



Deciphering the chain length effect of organic additives on Zn reversibility

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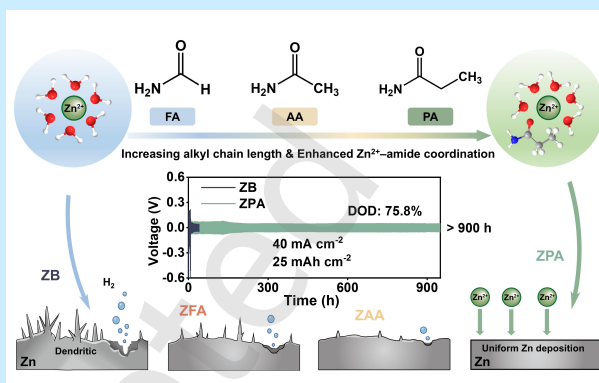
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Increasing alkyl chain length of amide additives strengthens Zn^{2+} -amide coordination, reshapes the Zn^{2+} solvation environment, and promotes uniform Zn nucleation while suppressing water-induced parasitic reactions. The optimized electrolyte achieves an average Coulombic efficiency of 99.6% and sustains Zn||Zn cycling for over 900 h at 40 mA cm^{-2} and 25 mAh cm^{-2} , outperforming most previously reported electrolyte systems.



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ABSTRACT

The practical deployment of zinc (Zn) metal anodes is severely hindered by uncontrolled dendrite growth and parasitic side reactions. Although organic additives can alleviate these issues, the fundamental relationship between their molecular structure and Zn deposition/stripping reversibility remains inadequately understood. Herein, a homologous series of amide additives is employed to establish the effect of molecular chain length on Zn reversibility. Complementary theoretical and experimental analyses reveal that alkyl chain extension increases the electron density of the carbonyl oxygen and strengthens Zn²⁺-amide coordination, thereby reorganizing the primary solvation sheath toward enhanced amide coordination. This regulation generates a dual effect: stronger coordination raises the nucleation overpotential and promotes dense, uniform Zn nucleation, while reduced interfacial water activity suppresses hydrogen evolution and corrosion reactions. Consequently, the optimized amides electrolyte delivers an average Coulombic efficiency of 99.6% and enables stable Zn||Zn cycling for over 900 h at 40 mA cm⁻² and 25 mAh cm⁻², corresponding to approximately 75.8% Zn utilization. Zn||VS₂ full cells retain 87.9% of their initial capacity after 1000 cycles. Notably, the same chain length-dependent enhancement is reproduced in carbonate additives, establishing molecular chain engineering as a transferable strategy for highly reversible Zn metal anodes.

KEYWORDS

Aqueous Zn metal batteries, Electrolyte additives, Amide, Nucleation, Alkyl chain length

1 Introduction

Aqueous zinc-ion batteries (AZIBs) have garnered significant attention as safe and cost-effective energy storage systems, owing to the intrinsic safety of aqueous electrolytes, the abundance of Zn resources, and the high theoretical capacity of Zn metal [1-4]. However, their practical application is severely constrained by the poor Zn reversibility in aqueous environments. Specifically, active water molecules promote parasitic hydrogen evolution and corrosion reactions, while an inhomogeneous Zn²⁺ flux induces uneven nucleation and dendritic growth [5-9]. Consequently, these adverse interfacial processes trigger severe active Zn and electrolyte depletion, resulting in electrically insulating byproducts and low Coulombic efficiency [10-14].

To mitigate these challenges, engineering Zn²⁺ solvation

structure has become a widely adopted strategy for stabilizing Zn metal anodes [15, 16]. Fundamentally, the primary solvation sheath dictates not only the activity of coordinated water molecules, but also the desolvation behavior of Zn²⁺ [17]. Consequently, tailoring the Zn²⁺ coordination environment can simultaneously suppress parasitic reactions and promote uniform Zn deposition [18-21]. On this basis, strategies such as highly concentrated “water-in-salt” electrolytes [22], organic cosolvent systems [23-25], and functional organic additives [26] have been developed to reconstruct the solvation structure. Among these approaches, organic additives stand out because they enable precise modulation of the local coordination chemistry without substantially altering the bulk electrolyte composition. Despite these advances, the molecular design of electrolyte additives remains largely empirical. Existing

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studies predominantly focus on identifying effective functional groups, whereas the influence of molecular skeleton parameters, such as alkyl chain length and steric structure, has received far less attention. More importantly, these structural effects have rarely been systematically isolated from the intrinsic chemical effects of the functional groups [27]. This knowledge gap hinders the establishment of explicit molecular structure-property relationships and limits the transition from trial and error additive screening to rational molecular engineering.

Amide-based molecules provide an ideal platform for investigating such molecular skeleton effects because the amide group can coordinate strongly with Zn^{2+} and directly regulate its local solvation environment [16]. Even within the same functional family, subtle variations in molecular structure can modify the electron donating ability of the amide group, molecular steric environment, and hydrogen bonding interactions with water. These changes may alter Zn^{2+} solvation structure, Zn nucleation behavior and side reactions. Establishing how the evolution of the molecular skeleton governs these processes is therefore essential for developing rational design principles for high performance electrolyte additives [28, 29].

Herein, a homologous series of amides—formamide, acetamide, and propionamide—is employed as a model platform to establish the molecular relationship between alkyl chain length and Zn reversibility. By varying the carbon skeleton while retaining the same amide functionality, the chain length effect is distinguished from the intrinsic chemistry of the functional group. It is found that alkyl chain extension increases the electron density of the carbonyl oxygen, thereby strengthening Zn^{2+} -amide coordination and partially displacing coordinated water, leading to a solvation structure with enhanced amide coordination and reduced water coordination. This reconstruction raises the interfacial activation barrier and nucleation overpotential, thereby promoting dense and uniform Zn nucleation, while the reduced availability of reactive water suppresses hydrogen evolution and corrosion reactions. Consequently, propionamide-containing electrolyte enables highly reversible Zn deposition/stripping under demanding conditions and substantially improves the cycling stability of $\text{Zn}||\text{VS}_2$ full cells. Moreover, the same chain length-dependent trend is reproduced with carbonate additives, demonstrating the transferability of this molecular design principle. This work establishes alkyl chain engineering as a rational strategy for coordinating Zn deposition kinetics with interfacial water regulation.

2 Results and discussion

To elucidate the effect of molecular chain length on Zn reversibility, a homologous series of primary amides, including formamide (FA), acetamide (AA), and propionamide (PA), are introduced into a conventional 1 mol kg^{-1} ZnSO_4 electrolyte, hereafter denoted as ZB. The additive concentration is fixed at 2 mol kg^{-1} to ensure an

equimolar comparison and induce a measurable change in the Zn^{2+} coordination environment while retaining the nonflammability of the aqueous electrolyte (Fig. S1). The resulting electrolytes are denoted as ZFA, ZAA, and ZPA, respectively (Fig. S2). Butyramide (BA) is excluded because its limited aqueous solubility prevents the formation of a homogeneous electrolyte. PA therefore represents the longest soluble amide investigated in this series. The electrolytes exhibit similar pH values and modest differences in wettability on Zn (Figs. S3 and S4). Notably, the ionic conductivities of ZB, ZFA, ZAA, and ZPA are 98.3, 73.2, 60.0, and 55.0 mS cm^{-1} , respectively (Fig. S5). Although the conductivity gradually decreases with increasing amide chain length, all values remain within the same order of magnitude. Therefore, the different electrochemical behaviors cannot be simply attributed to bulk ionic transport.

The carbonyl oxygen of the amide group can coordinate with Zn^{2+} , while the carbonyl and N-H moieties can reorganize the hydrogen bonding network of water [30]. Upon incorporation into the ZnSO_4 electrolyte, the ^1H NMR resonances of FA, AA, and PA shift upfield (Fig. 1(a)), indicating Zn^{2+} -induced changes in their local electronic environments. The chemical shift changes are approximately 0.19 ppm for FA and AA and increase to 0.22 ppm for PA, suggesting a stronger interaction between PA and Zn^{2+} . This trend is attributed to the enhanced electron donating effect of the progressively extended alkyl substituent, which increases the Lewis basicity of the carbonyl oxygen. Complementary evidence is provided by Fourier transform infrared spectroscopy (FTIR) (Fig. S6). The S=O stretching vibration of SO_4^{2-} (1050–1100 cm^{-1}) exhibits a progressive blue shift with increasing alkyl chain length, suggesting that amide coordination weakens the electrostatic coupling between Zn^{2+} and sulfate anions [31]. This trend further supports the stronger coordination of PA with Zn^{2+} compared with FA and AA. In addition to coordinating with Zn^{2+} , the amide additives reorganize the hydrogen bonding environment of the aqueous electrolyte. As shown by the ^1H NMR spectra (Fig. S7), the water-proton resonance varies after the introduction of different amides, with ZPA displaying the most pronounced change. These results indicate that chain extension strengthens the ability of the amide additives to regulate both Zn^{2+} coordination and the water hydrogen bonding network.

Density functional theory calculations further clarify the chain length-dependent Zn^{2+} affinity (Fig. 1(b)). The calculated binding energies become progressively more negative in the order H_2O (−4.52 eV), FA (−6.49 eV), AA (−6.85 eV), and PA (−7.08 eV), corresponding to the binding strength sequence $\text{H}_2\text{O} < \text{FA} < \text{AA} < \text{PA}$. Electrostatic potential maps identify the carbonyl oxygen as the principal coordination site, with PA exhibiting the most electron-rich region around this atom [32]. These results confirm that extending the molecular chain enhances the Lewis basicity of the carbonyl oxygen and strengthens

Zn^{2+} -amide coordination. Molecular dynamics simulations reveal the resulting evolution of Zn^{2+} solvation structure. The radial distribution functions and coordination numbers confirm that the carbonyl oxygen of the amides enters the primary Zn^{2+} solvation shell (Figs. 1(c), (d), and S8). From ZFA to ZPA, the coordination numbers of $\text{Zn-O}(\text{H}_2\text{O})$ and $\text{Zn-O}(\text{SO}_4^{2-})$ progressively decrease, whereas that of $\text{Zn-O}(\text{amide})$ increases. PA induces the greatest changes in the coordination of water and sulfate around Zn^{2+} , resulting in a solvation environment characterized by strengthened Zn^{2+} -amide coordination.

