{-12} , Broyden mixing ($\alpha=0.4$, NBROYDEN=8), and Fermi-Dirac smearing at an electronic temperature of 300 K. Binding energies of Zn²⁺ solvation clusters (e.g., [Zn(H₂O)₆]²⁺, [Zn(AA)(H₂O)₄]²⁺) were obtained using ORCA 6.0. Geometry optimizations were carried out with the r²SCAN-3c composite method (r²SCAN meta-GGA functional, def2-mTZVPP basis set, D4 dispersion, and gCP correction). Single-point energies were refined with the wB97M-V functional and the def2-TZVPP basis set, employing the SMD implicit solvation model (water). Binding energies were calculated as $E_{binding} = E_{complex} - (E_{Zn^{2+}} + \sum E_{ligands})$. Electrostatic potential (ESP) maps were generated with Multiwfn 3.8 and visualized using VMD.

2. Supplementary Figures (1-20)

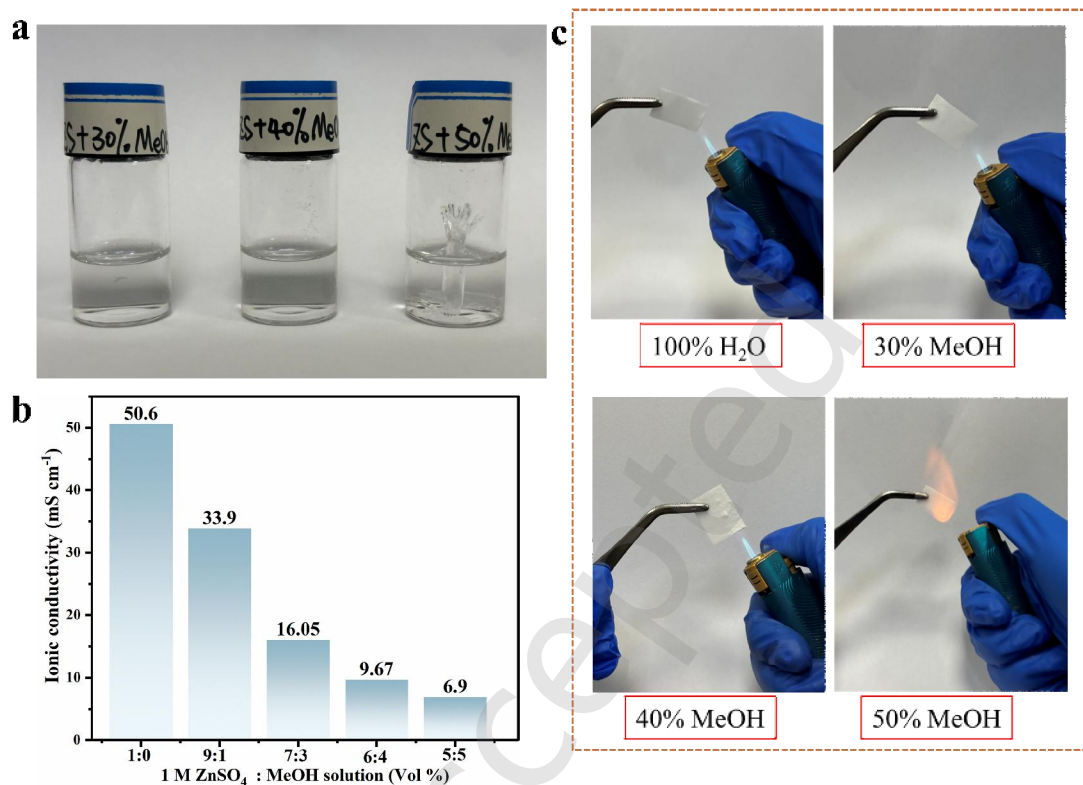


Figure S1 (a) Optical photographs of solubility, (b) Ionic conductivity and (c) Ignition test, of binary electrolytes composed of aqueous ZnSO₄ with different volume MeOH.

