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Article

Keywords:

Posted Date: December 15th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-1158034/v1>

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**Solvation Structure and Interfacial Regulation for Extremely Stable Zinc Metal Anodes
Operating in a Wide Range of Temperatures**

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Abstract

Aqueous zinc-metal batteries are promising for large-scale energy storage owing to their reasonable energy density, safety and low cost. However, their practical applications are limited by hydrogen evolution, corrosion, and dendrite formation of Zn anode and there is trade-off between efficiency and stability at high and low temperatures. Herein, we propose a solvation chemistry regulation strategy that can adjust the Zn^{2+} -solvation structure and *in situ* form a robust and Zn^{2+} -conducting $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ SEI on the Zn surface, using hybrid electrolytes of water and a polar aprotic N, N-dimethylformamide. As verified by experimental characterizations and computational analyses, the unique solvation structure and the newly formed solid electrolyte interface are created by hybrid electrolytes, resulting in highly reversible and dendrite-free Zn plating/stripping process as well as thermal stability and high ionic conductivity from -30 to 70 °C. The Zn||Zn symmetric cells in hybrid electrolytes are very stable over 2500 h at 25 °C and 2000 h even at -20 °C. Thus, the stability and reversibility of the hybrid zinc-ion capacitors with Zn metal anode in hybrid electrolytes are firstly achieved in a wide and extreme temperature range, demonstrating high capacity retentions and Coulombic efficiencies over 14000, 10000, and 600 cycles at 25 , -20 , and 70 °C, respectively.

1 Introduction

2 Rechargeable aqueous zinc metal batteries (AZMBs) have received significant attention to replace
3 conventional lithium-ion batteries because of the inherent advantages of the zinc (Zn) metal anodes,
4 including high theoretical gravimetric and volumetric capacities (820 mA h g^{-1} and $5855 \text{ mA h cm}^{-3}$),
5 low cost, and natural abundance¹⁻⁴. Given by the proper plating/stripping potential of Zn metals,
6 AZMBs further takes advantages in terms of high ionic conductivity and environmental benignity
7 when they are operated in aqueous electrolytes. Despite this harmonized electrochemistry between Zn
8 metal and aqueous electrolyte, electrochemical performance and stability of AZMBs are deteriorated
9 due to Zn dendrite formation and corrosion, and hydrogen evolution reaction⁵⁻⁹. More critical at higher
10 temperatures $> 60 \text{ }^{\circ}\text{C}$ are these unfavorable reactions that can be accelerated by thermal activation,
11 seriously degrading the stability of the batteries¹⁰. Moreover, the ionic conductivity can be dropped
12 due to water volatilization. On the other hand, even at low temperatures $< 0 \text{ }^{\circ}\text{C}$, the reversible
13 deposition/stripping of Zn metals becomes more sluggish due to the freezing and increased viscosity
14 and salt precipitation¹¹. This dilemma limit high efficiency and long-term stability of AZIBs operating
15 in a wide temperature range of “both below $0 \text{ }^{\circ}\text{C}$ and above $60 \text{ }^{\circ}\text{C}$ ”.

16 Herein, we first propose the rational design of hybrid electrolyte regulating solvation structure and
17 interfacial chemistry for highly efficient and stable ZMBs even at low ($-30 \text{ }^{\circ}\text{C}$) and high ($70 \text{ }^{\circ}\text{C}$)
18 temperatures. Recently, hybrid electrolytes consisting of water and another soluble substance (solid or
19 organic liquid) have been developed to modify the local and/or bulk solvated environment of water for
20 the improved thermodynamic stability¹²⁻¹⁶. Examples of hybrid electrolytes include triethyl
21 phosphate¹⁶, diethyl ether¹⁷, ethylene glycol¹⁸, dimethyl sulfoxide¹⁹, and acetonitrile²⁰ that could
22 enhance the reversibility of Zn deposition for long term cyclability up to 2000 h yet being limited by
23 narrow operating temperatures and/or rates (1 mA cm^{-2} and 1 mA h cm^{-2}).

