



Ester-mediated self-evolving electrolyte enables low-temperature aqueous zinc-ion batteries

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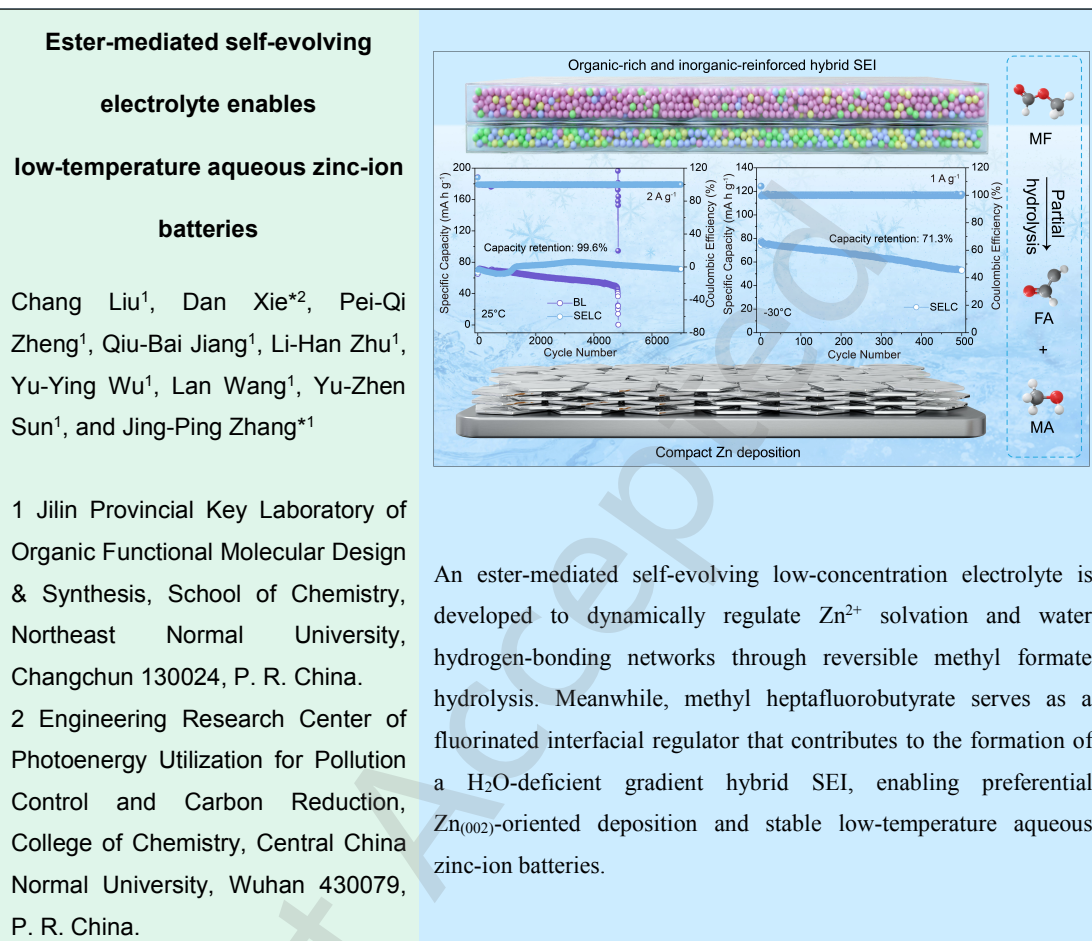
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An ester-mediated self-evolving low-concentration electrolyte is developed to dynamically regulate Zn^{2+} solvation and water hydrogen-bonding networks through reversible methyl formate hydrolysis. Meanwhile, methyl heptafluorobutyrate serves as a fluorinated interfacial regulator that contributes to the formation of a H_2O -deficient gradient hybrid SEI, enabling preferential $\text{Zn}_{(002)}$ -oriented deposition and stable low-temperature aqueous zinc-ion batteries.

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Abstract

The failure of low-concentration electrolytes in low-temperature aqueous zinc-ion batteries arises from the abundance of H₂O molecules that facilitate electrolyte freezing and induce sluggish ion transport and interfacial reaction kinetics, resulting in uneven Zn deposition and dendrite growth. Herein, we propose an ester-mediated self-evolving low-concentration electrolyte (SELC) developed through the incorporation of methyl formate (MF) and methyl heptafluorobutyrate (MH) into 1 M Zn(OTf)₂ aqueous solution. As a chemically transformable co-solvent, MF undergoes partial hydrolysis to generate formic acid and methanol in situ, which reorganize the hydrogen-bonding network of H₂O molecules, diversify Zn²⁺ coordination environments, and maintain efficient ion transport under subzero conditions. Meanwhile, MH serves as a fluorinated interfacial regulator that preferentially accumulates at the Zn interface and contributes to the formation of a H₂O-deficient organic-rich and inorganic-reinforced gradient solid electrolyte interphase, thereby suppressing side reactions and dendrite growth. Benefiting from the synergistic regulation of Zn²⁺ solvation and interfacial chemistry, the SELC electrolyte induces preferential Zn deposition along the (002) crystal plane. Consequently, Zn||Zn symmetric cells achieve stable cycling for 3800 h at room temperature, 2200 h at -30 °C, and 300 h at -50 °C, respectively, demonstrating outstanding wide-temperature adaptability. Zn||polyaniline (PANI) full cells deliver 99.6% of their initial capacity after 7000 cycles, while pouch cells maintain 81.0% capacity retention after 1200 cycles.

Keywords: self-evolving electrolyte, low-concentration electrolyte, solvation chemistry, interfacial reaction kinetics, low-temperature zinc-ion batteries

1. Introduction

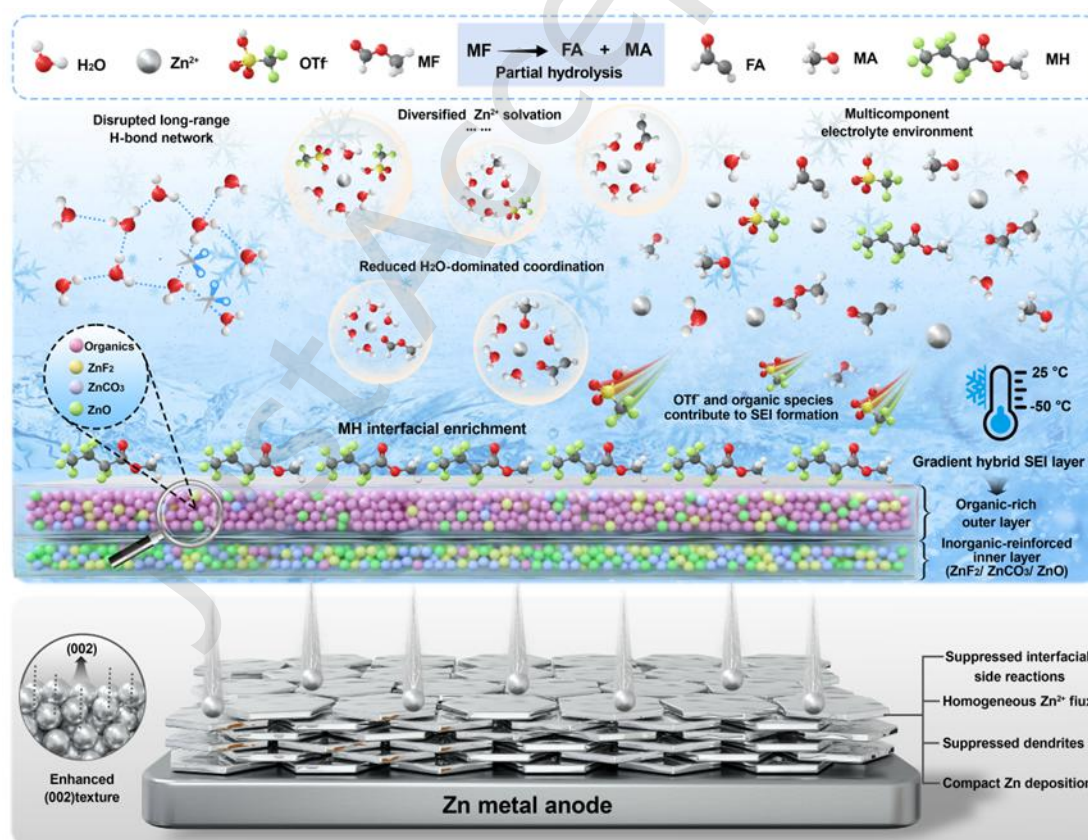
Aqueous zinc-ion batteries (AZIBs) are promising candidates for safe and cost-effective electrochemical energy storage, yet their operation under low-temperature conditions remains fundamentally limited by the strong temperature dependence of aqueous electrolyte chemistry [1-7]. The failure of low-temperature AZIBs is not merely associated with electrolyte freezing, but arises from the simultaneous deterioration of bulk electrolyte dynamics and interfacial stability [8,9]. As temperature drops, hydrogen-bonding networks among H₂O molecules becomes increasingly ordered, leading to increased viscosity, sluggish ion transport, and even electrolyte solidification [10-12]. Meanwhile, strong hydration of Zn²⁺ increases the desolvation barrier at the electrode/electrolyte interface (EEI), while interfacial H₂O molecules participate in hydrogen evolution reactions (HER), anode corrosion, and insulating by-product formation [13-15]. These detrimental processes continuously reconstruct the interfacial microenvironment, increase charge-transfer resistance, and induce uneven Zn nucleation and dendritic growth, which collectively leads to large polarization and compromise the reversibility of the Zn anode [16-18].

To mitigate these challenges, electrolyte engineering strategies such as organic co-solvents [19-21], functional additives [22-24], highly concentrated [25,26], and localized high-concentration electrolytes [27,28], have been extensively explored to regulate Zn²⁺ solvation, suppress H₂O activity, and stabilize the EEI. Organic co-solvents can partially reconstruct hydrogen-bonding network among H₂O molecules and improve anti-freezing capacity, whereas many of them mainly regulate the bulk electrolyte environment and lack programmable interfacial decomposition chemistry for constructing a durable Zn-protective interphase. Functional additives can modify the electric double layer (EDL) or passivate the Zn anode surface, but their low dosage often limits the ability to globally reconstruct the bulk H-bond network and suppress freezing. Highly concentrated and localized high-concentration

electrolytes can effectively reduce water activity, promote anion participation in Zn^{2+} solvation, and facilitate the formation of inorganic-rich interphases. However, these benefits are frequently accompanied by increased viscosity, sluggish ion transport, reduced wettability, and high salt cost. By comparison, low-concentration aqueous electrolytes are more attractive regarding fluidity, ionic conductivity, and scalability, but the abundance of free H_2O molecules makes them vulnerable to freezing and sluggish ion transport and interfacial reaction kinetics [29,30]. A core challenge is therefore how to endow a low-concentration electrolyte with both H_2O -regulating ability and interfacial stability typically associated with concentrated electrolytes while preserving fast ion transport under subzero conditions.

Herein, we propose an ester-mediated self-evolving low-concentration electrolyte (SELC) for low-temperature AZIBs. Specifically, the electrolyte is constructed by incorporating methyl formate (MF) as a chemically transformable co-solvent and methyl heptafluorobutyrate (MH) as a fluorinated interfacial regulator into a low-concentration $\text{Zn}(\text{OTf})_2$ aqueous electrolyte. Unlike conventional co-solvents that primarily act as anti-freezing agents, MF undergoes controlled partial hydrolysis to generate formic acid (FA) and methanol (MA) in situ. This molecular evolution not only increases the number of electrolyte components and diversifies Zn^{2+} coordination environments, but also disrupts the long-range hydrogen-bonding network among H_2O molecules and preserves unblocked ion transport under subzero conditions. Meanwhile, MH remains chemically stable against hydrolysis in the bulk electrolyte but preferentially enriches at the Zn interface owing to its strong affinity toward Zn and favorable reduction tendency under electric field. Together with anion- and organic-derived decomposition species, MH contributes to the formation of a H_2O -deficient organic-rich and inorganic-reinforced gradient hybrid solid electrolyte interphase (SEI). The resulting gradient organic-inorganic hybrid SEI suppresses corrosion reactions and induces preferential Zn deposition along the (002) crystal

plane, effectively inhibiting dendrite formation (**Scheme 1**). Benefiting from this synergistic regulation of bulk solvation and interfacial chemistry, the Zn||Zn symmetric cell employing the SELC electrolyte achieves a long cycle life of 3800 h at $1 \text{ mA} \cdot \text{cm}^{-2}$ and $0.5 \text{ mAh} \cdot \text{cm}^{-2}$ at room temperature. Remarkably, even at -30°C and -50°C , the Zn||Zn symmetric cells assembled with SELC electrolyte can stably cycle for 2200 h and 300 h, respectively. The Zn||polyaniline (PANI) full cell using SELC electrolyte maintains a high capacity retention of 99.6% after 7000 cycles at room temperature. The assembled Zn||PANI pouch cell still retains 81.0% of its capacity after 1200 cycles. This work demonstrates the potential of ester-mediated self-evolving electrolytes for next-generation low-temperature aqueous batteries.



Scheme 1 Schematic illustration of the bulk-phase and interfacial regulation mechanisms of the SELC electrolyte.

2. Results and discussion

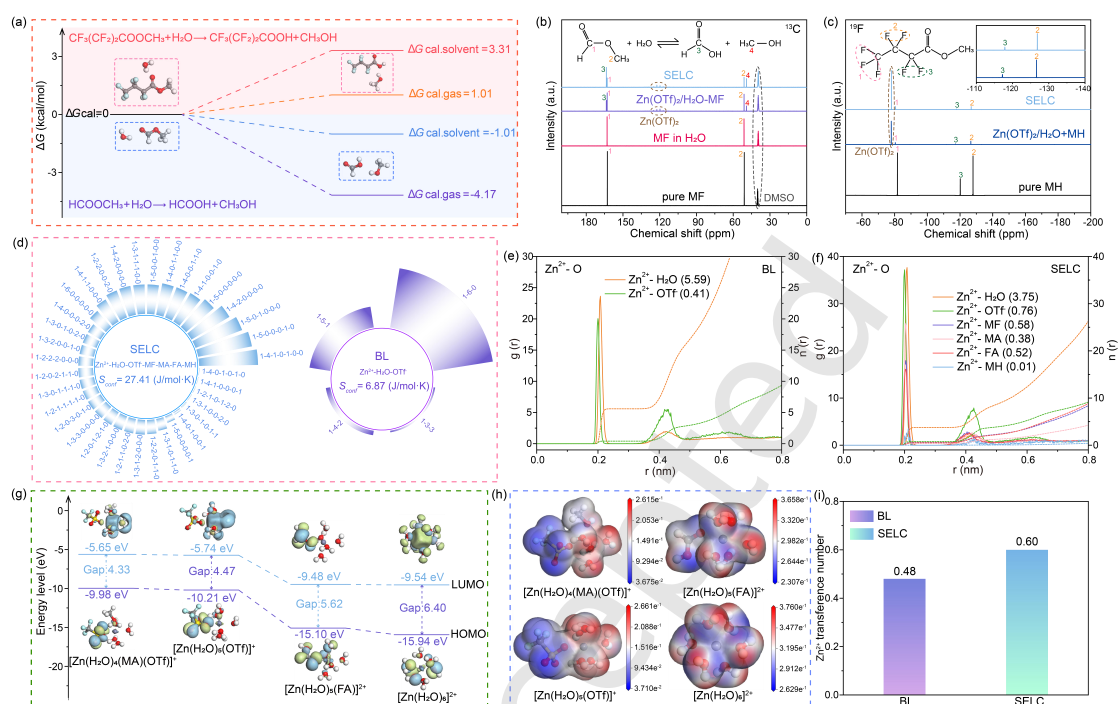


Figure 1 (a) ΔG value (gas and solvent phase) of the hydrolysis reaction of MF and MH. (b) ¹³C NMR spectra of pure MF, MF in H₂O, Zn(OTf)₂ in H₂O+MF, and SELC. (c) ¹⁹F NMR spectra of pure MH, MH in BL, and SELC. (d) Statistical comparison of the distribution proportions of different solvation structures in the SELC (left) and BL (right) electrolytes, along with their corresponding configurational entropy values. RDF and ACN calculated from MD simulations in the (e) BL and (f) SELC electrolytes. (g) Frontier molecular orbital energy and (h) electrostatic potential mapping of main solvation structure of Zn²⁺ in the BL and SELC electrolytes. (i) Zn²⁺ transference number in different electrolytes.

The design principle of the SELC electrolyte relies on the differentiated chemical functions of two ester molecules incorporated into a low-concentration Zn(OTf)₂ aqueous electrolyte. MF was selected as a chemically transformable co-solvent because its ester bond can undergo partial hydrolysis in the aqueous environment, generating additional small molecular species that participate in Zn²⁺ solvation regulation and hydrogen-bond network reconstruction. In contrast, MH was introduced as a fluorinated interfacial regulator because its highly fluorinated alkyl chain is expected to enhance affinity toward the Zn surface and provides fluorinated

components upon preferential interfacial decomposition, while maintaining chemical stability against hydrolysis in the bulk electrolyte. To evaluate the intrinsic hydrolysis tendencies of MF and MH, density functional theory (DFT) calculations were first performed to compare the Gibbs free energy changes associated with their hydrolysis reactions in both gas and solution phases (**Fig. 1(a)**). The calculated results indicate that MF exhibits a substantially higher thermodynamic tendency toward hydrolysis, producing FA and MA, whereas MH maintains much greater resistance to hydrolysis. These results provide the theoretical basis for assigning MF as the dynamically evolving component and MH as the bulk-stable fluorinated interfacial regulator. The chemical evolution of MF in the aqueous $\text{Zn}(\text{OTf})_2$ environment was subsequently verified by nuclear magnetic resonance (NMR) spectroscopy. As shown in **Fig. 1(b)**, when MF is introduced into pure H_2O , the characteristic MF signals remain unchanged without the appearance of additional peaks, indicating negligible hydrolysis under these conditions. After adding $\text{Zn}(\text{OTf})_2$, new carbon signals corresponding to FA (peak 3) and MA (peak 4) emerge, accompanied by a decrease in the intensity of the original MF signals (peaks 1 and 2), demonstrating that $\text{Zn}(\text{OTf})_2$ contributes to MF hydrolysis. Upon further incorporation of MH into the system, the signals assigned to FA and MA become further intensified, while the MF signals continue to decrease, suggesting that MH promotes the continued evolution of MF by modifying the local chemical environment. These results reveal a synergistic effect between $\text{Zn}(\text{OTf})_2$ and MH in accelerating the dynamic conversion of MF. To further quantify this chemical evolution, quantitative ^1H NMR measurements were performed using maleic acid as an internal standard. The MF hydrolysis degree is approximately 46.9% in the freshly prepared SELC electrolyte, indicating that partial hydrolysis has already occurred upon electrolyte preparation. After 7 days of storage and 10 cycles in a $\text{Zn}||\text{Zn}$ symmetric cell, the hydrolysis degree increases only slightly to 49.1% and 52.3%, respectively (**Fig. S1 and Table S1**). Notably, although MF hydrolysis

continues during storage and electrochemical cycling, the hydrolysis degree increases only modestly from 46.9% to 52.3%, indicating that the electrolyte composition remains relatively stable while undergoing gradual chemical evolution. These results reveal substantial yet incomplete MF hydrolysis followed by slow compositional evolution, indicating that the electrolyte maintains a relatively stable overall composition while retaining its self-evolving character. In comparison with the continuous evolution of MF, ^{19}F NMR spectra show no new characteristic peaks associated with MH-derived hydrolysis products in different electrolytes, verifying the excellent chemical stability of MH under the investigated bulk conditions (**Fig. 1(c)**). Therefore, the SELC can be regarded as a dynamically evolving multicomponent system, in which MF-derived FA and MA, together with H_2O , MF, OTf, and MH, collectively reconstruct the Zn^{2+} solvation environment and regulate interfacial chemistry.