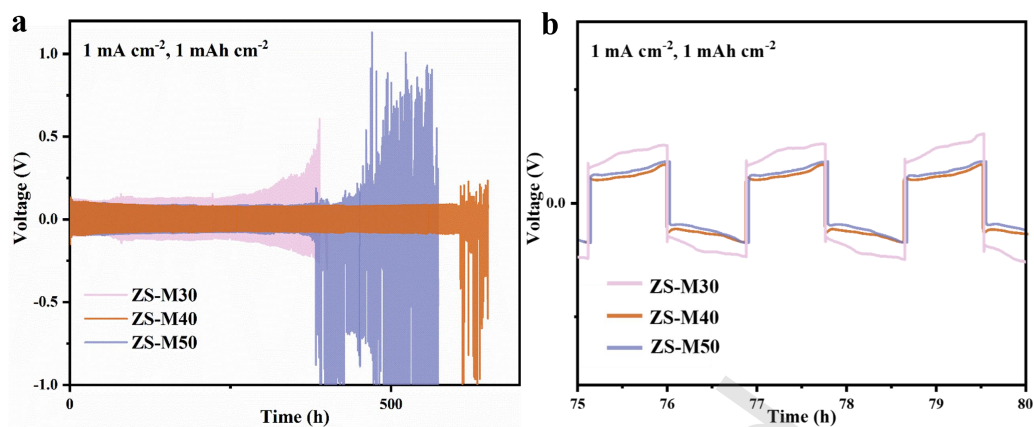


Figure S2 (a) Time–voltage curves of Zn||Zn symmetric cells in ZnSO₄ electrolytes with different volume ratios of MeOH (30%, 40%, 50%). (b) Corresponding locally magnified plots of the cycles from 75 h to 80 h.

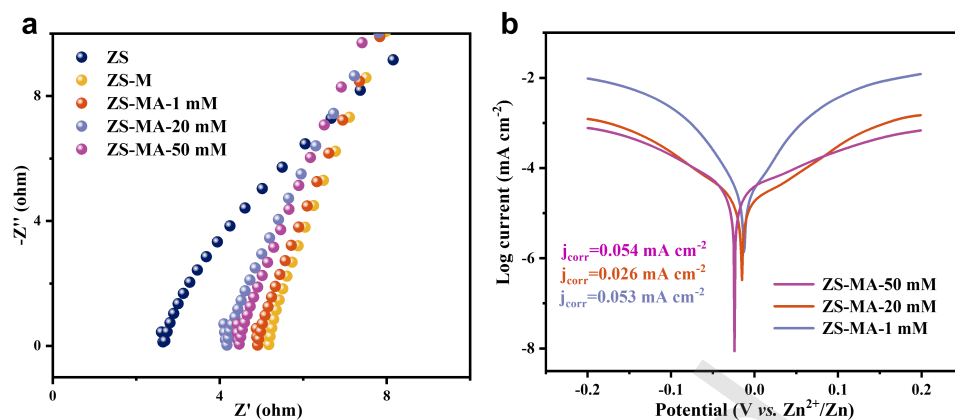


Figure S3 (a) Electrochemical impedance spectroscopy (EIS) tests of symmetric cells. (b) Tafel curves varying concentrations of ascorbic acid.

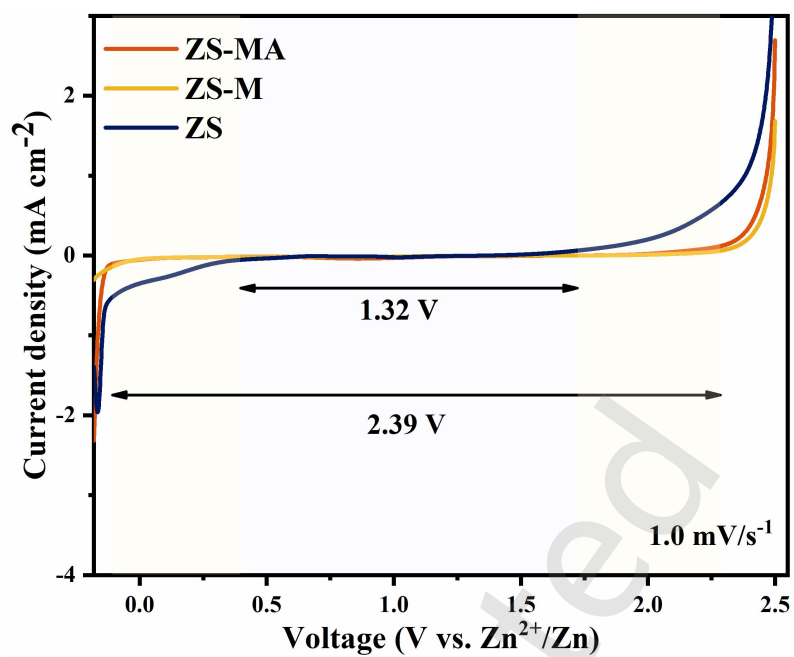


Figure S4 Electrochemical windows of different electrolytes.