The influence of this solvation reconstruction on interfacial kinetics is examined by temperature dependent electrochemical impedance spectroscopy (see Fig. S9 for details). The apparent activation energy derived from the temperature dependence of the charge transfer resistance is $27.27 \text{ kJ mol}^{-1}$ for ZB, which is comparable to previously reported values for ZnSO_4 electrolytes [33]. The value remains nearly unchanged after the addition of FA, reaching $27.44 \text{ kJ mol}^{-1}$ for ZFA, but increases substantially

to $40.74 \text{ kJ mol}^{-1}$ for ZAA and $51.71 \text{ kJ mol}^{-1}$ for ZPA (Fig. 1(e)). The activation energy of ZPA is approximately 1.9 times that of ZB, indicating a considerably larger energetic penalty for reorganizing and partially removing the primary solvation sheath before interfacial electron transfer.

This kinetic regulation is further reflected in the Zn nucleation overpotential (η), defined as the voltage difference between the initial dip and the subsequent plateau during galvanostatic Zn deposition. As shown in Fig. 1(f), ZB exhibits a low η of 33.6 mV at 1 mA cm^{-2} , while this value increases modestly to 41.0 mV (ZFA) and 44.8 mV (ZAA). In striking contrast, a significantly elevated η of 55.9 mV is observed in ZPA. This trend persists under higher current densities (Fig. S10) and is further supported by cyclic voltammetry measurement, which shows progressively decreased anodic current responses from ZB to ZPA (Fig. S11), consistent with the strongest Zn^{2+} -PA

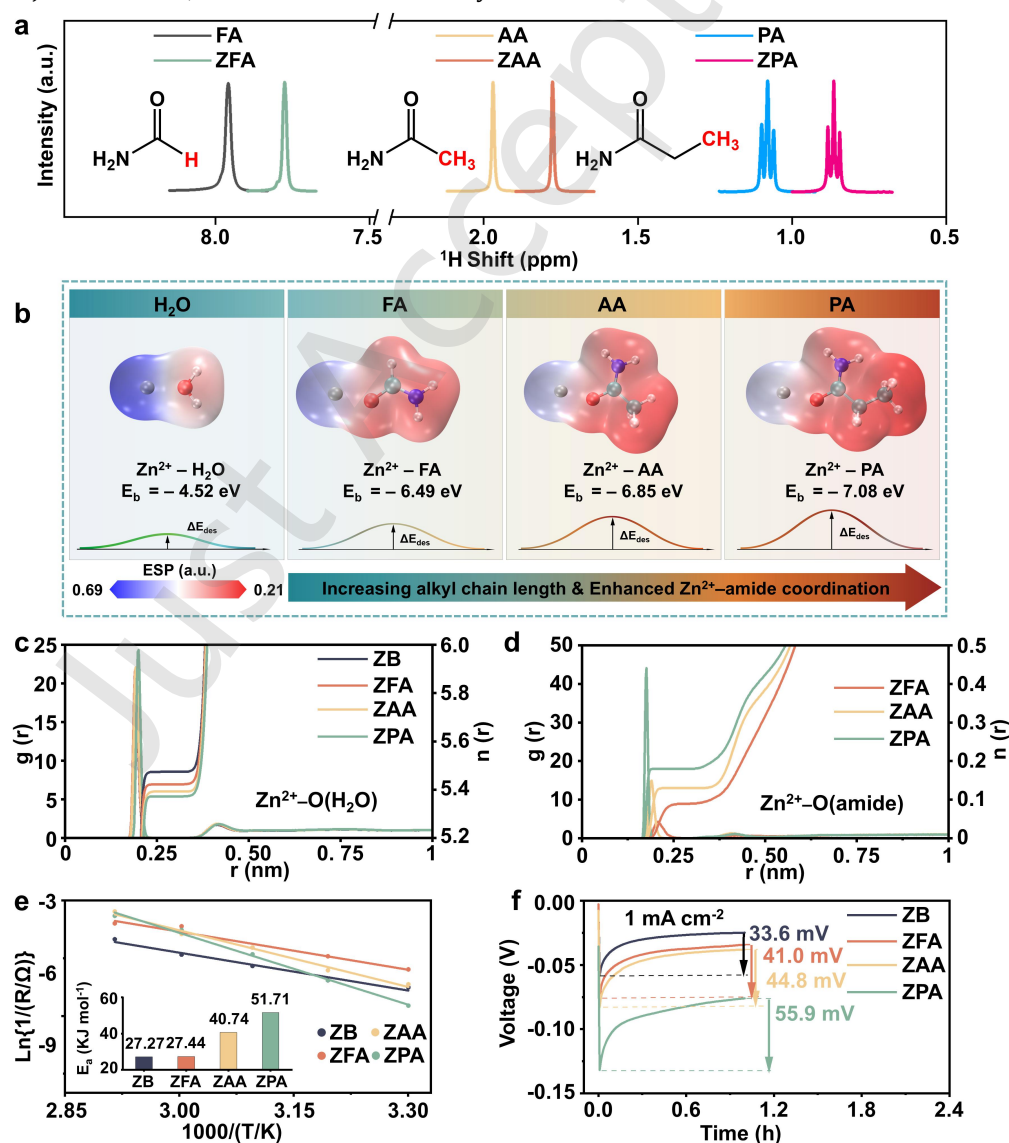


Figure 1 (a) ^1H NMR spectra of FA, AA, PA and ZFA, ZAA, ZPA electrolytes. (b) Calculated binding energies and corresponding electrostatic

potential maps of Zn^{2+} coordinated with different amides. Radial distribution functions and coordination numbers for (c) $\text{Zn}^{2+}\text{-O}(\text{H}_2\text{O})$ and (d) $\text{Zn}^{2+}\text{-O}(\text{amide})$ computed from molecular dynamics simulations. (e) Arrhenius curves fitted from the series of R_{ct} and corresponding desolvation activation energy at different temperatures with different electrolytes. (f) Galvanostatic discharge profile of $\text{Zn}||\text{Cu}$ cell with different electrolytes at 1 mA cm^{-2}

binding energy. Although an excessively high desolvation barrier could, in principle, hinder Zn^{2+} transfer, the ZPA electrolyte appears to achieve a balanced kinetic regulation: the increased nucleation overpotential provides a larger driving force for dense nucleation, while the electrolyte still allows stable Zn deposition/stripping without severe transport limitation (see Fig. 3 for details).

The chain length-dependent increase in nucleation overpotential established above is expected to directly influence the initial nucleation and subsequent growth of Zn. To verify this relationship, Zn deposition morphology is examined by ex-situ scanning electron microscopy (SEM) and in-situ optical microscopy. According to classical nucleation theory, increasing the nucleation overpotential decreases the critical nucleus radius and increases the nucleation rate, thereby favoring the formation of smaller and more densely distributed Zn nuclei [34]. After depositing $0.002 \text{ mAh cm}^{-2}$ of Zn onto Cu, sparse and isolated nuclei are observed in ZB, which readily develop into a rough and nonuniform deposit (Fig. 2(a)). In comparison, the nuclei become progressively smaller and more densely distributed from ZFA to ZPA, with ZPA exhibiting the most uniform nucleation pattern. These observations are consistent with the chain length-dependent increase in nucleation overpotential. In-situ optical microscopy is further employed to monitor the dynamic evolution of Zn deposition (Fig. 2(b)). In ZB electrolyte, prominent bulges and protrusions emerge on the Zn electrode surface at deposition capacities of 2 and 10 mAh cm^{-2} , indicative of irregular nucleation and preferential growth at high energy sites. The ZFA and ZAA electrolytes produce moderately improved morphologies, though a few protrusions remain visible (Fig. S12). In sharp contrast, ZPA markedly eliminates nonuniform deposition, yielding a smooth, bulge-free surface throughout the entire deposition process. This behavior directly reflects the kinetic control mechanism: the elevated nucleation overpotential promotes the formation of numerous small nuclei that grow uniformly, preventing the tip effect that otherwise drives dendritic morphology.

Beyond regulating Zn deposition, the reconstructed solvation environment is also expected to alleviate water-induced parasitic reactions. The chemical stability of Zn in the different electrolytes is therefore evaluated by X-ray diffraction (XRD) analysis (Fig. 2(c)) and confocal microscopy. After 24 hours immersion of Zn foil in each electrolyte, prominent diffraction peaks corresponding to the byproduct $\text{Zn}_4\text{SO}_4(\text{OH})_6 \cdot 5\text{H}_2\text{O}$ appear in ZB, indicating severe parasitic reactions between Zn metal and water. Notably, the intensity of these peaks progressively decreases with increasing alkyl chain length. In ZPA, the byproduct peaks are nearly undetectable, demonstrating the most effective suppression of Zn corrosion.

Consistently, topographic imaging reveals a porous and severely roughened Zn surface in ZB, whereas the Zn foil immersed in ZPA largely retains its structural integrity with minimal pitting or etching (Figs. 2(d), (e), and S13). Post-cycling characterizations further show that ZPA yields a denser and more uniform Zn deposition layer with fewer interfacial by-products than the other electrolytes (Figs. S14 and S15).

Electrochemical measurements further quantify the suppression of these parasitic reactions [35]. Tafel polarization analysis is employed to quantify corrosion currents (Fig. 2(f)). ZB exhibits a substantial corrosion current of 1.72 mA cm^{-2} , whereas corrosion is progressively suppressed across the amide series, with ZPA delivering the lowest value (0.13 mA cm^{-2}). A similar trend is observed for the hydrogen evolution reaction (HER). Linear sweep voltammetry shows a progressive negative shift in the HER onset potential from ZB to ZPA, indicating increasingly suppressed water reduction (Figs. 2(g), S16 and S17) [36]. This result is corroborated by direct optical observations: vigorous H_2 evolution occurs in ZB, fewer bubbles are generated in ZFA and ZAA (Fig. S16), and almost no visible bubbles are observed in ZPA (Fig. 2(g)). The mechanism underlying this suppression is that the solvation sheath of ZPA reduces the population of reactive water molecules at the electrode interface. These findings collectively demonstrate that PA, bearing the longest alkyl chain in the series, exerts the strongest regulation of the Zn^{2+} solvation environment. The enhanced $\text{Zn}^{2+}\text{-PA}$ coordination partially replaces coordinated water and increases the nucleation overpotential, thereby promoting dense and uniform Zn deposition. Meanwhile, the reduced availability of reactive water at the electrode interface suppresses both hydrogen evolution and chemical corrosion, ultimately stabilizing the Zn/electrolyte interface (Fig. 2(h)).