Molecular dynamics (MD) simulations were conducted to examine how the chemically evolved multicomponent environment reconstructs the Zn^{2+} solvation configurations. The experimentally quantified ratio of MF to FA to MA was adopted as the input composition for MD simulations to ensure that the calculated solvation environment reflects the real electrolyte state. Compared with the baseline (BL) electrolyte, in which the primary solvation shell of Zn^{2+} is predominantly occupied by H_2O molecules, the SELC electrolyte exhibits a much more diversified solvation landscape. Statistical analysis reveals that the SELC electrolyte contains 36 distinct Zn^{2+} solvation configurations, whereas only 4 configurations are observed in the BL electrolyte (**Figs. 1(d) and S2**). Accordingly, the calculated configurational entropy increases from 6.87 to 27.41 $\text{J mol}^{-1} \text{K}^{-1}$ after chemical evolution, further confirming the enhanced structural diversity of the solvation environment. The specific coordination environment of Zn^{2+} was investigated by the radial distribution function (RDF) and average coordination number (ACN). As illustrated in **Fig. 1(e)**, the

primary solvation shell of Zn^{2+} in the BL electrolyte is dominated by H_2O molecules, while most OTf^- anions remain in a free state. And the corresponding ACN of $\text{Zn}^{2+}\text{-H}_2\text{O}$ and $\text{Zn}^{2+}\text{-OTf}^-$ are 5.59 and 0.41, respectively, indicating a typical H_2O -dominated solvation structure. By contrast, in the SELC electrolyte, the hydration number of Zn^{2+} decreases markedly to 3.75, while the ACNs of $\text{Zn}^{2+}\text{-MF}$, $\text{Zn}^{2+}\text{-FA}$, and $\text{Zn}^{2+}\text{-MA}$ are 0.58, 0.52, and 0.38, respectively, verifying that MF, FA, and MA molecules competitively coordinate with Zn^{2+} and partially replace H_2O molecules in the primary solvation sheath (**Fig. 1(f)**). Notably, the ACN of $\text{Zn}^{2+}\text{-MH}$ is extremely low (0.01), indicating that MH barely enters into the solvation structure of Zn^{2+} . Meanwhile, the ACN of $\text{Zn}^{2+}\text{-OTf}^-$ increases to 0.78, suggesting enhanced anion involvement in the Zn^{2+} solvation shell. Such an anion-participating solvation structure is expected to promote OTf-derived interfacial decomposition, thereby contributing to the formation of a hybrid SEI with enriched inorganic components and improved mechanical robustness [31,32]. Furthermore, compared with room temperature, the ACN of $\text{Zn}^{2+}\text{-H}_2\text{O}$ is slightly reduced at both -30 and -50 °C, while the coordination contribution from organic components is correspondingly increased, indicating enhanced participation of organic molecules in the primary Zn^{2+} solvation environment at low temperatures. Notably, the coordination environment of Zn^{2+} and overall solvation structures at -30 and -50 °C are highly comparable, suggesting that the Zn^{2+} solvation sheath in the SELC electrolyte remains structurally stable, which may contribute to maintaining consistent interfacial Zn^{2+} transport behavior under subzero conditions (**Figs. S3-S4**). To investigate the impact of reconstructed solvation structure on interfacial charge transfer process, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels were calculated for the two most dominant solvation structures in both the BL and SELC electrolytes. As shown in **Fig. 1(g)**, the $[\text{Zn}(\text{H}_2\text{O})_4(\text{MA})(\text{OTf})]^+$ and $[\text{Zn}(\text{H}_2\text{O})_5(\text{FA})]^{2+}$ in the SELC electrolyte exhibit a smaller HOMO-LUMO gap compared to the

$[\text{Zn}(\text{H}_2\text{O})_5(\text{OTf})]^+$ and $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ in the BL electrolyte, indicating more favorable electron transfer and contributing to the involvement of OTf and organic solvents in the construction of a functional SEI [33,34]. In addition, we simulated the charge distribution surrounding the four primary solvation structures (**Fig. 1(h)**). The results reveal that the surface electrostatic potentials of $[\text{Zn}(\text{H}_2\text{O})_4(\text{MA})(\text{OTf})]^+$ and $[\text{Zn}(\text{H}_2\text{O})_5(\text{FA})]^{2+}$ are generally lower than those of $[\text{Zn}(\text{H}_2\text{O})_5(\text{OTf})]^+$ and $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$. This weakened electrostatic environment around Zn^{2+} helps mitigate electrostatic repulsion and accelerates Zn^{2+} migration within the electrolyte system [35]. This conclusion is further supported by Zn^{2+} transference number measurements (**Figs. 1(i) and S5**). As exhibited, the Zn^{2+} transference number in the SELC electrolyte reaches 0.60, higher than the 0.48 in the BL electrolyte, demonstrating enhanced Zn^{2+} transport ability in the self-evolving electrolyte, which is advantageous for reducing concentration polarization during Zn plating and stripping.

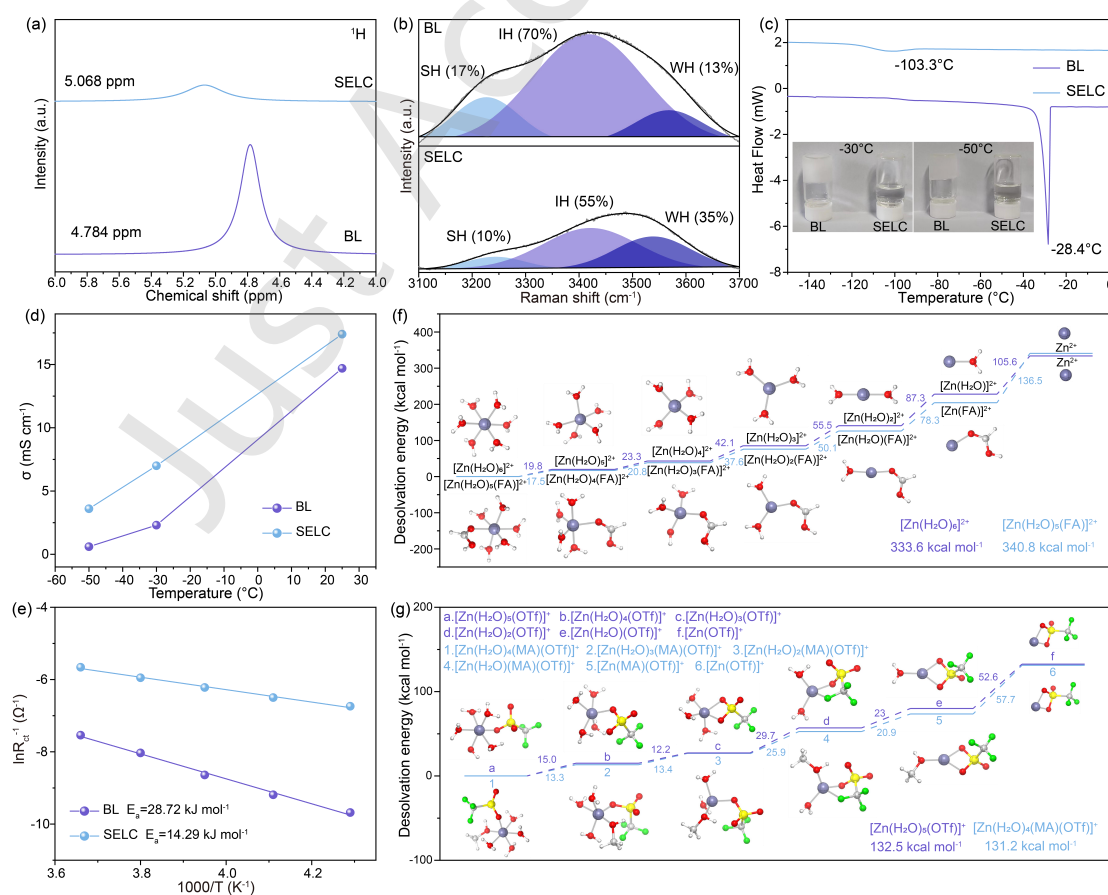


Figure 2 (a) ^1H NMR spectra of BL and SELC electrolytes. (b) Raman spectra of BL and SELC electrolytes. (c) The DSC curves of different electrolytes. The inset shows the digital images of the BL and SELC electrolytes stored at $-30\text{ }^\circ\text{C}$ and $-50\text{ }^\circ\text{C}$ for 12 h. (d) Ionic conductivity of BL and SELC electrolytes at different temperatures. (e) Arrhenius curves along with the corresponding activation energies in various electrolytes. (f-g) Diagrams of the energy barriers during the step-by-step de-solvation process of $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$, $[\text{Zn}(\text{H}_2\text{O})_5(\text{FA})]^{2+}$, $[\text{Zn}(\text{H}_2\text{O})_5(\text{OTf})]^+$ and $[\text{Zn}(\text{H}_2\text{O})_4(\text{MA})(\text{OTf})]^+$.

The reconstructed solvation environment also regulates the hydrogen-bonding network of H_2O molecules. As shown in **Fig. 2(a)**, compared with the ^1H resonance of H_2O molecules in the BL electrolyte at 4.784 ppm, the corresponding peak in the SELC electrolyte shifts downfield to 5.068 ppm, indicating an enhanced deshielding effect of the H_2O protons. This shift signifies a reconstructed local hydrogen-bonding environment rather than merely enhanced H_2O - H_2O interactions, which can be attributed to the introduction of organic molecules that disrupt the continuous intermolecular interactions among H_2O molecules while establishing new H_2O -organic hydrogen-bonding interactions [36]. This interpretation is further supported by calculating average number of hydrogen bonds in the two electrolyte systems using MD simulations. As displayed in **Fig. S6**, the average number of H_2O - H_2O hydrogen bonds in the SELC electrolyte is significantly lower than that in the BL electrolyte, whereas the number of hydrogen bonds between H_2O and organic molecules (H_2O -FA, H_2O -MH, H_2O -MA, and H_2O -MF) increases accordingly, indicating that the introduced organic components effectively break the continuous H_2O - H_2O hydrogen-bonding network. The reorganization of the H_2O hydrogen-bonding network in the SELC electrolyte primarily originates from stronger intermolecular interactions between H_2O and the organic components compared with those among H_2O molecules themselves, which provides a thermodynamic driving force for the formation of H_2O -organic hydrogen bonds (**Fig. S7**). Raman spectroscopy was subsequently conducted to experimentally analyze the O-H stretching vibrations of H_2O molecules in both electrolytes (**Fig. 2(b)**). Generally, the

broad band ranging from 3100 to 3700 cm^{-1} can be deconvoluted into three sub-peaks corresponding to distinct hydrogen-bonding states: strong hydrogen bonding (SH), intermediate hydrogen bonding (IH), and weak hydrogen bonding (WH) [37,38]. Quantitative analysis of the integrated peak areas shows that, compared with the BL electrolyte, the proportion of SH in the SELC electrolyte decreases from 17% to 10%, whereas the WH fraction increases substantially from 13% to 35%. This result confirms that the SELC electrolyte effectively disrupts the original hydrogen-bonding network among H_2O molecules, transforming ordered H_2O clusters into more disordered and loosely associated structures, which is beneficial for improving the anti-freezing capability of the electrolyte. This conclusion is verified by differential scanning calorimetry (DSC). As displayed in **Fig. 2(c)**, the BL electrolyte exhibits a sharp exothermic peak at $-28.4\text{ }^{\circ}\text{C}$, corresponding to electrolyte crystallization. In contrast, no obvious crystallization peak appears in the SELC electrolyte, while a glass transition is observed at approximately $-103.3\text{ }^{\circ}\text{C}$. Furthermore, after being stored at -30 and $-50\text{ }^{\circ}\text{C}$ for 12 h, the BL electrolyte solidifies, whereas the SELC electrolyte remains in a liquid state, further corroborating its superior resistance against electrolyte freezing. It is worth noting that the reconstructed solvation structure and suppressed crystallization contribute to improved ion transport. As exhibited in **Figs. 2(d) and S8**, the ionic conductivity of the SELC electrolyte is consistently higher than that of the BL electrolyte from 25 to $-50\text{ }^{\circ}\text{C}$, indicating that the SELC electrolyte maintains effective ion-conducting pathways even under deeply subzero conditions.

Although rapid bulk ion transport ensures sufficient ion flux toward the electrode surface, the subsequent desolvation process largely determines the interfacial reaction kinetics at the EEI. Accordingly, the activation energies (E_a) derived from Arrhenius plots were used to evaluate the Zn^{2+} transport kinetics at the interface [39,40]. As depicted in **Figs. 2(e) and S9**, the E_a value of the SELC electrolyte is 14.29 kJ mol^{-1} ,

markedly lower than that of the BL electrolyte ($28.72 \text{ kJ mol}^{-1}$), revealing enhanced Zn^{2+} desolvation ability and accelerated interfacial charge transfer, which are favorable for achieving uniform Zn deposition. To gain deeper insight into the desolvation process, the stepwise desolvation energy barriers of the two dominant Zn^{2+} solvation structures in both electrolytes were calculated by DFT (**Figs. 2(f) and 2(g)**). The results show that the energy required to release coordinated H_2O molecules from the Zn^{2+} solvation structure in the SELC electrolyte is generally lower than that in the BL electrolyte. This reduction can be attributed to the incorporation of organic ligands (FA/MA), which competitively coordinate with Zn^{2+} and redistribute the local solvation environment, thereby weakening the electrostatic interactions between Zn^{2+} and solvated H_2O molecules. Notably, the removal of organic molecules demands a higher energy barrier than the removal of H_2O molecules due to their stronger coordination with Zn^{2+} . This result suggests that Zn^{2+} tends to approach the Zn anode surface together with coordinated organic ligands, which is conducive to the formation of an organic-rich SEI layer.

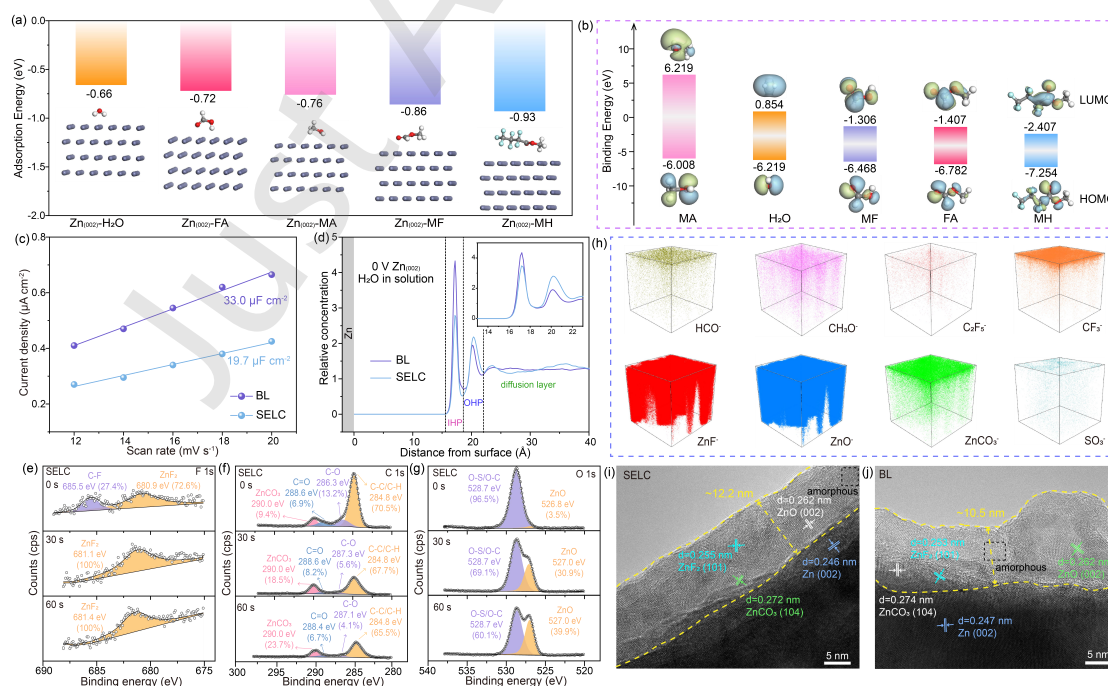


Figure 3 (a) Adsorption energy of H_2O , FA, MA, MF and MH molecules on $\text{Zn}_{(002)}$

crystal plane. (b) HOMO and LUMO energy levels of MA, H₂O, MF, FA and MH molecules. (c) Double layer capacitance at Zn anode surface in the BL and SELC electrolytes. (d) Density profiles of H₂O molecules as a function of the distance from the Zn anode in the BL and SELC electrolytes at 0 V. In-depth XPS spectra of (e) F 1s, (f) C 1s, and (g) O 1s of cycled Zn anode in the SELC electrolyte. (h) 3D render overlay for elements of TOF-SIMS for the SELC electrolyte. HRTEM images of Zn anode after cycling in the (i) SELC and (j) BL electrolytes.

It is generally accepted that the stability of the Zn anode is closely associated not only with the bulk solvation environment but also with the chemical properties of the EEI. In aqueous electrolytes, the decomposition of active H₂O molecules at the interface inevitably triggers side reactions and destroys interfacial stability [41]. Therefore, constructing a H₂O-poor interfacial environment is critical for stabilizing the EEI. On the basis of this consideration, DFT calculations were first performed to evaluate the adsorption energies of different electrolyte components on the Zn₍₀₀₂₎ crystal plane. As shown in **Fig. 3(a)**, the adsorption energies of the organic components are significantly more negative than that of H₂O molecules, representing their stronger interactions with the Zn anode and their tendency to construct a H₂O-poor and zincophilic organic adsorption layer. Among these components, MH exhibits the strongest affinity toward the Zn anode, signifying that MH preferentially occupies active sites on the Zn surface and participates in reductive decomposition. Subsequently, the reduction tendency of different species in the SELC electrolyte was evaluated by calculating their frontier molecular orbital energy levels. As displayed in **Fig. 3(b)**, the LUMO energy level of MH is significantly lower than those of the other molecules, indicating that MH is more susceptible to accept electrons and undergo preferential interfacial reduction at the Zn anode surface, which contributes to forming an organic-rich and inorganic-reinforced hybrid SEI [42]. To experimentally verify this preferential reduction tendency, comparative LSV measurements were further performed on Ti electrodes using the Zn(OTf)₂ -50%MF electrolyte with and without MH. As shown in **Fig. S10**, the SELC electrolyte exhibits a more pronounced cathodic current response. At a representative potential of 0.10 V, the current density

changes from approximately -2.12 mA cm^{-2} for the $\text{Zn}(\text{OTf})_2$ -50%MF electrolyte to -2.26 mA cm^{-2} for the SELC electrolyte. The enhanced cathodic current response after the introduction of MH indicates a promoted interfacial reduction process, which is consistent with the calculated lower LUMO energy of MH and further supports its preferential reduction tendency at the EEI [43]. Furthermore, the decreased EDL capacitance reveals an increased effective EDL thickness, further supporting the preferential adsorption of zincophilic organic molecules at the anode surface (**Figs. 3(c) and S11**). Owing to the enhanced electrode/electrolyte interfacial affinity induced by the H_2O -poor and zincophilic organic adsorption layer, the SELC electrolyte exhibits a much smaller contact angle of 12.59° than that of the BL electrolyte (83.79°), indicative of improved electrolyte wettability and a more homogeneous interfacial ion distribution (**Fig. S12**). To further elucidate the microstructure of the EDL in the two electrolytes, MD simulations were employed to reveal the spatial distribution of electrolyte components near the anode surface under applied potentials of 0, +1.5, and -1.5 V (**Figs. 3(d) and S13-S15**). The cross-sectional snapshots and density distribution profiles show that the proportion of H_2O molecules in the inner Helmholtz plane (IHP) of the SELC electrolyte is substantially lower than that in the BL electrolyte under all investigated potentials, which is advantageous for suppressing H_2O -induced side reactions and maintaining EEI stability. Notably, the relative concentrations of organic molecules (FA, MF, MH, and MA) near the SELC electrolyte interface are significantly higher than those of H_2O and OTf^- , demonstrating pronounced enrichment of organic components within the IHP driven by their stronger affinity toward the Zn surface. Such an organic-enriched EDL structure favors the construction of an organic-rich and inorganic-reinforced hybrid SEI with high flexibility and robustness through their preferential reduction decomposition, thereby more effectively isolating the Zn anode from active H_2O molecules and promoting homogeneous Zn^{2+} flux.