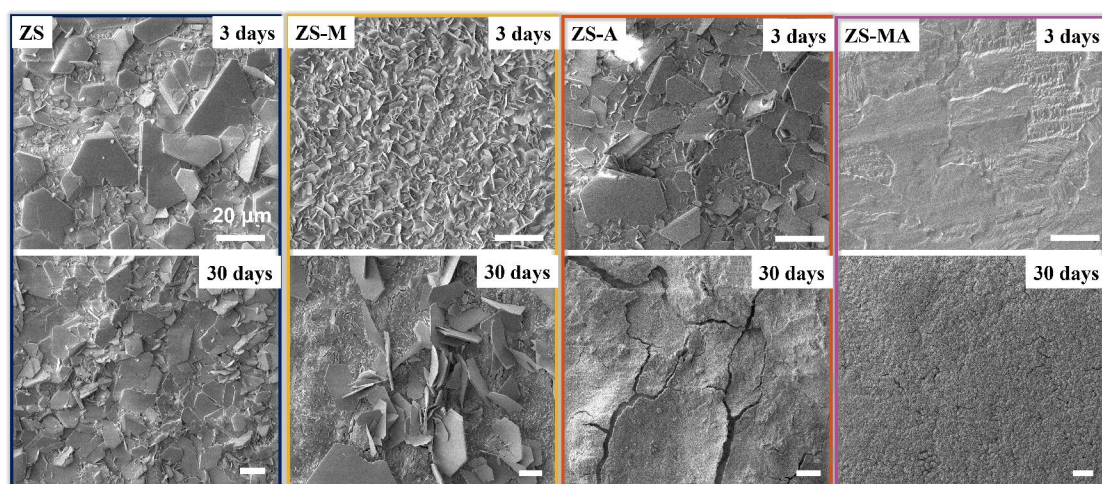


Figure S5 Morphologies of Zn foil after soaking in different electrolytes for various days: (a) ZS electrolyte, (b) ZS-M electrolyte, (c) ZS-MA electrolyte. Scale bar: 20 μm .

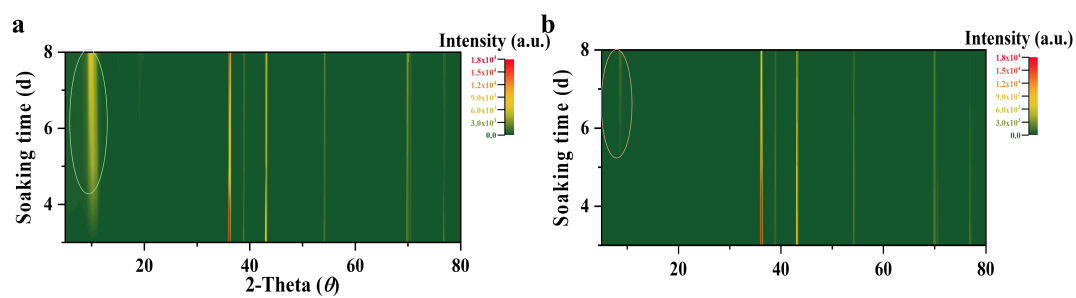


Figure S6 XRD patterns of Zn foil after soaking in different electrolytes for various days: (a) ZS-M electrolyte, (b) ZS-A electrolyte.

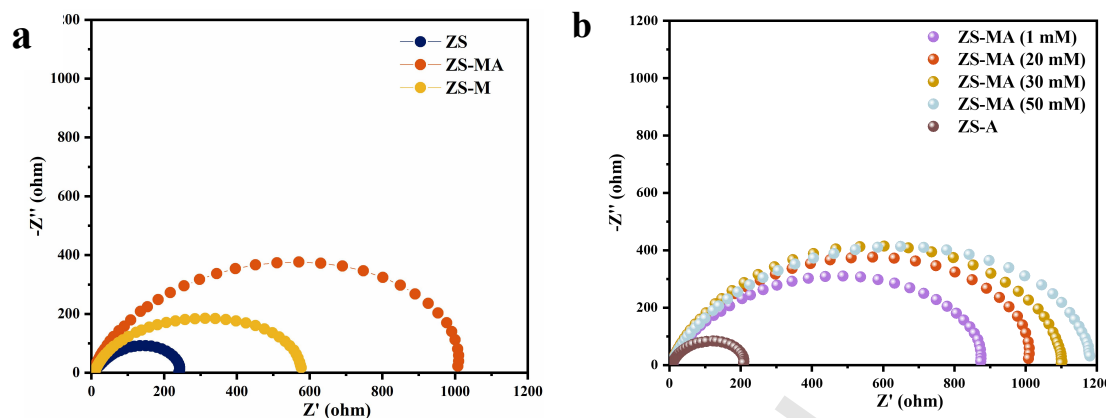


Figure S7 EIS curves of Zn||Zn cells of (a) ZS, ZS-M and ZS-MA electrolytes, and (b) different concentrations of AA.