To determine whether the regulated Zn nucleation and suppressed parasitic reactions translate into improved electrochemical reversibility, $\text{Zn}||\text{Zn}$ symmetric and $\text{Zn}||\text{Cu}$ asymmetric cells are assembled. Galvanostatic cycling of $\text{Zn}||\text{Zn}$ symmetric cells at 1 mA cm^{-2} with 1 mAh cm^{-2} reveals a stark contrast in stability (Fig. 3(a)): ZB cells suffer rapid short circuit failure after $\sim 150 \text{ h}$ due to uncontrolled dendrite propagation. The amide-containing electrolytes extend the cycle life substantially, from 200 h (ZFA) to 410 h (ZAA) to an impressive 1600 h (ZPA). The same chain length-dependent improvement is maintained at higher current densities (Fig. S18), demonstrating the superior interfacial stability of ZPA. Notably, the $\text{FA} < \text{AA} < \text{PA}$ trend is also retained at a lower amide concentration and in $\text{Zn}(\text{OTf})_2$ -based electrolytes (Figs. S19 and S20), indicating the robustness of the chain length effect across different electrolyte conditions. Reliable Zn

deposition/stripping under high current density, high areal capacity, and large depth of discharge (DOD) is essential for practical Zn metal batteries [37]. Accordingly, ZPA is further evaluated at 40 mA cm^{-2} and 25 mAh cm^{-2} , corresponding to a DOD of approximately 75.8% (Fig. 3(b)). Under these demanding conditions, the ZPA-based cell operates stably for over 900 h, approximately ten times longer than the ZB-based cell (Fig. 3(b)). ZPA also

exhibits good low temperature compatibility, enabling stable Zn deposition/stripping for over 1000 h at -10°C (Figs. 3(c) and S21). The ZPA-based cell delivers a cumulative capacity (CPC) exceeding 39.2 Ah cm^{-2} at 40 mA cm^{-2} and 25 mAh cm^{-2} [38, 39], outperforming most previously reported Zn anode electrolyte systems (Fig. 3(d) and Table S1) [40-51].

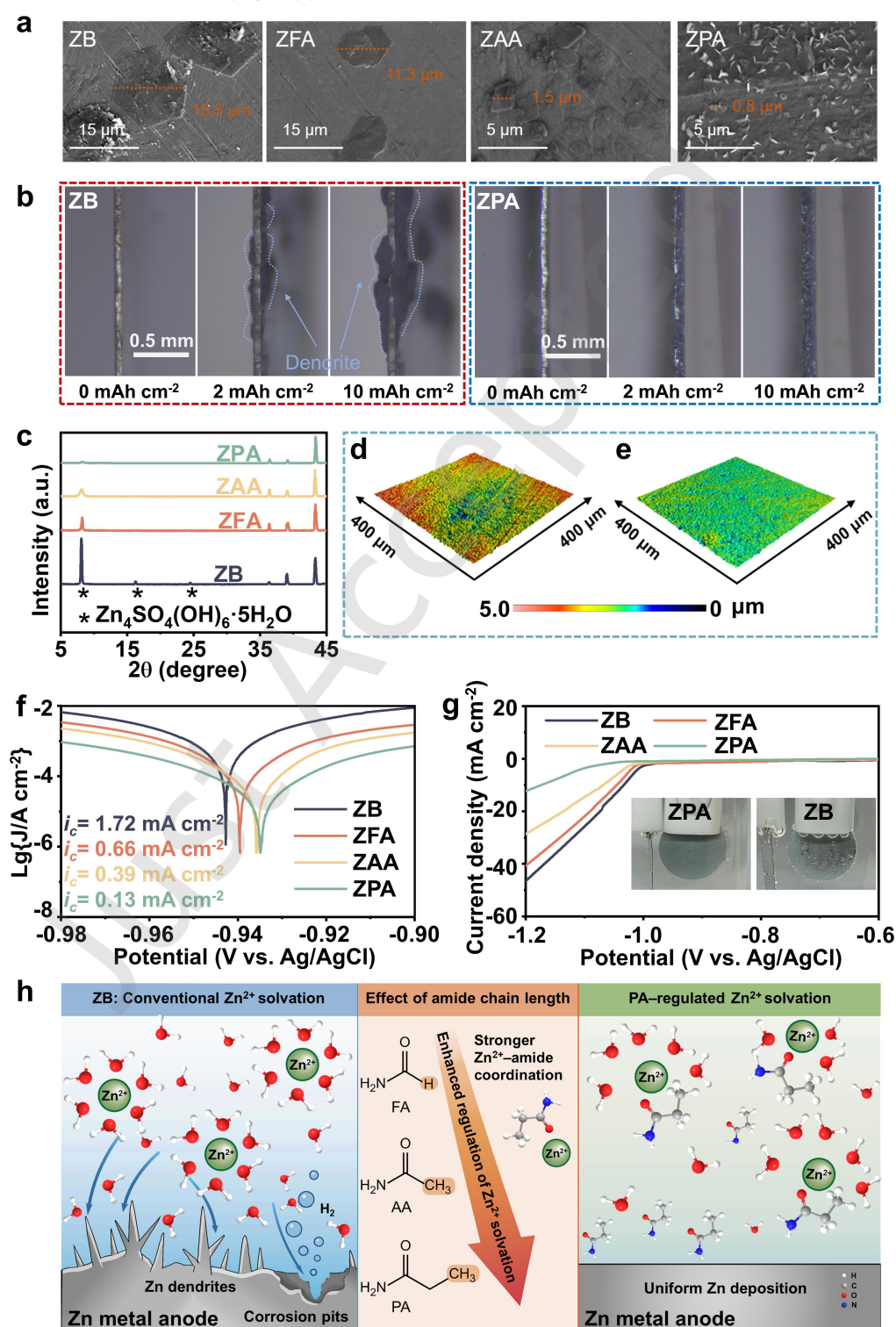


Figure 2 (a) SEM images of $0.002 \text{ mAh cm}^{-2}$ Zn deposition on Cu current collector with different electrolytes. (b) Optical images of Zn deposition

at 5 mA cm^{-2} with ZB and ZPA electrolytes. (c) XRD patterns of Zn anodes after immersion for 24 hours with different electrolytes. Topographic images of Zn foils after immersion for 24 hours with different electrolytes, (d) ZB, (e) ZPA. (f) The Tafel curves of Zn with different electrolytes. (g) LSV test with different electrolytes at 5 mV s^{-1} . (h) Schematic diagram of the mechanism of stabilizing Zn metal anode with ZPA electrolyte.

The improvement in Zn reversibility is further quantified using the Aurbach protocol, with the average Coulombic efficiency calculated as $\text{CE} = (nQ_c + Q_s)/(nQ_c + Q_p)$ [52]. The CE increases progressively from 97.0% in ZB to 98.9%, 99.1%, and 99.6% in ZFA, ZAA, and ZPA, respectively (Fig. 3(e)). This trend further supports the chain length-dependent enhancement of Zn reversibility. Combined with the mechanism analyses in Fig. 2, the superior performance of ZPA can be attributed to its ability to promote uniform Zn deposition while suppressing side reactions through the regulated solvation structure and interfacial kinetics [53].

The practical applicability of ZPA is subsequently examined in Zn||VS₂ and Zn||activated carbon (AC) full cells (Figs. 3(f), (g)). The prepared VS₂ cathode shows the expected phase, as confirmed by XRD (Fig. S22). The Zn||VS₂ cell using ZB retains only approximately 50% of its

initial capacity after 1000 cycles, whereas the cell using ZPA maintains 87.9% capacity retention under the same conditions (Fig. 3(f)). The corresponding charge-discharge profiles remain well preserved during cycling (Fig. 3(g)). The Zn||VS₂ full cell using ZPA consistently delivers higher capacities than its ZB counterpart as the current density increases from 0.2 to 5 A g^{-1} and subsequently returns to 0.2 A g^{-1} , demonstrating superior rate capability (Fig. S23). Even at an N/P ratio of 5:1, the ZPA cell delivers stable cycling for over 300 cycles at 1 A g^{-1} with negligible capacity decay (Fig. S24). A similar improvement is observed in Zn||AC cells, where ZPA enables nearly decay-free cycling over 10000 cycles, compared with a capacity retention of approximately 71.4% in ZB (Fig. S25). These results confirm that the solvation and interfacial regulation enabled by PA effectively improves Zn anode reversibility in different full cell configurations.