X-ray photoelectron spectroscopy (XPS) with Ar⁺ sputtering was performed to determine the chemical distribution and spatial configuration of SEI. As shown in the F 1s spectra, before sputtering, the proportion of C-F peaks in the SELC electrolyte (27.4%) is higher than that in the BL electrolyte (16.5%), which originates from the preferential adsorption of MH on the anode surface (**Figs. 3(e) and S16(a)**). The C 1s and O 1s spectra demonstrate that the proportions of organic species such as C-C/C-H, C-O, C=O, and O-S/O-C in the SELC electrolyte are significantly higher than those in the BL electrolyte throughout the sputtering process, resulting from the co-adsorption and preferential interfacial decomposition of organic molecules (**Figs. 3(f-g) and S16(b-c)**). Notably, the content of inorganic components gradually increases with prolonging sputtering depth, suggesting their progressive enrichment toward the deeper region of the SEI. Although the signal intensities of organic components decrease as the sputtering time increases, they remain detectable throughout the etching process, revealing a continuous compositional gradient across the SEI. To further elucidate the spatial distribution of the SEI components, three-dimensional time-of-flight secondary ion mass spectrometry (TOF-SIMS) was performed on the cycled Zn anode in the SELC electrolyte. The organic/fluorocarbon-related fragments, including HCO⁻, CHO⁻, C₂F₅⁻, and CF₃⁻, and inorganic-related fragments, including ZnF⁻, ZnO⁻, ZnCO₃⁻, and SO₃⁻, exhibit distinct spatial distributions across the interphase, further supporting the gradient composition of the SEI (**Fig. 3(h)**). High-resolution transmission electron microscopy (HRTEM) further reveals distinct interfacial morphologies for Zn anodes cycled in the two electrolytes. The SELC-derived SEI forms a relatively continuous and uniform interphase along the Zn surface, with a thickness of approximately 12.2 nm (**Fig. 3(i)**). Lattice fringes assigned to ZnF₂, ZnO, and ZnCO₃ can be identified within the interphase, confirming the incorporation of multiple inorganic components. In contrast, the BL-derived SEI exhibits a markedly nonuniform and irregular morphology with pronounced local

thickness variations (**Fig. 3(j)**). These results confirm that the SELC electrolyte induces the formation of a continuous gradient organic-inorganic hybrid SEI, which not only serves as a physical barrier against dendrite penetration and prevents direct corrosion of the Zn anode by the bulk electrolyte, but also accommodates mechanical stress and regulates interfacial Zn^{2+} flux, thereby enhancing the long-term stability of the EEI [44].

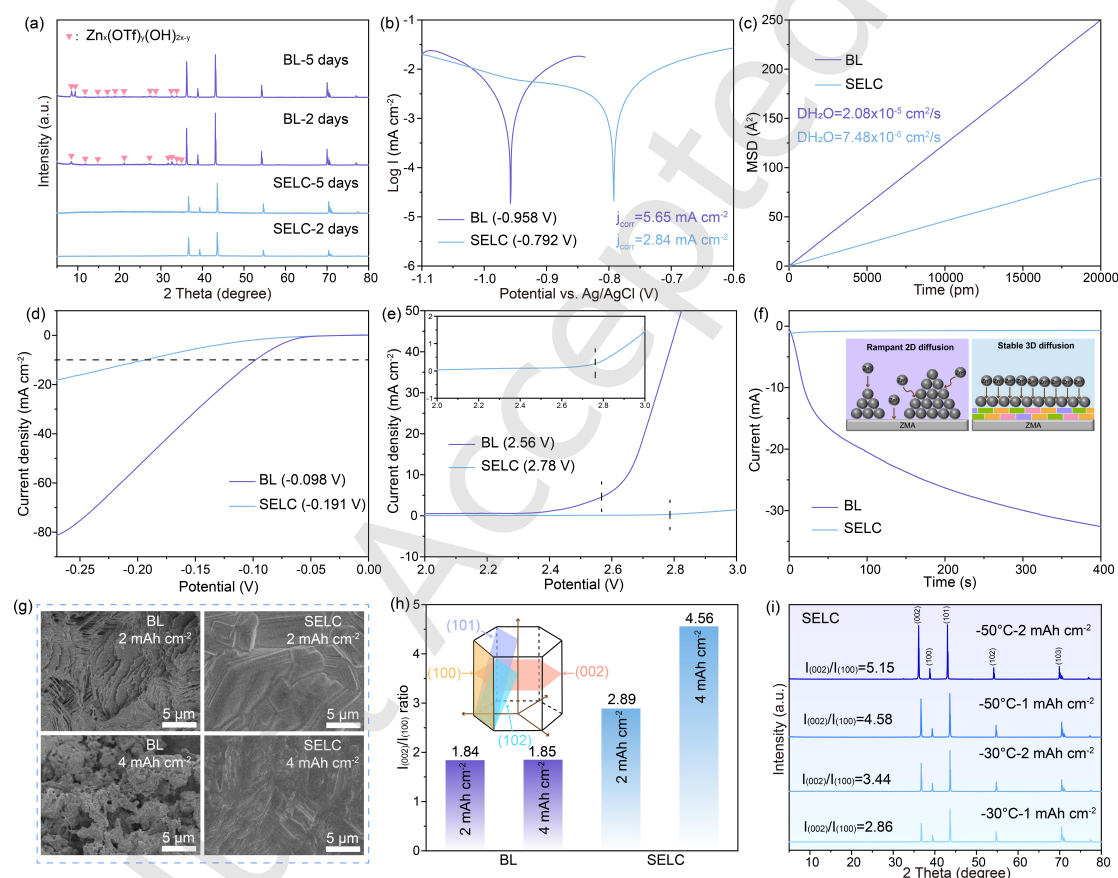


Figure 4 (a) XRD patterns of Zn foil after immersing in the BL and SELC electrolytes for 2 and 5 days. (b) Tafel curves of Zn anode in different electrolytes. (c) Diffusion coefficients of H_2O molecules in various electrolyte simulated by MD. (d) HER and (e) LSV curves of Zn anode in the BL and SELC electrolytes. (f) CA curves of Zn anode in the BL and SELC electrolytes. (g) SEM images of Zn deposits in the BL and SELC electrolytes at a current density of 1 mA cm^{-2} and a deposition capacity of 2 and 4 mAh cm^{-2} . (h) I_{002}/I_{100} peak intensity of Zn deposits in the BL and SELC electrolytes. (i) XRD patterns of Zn deposits in the SELC electrolytes at -30 °C and -50 °C.

Because the construction of a H_2O -deficient interfacial environment and gradient

SEI on the anode surface can effectively shield the Zn anode from active H₂O molecules, the corrosion resistance of the Zn anode is markedly improved. Before immersion, the Zn foils in both groups exhibit relatively smooth surfaces, providing a comparable initial morphological (**Figs. S17(a) and S17(d)**). As shown in **Figs. S17(b) and S17(c)**, after immersion in the BL electrolyte for 2 days, the Zn foil surface is covered with numerous dendrite-like corrosion products. With prolonged immersion for 5 days, these protrusions become larger and sharper. The corresponding X-ray diffraction (XRD) patterns reveal distinct characteristic peaks assigned to $\text{Zn}_x(\text{OTf})_y(\text{OH})_{2x-y}$, indicating the formation of corrosion by-products (**Fig. 4(a)**). In contrast, the Zn foil immersed in the SELC electrolyte consistently maintains a smooth and compact morphology without detectable diffraction peaks from corrosion by-products, confirming the enhanced corrosion resistance of the Zn anode in the SELC electrolyte (**Figs. S17(e) and S17(f)**). Given that acidic conditions are generally known to promote HER kinetics, time-resolved pH measurements were conducted during both storage and Zn||Zn symmetric cells cycling to clarify the relationship between bulk electrolyte acidity and interfacial parasitic reactions. As shown in **Figs. S18 and S19(a)**, the pH of the BL electrolyte remains essentially unchanged during 48 h of storage but gradually increases from 5.17 to 5.44 during cycling. This increase is attributed to the generation and accumulation of OH⁻ through parasitic interfacial reactions, which may subsequently induce the precipitation of hydroxyl-containing Zn salts. In contrast, the apparent pH of the SELC electrolyte is close to 0.00 throughout both storage and cycling (**Figs. S18 and S19(b)**). This stable value indicates that the reversible hydrolysis of MF establishes a highly acidic equilibrium state, which is conducive to neutralizing locally generated OH⁻, thereby limiting its accumulation and the subsequent precipitation of hydroxyl-containing corrosion products. Although the low bulk pH increases the thermodynamic driving force for HER, the actual rates of HER and corrosion are also governed by the

accessibility and activity of interfacial H₂O/proton species, interfacial charge-transfer kinetics, and the properties of the SEI. In the SELC electrolyte, preferential adsorption of organic species, reduced H₂O mobility, and the formation of a protective gradient SEI collectively establish an H₂O-deficient interfacial environment that kinetically suppresses these parasitic reactions. These interfacial kinetic effects surpass the thermodynamic tendency associated with the acidic bulk electrolyte, thereby reconciling the low apparent pH with the experimentally observed improvements in corrosion resistance and interfacial stability. The inhibitory effect of the SELC electrolyte on Zn corrosion was further quantified by Tafel polarization measurements. As illustrated in **Fig. 4(b)**, compared with the BL electrolyte, the SELC electrolyte shifts the corrosion potential positively from -0.958 to -0.792 V and reduces the corrosion current density from 5.65 to 2.84 mA cm⁻², demonstrating reduced corrosion tendency and suppressed corrosion kinetics. Meanwhile, the diffusion coefficient of H₂O molecules in the SELC electrolyte is 7.48×10^{-6} cm² s⁻¹, much lower than that in the BL electrolyte (2.08×10^{-5} cm² s⁻¹), suggesting restricted H₂O mobility and reduced transport of active H₂O molecules toward the electrode interface (**Fig. 4(c)**). In addition, compared with the BL electrolyte, the SELC electrolyte presents a more negative HER potential (-0.191 vs. -0.098 V) and a higher oxygen evolution reaction overpotential (2.78 vs. 2.56 V) (**Figs. 4(d) and 4(e)**), further evidencing the kinetic suppression of H₂O-induced side reactions.

Generally, Zn dendrite formation originates from uncontrolled nucleation and excessive growth [45]. Therefore, in addition to corrosion inhibition, the regulation of Zn nucleation and growth behavior by the SELC electrolyte is also critical. To investigate the initial nucleation behavior, voltage-capacity profiles during Zn²⁺ deposition were collected (**Fig. S20**). As shown, the SELC electrolyte (73 mV) exhibits a higher nucleation overpotential than the BL electrolyte (54 mV). Such a moderately increased nucleation overpotential is favorable for reducing the nucleation

radius and increasing the nucleation density, thereby facilitating uniform and compact Zn deposition without dendrite formation [46]. The nucleation behavior and deposition mode of Zn^{2+} were further investigated by chronoamperometry (CA) under an applied potential of -150 mV (**Fig. 4(f)**). In the BL electrolyte, the current density of the Zn anode continuously increases within 400 s, corresponding to typical two-dimensional diffusion behavior, in which Zn^{2+} tends to diffuse along the surface and accumulate at energetically favorable protrusion sites, thereby inducing dendrite growth. In contrast, the current response in the SELC electrolyte rapidly stabilizes within only 10 s. This behavior indicates that the H_2O -deficient interfacial environment and gradient SEI inhibit lateral two-dimensional diffusion while promoting three-dimensional diffusion-controlled nucleation, thereby ensuring a homogeneous Zn^{2+} flux throughout the deposition process and suppressing dendrite formation. Ex situ SEM observations further confirm the distinct Zn deposition morphologies in the two electrolytes. As depicted in **Fig. 4(g)**, in the BL electrolyte, the Zn anode surface exhibits vertically aligned flake-like structures at a deposition capacity of 2 mAh cm^{-2} . When the deposition capacity increases to 4 mAh cm^{-2} , these structures become increasingly aggregated, posing a high risk of separator puncture. By contrast, Zn deposits formed in the SELC electrolyte consistently maintain a dense and smooth surface. To uncover the crystallographic origin of this compact morphology, the evolution of Zn crystal facets was monitored by XRD at different areal capacities. As shown in **Figs. 4(h) and S21**, the $I_{(002)}/I_{(100)}$ intensity ratio in the SELC electrolyte is consistently higher than that in the BL electrolyte. Notably, as the deposition capacity increases from 2 to 4 mAh cm^{-2} , the $I_{(002)}/I_{(100)}$ ratio in the SELC electrolyte increases markedly from 2.89 to 4.56, whereas that in the BL electrolyte shows only a negligible increase of 0.01. These results demonstrate that the synergistic regulation of bulk solvation and interfacial chemistry not only suppresses H_2O decomposition on the anode surface but also favors Zn deposition with

preferential (002) orientation, thereby simultaneously mitigating side reactions and impeding dendrite growth. Furthermore, the Zn deposition behavior in the SELC electrolyte at low temperatures was investigated. After deposition at -30 °C, the Zn anode surface presents an ordered morphology composed of hexagonally aligned platelets. When the temperature is further reduced to -50 °C, the Zn deposits become more compact and flatter (**Fig. S22**). The corresponding XRD patterns reveal that, with decreasing temperature, the $I_{(002)}/I_{(100)}$ ratio increases markedly without detectable by-product formation (**Fig. 4(i)**). This enhanced $Zn_{(002)}$ preferential orientation is probably attributed to the coupled effects of increased nucleation barriers, regulated ion transport, and stabilized interfacial chemistry enabled by the H_2O -deficient environment and gradient SEI, which collectively promote low-surface-energy $Zn_{(002)}$ -oriented deposition, enabling uniform Zn growth and stabilizing the Zn anode over a wide temperature range.

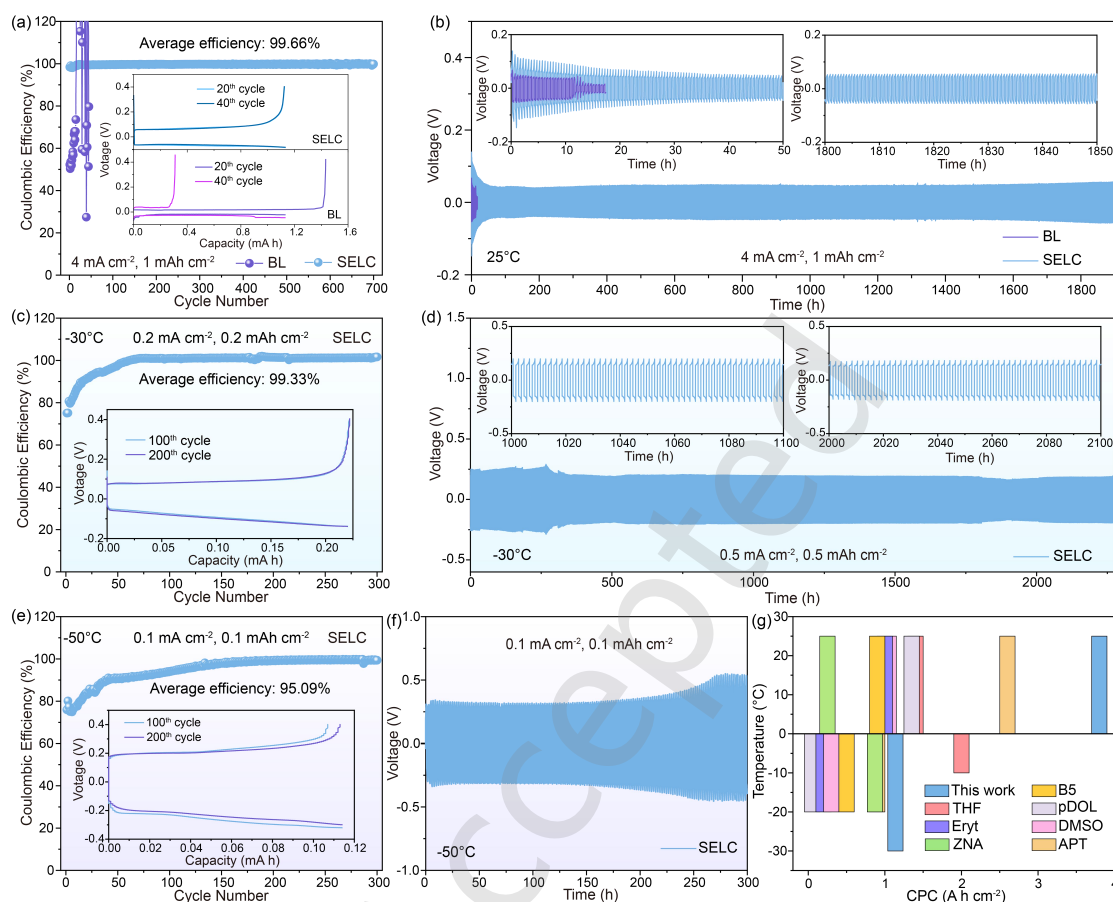


Figure 5 (a) The CE of the BL and SELC electrolytes at 4 mA cm⁻², 1 mAh cm⁻². The inset shows the voltage profiles of Zn plating/stripping at different cycles. (b) Cycling performance of Zn||Zn symmetric cells in the BL and SELC electrolytes at 4 mA cm⁻², 1 mAh cm⁻². (c) The CE of Zn||Cu asymmetrical cells and (d) the long-term cycling performance of Zn||Zn symmetric cells in the SELC electrolyte at -30 °C. (e) The CE of Zn||Cu asymmetrical cells and (f) the long-term cycling performance of Zn||Zn symmetric cells in the SELC electrolyte at -50 °C. (g) Performance comparison of Zn||Zn symmetric cells in this work with the previously reported research.

Through systematic optimization of the MF/H₂O ratio and MH content, together with comparative tests using the complete-hydrolysis products and non-hydrolyzable co-solvent control electrolytes, the optimal SELC electrolyte formulation and its composition-specific electrochemical advantages were established (**Figs. S23-S24**). Subsequently, Zn||Cu asymmetric cells were assembled to evaluate the reversibility of the Zn anode in different electrolytes. Benefiting from the enhanced stability of the EEI and the suppressed activity of H₂O molecules in the SELC electrolyte, the

assembled Zn||Cu asymmetric cells exhibit outstanding reversibility. As shown in **Fig. S25**, the Zn||Cu asymmetric cell using the BL electrolyte suffers from severe corrosion and dendrite formation, leading to large CE fluctuations and rapid failure after only 30 cycles. In contrast, the Zn||Cu asymmetric cell with the SELC electrolyte maintains a high average CE of 99.54% for 1050 cycles at 2 mA cm^{-2} with a capacity of 1 mAh cm^{-2} , demonstrating highly reversible Zn plating/stripping behavior. Even at a higher current density of 4 mA cm^{-2} , the SELC-based cell sustains a superior average CE of 99.66% for up to 700 cycles (**Fig. 5(a)**). Representative capacity-voltage profiles indicate that the BL-based cells exhibit pronounced voltage fluctuations at both tested current densities. In contrast, the SELC-based cells display highly reproducible voltage-capacity profile over cycling, further confirming the enhanced Zn plating/stripping reversibility and interfacial stability afforded by the SELC electrolyte. Encouraged by the high reversibility observed in asymmetric cells, the long-term cycling stability of the Zn anode was evaluated using Zn||Zn symmetric cells. As illustrated in **Fig. S26**, the Zn||Zn symmetric cell with the BL electrolyte exhibits a sudden increase in polarization voltage after only 187 h of cycling at 1 mA cm^{-2} and 0.5 mAh cm^{-2} , which is associated with severe interfacial degradation induced by H_2O -related parasitic reaction. In sharp contrast, the SELC-based cell operates stably for 3800 h under the same conditions. When the current density and deposition capacity are increased to 4 mA cm^{-2} and 1 mAh cm^{-2} , respectively, the Zn||Zn symmetric cell with the SELC electrolyte still cycles stably for 1900 h, whereas the cell with the BL electrolyte short-circuits and fails after only 15 h due to uncontrolled dendritic growth caused by insufficient solvation regulation and weak interfacial protection (**Fig. 5(b)**). To further investigate the impact of SELC electrolyte on the stability and reversibility of the Zn anode, rate performances were performed by stepwise increasing the current density from 0.5 to 1, 2, 3, 4, 5, and 10 mA cm^{-2} , followed by recovery to 0.5 mA cm^{-2} (**Fig. S27**). The Zn||Zn symmetric cell

in the BL electrolyte fails to sustain stable cycling at elevated current densities, indicative of compromised interfacial stability under high-rate conditions. For comparison, the SELC-based Zn||Zn symmetric cell maintains stable Zn plating/stripping profiles during the entire testing process, with the polarization increasing gradually as the current density increases. Notably, when the current density is returned to 0.5 mA cm^{-2} , the SELC-based cell rapidly recovers to a stable voltage response. This improved rate performance strongly confirms that the SELC electrolyte enables highly reversible Zn plating/stripping and stabilizes the anode/electrolyte interface over a wide range of current densities. To better simulate practical intermittent operation scenarios, the Zn symmetric cells were evaluated under a rest-recovery protocol. As shown in **Fig. S28**, the Zn||Zn symmetric cell with the BL electrolyte exhibits pronounced polarization fluctuations after the first rest period due to serious side reactions. In contrast, the symmetric cell using the SELC electrolyte can operate stably for 1800 h, demonstrating markedly improved long-term stability. To uncover the origin of the distinct cycling stability, the morphology and composition of Zn anodes after cycling were characterized. **Fig. S29** presents SEM images of Zn anodes after 50 and 100 cycles at 4 mA cm^{-2} and 1 mAh cm^{-2} . As exhibited, the surface of the Zn anode cycled in the BL electrolyte is covered with vertically aligned Zn dendrites. In stark contrast, the Zn anode cycled in the SELC electrolyte retains a highly compact and smooth surface without obvious dendritic accumulation or “dead Zn” deposits. Meanwhile, energy-dispersive spectroscopy (EDS) elemental mapping of the Zn anode cycled in the SELC electrolyte reveals the uniform distribution of Zn, O, C, S, and F elements across the surface (**Fig. S30**). Notably, compared with the BL electrolyte, the surface O signal is significantly reduced after cycling in the SELC electrolyte, which is attributed to the suppressed formation of $\text{Zn}_x(\text{OTf})_y(\text{OH})_{2x-y}$ by-products. This conclusion is further corroborated by the post-cycling XRD patterns (**Fig. S31**). Distinct characteristic

peaks corresponding to $\text{Zn}_x(\text{OTf})_y(\text{OH})_{2x-y}$ are detected on the cycled Zn anode surface in the BL electrolyte. Conversely, these characteristic peaks disappear in the SELC electrolyte even after 100 cycles. It is worth noting that, as the cycle number increases, the $I_{(002)}/I_{(100)}$ intensity ratio of the Zn anode surface in the SELC electrolyte remains markedly higher than that in the BL electrolyte, indicating that the SELC electrolyte can sustain preferential Zn deposition along the (002) plane, thereby continuously suppressing dendrite growth. These results highlight the crucial role of the SELC electrolyte in simultaneously regulating Zn^{2+} solvation structure and interfacial chemistry, effectively suppressing side reactions and achieving homogeneous Zn plating and stripping behavior.