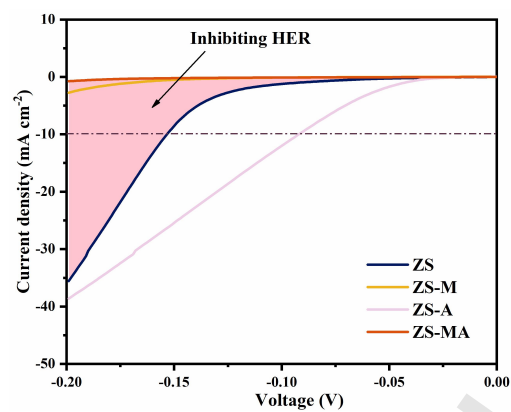


Figure S8 LSV curves of Zn||Zn cells with ZS, ZS-M, ZS-A and ZS-MA electrolytes.

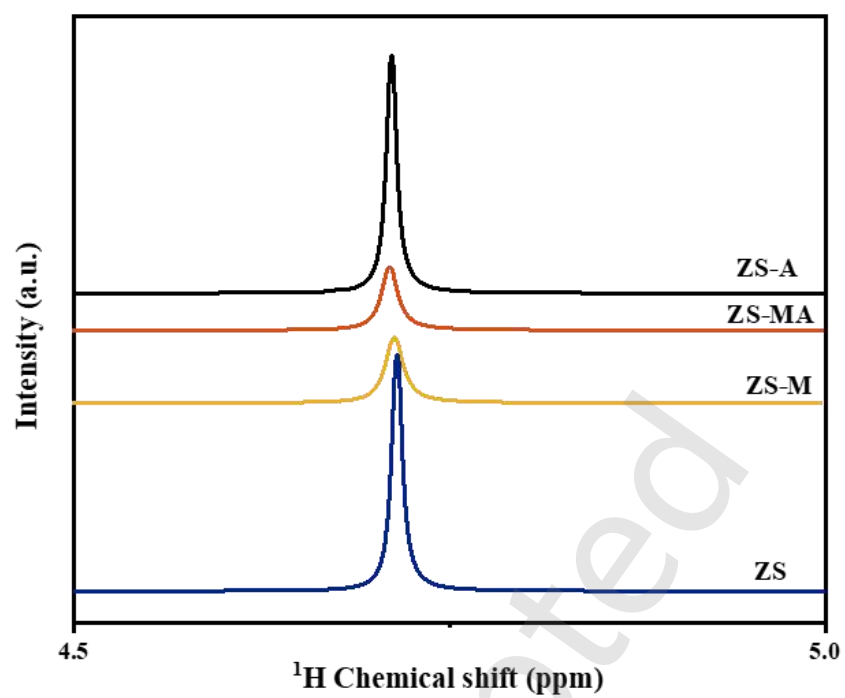


Figure S9 Nuclear magnetic hydrogen spectra of different electrolytes.

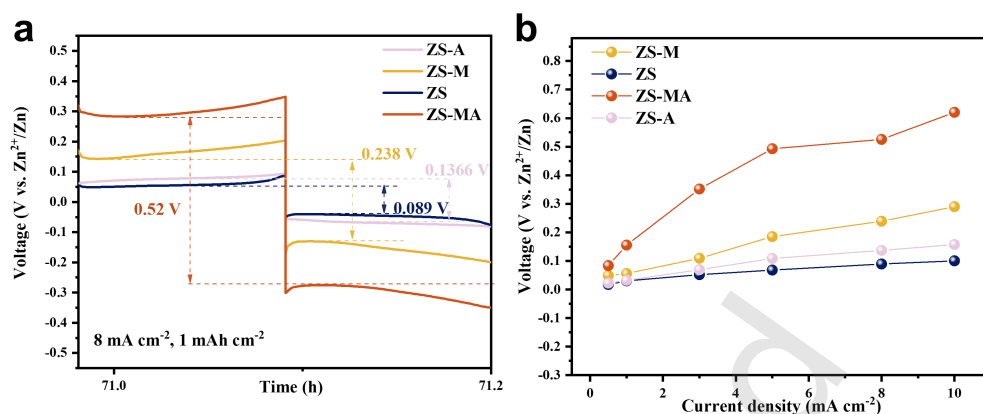


Figure S10 (a) Time-voltage curves of symmetric cells at an areal capacity of 1 mAh cm^{-2} and current density of 8 mA cm^{-2} . (b) Statistical plots of polarization voltages at current densities of 0.5, 1, 3, 5, 8 and 10 mA cm^{-2} in different electrolytes.