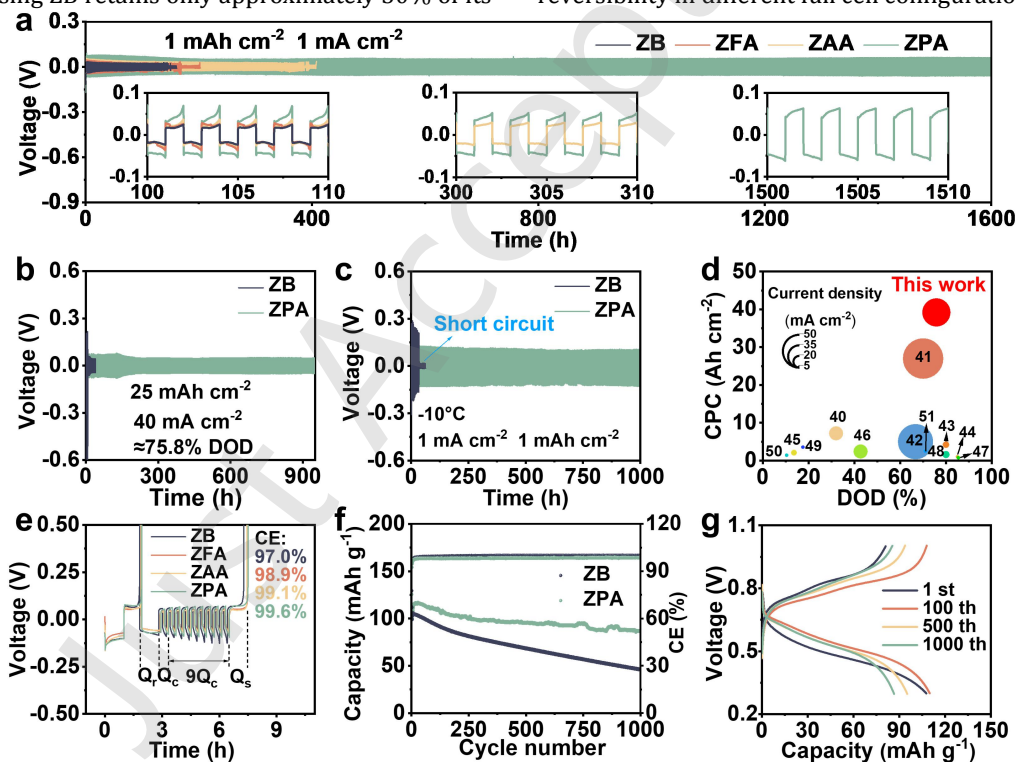


Figure 3 (a) Galvanostatic Zn deposition/stripping of Zn||Zn symmetric cell at a current density of 1 mA cm^{-2} and a capacity of 1 mAh cm^{-2} . (b) Galvanostatic Zn deposition/stripping of Zn||Zn cell at a current density of 40 mA cm^{-2} and a capacity of 25 mAh cm^{-2} . (c) Galvanostatic Zn deposition/stripping of Zn||Zn symmetric cell at -10°C . (d) Comparison of the proposed ZPA electrolyte with other reported work [40–51]. (e) CE tests of Zn||Cu cells at a current density of 5 mA cm^{-2} . (f) Cycle performance of the Zn||VS₂ full cell at 1 A g^{-1} and (g) corresponding discharge-charge profile with ZPA electrolyte.

To examine whether the chain length-dependent design principle extends beyond amide additives, a structurally related carbonate series comprising dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), and diethyl carbonate (DEC) is investigated [54]. Because of the limited solubility of these carbonates in ZnSO₄ electrolytes, Zn(OTf)₂ is used as the supporting salt (Fig. S26(a)). The baseline electrolyte is denoted as ZOTF, while those

containing DMC, EMC, and DEC are designated as ZDMC, ZEMC, and ZDEC, respectively. As shown in Fig. 4(a), the Zn||Zn cell using ZOTF fails within 20 h at 5 mA cm^{-2} with 5 mAh cm^{-2} . The cycling life increases to approximately 40 h in ZDMC, 50 h in ZEMC, and 600 h in ZDEC, corresponding to a 30 fold extension relative to ZOTF. Consistently, Zn||Cu cells exhibit progressively improved Coulombic efficiency across the carbonate series, with

ZDEC achieving the highest average CE of 99.8% (Fig. 4(b)). These results reproduce the chain length-dependent performance trend observed for the amide additives.

To identify the interfacial origin of this improvement, we examine the nucleation overpotential and deposition morphology. ZDEC exhibits the largest η (88.0 mV, Fig. 4(c)), indicating that extension of the carbonate alkyl groups also increases the polarization required for initial Zn nucleation. XRD patterns and SEM images of cycled Zn anodes (Figs. 4(d), (e)) reveal that ZOTF produces a rough, dendrite ridden surface with abundant byproduct accumulation. Carbonate-containing electrolytes, particularly ZDEC, yield nearly byproduct-free surfaces with smooth and compact morphology. High magnification

images further reveal laterally ordered Zn deposition, demonstrating that DEC effectively suppresses both dendrite growth and water related side reactions. Importantly, the low additive content preserves the nonflammable nature of the electrolyte (Fig. S26(b)). Although amides and carbonates possess different coordination structures, both series exhibit a consistent dependence of Zn nucleation and reversibility on molecular chain length. These results support the broader applicability of molecular skeleton regulation and establish alkyl chain engineering as a versatile strategy for designing electrolyte additives for reversible Zn metal anodes.

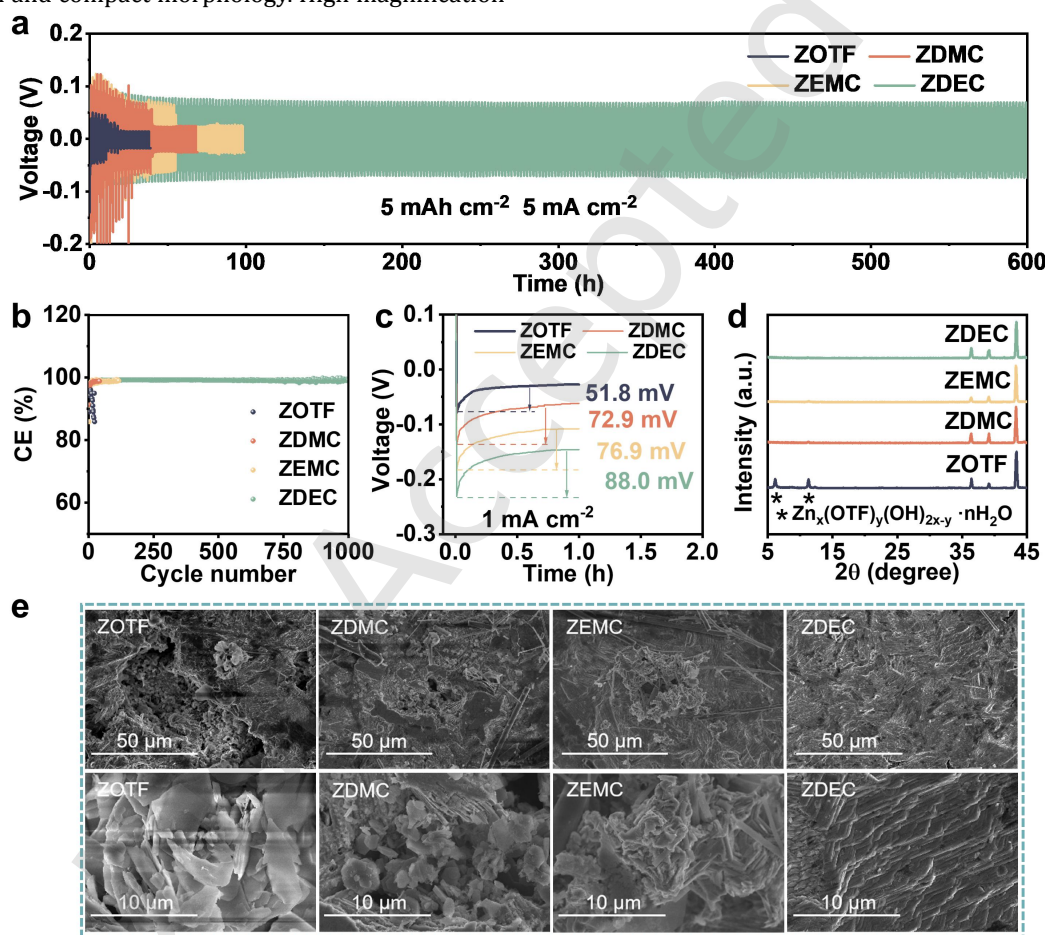


Figure 4 (a) Galvanostatic Zn deposition/stripping of Zn||Zn symmetric cell at a current density of 5 mA cm⁻² and a capacity of 5 mAh cm⁻². (b) CE tests of Zn||Cu cells at a current density of 5 mA cm⁻². (c) Galvanostatic discharge profile of Zn||Cu cell with different electrolytes at 1 mA cm⁻². (d) XRD patterns of Zn anodes after 10 cycles of Zn||Zn symmetric cell with different electrolytes. (e) SEM images of Zn anodes after 10 cycles of Zn||Zn symmetric cell with different electrolytes.

3 Conclusion

In summary, this work establishes alkyl chain engineering as a rational strategy for designing organic additives for aqueous Zn electrolytes. Using a homologous amide series, we demonstrate that extending the alkyl chain increases the electron density and Lewis basicity of the carbonyl oxygen, thereby strengthening Zn²⁺-amide coordination and progressively reconstructing the primary solvation sheath into enhanced amide coordination and reduced

water coordination. This solvation evolution simultaneously regulates interfacial kinetics and suppresses water activity: the increased activation barrier and nucleation overpotential favor dense and uniform Zn nucleation, while the reduced availability of reactive water mitigates hydrogen evolution and corrosion reactions. Consequently, the optimized ZPA electrolyte enables stable Zn||Zn cycling for over 1600 h under conventional conditions and over 900 h at 40 mA cm⁻² and 25 mAh cm⁻²,

corresponding to approximately 75.8% DOD. It also supports prolonged operation at -10°C and 87.9% capacity retention in $\text{Zn}||\text{VS}_2$ cells after 1000 cycles. More importantly, the same chain length-dependent enhancement is reproduced in carbonate additives, confirming that this design principle extends beyond amide chemistry. Moving forward, this predictive structure activity framework provides a rational evolution pathway for expanding into diverse functional groups and complex architectures, accelerating the development of application ready, high-performance electrolytes for next generation energy storage.

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Declaration of conflicting interests

The authors declare no conflicting interests regarding the content of this article.

Data availability

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

Electronic Supplementary Material: Supplementary Material (experimental and computational details, flammability and storage-stability tests of the electrolytes, ionic conductivities, FTIR and ^1H NMR spectra, molecular dynamics simulation results, temperature-dependent electrochemical impedance spectra, Zn nucleation overpotentials and galvanostatic discharge profiles, optical and topographic images of Zn deposition, SEM images and XRD patterns of cycled Zn anodes, linear sweep voltammetry results, cycling performance of $\text{Zn}||\text{Zn}$ symmetric cells, rate and cycling performance of $\text{Zn}||\text{VS}_2$ and $\text{Zn}||\text{AC}$ full cells, and a comparison with previously reported Zn batteries) is available in the online version of this article at <https://doi.org/10.26599/NRE.2026.9120275>.