24 Our chemical strategy that can overcome these bottlenecks is to simply yet more effectively
25 formulate hybrid electrolytes with a polar aprotic solvent including higher Gutmann donor number
26 than water and *in situ* solid electrolyte interphase (SEI) forming capability as illustrated by **Figure 1**.
27 Firstly, this solvent is chosen to disrupt hydrogen bonding networks coordinating with Zn^{2+} , to partially
28 substitute the coordinating H_2O , and finally to modify the solvated structure. Such the modified
29 solvated structure is postulated to increase the Zn^{2+} de-solvation energy, which leads to regulate the

kinetics for homogeneous Zn deposition while not seriously slowing the Zn^{2+} transport^{16–20}. Moreover, the Zn^{2+} transport of solvated structure is persistent even at $-30\text{ }^{\circ}\text{C}$, where the freezing of H_2O is inhibited, for a low temperature operation of AZMBs. Secondly, this solvent can be decomposed at the interface to *in situ* construct a dense and self-repairable SEI onto Zn anode. Thus, the newly formed *in situ* $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ SEI is so electrochemically, mechanically, and thermally stable that the dendrite formation can be suppressed at extreme conditions at $70\text{ }^{\circ}\text{C}$. In order to prove our hypothesis, we chose a polar aprotic N, N-dimethylformamide (DMF) – donor number of 26.6 larger than 18 of H_2O ²¹ and freezing and boiling points of $-61\text{ }^{\circ}\text{C}$ and $153\text{ }^{\circ}\text{C}$ ²² – that can satisfy all of the requirements as discussed above. The superiority of the rationally designed hybrid electrolyte is also confirmed demonstrating highly reversible and dendrite-free Zn plating/stripping performance of over 2500 h operated at $25\text{ }^{\circ}\text{C}$ (1 mA cm^{-2} and 1 mA h cm^{-2}) and 2000 h operated at $-20\text{ }^{\circ}\text{C}$ (0.5 mA cm^{-2} and 0.5 mA h cm^{-2}) in the $\text{Zn}||\text{Zn}$ symmetric cells. Furthermore, the hybrid zinc-ion capacitors (HZICs) with hybrid electrolyte are stably operated in a wide temperature range from -30 to $70\text{ }^{\circ}\text{C}$, achieving a long term cyclability and high Coulombic efficiency.

Results

Solution structure analysis of electrolyte:

It has been known that the free water molecules can combine with Zn^{2+} ions and solvate to form a hydrated zinc ion of $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ in the most common ZnSO_4 electrolytes^{12,23}. In this study, a series of 2 M $\text{ZnSO}_4/\text{H}_2\text{O}/\text{DMF}$ hybrid electrolytes with various volume ratios of H_2O to DMF (6:0, 5:1, 4:2, 3:3, 2:4, 1:5, and 0:6) were prepared (**Supplementary Figure 1**). Homogenous solutions could be formed when the $\text{H}_2\text{O}/\text{DMF}$ ratios were 5:1 and 4:2. However, apparent recrystallization of ZnSO_4 occurred when the H_2O to DMF ratio increased up to 3:3, indicating that DMF was involved in the solvation structure of Zn^{2+} with water and the excess DMF could damage it (**Supplementary Figure 1 and Figure 1**)²⁴. Although DMF is dissolved in H_2O in any proportion constructing an hydrogen bonding (HB), it is not readily soluble with ZnSO_4 due to an antisolvent against aqueous ZnSO_4 electrolyte^{25,26}. Accordingly, the H_2O to DMF ratio is controlled in the range of 6:0 to 2:4.

In order to confirm our strategical hypothesis, the solvation structure of the hybrid electrolytes was investigated by molecular dynamics (MD) simulations and density functional theory (DFT) calculations. The particular number of ions and molecules in the MD simulations box is summarized