Considering the superior low-temperature adaptability of the SELC electrolyte, Zn||Cu asymmetric cells were assembled to assess the Zn deposition and stripping reversibility under subzero conditions. As shown in **Fig. 5(c)**, at $-30\text{ }^{\circ}\text{C}$, the SELC-based cell maintains a high average CE of 99.33% over 300 cycles. Even at an extremely low temperature of $-50\text{ }^{\circ}\text{C}$, the cell with the SELC electrolyte still enables highly reversible Zn deposition, maintaining an average CE of 95.09% after 300 cycles (**Fig. 5(e)**). Moreover, the Zn||Zn symmetric cell with the SELC electrolyte also exhibits excellent cycling stability, operating steadily for more than 2200 h at $-30\text{ }^{\circ}\text{C}$ and cycling for 300 h without short-circuiting at $-50\text{ }^{\circ}\text{C}$ (**Figs. 5(d) and 5(f)**). The superior cycling stability and reversibility can be attributed to the dynamically regulated solvation and interfacial chemistry of the SELC electrolyte, which alleviates the kinetic barriers under extreme cryogenic conditions, facilitates rapid ion transport, and ensures homogeneous Zn plating and stripping behavior. Encouragingly, compared with previously reported low-temperature aqueous electrolytes, the Zn||Zn symmetric cell with the SELC electrolyte delivers an exceptional cumulative plating capacity (CPC) at both room and low temperatures [28,47-52] (**Fig. 5(g)**). Furthermore, to verify the structural integrity of the cycled Zn anode under harsh

low-temperature conditions, the morphology and composition of Zn anodes were characterized by SEM and XRD. The SEM images in **Fig. S32** show that Zn anodes cycled at -30 and -50 °C both maintain compact and dendrite-free surfaces. The corresponding XRD patterns confirm the effective suppression of by-product formation by the SELC electrolyte at low temperatures. In addition, the intensity of the $\text{Zn}_{(002)}$ reflection increases as the temperature decreases, which is consistent with the low-temperature Zn deposition behavior in the SELC electrolyte and suggests that regulation of the $\text{Zn}_{(002)}$ crystallographic orientation plays an important role in ensuring stable battery operation over a wide temperature range (**Fig. S33**).

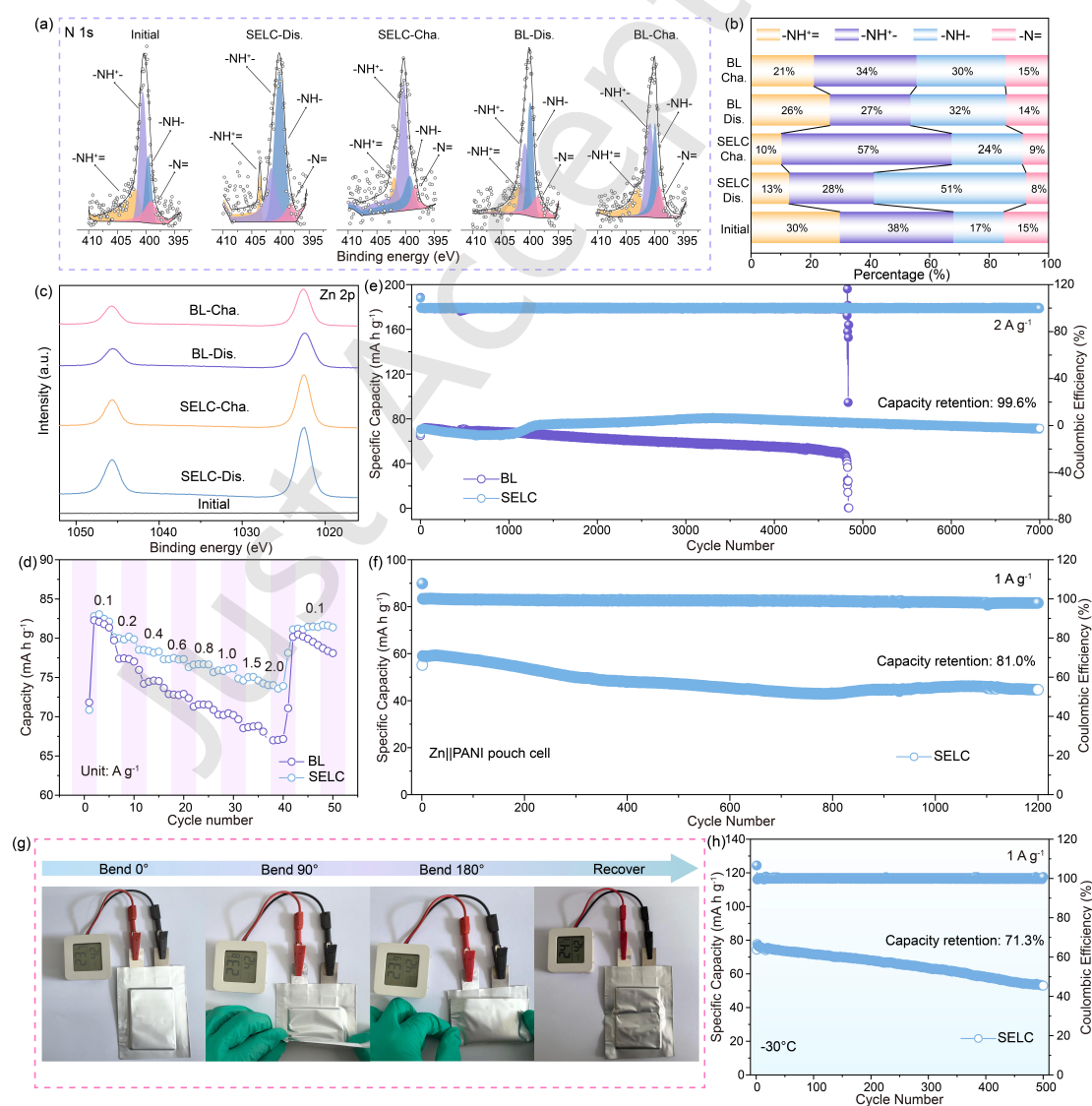


Figure 6 (a) High-resolution N 1s XPS spectra of PANI cathodes at selected electrochemical states. (b) Relative proportions of different nitrogen species obtained from N 1s peak deconvolution in the SELC and BL electrolytes. (c) High-resolution Zn 2p XPS spectra of PANI cathodes at the corresponding electrochemical states. (d) Rate performance of Zn||PANI full cells in different electrolytes. (e) Long cycling performance of Zn||PANI full cells in the BL and SELC electrolytes at 2 A g⁻¹. (f) The cycling performance of the Zn||PANI pouch cell in the SELC electrolyte at a current density of 1 A g⁻¹. (g) Optical photographs of the Zn||PANI pouch cell in the SELC electrolyte powering an electronic thermometer under different bending angles. (h) The cycling stability of Zn||PANI full cell under 1 A g⁻¹ at -30 °C.

To demonstrate practical applicability of the SELC electrolyte for energy storage systems, Zn anodes were paired with polyaniline (PANI) cathodes to assemble full cells. The SEM image in **Fig. S34** reveals that the synthesized PANI possesses a uniform nanofiber morphology, which is favorable for electrolyte penetration and ion transport. Subsequently, cyclic voltammetry (CV) was employed to investigate the electrochemical behavior of Zn||PANI full cells in the two electrolytes. As shown in **Fig. S35**, the Zn||PANI full cell with the SELC electrolyte exhibits lower polarization than that using the BL electrolyte, indicating improved electrochemical reversibility and accelerated charge-transfer kinetics. Notably, the full cell using the BL electrolyte exhibits three distinct reduction peaks and two oxidation peaks, which can be assigned to the transitions among the leucoemeraldine, emeraldine, and pernigraniline states of PANI, accompanied by anion interactions with the PANI chains [53]. These complex redox features are likely attributed to the H₂O-dominated solvation environment and stronger protonation and anion-interaction effects in the BL electrolyte. In contrast, because the introduced organic components reshape the primary Zn²⁺ solvation shell and reduce the influence of free H₂O and proton-related side processes, the Zn||PANI full cell using the SELC electrolyte displays only a single well-defined pair of redox peaks, which is associated with the reversible transformation between the emeraldine and leucoemeraldine states through H⁺ and Zn²⁺ insertion and extraction [54]. This simplified electrochemical response is

attributed to the reconstructed Zn^{2+} solvation environment and reduced influence of free H_2O and proton-related parasitic processes, which promotes a more reversible proton-assisted Zn^{2+} insertion and extraction within the PANI. This interpretation is further supported by ex situ XPS analysis of PANI cathodes collected at selected charge and discharge states during the second cycle [55]. The N 1s spectra show that, in the initial PANI cathode, the fractions of $-\text{NH}^+=$, $-\text{NH}^+$, $-\text{NH}-$, and $-\text{N}=$ are about 30%, 38%, 17%, and 15%, respectively. Upon discharge in the SELC electrolyte, $-\text{NH}-$ markedly increases to 51%, whereas $-\text{NH}^+$ and $-\text{N}=$ decrease to 28% and 8%, respectively, indicating a pronounced conversion toward reduced amine-type nitrogen related to leucoemeraldine. Upon charge, $-\text{NH}^+$ rises to 57% and $-\text{NH}-$ decreases to 24%, while $-\text{N}=$ slightly recovers to 9%, evidencing reversible oxidation and protonation toward an emeraldine-salt-dominant state. In contrast, the BL electrolyte exhibits much smaller variations in nitrogen-state composition during discharge and charge, suggesting less reversible redox evolution of PANI (**Figs. 6(a-b)**). To investigate the involvement of Zn species during charge storage, Zn 2p spectra were collected at the same states (**Fig. 6(c)**). The Zn 2p signals are clearly observed for both electrolytes, indicating the presence of Zn-containing species on the PANI cathode and supporting Zn^{2+} involvement in the charge-storage process [56]. In the SELC electrolyte, the Zn 2p signal exhibits clearly state-dependent evolution between discharge and charge, with reversible variations in peak intensity, indicating reversible Zn^{2+} coordination and decoordination with nitrogen-containing sites in PANI. By contrast, the BL electrolyte exhibits weaker reversibility in the Zn 2p evolution, suggesting less efficient Zn^{2+} exchange and slower interfacial reaction kinetics. These results support a highly reversible H^+ and Zn^{2+} co-insertion and extraction mechanism in the SELC electrolyte. To further quantify the relative contributions of Zn^{2+} and H^+ , inductively coupled plasma-optical emission spectrometry analysis was performed on PANI cathodes at the charged and discharged states of the second cycle [57,58]. The

Zn^{2+} -associated capacity contributions were estimated to be approximately 8.7% and 7.1% in the SELC and BL electrolytes, respectively, indicating that proton-associated storage dominates in both systems while SELC electrolyte enables a slightly higher reversible Zn^{2+} contribution (**Fig. S36 and Table S2**). This more effective participation of Zn^{2+} , together with the highly reversible proton-associated redox process revealed by XPS, supports the enhanced $\text{H}^+/\text{Zn}^{2+}$ co-storage behavior in the SELC electrolyte. Consequently, compared with the BL electrolyte, the $\text{Zn}||\text{PANI}$ full cell using the SELC electrolyte exhibits excellent rate performance (**Fig. 6(d)**). The long-term cycling stability of the full cells was evaluated at a current density of 2 A g^{-1} . The full cell using the BL electrolyte suffers from rapid capacity decay, with the capacity approaching zero after approximately 4800 cycles. In contrast, the $\text{Zn}||\text{PANI}$ full cell employing the SELC electrolyte demonstrates superior cycling stability, maintaining a high capacity retention of 99.6% even after 7000 cycles (**Fig. 6(e)**). Representative galvanostatic charge-discharge profiles further reveal that, In the second cycle, the full cells employing the SELC and BL electrolytes deliver comparable discharge specific capacities of 71.25 and 70.31 mAh g^{-1} , respectively, demonstrating that the H_2O -deficient interfacial environment does not compromise the initial charge-storage capability of PANI. In the 2000th cycle, the SELC-based full cell still delivers a discharge specific capacity of 75.70 mAh g^{-1} with lower voltage polarization, whereas the capacity of the BL-based full cell decreases to 62.81 mAh g^{-1} . These results highlight that the interfacial environment reconstructed by the SELC electrolyte improves the stability of Zn anode and suppresses the interfacial parasitic reactions, thereby enhancing the cycling stability. Subsequently, SEM characterization was employed to investigate the morphological difference of the Zn anodes after 50 cycles in the full cells. As shown in **Fig. S38(a)**, the Zn anode cycled in the BL electrolyte is covered with numerous dendrites and loose by-products, indicating severe side reactions. Conversely, the Zn anode cycled in the SELC electrolyte

maintains a smooth, dense, and dendrite-free morphology (**Fig. S38(b)**). This improvement originates from the synergistic regulation of Zn^{2+} solvation chemistry and the organic-rich and inorganic-reinforced gradient hybrid SEI formed in the SELC electrolyte, which regulates Zn deposition behavior and isolates the Zn anode from active H_2O molecules. Furthermore, the corrosion resistance enabled by the SELC electrolyte was evaluated through self-discharge tests (**Fig. S39**). After resting for 24 h at the fully charged state, the full cell with the SELC electrolyte retains 89.03% of its capacity, significantly higher than that with the BL electrolyte, 84.22%. Encouragingly, the $\text{Zn}||\text{PANI}$ pouch cell assembled with the SELC electrolyte maintains a capacity retention of 81.0% after 1200 cycles at 1 A g^{-1} (**Fig. 6(f)**) and powers a digital electronic thermometer under different bending angles (**Fig. 6(g)**), further indicating its potential for flexible energy-storage applications. Finally, the low-temperature performance of the $\text{Zn}||\text{PANI}$ full cell with the SELC electrolyte was assessed. The full cell exhibits good rate capability at both -30 and -50 $^{\circ}\text{C}$ (**Fig. S40**). Furthermore, at -30 $^{\circ}\text{C}$, the full cell retains 71.3% of its initial capacity after 500 cycles at 1 A g^{-1} (**Fig. 6(h)**). Notably, even at an ultralow temperature of -50 $^{\circ}\text{C}$, it can operate for 100 cycles while maintaining a capacity retention of 83.6% (**Fig. S41**). These results strongly demonstrate that the SELC electrolyte, by virtue of its freezing-point depression effect and preserved fast ion-transport channels enabled by dynamically regulated solvation and interfacial chemistry, can support reliable battery operation under extreme freezing conditions.

3. Conclusion

In summary, we have developed an ester-mediated SELC electrolyte for enabling highly reversible AZIBs under low-temperature conditions. By introducing MF as a chemically transformable co-solvent, the electrolyte undergoes in situ molecular evolution through partial hydrolysis, generating FA and MA to reconstruct the

hydrogen-bonding network of H₂O molecules, diversify Zn²⁺ solvation environments, and maintain favorable ion-transport kinetics at subzero temperatures. Meanwhile, MH serves as an interfacial regulator that preferentially enriches at the Zn surface and participates in the formation of a H₂O-deficient organic-rich and inorganic-reinforced gradient SEI. This robust interphase effectively suppresses H₂O-triggered side reactions, mitigates dendrite growth, and guides preferential Zn deposition along the (002) crystal plane. As a consequence of this dual regulation in the electrolyte bulk and at the Zn interface, the SELC electrolyte enables long-term stable Zn plating and stripping in Zn||Zn symmetric cells for 3800 h at room temperature, 2200 h at -30 °C, and 300 h at -50 °C. Moreover, Zn||PANI full cells deliver excellent cycling stability with 99.6% capacity retention after 7000 cycles, and the assembled pouch cell retains 81.0% of its capacity after 1200 cycles. This work provides a feasible strategy for constructing low-concentration aqueous electrolytes with both anti-freezing capability and interfacial stability, offering new insights into the design of practical low-temperature AZIBs.

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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 details of electrolyte and electrode preparation, material characterization, electrochemical measurements, DFT and MD simulations, together with supplementary data on solvation structures, hydrogen-bonding networks, interfacial chemistry, Zn deposition behavior, and room- and low-temperature electrochemical performance) is available in the online version of this article at <https://doi.org/10.26599/NRE.2026.9120277>.

References

- [1] Cai, S.; Hu, J.; Wei, C.; Yang, Y.; Dai, J.; Zou, G.; Hou, H.; Ji, X. Adaptive Hydration Chemistry Enables Fast and Durable Zinc - Ion Batteries. *Angew. Chem. Int. Ed.* **2025**, *64*, e202515095.
- [2] Chu, J.; Liu, Z.; Yu, J.; Cheng, L.; Wang, H.; Cui, F.; Zhu, G. Boosting H⁺ Storage in Aqueous Zinc Ion Batteries via Integrating Redox - Active Sites into Hydrogen - Bonded Organic Frameworks with Strong π - π Stacking. *Angew. Chem. Int. Ed.* **2024**, *63*, e202314411.
- [3] Lin, D.; Li, Y. Recent Advances of Aqueous Rechargeable Zinc - Iodine Batteries: Challenges, Solutions, and Prospects. *Adv. Mater.* **2022**, *34*, 2108856.
- [4] Li, Y.; Jia, H.; Fu, L.; Ali, U.; Zhao, L.; Zhang, L.; Li, L.; Yang, Y.; Wang, C.; Liu, B. Graded desolvation accelerators based on high-entropy alloys with widely distributed d-band centers for high-performance aqueous zinc-ion batteries. *Energy Environ. Sci.* **2025**, *18*, 6676-6689.
- [5] Diao, W.-Y.; Xie, D.; Wang, J.-W.; Liu, H.-H.; Sang, Y.; Tao, F.-Y.; Liu, C.; Gahungu, G.; Yu, H.; Li, W.-L.; Wu, X.-L.; Zhang, J.-P. Anion Receptor-manipulated solvation chemistry and electric double layer enables high Zn-Utilization rate and lean Zn metal batteries. *J. Colloid Interface Sci.* **2025**, *679*, 947-957.
- [6] Yin, L.; Guo, X.; Hu, J.; Yan, K.; Liu, L.; Shi, X.; Cui, F.; Zhu, G.; Zhang, N., Strategic Nitrogen Site Alignment in Covalent Organic Frameworks for Enhanced Performance in Aqueous Zinc-Iodide Batteries. *Angew. Chem. Int. Ed.* **2025**, *64*, e202423265.
- [7] Zhang, X.-Y.; Yin, H.; Liu, H.-H.; Ge, Y.-D.; Dang, C.-C.; Zheng, S.-H.; Gu, Z.-Y.; Cao, J.-M.; Guo, J.-Z.; Wu, X.-L. Decoupling Adsorption of Key Intermediates Enabled by Asymmetric 3d-5d-Orbital Hybridization: Durable High-Performance AEM Water Electrolysis and Zn-Air Batteries. *Angew. Chem. Int. Ed.* **2026**, *65*, e24805.
- [8] Li, X.; Jin, T.; Wang, Z.; Chen, Y.; Yun, C.; Shang, J.; Ge, Y.; Lu, T.; Zhuang, W.; Ma, Y.; Qi, Z. Hydroxyl - Rich Hyperbranched Polyglycerol Additive for Low - Temperature Aqueous Zinc Batteries: Sustained and Efficient Dehydration and High - Conductivity. *Adv. Sci.* **2026**, *13*, e16639.