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Electronic Supplementary Material

Deciphering the chain length effect of organic additives on Zn reversibility

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1 Experimental Section

1.1 Materials

Zinc sulfate heptahydrate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, Sigma-Aldrich, $\geq 99.0\%$) is dissolved in deionized (DI) water to prepare 1 M ZnSO_4 solution (ZB). Formamide (FA, Aladdin, $\geq 99.5\%$), acetamide (AA, Macklin, $\geq 99.5\%$) and propionamide (PA, J&K Scientific, 99%) are added into 1 M ZnSO_4 to prepare ZFA, ZAA and ZPA at a molality of 2 M, respectively. For the carbonate-based system, a 2 M ($\text{Zn}(\text{OTf})_2$) solution is prepared as the baseline electrolyte, denoted as ZOTF. To evaluate the effect of carbonate chain length, electrolytes containing 2 M of dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), and diethyl carbonate (DEC) are formulated and designated as ZDMC, ZEMC, and ZDEC, respectively. Zinc (Zn) foil, titanium (Ti) foil, copper (Cu) foil and stainless steel (SS) mesh are stamped into 1.2 cm diameter discs for coin cell assembly, immersion and electrochemical measurement. 1×0.5 cm area of Cu sheet is prepared for optical observation of various capacity Zn deposition.

1.2 Preparation of VS_2 cathode

VS_2 synthesis: According to previous research, VS_2 nanosheets are synthesized by hydrothermal method. Generally, 2 mmol ammonium metavanadate (NH_4VO_3 , Aladdin, 99.0%) is dissolved in a mixture of 30 mL DI water and 2 mL ammonia ($\text{NH}_3 \cdot \text{H}_2\text{O}$, AR). After stirring for 15 mins, 15 mmol thioacetamide ($\text{C}_2\text{H}_5\text{NS}$, Aladdin, $\geq 99.0\%$) is added into the solution and well-stirred for 1 hour at room temperature and the homogenous solution is transferred into steel reactor and maintained for 20 hours at 180°C . After cooling at room temperature, the mixture is filtered and washed three times with ethanol and DI water. The product is taken finally after 12 hours vacuum drying. VS_2 cathode: VS_2 synthesized by the method above is well-mixed with super P and 8% polyvinylidene difluoride (PVDF) following the weight ratio of 8: 1: 1. The mixture is added 1-methyl-2-pyrrolidinone (NMP, Macklin, 98%) and stirred overnight. Ti foil is coated with the mixture and used as cathode after 12 hours vacuum drying at 80°C .

1.3 Electrochemical measurements

The cell performance of galvanostatic charge/discharge cycles is tested by Neware battery system. The $\text{Zn}||\text{Zn}$ symmetric cells are cycled with current densities of 1, 5, 40 mA cm^{-2} and area capacities of 1, 2, 25 mAh cm^{-2} . The $\text{Zn}||\text{VS}_2$ full cell is cycled in the voltage range of 0.3-1.0 V. $\text{Zn}||\text{Cu}$ asymmetric cells are used for 50% DOD test and discharge profile of Zn nucleation overpotential. Tafel plot, Linear sweep voltammetry (LSV), Cyclic voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS) are investigated by Princeton P4000 electrochemical workstation. Generally, the three-electrode system is used for electrochemical measurement equipped with Pt as counter electrode and Ag/AgCl as reference electrode. Tafel plot is tested using a three-electrode system with a scan rate of 1 mV s^{-1} (Work electrode: Zn). CV and LSV test are carried out with a three-electrode system with a scan rate of 5 mV s^{-1} (Working electrode: SS). The EIS at different temperature is employed by testing $\text{Zn}||\text{Zn}$ symmetric cell with a scan range from 10^5 to 0.1 Hz. The ionic conductivity is gained by calculating the EIS data of $\text{SS}||\text{SS}$ symmetric cell at room temperature obeying the following equation:[1]

$$\sigma = \frac{Z'^2}{Z'^2 + Z''^2} \cdot \frac{l}{A}$$

where σ , l and A represent ionic conductivity, the distance between two electrodes and the area of the separator, respectively. Z' and Z'' are the real and imaginary components of the impedance, respectively.

1.4 Characterizations

X-ray diffraction (XRD) patterns are detected by a Rigaku SmartLab X-ray diffractometer using Cu $K\alpha$ radiation. Scanning electron microscope (SEM) images are observed by a Zeiss Merlin microscope for scanning the sample surface. NMR measurements are performed on an AVANCE III 400 MHz spectrometer. For NMR analysis, D_2O is used in place of H_2O ; FA, AA, and PA denote the corresponding salt-free amide/ D_2O mixtures, whereas ZFA, ZAA, and ZPA contain ZnSO_4 with otherwise identical compositions to their respective electrolytes. Fourier Transform Infrared (FT-IR) Spectrometer (Bruker VERTEX 70) is used for IR analysis. Electrolyte pH is measured at room temperature using a PHS-3C pH meter. Contact angles on Zn foil are measured using a DSA20 contact-angle goniometer. Optical images are taken by a FHD camera on the sample surface.

1.5 Theoretical calculations

Molecular dynamics (MD) simulations are conducted using GROMACS [2]. The initial configurations are generated with Packmol [3]. Zn^{2+} , SO_4^{2-} , and water molecules are described using the Amber99SB force field, whereas the parameters of FA, AA, and PA are generated with Sobtop based on GAFF2 [4]. Atomic charges of the additives are obtained via RESP fitting using Multiwfn [5]. Each amide-containing system comprised 100 Zn^{2+} , 100 SO_4^{2-} , 5550 H_2O , and 200 additive molecules, while the additive-free ZnSO_4 electrolyte is employed as the reference. Periodic boundary conditions are applied in all directions. Electrostatic interactions are treated with the particle mesh Ewald method, and van der Waals interactions are truncated at 1.6 nm. After energy minimization and successive NVT/NPT equilibration, production

simulations are performed for RDF and coordination-number analyses.

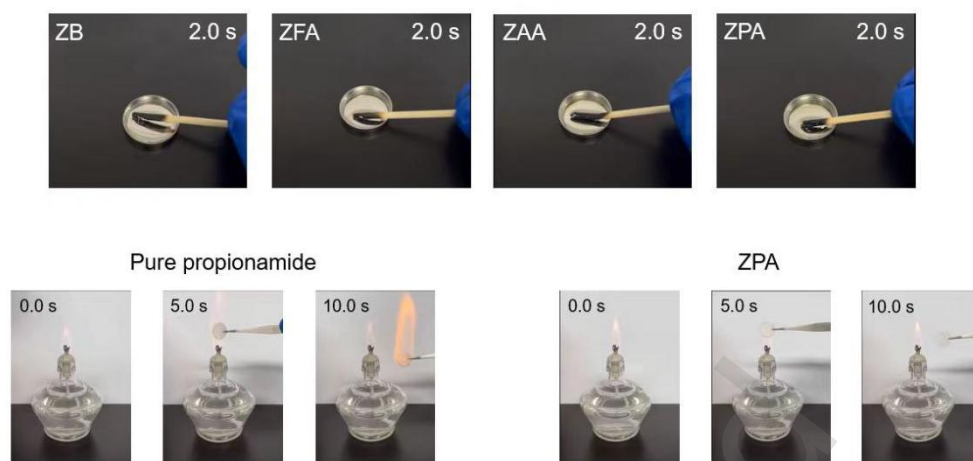


Fig. S1 Flammability testing of different hybrid electrolytes and amides.

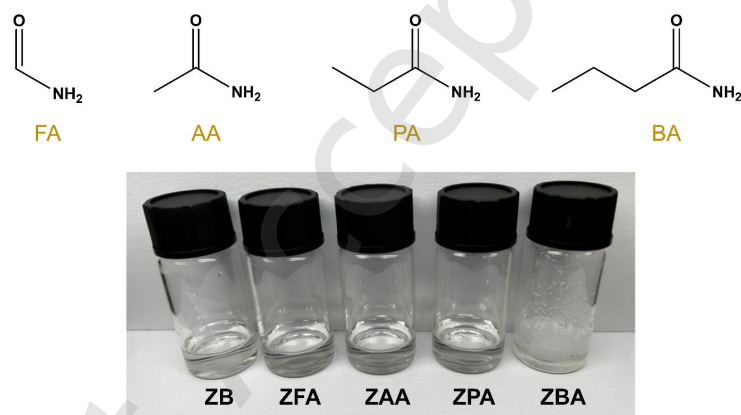


Fig. S2 Photographs of electrolytes with different amides after standing for one month.

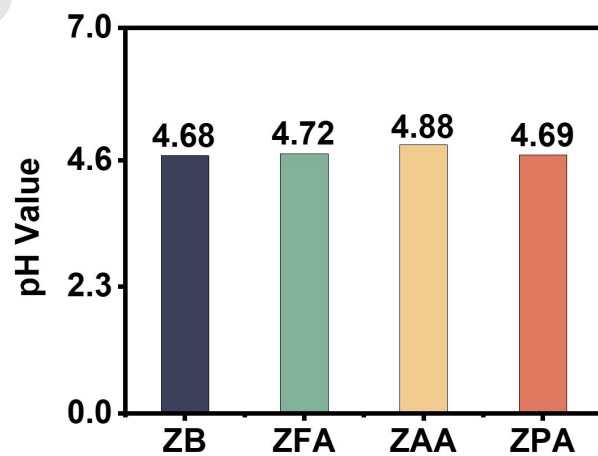


Fig. S3 The pH values with different electrolytes at room temperature.

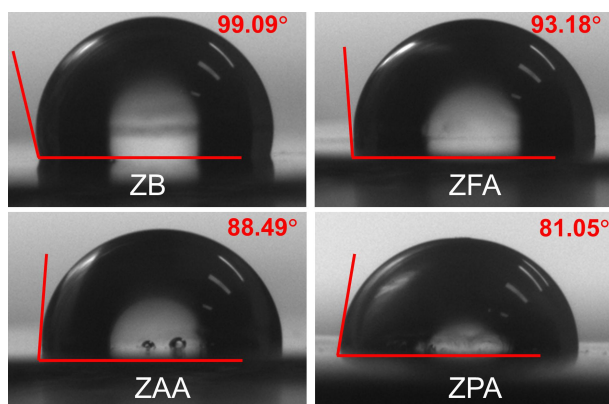


Fig. S4 Contact angle test with different electrolytes on zinc foil.