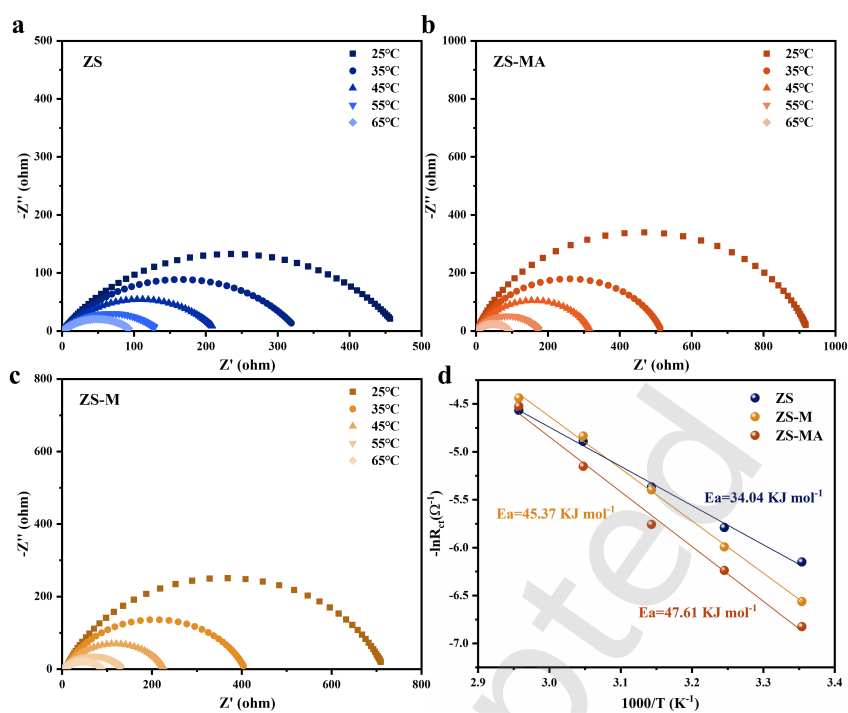


Figure S11 EIS of symmetric cells at different temperatures. (a) ZS electrolyte, (b) ZS-MA electrolyte, (c) ZS-M electrolyte. (d) Arrhenius curves and comparison of activation energies.

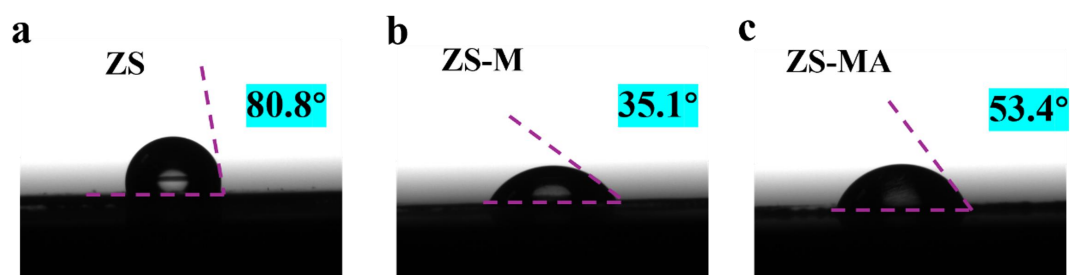


Figure S12 Contact angles of different electrolytes on bare Zn foil. (a) ZS, (b) ZS-M, (c) ZS-MA..