- [9] Lin, Z.; Cai, Y.; Zhang, S.; Sun, J.; Liu, Y.; Zheng, Y.; Huo, K. Wide-Temperature Electrolytes for Aqueous Alkali Metal-Ion Batteries: Challenges, Progress, and Prospects. *Nano-Micro Lett.* **2026**, *18*, 27.
- [10] Chen, Y.; Hu, Y.; Lu, C.; Zhou, S.; Pan, A. Thermodynamics and Kinetics of Aqueous Zinc Electrolytes in Extreme Temperatures: Challenges, Advances, and Future. *Small* **2025**, *21*, e05865.
- [11] Yang, Y.; Zhao, L.; Zhang, Y.; Yang, Z.; Lai, W.; Liang, Y.; Dou, S.; Liu, M.; Wang, Y. Challenges and Prospects of Low - Temperature Rechargeable Batteries: Electrolytes, Interfaces, and Electrodes. *Adv. Sci.* **2024**, *11*, 2410318.
- [12] Nian, Q.; Wang, J.; Liu, S.; Sun, T.; Zheng, S.; Zhang, Y.; Tao, Z.; Chen, J. Aqueous Batteries Operated at -50 °C. *Angew. Chem. Int. Ed.* **2019**, *58*, 16994-16999.
- [13] Li, Y.; Li, X.; Peng, X.; Yang, X.; Kang, F.; Dong, L. Electrolyte Additive-Assembled Interconnecting Molecules-Zinc Anode Interface for Zinc-Ion Hybrid Supercapacitors. *Nano-Micro Lett.* **2025**, *17*, 268.
- [14] Zhang, H.; Gan, X.; Song, Z.; Zhou, J. Amphoteric Cellulose - Based Double - Network Hydrogel Electrolyte Toward Ultra - Stable Zn Anode. *Angew. Chem. Int. Ed.* **2023**, *62*, e202217833.
- [15] Yang, J.-L.; Liu, H.-H.; Liu, Y.; Du, M.; Zhang, J.-P.; Cao, J.-M.; Wu, X.-L. A Bio-Chemical Synergy Strategy: Mycelium Separator Breaks the Coupled Degradation Cycle in Aqueous Zn-I₂ Batteries. *Adv. Mater.* **2026**, *38*, e72967.
- [16] Hu, Q.; Wang, X.; Cui, J.; Hou, J.; Liu, X.; Yang, J.-L.; Gu, Z.-Y.; Zhao, J.; Xu, B.; Wu, X.-L. A Three-Tiered Golf Anode towards Ultralong-Life Zn-Mn Aqueous Batteries. *Angew. Chem. Int. Ed.* **2025**, *64*, e202421217.
- [17] Xie, D.; Sang, Y.; Wang, D.; Diao, W.; Tao, F.; Liu, C.; Wang, J.; Sun, H.; Zhang, J.; Wu, X. ZnF₂ - Riched Inorganic/Organic Hybrid SEI: in situ - Chemical Construction and Performance - Improving Mechanism for Aqueous Zinc - ion Batteries. *Angew. Chem. Int. Ed.* **2023**, *62*, e202216934.
- [18] Deng, H.; Qiu, B.; Gao, J.; He, C.; Zhang, P.; Mi, H. Synergistic Piezoelectric-Field and Crystal Plane Manipulation in Composite Solid Electrolytes Toward High-Rate Zinc Metal Batteries. *Adv. Funct. Mater.* **2026**, *36*, e75614.
- [19] Ming, F.; Zhu, Y.; Huang, G.; Emwas, A.-H.; Liang, H.; Cui, Y.; Alshareef, H. N. Co-Solvent Electrolyte Engineering for Stable Anode-Free Zinc Metal Batteries. *J. Am. Chem. Soc.* **2022**, *144*, 7160-7170.
- [20] Wang, W.; Chen, S.; Liao, X.; Huang, R.; Wang, F.; Chen, J.; Wang, Y.; Wang, F.; Wang, H. Regulating interfacial reaction through electrolyte chemistry enables gradient interphase for low-temperature zinc metal batteries. *Nat. Commun.* **2023**, *14*, 5443.
- [21] Ni, Q.; Zheng, L.; Tamwattana, O.; Yoo, J.; Bai, S.; Lee, M. H.; Noh, J. H.; Wu, C.; Kang, K. Subzero Temperature Operation of Aqueous Zn Metal Batteries by Tailoring Electrolyte Solvation Structure. *ACS Energy Lett.* **2025**, *10*, 2650-2659.
- [22] Liu, C.; Xie, D.; Tao, F.; Diao, W.; Yu, H.; Gahungu, G.; Li, W.; Wu, X.; Zhang, J. Revealing the Triangular Entanglement of Hydrogen Bond Network via Kosmotropic

- Effect for Durable Aqueous Zinc - Ion Batteries. *Adv. Funct. Mater.* **2025**, *35*, 2422628.
- [23] Zhang, S.; Wang, S.; Zhang, J.; Liu, J.; Xie, J.; Tang, W.; Guan, L.; Huang, H.; Xue, Q.; Zhi, C. A Dual - Functional Electrolyte Additive for Highly Reversible Zinc - Ion Batteries. *Adv. Funct. Mater.* **2026**, *36*, e76283.
- [24] Li, Y.-M.; Li, W.-H.; Li, K.; Jiang, W.-B.; Tang, Y.-Z.; Zhang, X.-Y.; Yuan, H.-Y.; Zhang, J.-P.; Wu, X.-L. Molecular Synergistic Effects Mediate Efficient Interfacial Chemistry: Enabling Dendrite-Free Zinc Anode for Aqueous Zinc-Ion Batteries. *J. Am. Chem. Soc.* **2024**, *146*, 30998-31011.
- [25] Zhang, C.; Holoubek, J.; Wu, X.; Daniyar, A.; Zhu, L.; Chen, C.; Leonard, D. P.; Rodríguez-Pérez, I. A.; Jiang, J.-X.; Fang, C.; Ji, X. A ZnCl_2 water-in-salt electrolyte for a reversible Zn metal anode. *Chem. Commun.* **2018**, *54*, 14097-14099.
- [26] Wang, F.; Borodin, O.; Gao, T.; Fan, X.; Sun, W.; Han, F.; Faraone, A.; Dura, J. A.; Xu, K.; Wang, C. Highly reversible zinc metal anode for aqueous batteries. *Nat. Mater.* **2018**, *17*, 543-549.
- [27] Huang, S.; Hu, Z.; Mo, X. W.; Park, Y.; Kim, J. S.; Jang, G.; Min, D. H.; Fu, H.; Xiong, P.; Wen, Z.; Jung, Y. M.; Kim, J.; Lee, H.; Hwang, C.; Kim, Y.; Li, C. C.; Dou, Q.; Park, H. S. Self-Assembled Ordered Nanostructure of Zwitterionic Co-Solutes Induces Localized High-Concentration Electrolytes for Ultrastable and Efficient Zinc Metal Anodes. *Nano-Micro Lett.* **2026**, *18*, 194.
- [28] Yang, K.; Liu, Y.; Yuan, C.; Wang, Y.; Hu, Y.; Zhao, J.; Miao, L. Trace Diluent - Like Polyoxometalate Modulated Localized High - Concentration Electrolyte Enables Highly Reversible Zinc Metal Chemistry. *Adv. Funct. Mater.* **2026**, *36*, e15837.
- [29] Hou, Z.; Lu, W.; Zheng, H.; Chen, N.; Jiang, H.; Zhang, D.; Du, F. An Mn-Enriched Interfacial Layer for Reversible Aqueous Mn Metal Batteries. *Nano Lett.* **2024**, *24*, 14034-14041.
- [30] Wei, H.; Li, B.; Liu, Q. Insights on Lean-Water Hydrogel Electrolyte Designs for Next-Generation Zinc Batteries. *Energy Mater. Devices* **2025**, *3*, 9370080.
- [31] Xu, W.; Li, J.; Liao, X.; Zhang, L.; Zhang, X.; Liu, C.; Amine, K.; Zhao, K.; Lu, J. Fluoride-Rich, Organic-Inorganic Gradient Interphase Enabled by Sacrificial Solvation Shells for Reversible Zinc Metal Batteries. *J. Am. Chem. Soc.* **2023**, *145*, 22456-22465.
- [32] Dong, Y.; Miao, L.; Ma, G.; Di, S.; Wang, Y.; Wang, L.; Xu, J.; Zhang, N. Non-concentrated aqueous electrolytes with organic solvent additives for stable zinc batteries. *Chem. Sci.* **2021**, *12*, 5843-5852.
- [33] Hei, P.; Sai, Y.; Yu, L.; Lin, Y.; Li, B.; Hu, G.; Wu, W.; Wang, J.; Sun, X.; Liu, X.-X.; Song, Y. Cosolvent Electrolyte Design for High-Voltage Aqueous Zinc-Sulfur Batteries. *J. Am. Chem. Soc.* **2025**, *147*, 27802-27811.
- [34] Zhu, X.; Wang, Z.; Zhang, T.; Zhang, J.; Ge, A.; Cao, Y.; Gao, R.; Yu, Z.; Wang, Y.; Xu, S.; Law, H. M.; Wang, F.; Ciucci, F.; Xu, G.; Zhu, M. Solvation chemistry tailored via dielectric constant engineering for stable low-temperature aqueous zinc batteries. *Nat. Commun.* **2026**, *17*, 3170.
- [35] Wang, G.; Fu, H.; Lu, J.; Huang, S.; Pei, C.; Min, D.; Zhang, Q.; Park, H. S.

Gradient - Structured and Robust Solid Electrolyte Interphase In Situ Formed by Hydrated Eutectic Electrolytes for High - Performance Zinc Metal Batteries. *Adv. Energy Mater.* **2024**, *14*, 2303549.

- [36] Dong, D.; Wang, T.; Sun, Y.; Fan, J.; Lu, Y.-C. Hydrotropic solubilization of zinc acetates for sustainable aqueous battery electrolytes. *Nat. Sustain.* **2023**, *6*, 1474-1484.
- [37] Hu, B.; Chen, T.; Wang, Y.; Qian, X.; Zhang, Q.; Fu, J. Reconfiguring the Electrolyte Network Structure with Bio - Inspired Cryoprotective Additive for Low - Temperature Aqueous Zinc Batteries. *Adv. Energy Mater.* **2024**, *14*, 2401470.
- [38] Zhao, J.; Wang, X.; Tang, B.; Li, Y.; Liu, D.; Zhu, G., Amidoxime-functionalized hydrogel electrolyte enables dendrite-free and shuttle-free zinc-iodine batteries. *J. Energy Chem.* **2026**, *114*, 536-545.
- [39] Zhou, T.; Mu, Y.; Chen, L.; Li, D.; Liu, W.; Yang, C.; Zhang, S.; Wang, Q.; Jiang, P.; Ge, G.; Zhou, H. Toward stable zinc aqueous rechargeable batteries by anode morphology modulation via polyaspartic acid additive. *Energy Storage Mater.* **2022**, *45*, 777-785.
- [40] Lv, D.; Zhang, X.; Cheng, L.; Yu, J.; Liu, Y.; Wang, H.; Zhu, G., Multiple Strong Ion-Dipole Interactions in Hierarchical Porous Polymer/Covalent Organic Framework Electrolytes Accelerating Stable and Efficient Ion Transport. *Angew. Chem. Int. Ed.* **2026**, e1155052.
- [41] Peng, Z.; Li, S.; Tang, L.; Zheng, J.; Tan, L.; Chen, Y. Water-shielding electric double layer and stable interphase engineering for durable aqueous zinc-ion batteries. *Nat. Commun.* **2025**, *16*, 4490.
- [42] Li, J.; Fang, Z.; Chen, H.; Liu, K.; Pan, Y.; Li, X.; Lin, D.; Wang, N.; Guo, C.; Han, C.; Yao, Y.; Xue, P.; Hong, G. Synergistic Construction of In Situ Self - Polymerized Interface and Localized pH Buffer Zone for High - Performance Aqueous Zinc-Iodine Batteries. *Angew. Chem. Int. Ed.* **2025**, *64*, e202511490.
- [43] Luo, J.; Xu, L.; Yang, Y.; Huang, S.; Zhou, Y.; Shao, Y.; Wang, T.; Tian, J.; Guo, S.; Zhao, J.; Zhao, X.; Cheng, T.; Shao, Y.; Zhang, J. Stable Zinc Anode Solid Electrolyte Interphase via Inner Helmholtz Plane Engineering. *Nat. Commun.* **2024**, *15*, 6471.
- [44] Cao, L.; Li, D.; Pollard, T.; Deng, T.; Zhang, B.; Yang, C.; Chen, L.; Vatamanu, J.; Hu, E.; Hourwitz, M. J.; Ma, L.; Ding, M.; Li, Q.; Hou, S.; Gaskell, K.; Fourkas, J. T.; Yang, X.-Q.; Xu, K.; Borodin, O.; Wang, C. Fluorinated interphase enables reversible aqueous zinc battery chemistries. *Nat. Nanotechnol.* **2021**, *16*, 902-910.
- [45] Cao, P.; Tang, J.; Wei, A.; Bai, Q.; Meng, Q.; Fan, S.; Ye, H.; Zhou, Y.; Zhou, X.; Yang, J. Manipulating Uniform Nucleation to Achieve Dendrite-Free Zn Anodes for Aqueous Zn-Ion Batteries. *ACS Appl. Mater. Interfaces* **2021**, *13*, 48855-48864.
- [46] Hu, Z.; Zhang, F.; Zhou, A.; Hu, X.; Yan, Q.; Liu, Y.; Arshad, F.; Li, Z.; Chen, R.; Wu, F.; Li, L. Highly Reversible Zn Metal Anodes Enabled by Increased Nucleation Overpotential. *Nano-Micro Lett.* **2023**, *15*, 171.
- [47] Li, X.; Li, S.; Quan, Y.; Wang, M.; Shen, H.; Wang, P.; Yan, J.; Cui, X.; Zhang, N. Promoting Desolvation by Hydrophobic and Zincophilic Adsorption Layer To Achieve Stable Zn Anodes at Low Temperature. *ACS Sustainable Chem. Eng.* **2024**, *12*,

7858-7868.

- [48] You, S.; Deng, Q.; Wang, Z.; Chu, Y.; Xu, Y.; Lu, J.; Yang, C. Achieving Highly Stable Zn Metal Anodes at Low Temperature via Regulating Electrolyte Solvation Structure. *Adv. Mater.* **2024**, *36*, 2402245.
- [49] Sun, M.; Zhang, Z.; Fu, S.; Zhang, Y.; Wang, R.; Mu, H.; Lian, C.; Wang, W.; Wang, G. A multifunctional electrolyte additive for zinc-ion capacitors with low temperature resistant and long lifespan. *J. Energy Chem.* **2024**, *94*, 477-485.
- [50] Zhu, M.; Cheng, W.; Wang, H.; Li, C.; Wang, H.; Yang, J.; Chen, Y.; Li, S.; Wu, H.; Chen, S.; Gao, T.; Tang, Y.; Zhang, Y. Dual - Salt Chaotropic Eutectic Electrolyte for Enhancing Low - Temperature Zinc - Ion Batteries. *ACS Energy Lett.* **2024**, *9*, 3380-3390.
- [51] Xi, M.; Liu, Z.; Qi, Z.; Huang, Y.; Wang, W.; Ding, J.; Tan, Z.; Liu, H. Electrolyte for Zn metal battery under extreme temperature operations design by Lewis acid-base chemically mediated polymerization of cyclic ether. *Energy Storage Mater.* **2025**, *75*, 104091.
- [52] Feng, D.; Cao, F.; Hou, L.; Li, T.; Jiao, Y.; Wu, P. Immunizing Aqueous Zn Batteries against Dendrite Formation and Side Reactions at Various Temperatures via Electrolyte Additives. *Small* **2021**, *17*, 2103195.
- [53] Luo, K.-H.; Yan, M.; Hung, Y.-H.; Kuang, J.-Y.; Chang, H.-C.; Lai, Y.-J.; Yeh, J.-M. Polyaniline Composites Containing Eco-Friendly Biomass Carbon from Agricultural-Waste Coconut Husk for Enhancing Gas Sensor Performance in Hydrogen Sulfide Detection. *Polymers* **2023**, *15*, 4554.
- [54] Gu, J.; Yuan, Z.; Wang, H.; Shen, J.; Ning, J.; Zhong, Y.; Hu, Y. Local protonation of polyaniline induced by nitrogen-doped carbon skeleton towards ultra-stable Zn-organic batteries with a dual-ion insertion/extraction mechanism. *Chem. Eng. J.* **2022**, *448*, 137711.
- [55] Feng, D.; Jiao, Y.; Wu, P. Proton - Reservoir Hydrogel Electrolyte for Long - Term Cycling Zn/PANI Batteries in Wide Temperature Range. *Angew. Chem. Int. Ed.* **2023**, *62*, e202215060.
- [56] Lin, X.; Zhou, G.; Robson, M. J.; Yu, J.; Kwok, S. C. T.; Ciucci, F. Hydrated Deep Eutectic Electrolytes for High - Performance Zn - Ion Batteries Capable of Low - Temperature Operation. *Adv. Funct. Mater.* **2022**, *32*, 2109322.
- [57] Shi, J.; Mao, K.; Zhang, Q.; Liu, Z.; Long, F.; Wen, L.; Hou, Y.; Li, X.; Ma, Y.; Yue, Y.; Li, L.; Zhi, C.; Gao, Y. An Air-Rechargeable Zn Battery Enabled by Organic-Inorganic Hybrid Cathode. *Nano-Micro Lett.* **2023**, *15*, 53.
- [58] Wang, W.; Kale, V. S.; Cao, Z.; Kandambeth, S.; Zhang, W.; Ming, J.; Parvatkar, P. T.; Abou-Hamad, E.; Shekhah, O.; Cavallo, L.; Eddaoudi, M.; Alshareef, H. N. Phenanthroline Covalent Organic Framework Electrodes for High-Performance Zinc-Ion Supercapattery. *ACS Energy Lett.* **2020**, *5*, 2256-2264.



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Electronic Supplementary Material

Ester-mediated self-evolving electrolyte enables low-temperature aqueous zinc-ion batteries

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1. Experimental Section

1.1 Chemical reagent: Zn(OTf)₂ (Macklin, 98%), Ultrapure water (Macklin), Methyl formate (MF, Macklin, 99%), Methyl heptafluorobutyrate (MH, Acme, 97%), Zn foil (Qinghe County Guantai Metal Material Co., Ltd., 99.999%, $\delta = 0.1$ mm)

1.2 Preparation of electrolyte: The baseline (BL) electrolyte was prepared by dissolving 1 M Zn(OTf)₂ in ultrapure water. The SELC electrolyte was obtained by dissolving 1 M Zn(OTf)₂ in a mixed solvent of MF and H₂O (1:1 by volume), with the addition of 5 vol% MH as an additive.