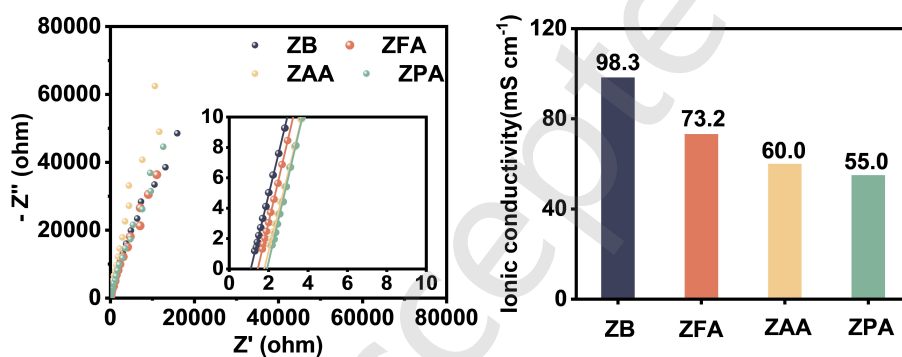


Fig. S5 Ionic conductivity of different electrolytes.

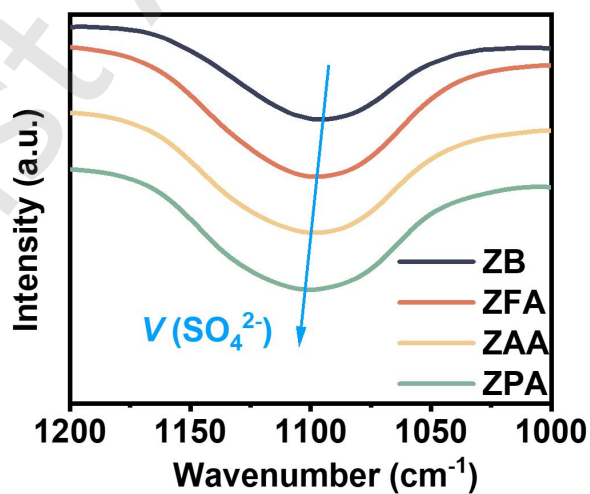


Fig. S6 FTIR of ZFA, ZAA, ZPA and ZB electrolytes.

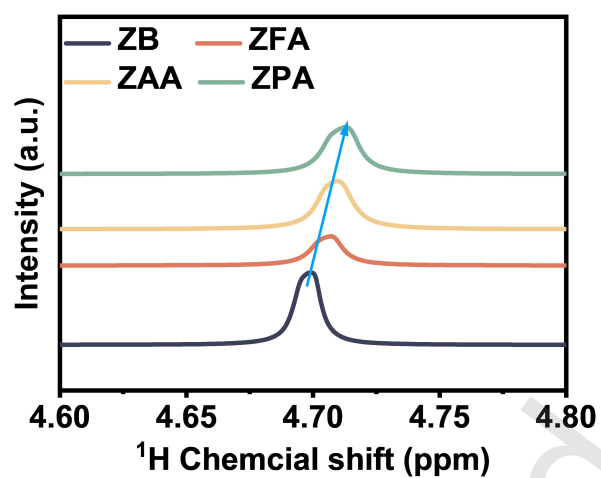


Fig. S7 ^1H NMR spectra of ZFA, ZAA, ZPA and ZB electrolytes.

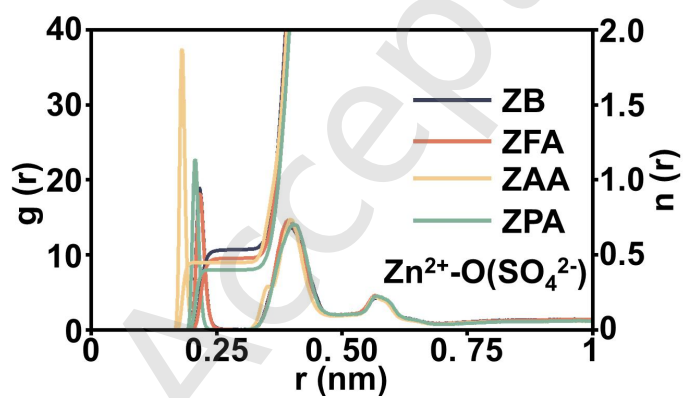


Fig. S8 Radial distribution functions and coordination numbers for $\text{Zn}^{2+}\text{-O}(\text{SO}_4^{2-})$ computed from molecular dynamics simulations.

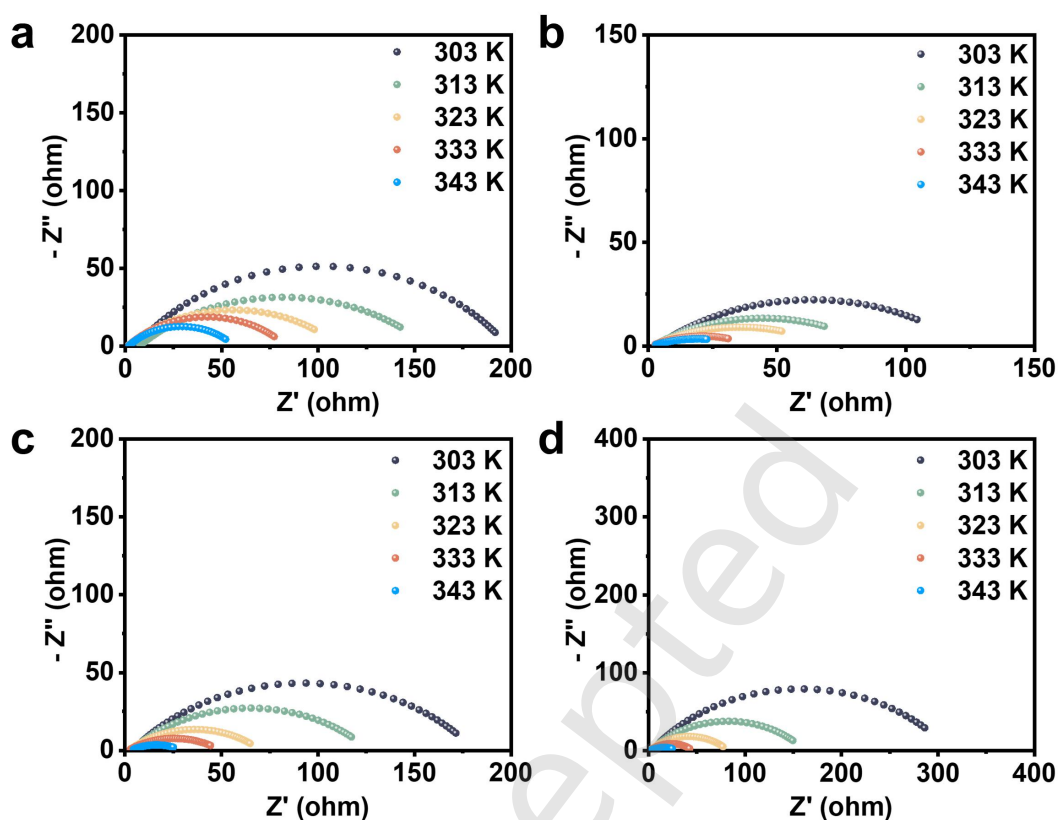


Fig. S9 EIS measurements at different temperatures from 30 to 70°C for different electrolytes: (a) ZB; (b) ZFA; (c) ZAA and (d) ZPA.

The parameter R_{ct} represents the interfacial charge-transfer resistance and reflects the kinetic barrier associated with the desolvation of Zn^{2+} . Its value is obtained from the diameter of the characteristic semicircle in the electrochemical impedance spectrum. The determination of the activation energy (E_a) is achieved through the application of the Arrhenius equation, as delineated below:[6]

$$\frac{1}{R_{ct}} = A \exp\left(\frac{-E_a}{RT}\right)$$

Where A , R , T respectively correspond to Arrhenius constant, gas constant and Kelvin temperature.

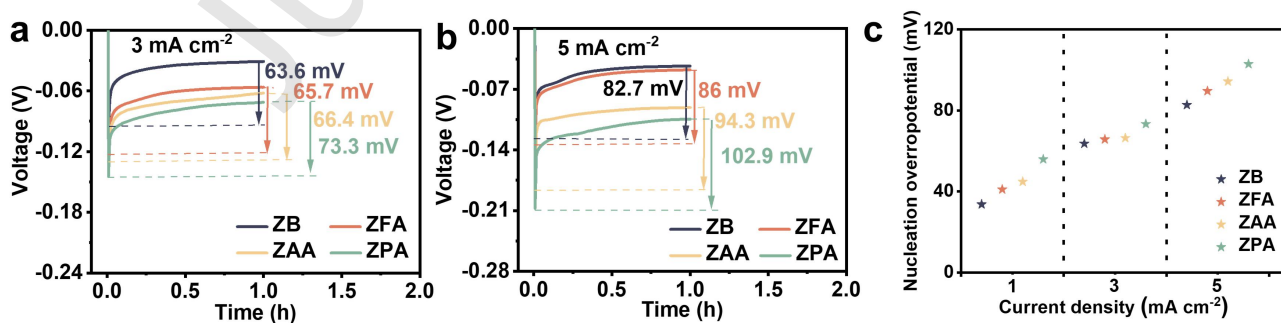


Fig. S10 Galvanostatic discharge profile of Zn||Cu half cells with different electrolytes at (a) 3 mA cm⁻² and (b) 5 mA cm⁻². (c) Statistical analysis of nucleation overpotential with different electrolytes at varying current densities.

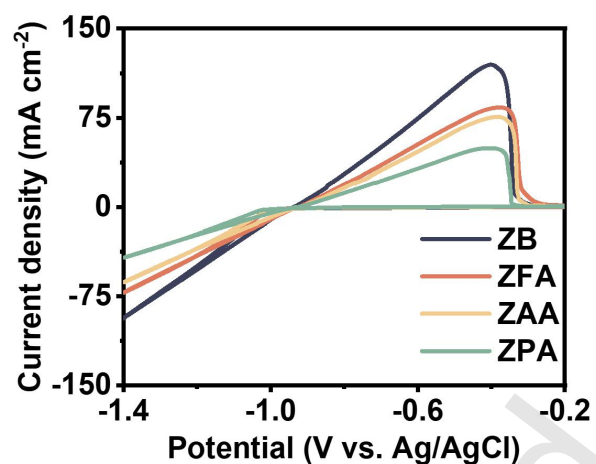


Fig. S11 Cyclic voltammetry plots with different electrolytes.