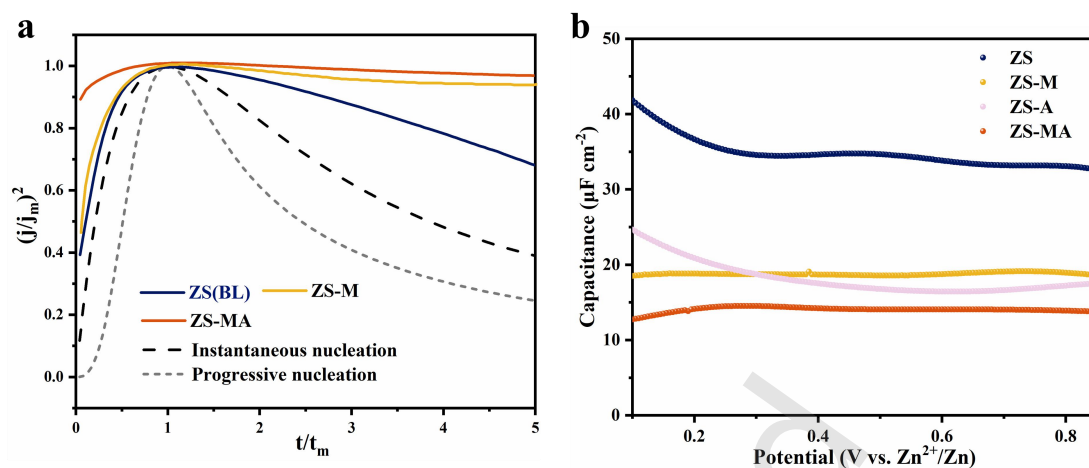


Figure S13 (a) Comparison of theoretical and experimental dimensionless current-time transients for nucleation model comparison. (b) Differential capacitance curves of zinc anode in ZS, ZS-M and ZS-MA electrolytes.

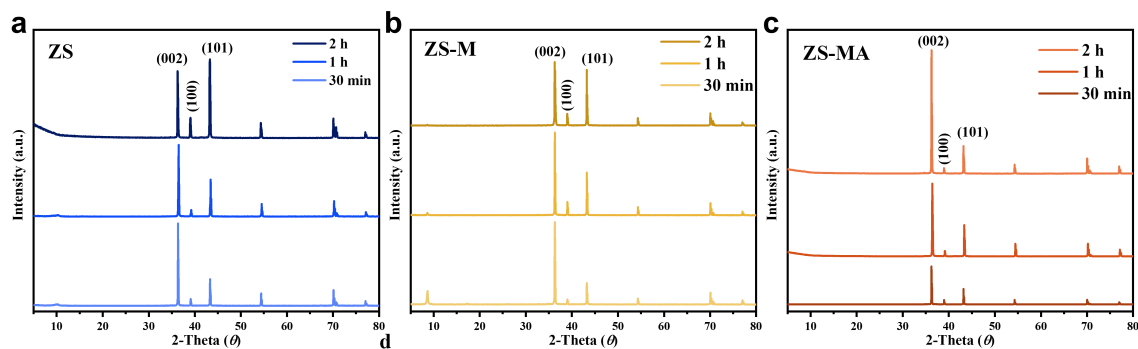


Figure S14 XRD patterns of Zn foils after deposition with different areal capacities in various electrolytes: (a) ZS electrolyte, (b) ZS- M electrolyte, (c) ZS- MA electrolyte.

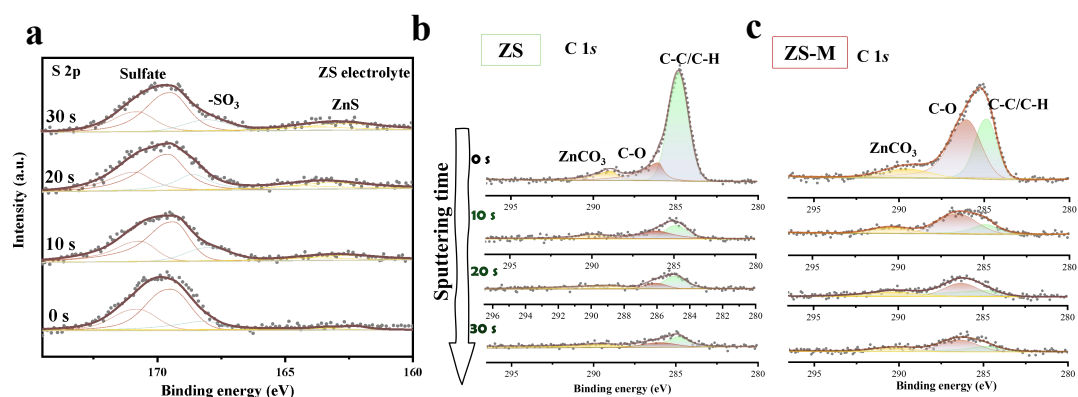


Figure S15 Depth-dependent XPS spectra of Zn foils after 10 cycles in (a) S 2p spectra in ZS electrolyte and (b) ZS and (c) ZS-M electrolytes for C 1s at different Ar^+ sputtering times.