1.3 Preparation of PANI cathode materials: Polyaniline (PANI) was prepared using a previously reported traditional approach. Initially, 0.365 mL of aniline monomer was dissolved in 15 mL of 1 M hydrochloric acid (HCl) and stirred for 30 min to ensure a

homogeneous solution. Then, 5 mL of 1 M HCl containing 0.228 g of ammonium persulfate was added slowly drop by drop to the above-mentioned solution. Upon mixing, the solution quickly turned dark green, suggesting the start of polymerization, and the reaction was allowed to continue for 1 h. The resulting sample was washed successively with deionized water and ethanol, and then dried in an oven at 60 °C for 12 hours. To fabricate the cathode, a composite slurry was created by mixing the synthesized PANI, Super P carbon, and polyvinylidene fluoride binder in a 7:2:1 mass ratio within N-methyl-2-pyrrolidone. This slurry was coated onto a carbon paper current collector and vacuum-dried at 100 °C for 24 h. The final areal mass loading of the active material was controlled at approximately 1.5 mg cm⁻².

1.4 Material characterization: The crystallographic structure of the Zn anodes was investigated using X-ray diffraction (XRD) on a Rigaku P/max 2200VPC diffractometer equipped with a Cu K α source, scanning a 2 θ range of 5-80° at a speed of 20° min⁻¹. Surface chemical states were resolved via X-ray photoelectron spectroscopy (XPS) using a Thermo ESCALAB 250 system with Al K α radiation. For morphological and elemental analysis of the cycled electrodes, a scanning electron microscope (FEI XL 30 ESEM-14 FEG) and an energy-dispersive X-ray spectrometer (JEOL-2100F Plus S3) were utilized, respectively. To probe the solvation structure and molecular interactions within the electrolytes, Raman spectroscopy (Horiba Jobin-Yvon LabRAM HR Evolution, 532 nm laser) and nuclear magnetic resonance (NMR, AVANCE Neo 400 MHz) were performed. Additionally, the interfacial wettability was assessed by measuring contact angles with a Kino sl200kb goniometer.

1.5 Electrode preparation and electrochemical measurements: All electrochemical performance evaluations were conducted using CR2032 coin-type cells. The specific cell configurations included Zn||Zn symmetric cells for stability tests, Zn||Cu asymmetric cells for Coulombic efficiency analysis, and Zn||PANI full cells for practical application assessment. Both the cathode and anode were punched into 12 mm diameter discs, while a 16 mm diameter glass fiber separator was used. The

amount of electrolyte was fixed at 100 μL for each cell. After assembly, the cells were rested for 4 h before galvanostatic measurements on a Neware battery test system. A suite of electrochemical analyses, including cyclic voltammetry, linear sweep voltammetry, chronoamperometry, and electrochemical impedance spectroscopy (EIS) was performed on a CHI660E workstation. Corrosion behavior was assessed via linear polarization in a three-electrode setup (Zn working, Pt counter, Ag/AgCl reference), recording Tafel plots from -0.6 to -1.1 V at 1 mV s⁻¹. The Zn²⁺ transference number was calculated based on the chronoamperometric response to a 25 mV polarization over 4000 s. Ionic conductivity was measured via EIS in SS||SS blocking cells. Zn||PANI full cells operated within a voltage window of 0.4-1.4 V.

1.6 Density functional theory simulation methods (DFT):

Density functional theory (DFT) computations were carried out using the Dmol3 module. The Perdew-Burke-Ernzerhof (PBE) functional under the generalized gradient approximation (GGA) was employed as the exchange-correlation functional, supplemented with Grimme's dispersion correction. The binding energy (E_b) was calculated by the following equation:

$$E_b = E_{AB} - (E_A + E_B)$$

where E_{AB} represents the total energy of the AB complex, and E_A and E_B correspond to the total energies of isolated A and isolated B, respectively.

1.7 Molecular dynamics (MD) simulations for solvation structure analysis: MD simulations were carried out using the GROMACS 2023 package. According to the molecular proportions used in experimental settings, four electrolyte models were built within a cubic simulation box of 5 nm $\times$ 5 nm $\times$ 5 nm (detailed composition: BL electrolyte contained 50 Zn²⁺, 100 OTf, and 2778 H₂O molecules; SELC electrolyte comprised 50 Zn²⁺, 100 OTf, and 1168 H₂O, 203 MF, 203 FA, 203 MA, and 16 MH molecules). The GAFF force field was adopted alongside the TIP4P water model, and the corresponding force field parameters were retrieved from the AuToFF database. All constructed systems were subjected to equilibration under the NPT ensemble,

starting with a 5 ns equilibration period at 298.15 K and 1 bar pressure. After completion of equilibration, production simulations were run under the same NPT ensemble for 20 ns, and the resulting trajectories were analyzed to determine the local coordination configuration of Zn^{2+} . During the production simulation process, the temperature (298.15 K, 243.15 K and 223.15 K) and pressure (1 bar) were regulated by the V-rescale and C-rescale methods, respectively. A cut-off distance of 1.5 nm was set for both van der Waals and electrostatic interactions.

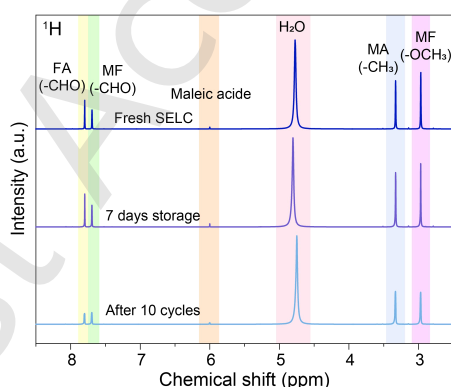


Figure S1. Quantitative ^1H NMR spectra of the SELC electrolyte under different conditions.

Table S1: Quantitative ^1H NMR analysis of MF hydrolysis in the SELC electrolyte under different conditions.

Sample	MF (mmol)	FA (mmol)	MA (mmol)	MF hydrolysis degree (%)
Fresh SELC	1.109	0.927	1.034	46.9
7-day storage	1.140	1.061	1.140	49.1

After 10 cycles	0.959	1.004	1.097	52.3
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The amount of hydrolyzed MF was estimated according to the 1:1 stoichiometry of MF hydrolysis:

$$n_{hyd} = \frac{n_{FA} + n_{MA}}{2}$$

The hydrolysis degree of MF was then calculated as:

$$X_{MF} = \frac{n_{hyd}}{n_{MF} + n_{hyd}} \times 100\%$$

where n_{MF} , n_{FA} , and n_{MA} are the molar amounts of MF, FA, and MA determined by quantitative ^1H NMR, respectively.

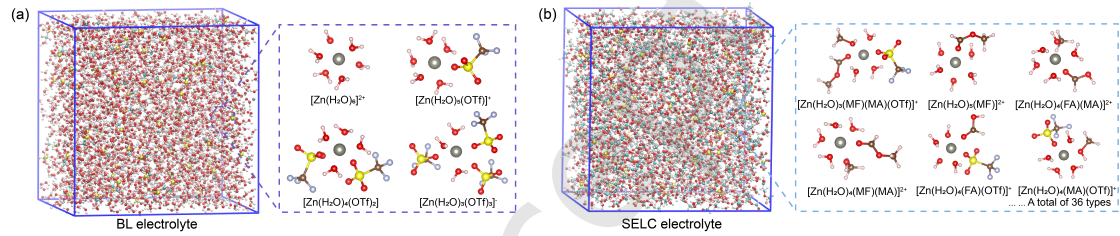


Figure S2. Snapshot of (a) BL and (b) SELC electrolytes from MD simulations.

The configurational entropy (S_{conf}) was calculated according to the Boltzmann-Gibbs expression:

$$S_{\text{conf}} = -R \sum_{i=1}^n x_i \ln x_i$$

where R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), n denotes the number of constituent Zn^{2+} solvation structure types, and x_i represents the mole fraction of each solvation structure obtained from the MD simulations.

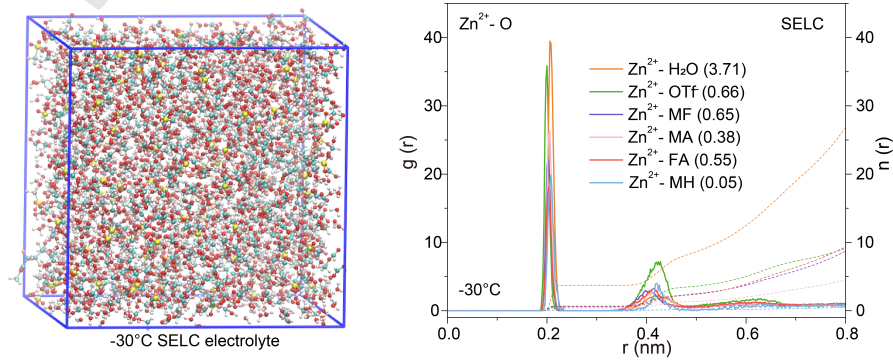


Figure S3. Snapshot of SELC electrolytes from MD simulations and corresponding ACN at -30 °C.

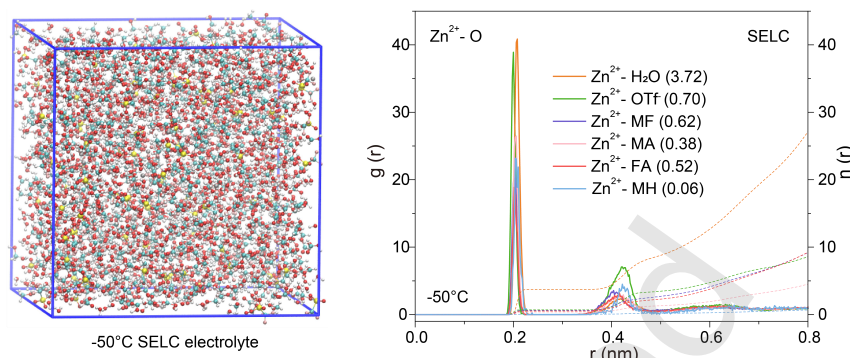


Figure S4. Snapshot of SELC electrolytes from MD simulations and corresponding ACN at -50 °C.

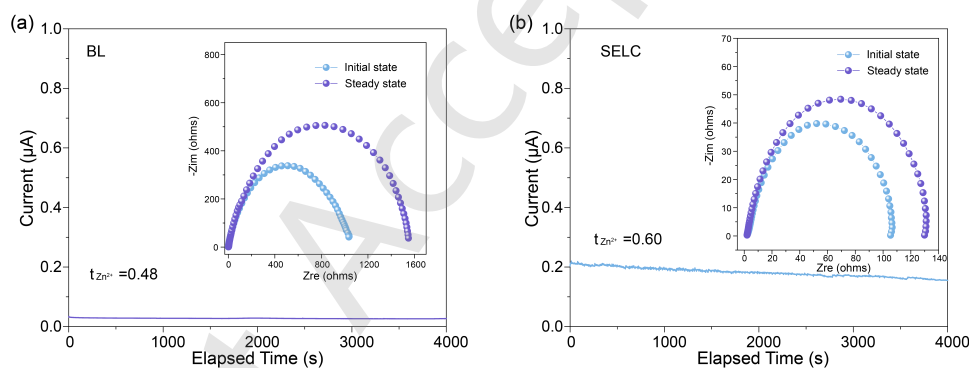


Figure S5. The transference number of Zn^{2+} in the (a) BL and (b) SELC electrolytes.

The transference number of ($t_{Zn^{2+}}$) was calculated by the following equation:

$$t_{Zn^{2+}} = \frac{I_s(\Delta V - I_o R_o)}{I_o(\Delta V - I_s R_s)}$$

In this equation, I_o and R_o denote the initial current and interfacial resistance, respectively, while I_s and R_s refer to their steady-state counterparts. ΔV represents the applied constant polarization voltage of 25 mV.

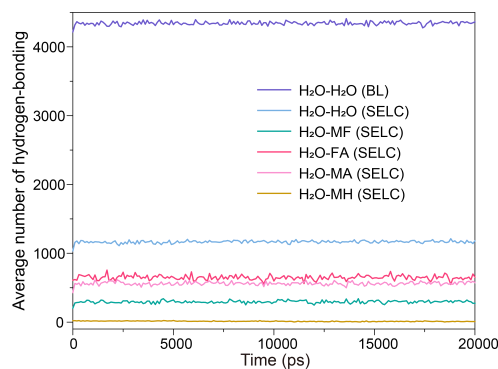


Figure S6. The average number of hydrogen-bonding in the BL and SELC electrolytes obtained from MD simulation.

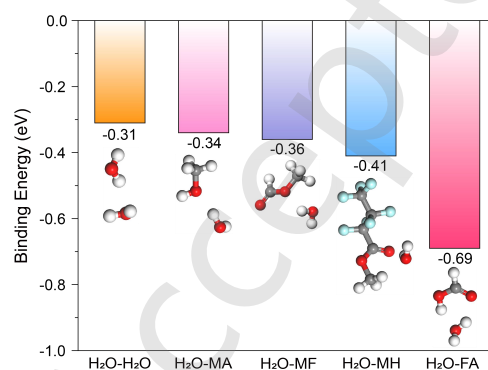


Figure S7. Calculated binding energies between H₂O and various molecules.

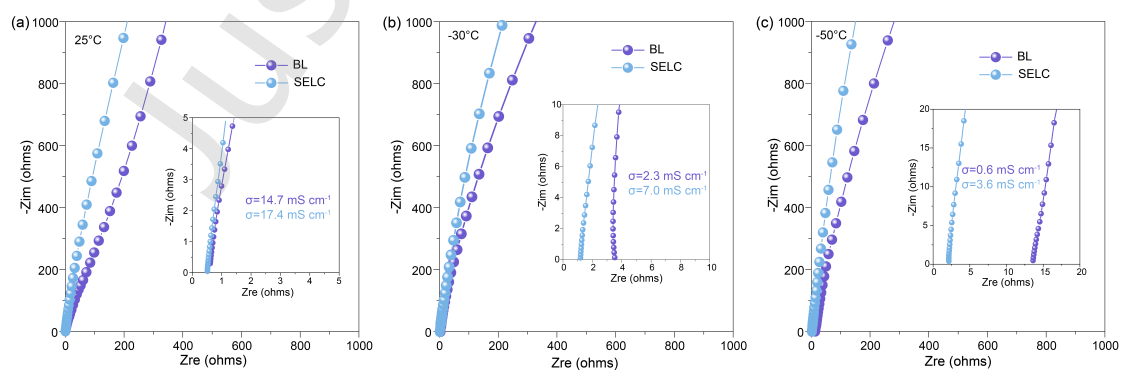


Figure S8. Ionic conductivity of BL and SELC electrolytes at (a) 25 °C, (b) -30 °C and (c) -50 °C.

The ionic conductivity (σ) was calculated according to the following equation:

$$\sigma = \frac{l}{RA}$$

Where l is the thickness of the separator, A is the effective contact area between the separator and the stainless-steel electrodes, and R is the bulk resistance of the electrolyte obtained from the electrochemical impedance spectroscopy measurement.

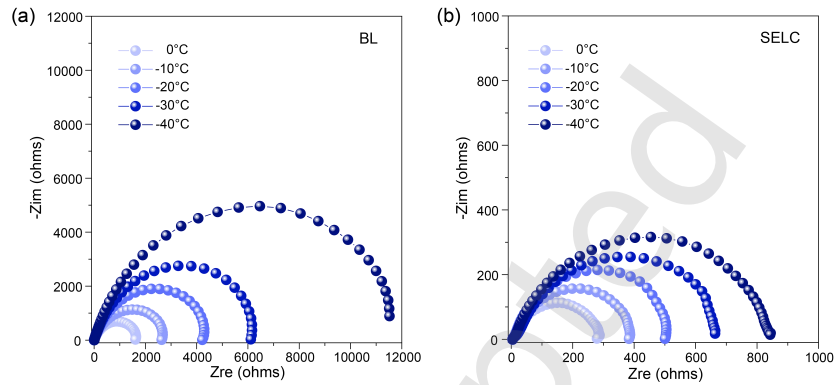


Figure S9. Nyquist plots of the Zn||Zn symmetrical cells in various electrolytes at different temperatures.

The E_a could be calculated through the Arrhenius equation:

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

Where R_{ct} denotes the charge-transfer resistance, A is the pre-exponential factor, R is the universal gas constant, and T stands for the absolute temperature in Kelvin.

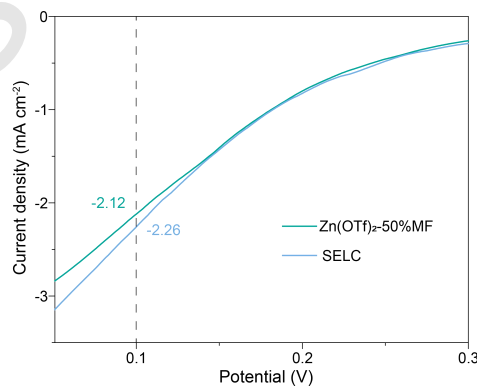


Figure S10. LSV curves of different electrolytes.

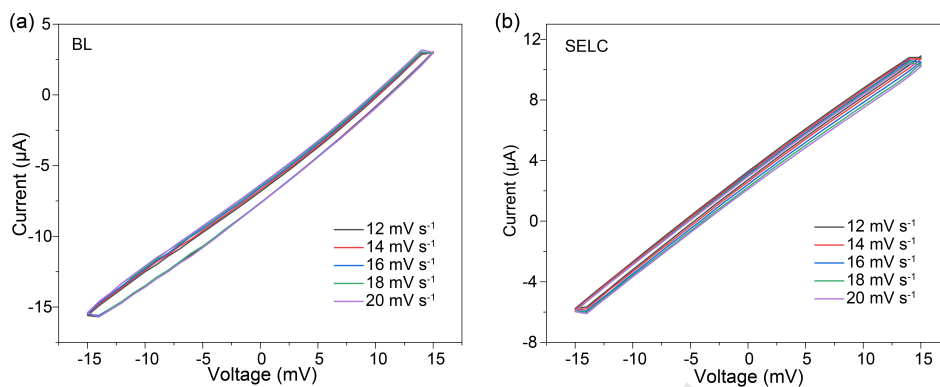


Figure S11. The CV curves for Zn||Zn symmetrical cells in the (a) BL and (b) SELC electrolytes.

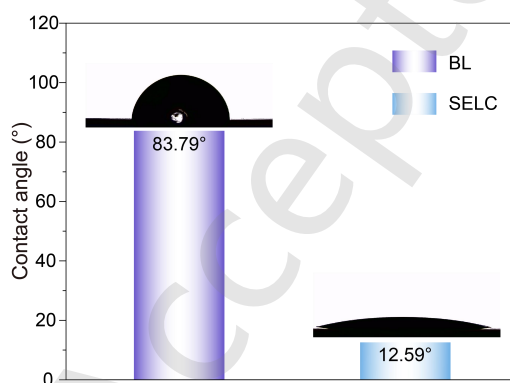


Figure S12. The contact angle of BL and SELC electrolytes on the Zn anode.

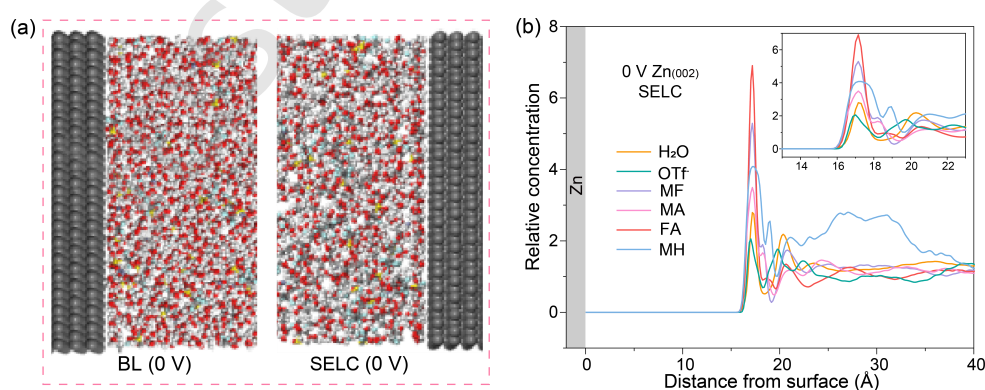


Figure S13. (a) 3D snapshots from MD simulations of the EDL on the Zn₍₀₀₂₎ crystal plane in different electrolytes at 0 V. (b) Density profiles of different components as a function of the distance from the Zn anode in the SELC electrolytes at 0 V.