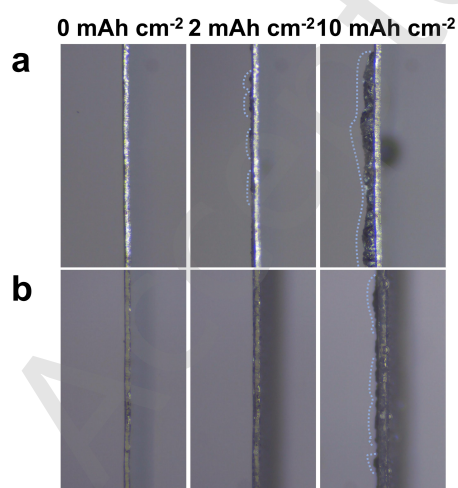


Fig. S12 Optical images of Zn deposition at 5 mA cm⁻² on Zn current collector with (a) ZFA and (b) ZAA electrolytes.

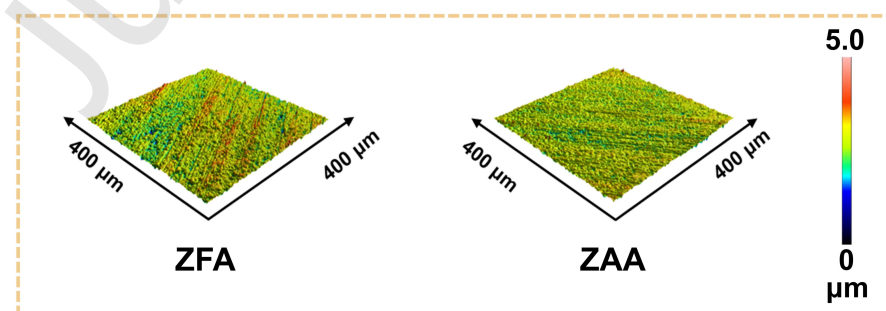


Fig. S13 Topographic images of Zn foils after immersed for 24 hours with different electrolytes.

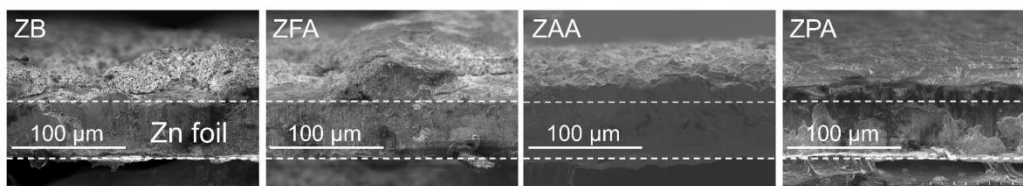


Fig. S14 Cross sectional SEM images of Zn deposition after 10 cycles of Zn||Zn symmetrical cell with different electrolytes.

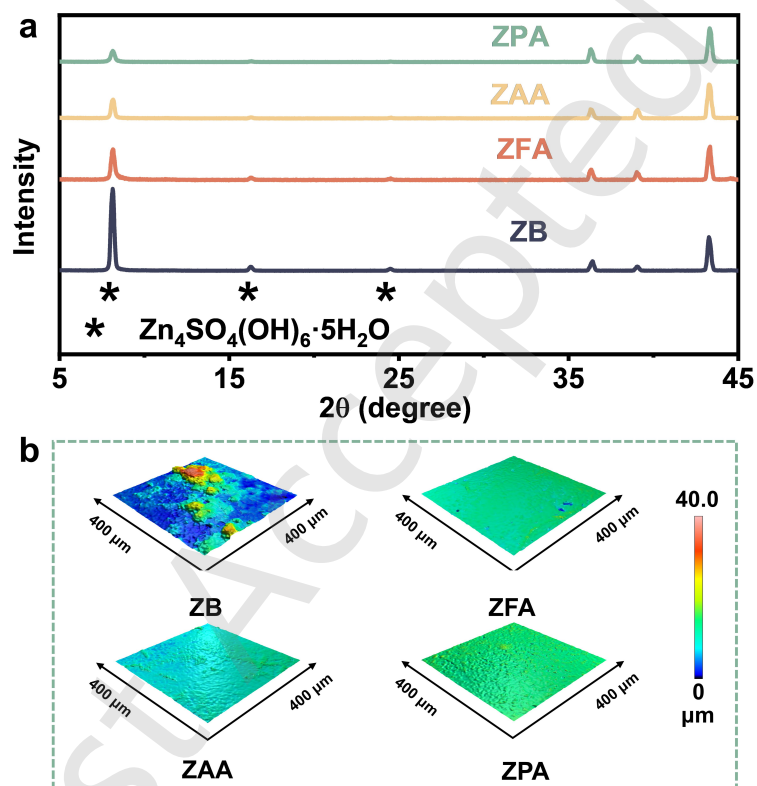


Fig. S15 (a) XRD patterns of Zn anodes after 10 cycles of Zn||Zn symmetrical cell with different electrolytes. (b) Topographic images of Zn foils after 10 cycles with different electrolytes.

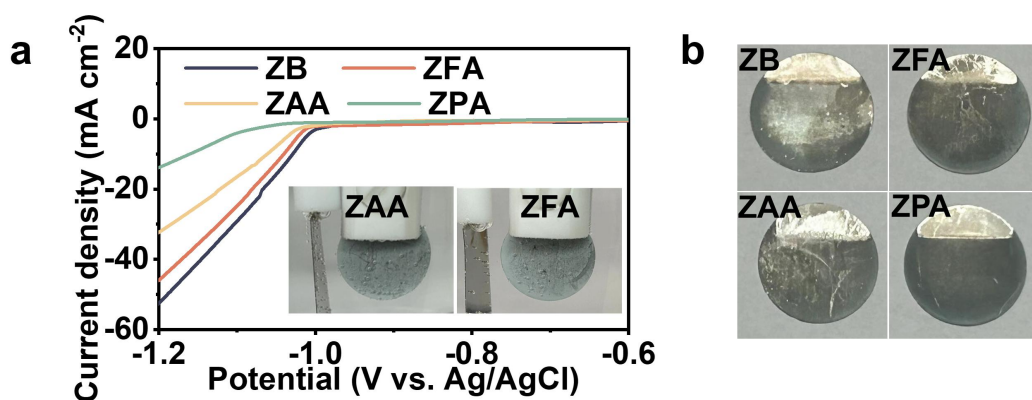


Fig. S16 (a) LSV test with different electrolytes at 5 mV s^{-1} . (b) Optical images of Zn foils after LSV test with different electrolytes.

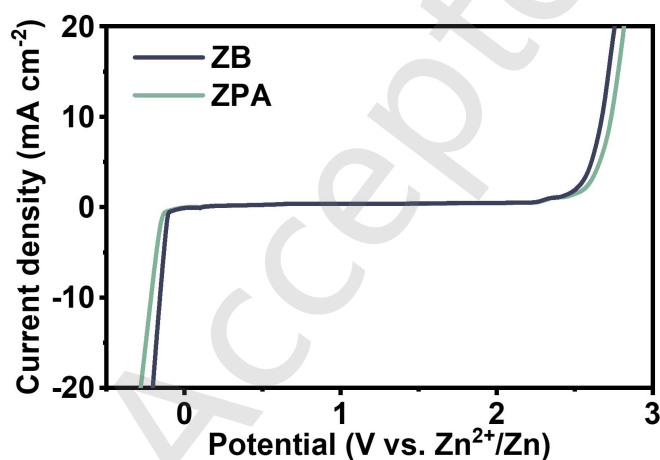


Fig. S17 Electrochemical stability windows of different electrolytes.

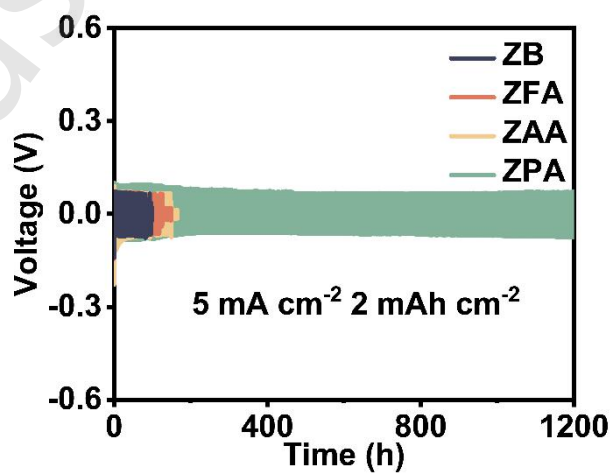


Fig. S18 Galvanostatic Zn deposition/stripping of Zn||Zn symmetrical cell at a current density of 5 mA cm^{-2} and a capacity of 2 mAh cm^{-2} .

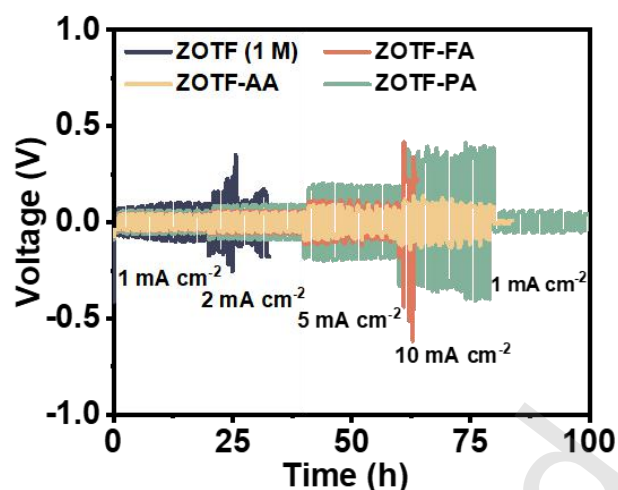


Fig. S19 Rate performance of Zn||Zn symmetric cells using Zn(OTf)₂-based ZB, ZFA, ZAA, and ZPA electrolytes at current densities ranging from 1 to 10 mA cm⁻².

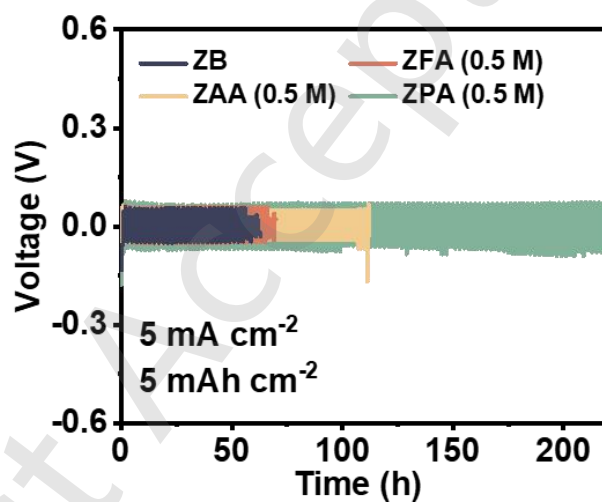


Fig. S20 Galvanostatic Zn deposition/stripping of Zn||Zn symmetrical cell with 0.5 M electrolyte additives (FA, AA, and PA) at a current density of 5 mA cm⁻² and a capacity of 5 mAh cm⁻².