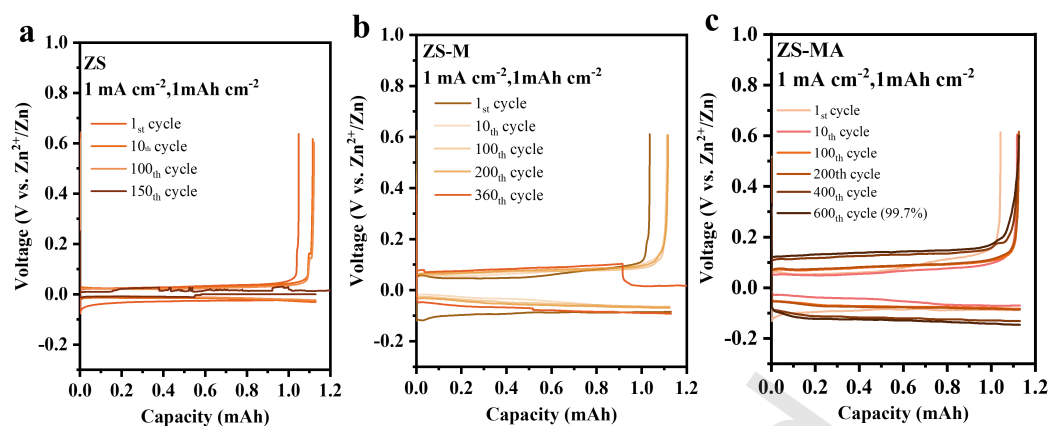


Figure S16 Capacity-voltage curves at different cycles for (a) ZS, (b) ZS-M, and (c) ZS-MA electrolytes.

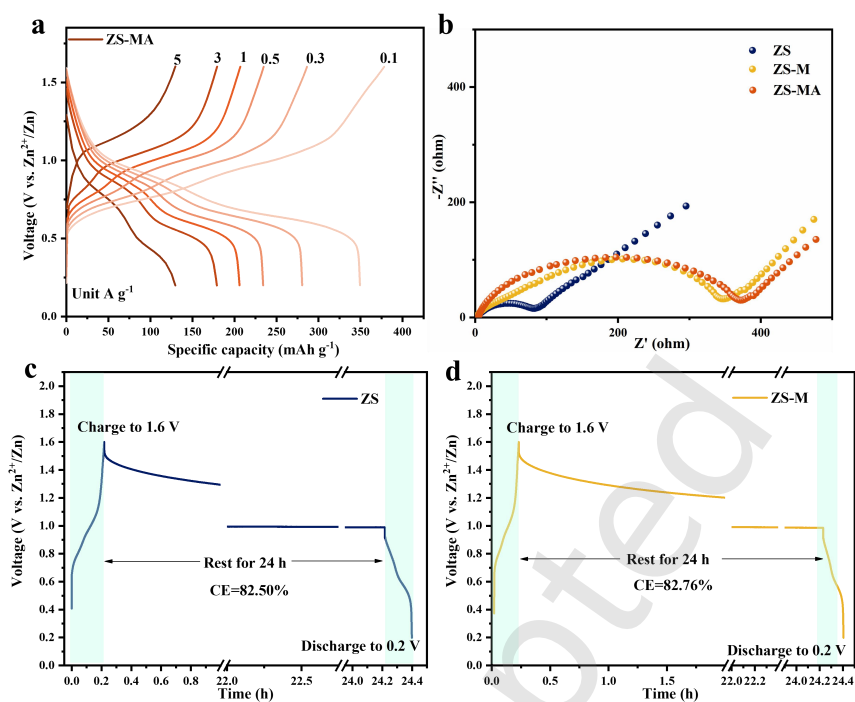


Figure S17 (a) GCD curves at different current density. (b) EIS of the full cells with various electrolytes. Self-discharge curves of Zn||V₂O₅ full cells with different electrolytes (c) ZS, (d) ZS-M.