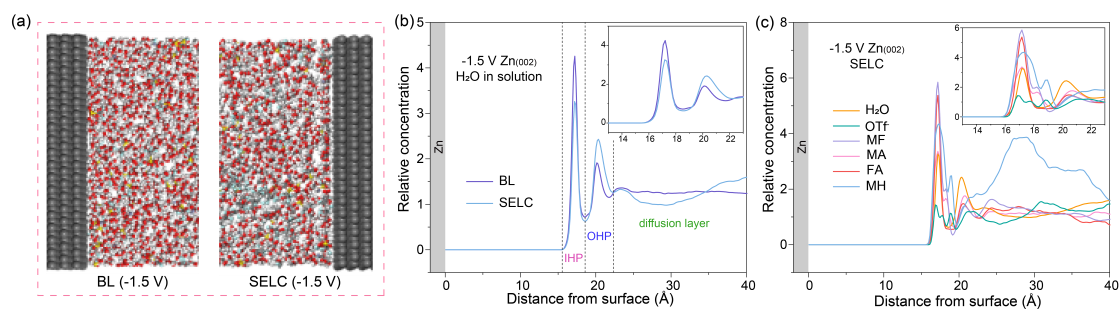


Figure S14. (a) 3D snapshots from MD simulations of the EDL on the Zn₍₀₀₂₎ crystal plane in different electrolytes at -1.5 V. (b) Density profiles of H₂O molecules as a function of the distance from the Zn anode in the BL and SELC electrolytes at -1.5 V. (c) Density profiles of different components as a function of the distance from the Zn anode in the SELC electrolytes at -1.5 V.

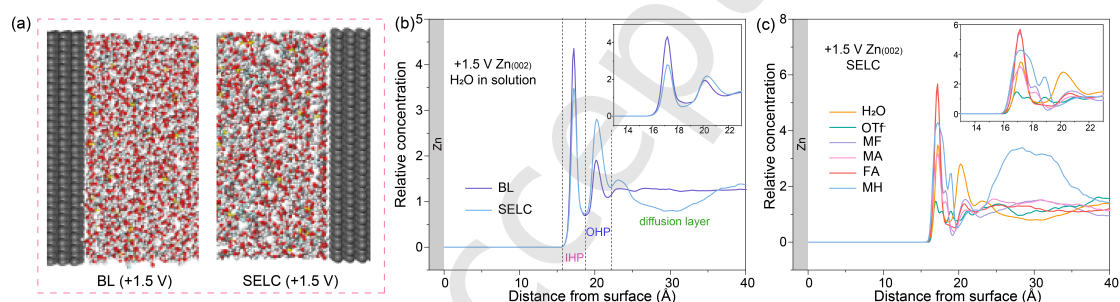


Figure S15. (a) 3D snapshots from MD simulations of the EDL on the Zn₍₀₀₂₎ crystal plane in different electrolytes at +1.5 V. (b) Density profiles of H₂O molecules as a function of the distance from the Zn anode in the BL and SELC electrolytes at +1.5 V. (c) Density profiles of different components as a function of the distance from the Zn anode in the SELC electrolytes at +1.5 V.

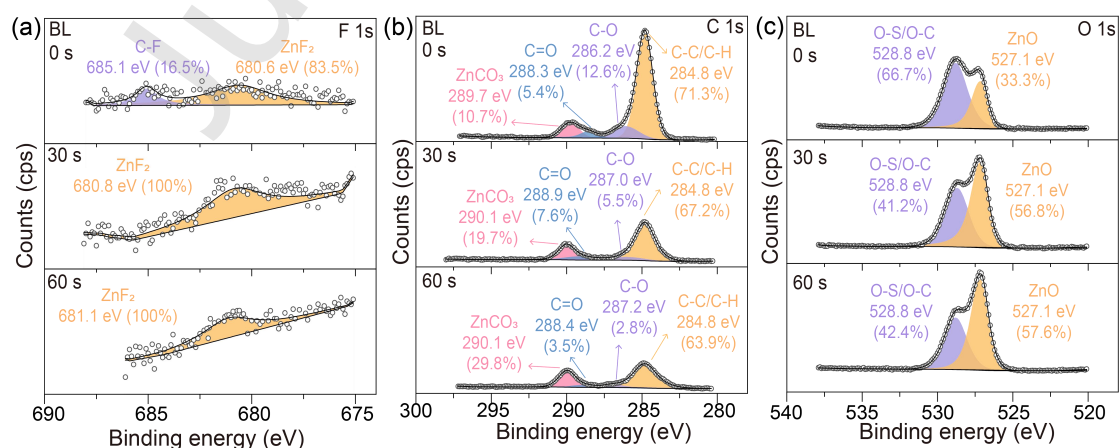


Figure S16. In-depth XPS spectra of (a) F 1s, (b) C 1s, and (c) O 1s of cycled Zn anode in the BL electrolyte.

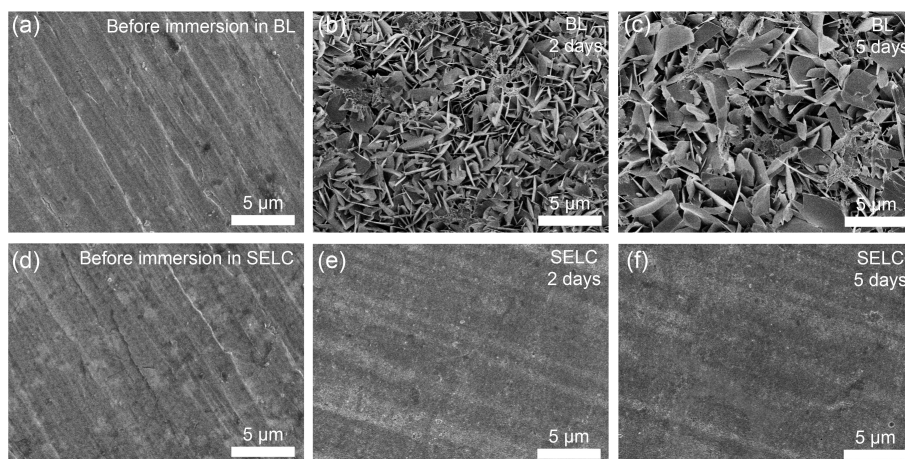


Figure S17. SEM images of Zn foils before and after immersed in the BL and SELC electrolytes and for 2 and 5 days.

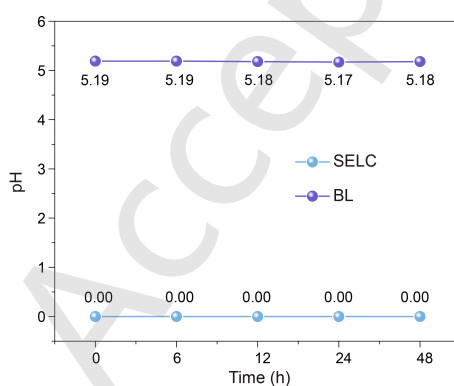


Figure S18. pH value during the storage process of BL and SELC electrolytes.

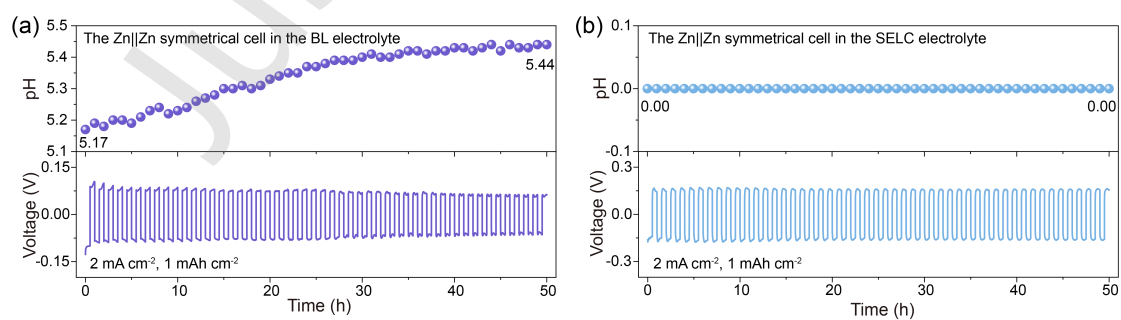


Figure S19. In situ pH monitoring of (a) BL and (b) SELC electrolytes within Zn||Zn symmetric cells upon cycling at 2 mA cm^{-2} , 1 mAh cm^{-2} .

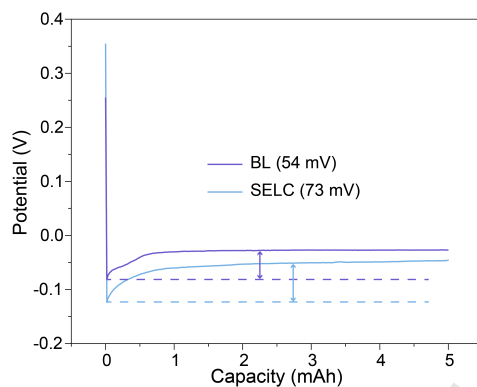


Figure S20. Nucleation overpotential of different electrolytes in Zn||Cu asymmetric cells.

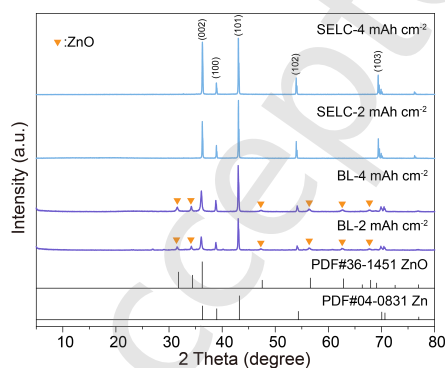


Figure S21. XRD patterns of Zn deposits in the BL and SELC electrolytes.

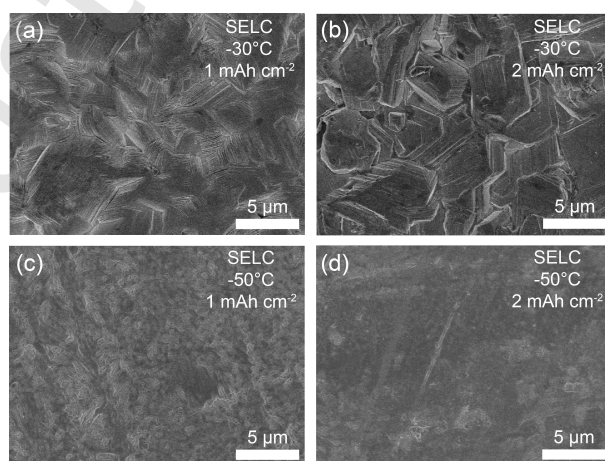


Figure S22. SEM images of Zn deposits in the SELC electrolyte at a current density of 1 mA cm⁻² and a deposition capacity of 1 and 2 mAh cm⁻² at (a-b) -30 °C and (c-d) -50 °C.

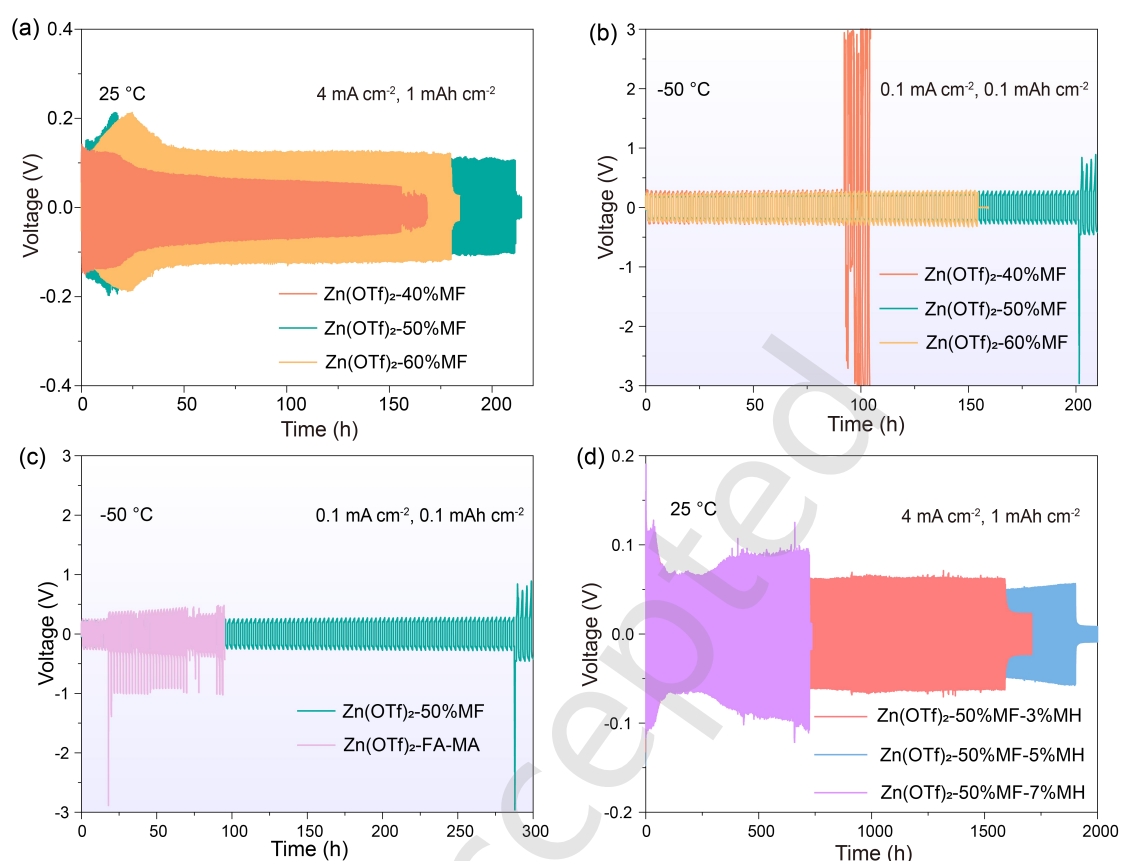


Figure S23. Galvanostatic plating/stripping of Zn||Zn symmetric cells with electrolytes containing different ratio of MF and H₂O at (a) 25 °C and (b) -50 °C. (c) Comparison of Zn||Zn symmetric-cell cycling performance between the Zn(OTf)₂-50% MF electrolyte and the FA/MA control corresponding to complete MF hydrolysis at -50 °C. (d) Cycling performance of Zn||Zn symmetric cells using electrolytes with different MH concentrations.

To minimize material costs, the salt concentration was fixed at 1 M Zn(OTf)₂, followed by systematic optimization of the MF/H₂O solvent ratio. As shown in **Figure S23a**, the Zn||Zn symmetric cell achieves the longest cycling lifespan when the initial volume ratio of MF to H₂O is 1:1. The influence of initial MF content on the low-temperature performance was further evaluated at -50 °C. Among the electrolytes containing 40%, 50%, and 60% MF, the Zn(OTf)₂-50% MF electrolyte exhibits the most stable Zn plating/stripping behavior (**Figure S23b**). The inferior performance at higher MF content may be associated with increased FA generation and the

consequent aggravation of acid-induced Zn corrosion. Meanwhile, an excessive MF content decreases the proportion of the aqueous phase, which can impede Zn^{2+} transport within bulk electrolyte and increase the resistance associated with Zn^{2+} desolvation and interfacial charge transfer, thereby increasing voltage polarization. Conversely, an insufficient MF content may not provide effective coupled regulation of the bulk Zn^{2+} solvation environment and interfacial chemistry. Accordingly, these results identify 50 vol% MF as the optimal initial content within the investigated compositional range. To evaluate the roles of MF hydrolysis products, we prepared an FA/MA control electrolyte containing the stoichiometric products corresponding to complete MF hydrolysis. As exhibited, the FA/MA control electrolyte corresponding to the complete hydrolysis products of MF shows much poorer cycling stability than the $\text{Zn}(\text{OTf})_2$ -50% MF electrolyte. This comparison demonstrates that the preformed products corresponding to complete MF hydrolysis cannot independently reproduce the superior low-temperature cycling stability of the optimized electrolyte. The result is consistent with the importance of the partially hydrolyzed multicomponent state and its gradual compositional evolution in regulating Zn^{2+} solvation and interfacial chemistry (**Figure S23c**). Building on the optimized MF/ H_2O binary-solvent composition, the optimal MH content was subsequently determined. As depicted in **Figure S23d**, the symmetric cell containing 3 vol% MH initially exhibits stable voltage polarization but undergoes a short circuit after 1580 h, indicating insufficient long-term interfacial protection. Increasing the MH content to 7 vol% results in pronounced voltage polarization and premature cell failure after only 720 h, likely because excessive MH enrichment increases interfacial resistance. By contrast, the electrolyte containing 5 vol% MH enables both stable polarization and prolonged cycling. Accordingly, the optimized SELC formulation consists of 1 M $\text{Zn}(\text{OTf})_2$ in an MF/ H_2O binary solvent with an initial volume ratio of 1:1 and 5 vol% MH as the interfacial additive.

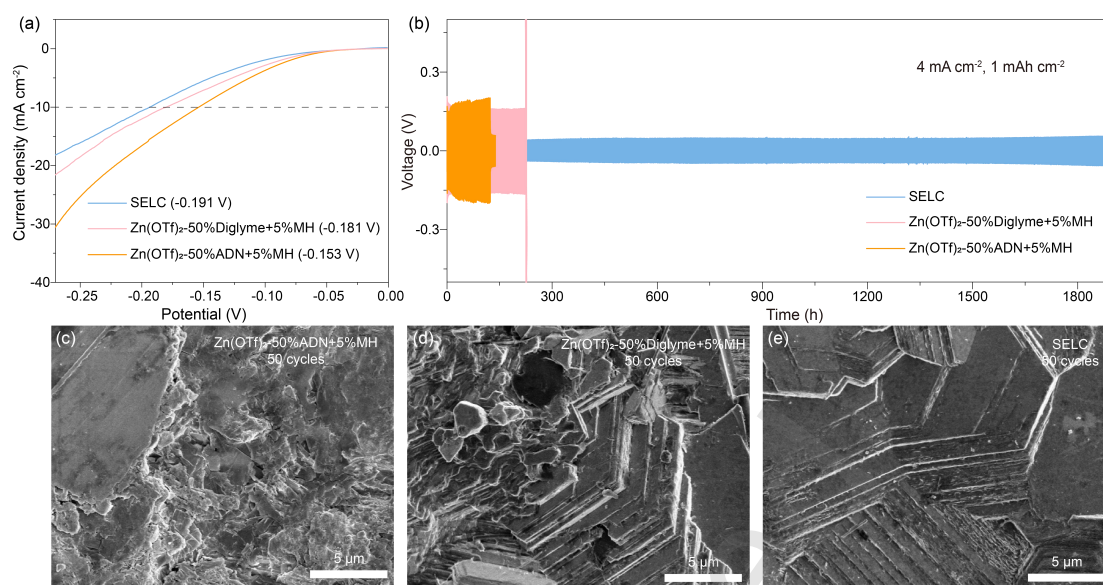


Figure S24. (a) HER curves of different electrolytes. (b) Galvanostatic cycling performance of Zn||Zn symmetric cells at 4 mA cm⁻² and 1 mAh cm⁻². (c-e) SEM images of Zn anodes after 50 cycles in different electrolytes.

To distinguish the specific chemical effects of the SELC electrolyte design from those arising simply from the reduced H₂O content, we introduced two non-hydrolyzable co-solvents, adiponitrile (ADN) and diethylene glycol dimethyl ether (Diglyme), as control solvents. The corresponding control electrolytes were formulated with comparable H₂O contents and the same MH content as the SELC electrolyte, and were denoted as Zn(OTf)₂-50%ADN+5%MH and Zn(OTf)₂-50%Diglyme+5%MH.

As shown in **Figure S24a**, despite their H₂O contents being comparable to that of SELC electrolyte, both control electrolytes exhibit substantially weaker HER suppression. The HER potentials at a current density of -10 mA cm⁻² are -0.153, -0.181, and -0.191 V for the Zn(OTf)₂-50%ADN+5%MH, Zn(OTf)₂-50%Diglyme+5%MH, and SELC electrolytes, respectively. This result indicates that reducing the water content alone is insufficient to reproduce the pronounced HER suppression achieved by the SELC electrolyte.

The difference becomes even more evident in Zn||Zn symmetric cell cycling (**Figure S24b**). Both the Zn(OTf)₂-50%ADN+5%MH and Zn(OTf)₂-50%Diglyme+5%MH electrolytes exhibit substantially larger voltage

hysteresis and premature cell failure, whereas the SELC-based cell maintains stable Zn plating/stripping for approximately 1900 h at 4 mA cm^{-2} and 1 mAh cm^{-2} . Consistently, SEM images of the Zn anodes after 50 cycles reveal severe surface degradation and highly nonuniform Zn deposits in the $\text{Zn}(\text{OTf})_2$ -50%ADN+5%MH and $\text{Zn}(\text{OTf})_2$ -50%Diglyme+5%MH electrolytes, while the Zn anode cycled in SELC electrolyte retains a much more compact and uniform surface morphology (**Figure S24c-e**).