Fig. S21 Electrolytes after resting at -10°C for 24 h.

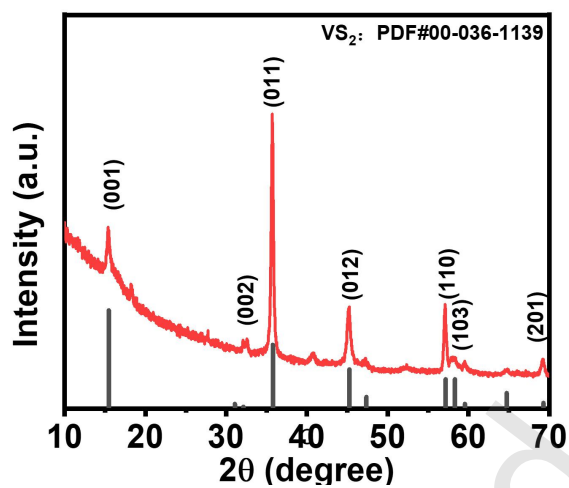


Fig. S22 XRD pattern of the as-synthesized VS₂.

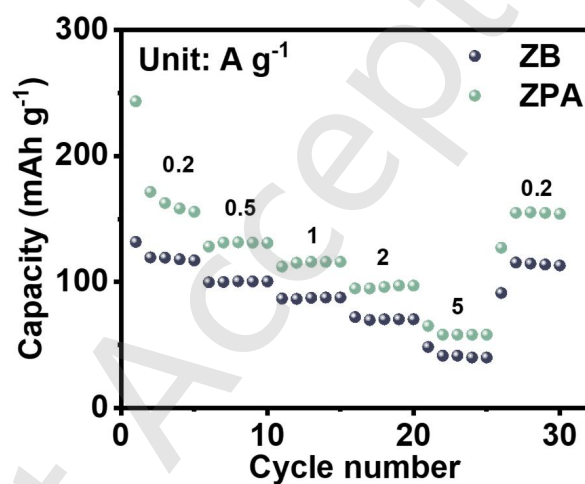


Fig. S23 The rate performance of Zn||VS₂ full cell with different electrolytes.

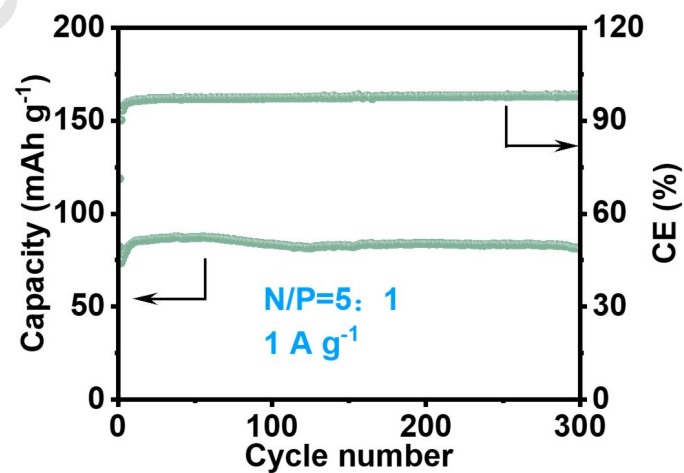


Fig. S24 Cycling performance of the Zn||VS₂ full cell in ZPA electrolyte with an N/P ratio of 5:1.

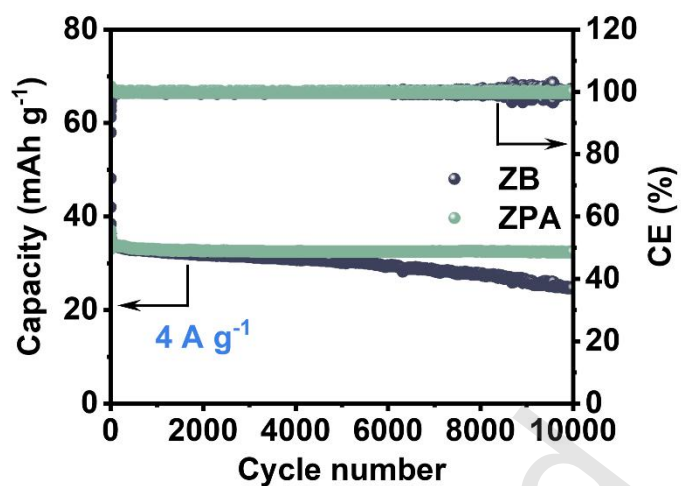


Fig. S25 Cycling performance of the Zn||AC full cell at a current density of 4 A g^{-1} .

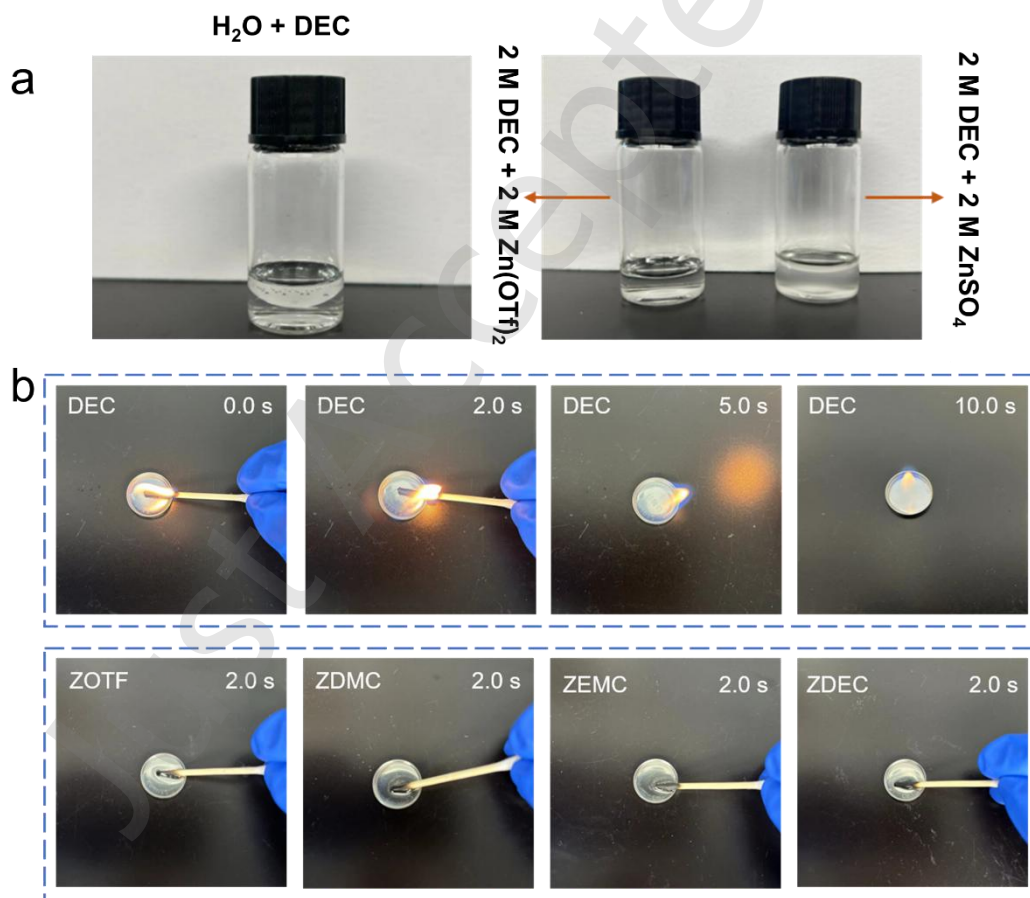


Fig. S26 (a) Optical images of the electrolyte at room temperature. (b) Flammability tests of DEC and different electrolytes.

Table S1. Comparison of cumulative capacities of Zn batteries reported in different studies.

Electrolyte	Current density (mA cm ⁻²)	depth of discharge	Cumulative Plated Capacity (Ah cm ⁻²)	Ref.
2 M ZnSO ₄ + 2 mM KTPP	20	32%	7.2	[7]
2 M Zn(OTf) ₂ + DMF	57.4	70%	27	[8]
2 M ZnSO ₄ + 20 v/v% Acetone	50	73.5%	40	[9]
2 M Zn(OTf) ₂ + 5 vol% TEP	10	17%	11.07	[10]
2 M ZnSO ₄ + 2 wt% DMU (N,N-Dimethylurea)	3.51	60%	36.62	[11]
2 M ZnSO ₄ + 10 mM HAM (2-(4-Imidazolyl)ethylamine)	1	17.1%	14.64	[12]
2 M ZnSO ₄ + 0.025 M Hmim (2-methylimidazole)	8	13.6%	2.08	[13]
2 M ZnSO ₄ + 2 wt% 15-CR-5 (15-crown-5 ether)	20	42.7%	2.4	[14]
2 M ZnSO ₄ + 10% sorbitol	5	85.4%	0.75	[15]
2 M Zn(OTf) ₂ + C10 (3-(decyldimethylammonio)propanesulfonate salt)	5	42.7%	0.129	[16]
2 M ZnSO ₄ + 30 mM allantoin	5	10.4%	1.425	[17]
2 M ZnSO ₄ + 0.2 M SADS (disodium succinate)	5	71%	2.5	[18]
1 M Zn(OTf) ₂ + 75 vol% DMI (1,3-dimethyl-2-imidazolidinone)	5	17.5%	3.55	[19]
2 M ZnSO ₄ + 0.005 M ADH (adipic dihydrazide)	1	-	2.4	[20]
2 M ZnSO ₄ + 0.8 mg mL ⁻¹ FCDs (functionalized carbon dots)	0.5	-	3.2	[21]
0.8 M Zn(OAc) ₂ + 2.5 M Ba(OAc) ₂	0.25	-	0.7	[22]
1 M ZnSO ₄ + 2 M propionamide	40	75.8%	39.2	This work

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