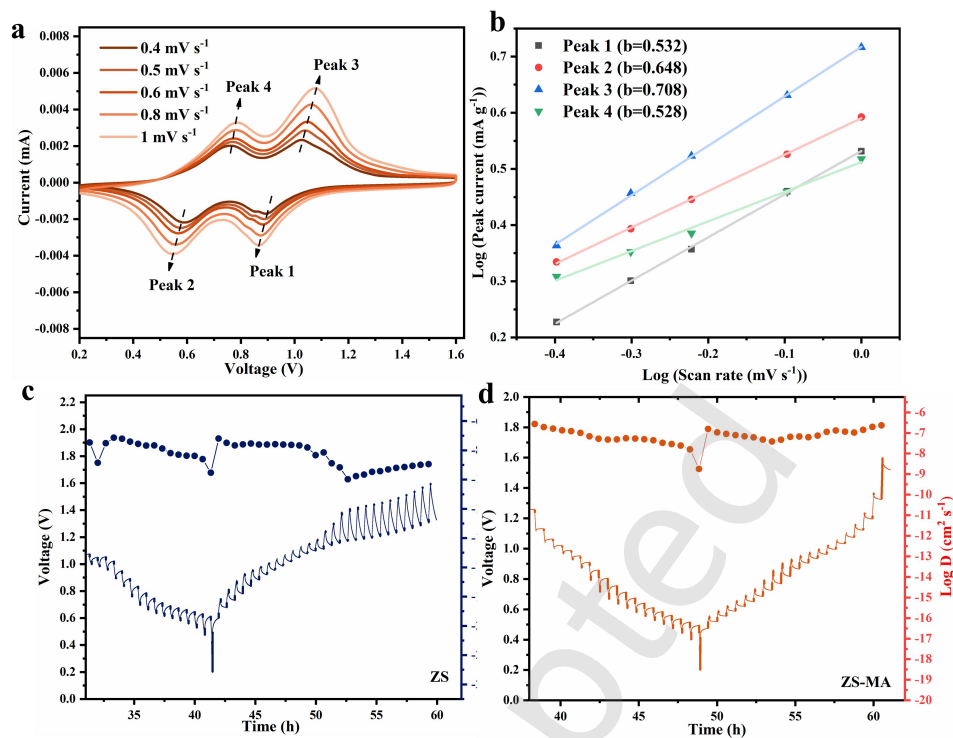


Figure S18 (a) CV curves of Zn||V₂O₅ full cells in the ZS-MA electrolyte at different scan rates. (b) Corresponding peak fitting plots of $\log(i)$ vs. $\log(v)$. GITT curves of the fully activated full cells for (c) ZS electrolyte and (d) ZS-MA electrolyte.

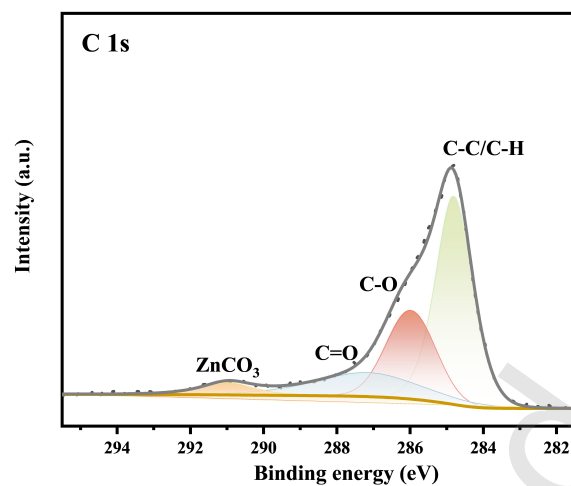


Figure S19 C 1s spectra of Zn anode after cycling with ZS-MA electrolyte for full cell.

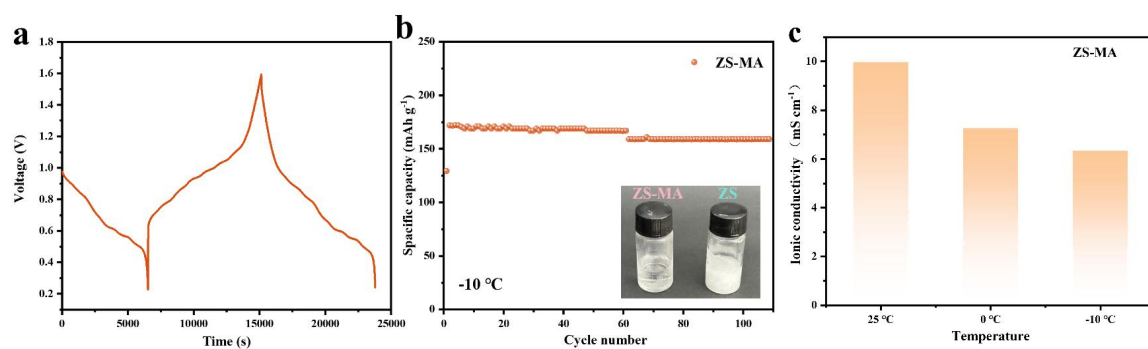


Figure S20 (a) GCD curves of the full battery at -10°C . (b) Long-term cycling performance at -10°C ; the inset shows the optical image of the electrolyte after being frozen. (c) Ionic conductivity at 25°C , 0°C and -10°C for ZS-MA electrolyte.