These control experiments therefore confirm that the improved electrochemical performance of the SELC electrolyte cannot be explained solely by its reduced H_2O content. Rather, the hydrolysis-mediated chemical evolution of MF reconstructs and diversifies the Zn^{2+} solvation environment while disrupting the continuous hydrogen-bonding network of H_2O molecules. Together with the MH-mediated regulation of interfacial chemistry, these effects suppress H_2O -related parasitic reactions, promote more reversible Zn plating/stripping, and stabilize the anode/electrolyte interface. Accordingly, the superior performance of the SELC electrolyte arises from the combined regulation of bulk solvation environment and interfacial chemistry rather than from a simple water-dilution effect.

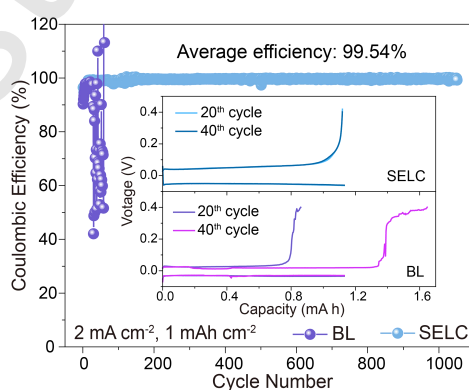


Figure S25. The CE of the BL and SELC electrolytes at 2 mA cm^{-2} , 1 mAh cm^{-2} . The inset shows the voltage profiles of Zn plating/stripping at different cycles.

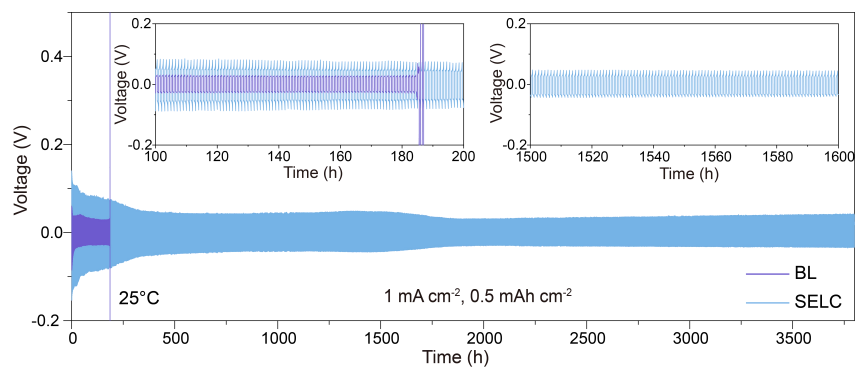


Figure S26. Cycling performance of Zn||Zn symmetric cells in the BL and SELC electrolytes at 1 mA cm^{-2} , 0.5 mAh cm^{-2} .

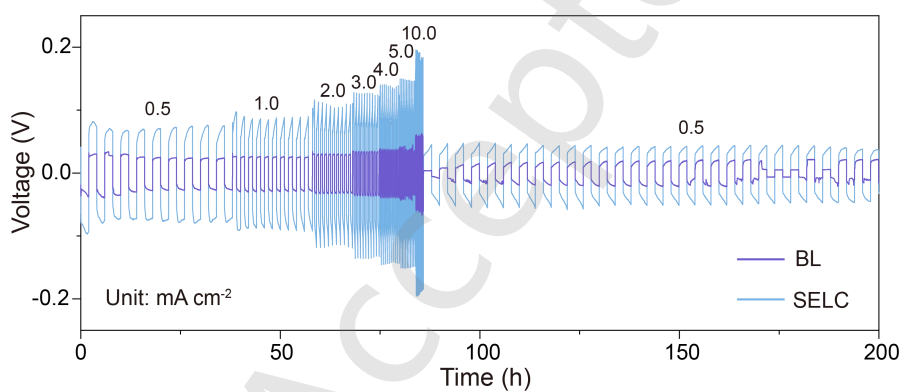


Figure S27. Rate performance of Zn||Zn symmetric cells in different electrolytes.

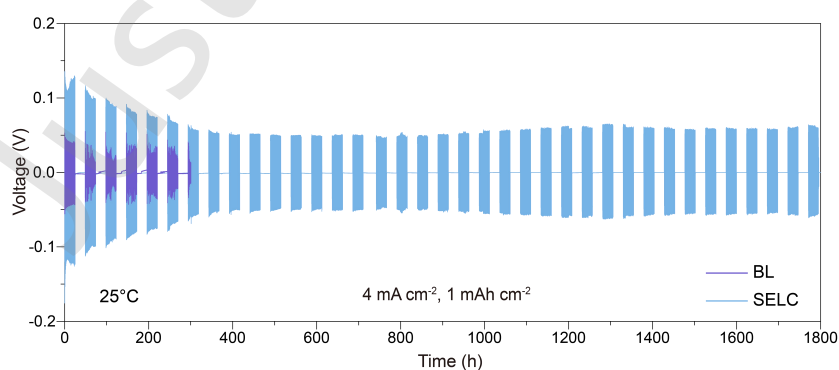


Figure S28. Rest-recovery cycling performance of Zn||Zn symmetric cells in different electrolytes at 4 mA cm^{-2} with a fixed areal capacity of 1 mAh cm^{-2} .

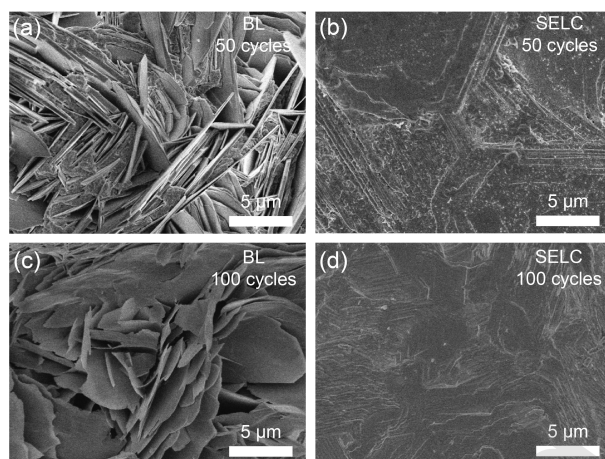


Figure S29. SEM images of the Zn anode after 50 and 100 cycles in the BL and SELC electrolytes.

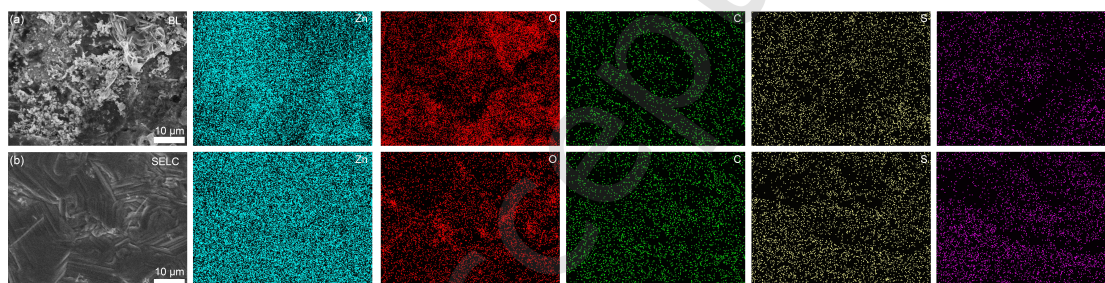


Figure S30. The EDS elemental mapping of the zinc anode after 50 cycles under the conditions of 4 mA cm^{-2} and 1 mAh cm^{-2} in the (a) BL and (b) SELC electrolytes.

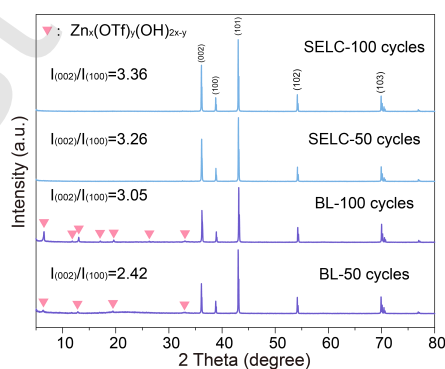


Figure S31. XRD patterns of the Zn anode after 50 and 100 cycles in the BL and SELC electrolytes.

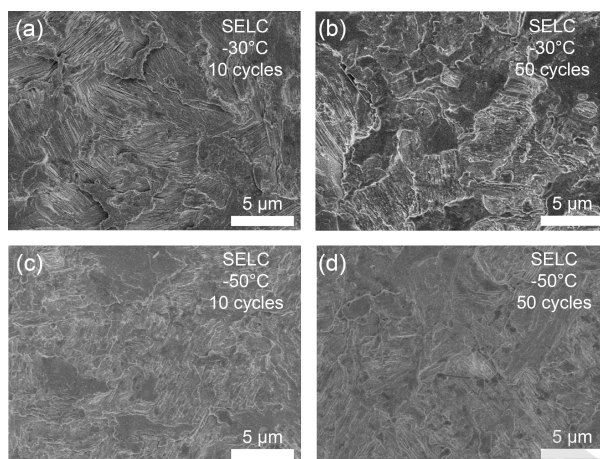


Figure S32. SEM images of the Zn anode after 10 and 50 cycles in the SELC electrolyte at -30 °C and -50 °C.

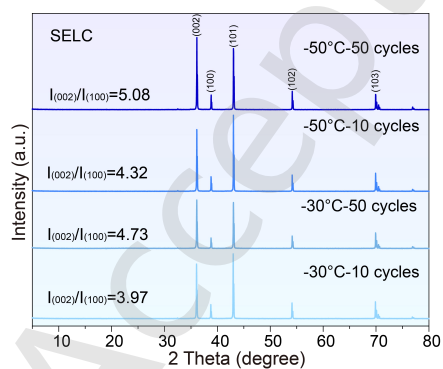


Figure S33. XRD patterns of the Zn anode after 10 and 50 cycles in the SELC electrolyte at -30 °C and -50 °C.

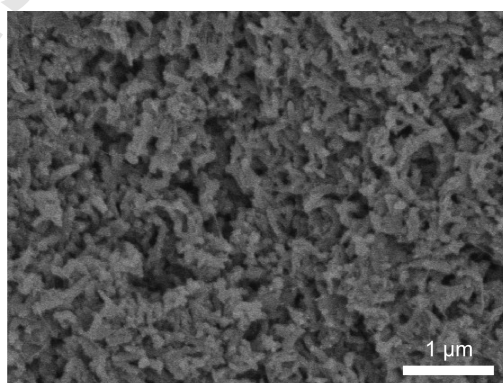


Figure S34. SEM image of the PANI cathode.

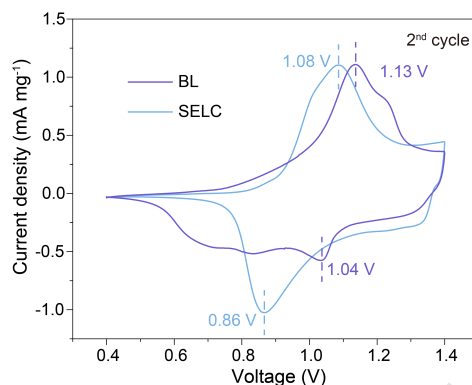


Figure S35. CV curves of Zn||PANI full cells in different electrolytes.

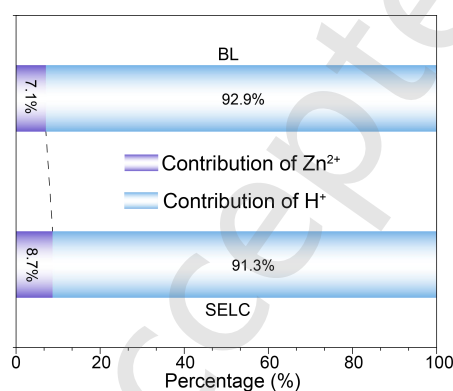


Figure S36. Estimated relative contributions of Zn^{2+} and H^+ to the second-cycle discharge capacity of Zn||PANI full cells using the BL and SELC electrolytes.

To quantitatively distinguish the relative contributions of Zn^{2+} and H^+ to the charge-storage process, inductively coupled plasma-optical emission spectrometry (ICP-OES) measurements were performed on PANI cathodes collected at the charged and discharged states of the second cycle in both the SELC and BL electrolytes. The reversible Zn^{2+} contribution during discharge was quantified from the difference in Zn content between these two electrochemical states.

The absolute amount of Zn in each electrode was first calculated according to:

$$m_{\text{Zn}} = \frac{C_{\text{Zn}} \times V}{1000}$$

where C_{Zn} is the Zn concentration measured by ICP-OES (mg L^{-1}) and V is the digestion volume (25 mL). The Zn content normalized to the PANI active material

was then calculated as:

$$w_{Zn} = \frac{m_{Zn}}{m_{PANI}}$$

where m_{PANI} is the actual mass of PANI in the corresponding electrode.

Table S2. ICP-OES analysis of Zn content in PANI cathodes at the charged and discharged states of the second cycle.

Cathode state	ICP Zn concentration (mg L ⁻¹)	PANI mass (mg)	Zn amount (mg)	Zn content normalized to PANI (mg g ⁻¹)
SELC-Dis.	8.1904	1.559	0.20476	131.34
SELC-Cha.	7.5879	1.533	0.18970	123.74
BL-Dis.	7.0523	1.624	0.17631	108.56
BL-Cha.	6.7349	1.638	0.16837	102.79

For the SELC electrolyte, the ICP-OES concentrations of the second-cycle discharged and charged cathodes are 8.1904 and 7.5879 mg L⁻¹, respectively. With PANI masses of 1.559 and 1.533 mg, the corresponding Zn contents are calculated as:

$$w_{Zn,dis.} = \frac{8.1904 \times 0.025}{0.001559} = 131.34 \text{ mg g}^{-1}$$

And

$$w_{Zn,cha.} = \frac{7.5879 \times 0.025}{0.001533} = 123.74 \text{ mg g}^{-1}$$

Therefore, the reversible Zn uptake during the second discharge is:

$$\Delta w_{Zn} = 131.34 - 123.74 = 7.60 \text{ mg g}^{-1}$$

According to the two-electron redox reaction of Zn²⁺, 1 mg of Zn corresponds to approximately 0.82 mAh. Thus, the capacity associated with reversible Zn²⁺ insertion is:

$$Q_{Zn^{2+}} = 7.60 \times 0.82 = 6.23 \text{ mAh g}^{-1}$$

Given the measured second-cycle discharge capacity of 71.56 mAh g⁻¹, the relative Zn²⁺ contribution is:

$$Contribution_{Zn^{2+}} = \frac{6.23}{71.56} \times 100\% = 8.7\%$$

The same calculation was performed for the BL electrolyte. The Zn concentrations of

the second-cycle discharged and charged cathodes are 7.0523 and 6.7349 mg L⁻¹, respectively, with corresponding PANI masses of 1.624 and 1.638 mg. The normalized Zn contents are therefore 108.56 and 102.79 mg g⁻¹, giving:

$$\Delta w_{Zn} = 108.56 - 102.79 = 5.77 \text{ mg g}^{-1}$$

$$Q_{Zn^{2+}} = 5.77 \times 0.82 = 4.73 \text{ mAh g}^{-1}$$

Based on the second-cycle discharge capacity of 66.94 mAh g⁻¹, the Zn²⁺-associated capacity contribution in the BL electrolyte is estimated to be:

$$Contribution_{Zn^{2+}} = \frac{4.73}{66.94} \times 100\% = 7.1\%$$

Assuming that the reversible capacity is predominantly contributed by H⁺ and Zn²⁺ storage, the remaining H⁺-associated contributions are therefore estimated to be approximately 91.3% for SELC electrolyte and 92.9% for BL electrolyte. These quantitative results demonstrate that proton-associated storage dominates the capacity while a measurable reversible Zn²⁺ contribution is retained in both electrolytes, thereby substantiating the proposed H⁺/Zn²⁺ co-insertion/extraction mechanism.

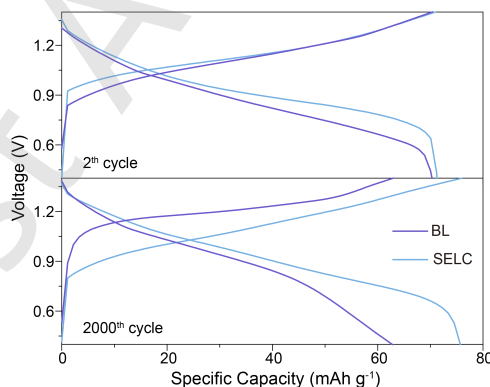


Figure S37. Specific capacity-voltage curves of Zn||PANI full cells with different cycle numbers at a current density of 2 A g⁻¹ in the BL and SELC electrolytes.

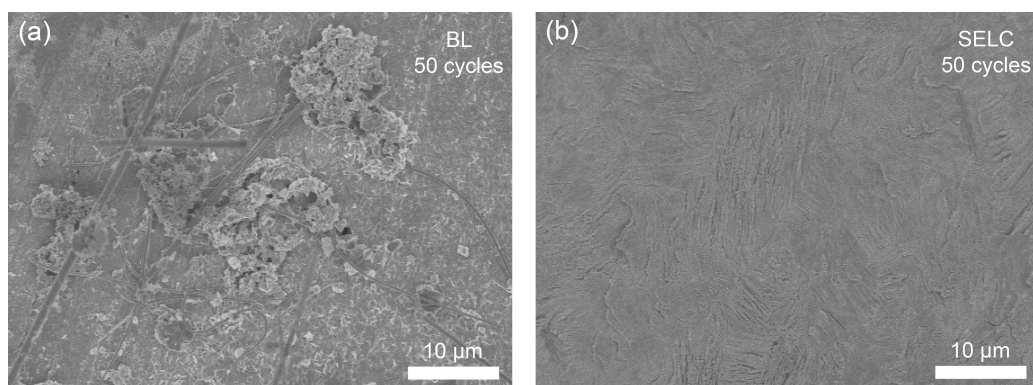


Figure S38. SEM images of the Zn anode after 50 cycles of the Zn||PANI full cell in the (a) BL and (b) SELC electrolytes.

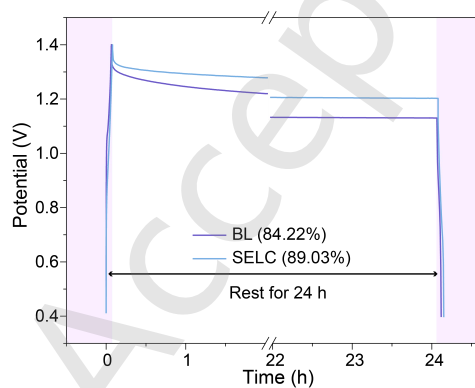


Figure S39. Self-discharge tests after a rest of 24 h.

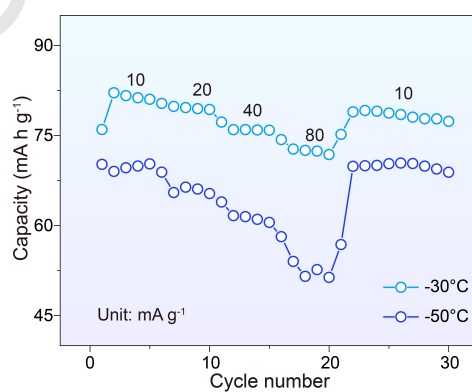


Figure S40. Rate performance of Zn||PANI full cells in the SELC electrolytes at -30°C and -50°C .

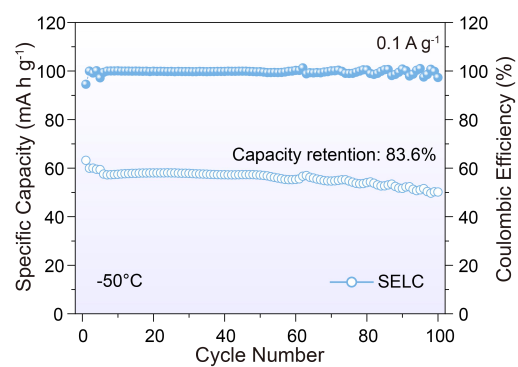


Figure S41. The cycling stability of Zn||PANI full cell under 0.1 A g⁻¹ at -50 °C.