in **Supplementary Table 1**. The snapshots of the simulated electrolyte structure (**Figure 2a**, **Figure 2c** and **Supplementary Figure 2**) along with the radial distribution functions (RDFs) and coordination number (CN) analyses (**Figure 2b**, **Figure 2d** and **Supplementary Figure 3**) revealed the pronounced ionic solvation cluster for Zn^{2+} coordinated with SO_4^{2-} , H_2O and DMF. The RDFs of $\text{ZnSO}_4\text{-H}_2\text{O}$ electrolyte present that the primary solvation shell of Zn^{2+} (central ion) is ~ 2.50 Å in distance (**Figure 2b**). After the introduction of DMF, distinct Zn-O (DMF) pair is observed at ~ 1.88 Å, implying that DMF could be incorporated into the Zn^{2+} -solvation structure (**Figure 2d** and **Supplementary Figure 3**). At the increased DMF-to- H_2O ratio, the CN of H_2O in the solvation layer decreases from 3.82 to 3.48, whereas the CN of DMF increases from 0 to 0.44, supporting that DMF molecules are participated in the Zn^{2+} -solvation structure (**Supplementary Figure 4** and **Supplementary Table 2**). In addition, new complexes of $\text{Zn}^{2+}[\text{DMF}]_1[\text{H}_2\text{O}]_4[\text{SO}_4^{2-}]_1$ and $\text{Zn}^{2+}[\text{DMF}]_2[\text{H}_2\text{O}]_3[\text{SO}_4^{2-}]_1$ could be found in the hybrid electrolytes (**Supplementary Figure 5**), which exhibit larger dissociation energies than that of $\text{Zn}^{2+}[\text{H}_2\text{O}]_5[\text{SO}_4^{2-}]_1$ complex (**Figure 2e**). The results elucidate that the DMF molecules have a much stronger affinity to the Zn^{2+} and may significantly change the Zn^{2+} -solvation structure. Meanwhile, the content of $\text{Zn}^{2+}[\text{H}_2\text{O}]_5[\text{SO}_4^{2-}]_1$ complex also decreases from 65.4% in $\text{ZnSO}_4\text{-H}_2\text{O}$ to 51.4% in $\text{ZnSO}_4\text{-H}_2\text{O-DMF}$ (5:1) and 39.6% in $\text{ZnSO}_4\text{-H}_2\text{O-DMF}$ (4:2), respectively (**Supplementary Figure 5**). Furthermore, the relative binding energies of Zn^{2+} to other species can be ranked in the sequence of $\text{Zn}^{2+}\text{-SO}_4^{2-} > \text{Zn}^{2+}\text{-DMF} > \text{Zn}^{2+}\text{-H}_2\text{O}$, suggesting that Zn^{2+} preferentially coordinate with DMF rather than H_2O (**Figure 2f**). Hence, the decreased number of coordinating H_2O would suggest a lower opportunity for side reactions (e.g., HER) during the Zn deposition process.

In order to further explore the solvation structure of the hybrid electrolytes and the interaction between ZnSO_4 and the solvents, various spectroscopic analyses, including nuclear magnetic resonance (NMR), Raman spectrum, and Fourier transform infrared spectroscopy (FTIR) measurements, were conducted. As shown in **Figure 2g**, ^{67}Zn chemical shift of $\text{ZnSO}_4\text{-H}_2\text{O-DMF}$ electrolyte (4.89 ppm) is higher than that of $\text{ZnSO}_4\text{-H}_2\text{O}$ electrolyte (4.73 ppm), indicating an increased surrounding electron density of Zn^{2+} . This finding suggests that DMF is involved in the solvation sheath and replaces some H_2O molecules due to the higher donor number of DMF (26.6) than that of H_2O (18)²¹. Moreover, the ^{17}O chemical shift showed a downshift from 4.56 ppm in $\text{ZnSO}_4\text{-H}_2\text{O}$ electrolyte to 4.26 ppm in $\text{ZnSO}_4\text{-H}_2\text{O-DMF}$ electrolyte, confirming that DMF could be incorporated

into the solvation structure of Zn^{2+} with H_2O (**Supplementary Figure 6**). The Raman spectra of H_2O can be resolved into three component bands centered at 3229, 3409, and 3554 cm^{-1} , which are attributed to be symmetric and asymmetric OH stretching and the free OH of water, respectively (**Figure 2h**)²⁵. Accordingly, the addition of DMF significantly breaks down the strong HB networks consisting of water as confirmed by the weakened OH stretching. Consequently, the blue shift of C-H stretching for DMF is attributed to the reformation of HB between the C=O group of DMF and H_2O molecules. The FTIR spectrum also shows discernible blue-shift in the OH bending vibration at 1600~1700 cm^{-1} and red-shift in the OH stretching vibration at 3000~3500 cm^{-1} of H_2O as the DMF content increases, verifying the reformation of HB between DMF and H_2O ²⁵. Besides, the blue-shift in the C=O bending vibration of DMF (~1661 cm^{-1}) could be observed in the hybrid electrolytes due to the HB between C=O and H_2O . The electrochemical stability windows of various electrolytes were investigated on non-active stain-steel electrodes by linear sweep voltammetry (LSV).

The above calculation (MD and DFT) and experimental (NMR, FTIR, and Raman spectra) results show strong implication on the change of the Zn^{2+} -solvation structure when DMF is incorporated into the electrolyte. As shown in **Figure 2i**, the $\text{ZnSO}_4\text{-H}_2\text{O}$ electrolyte undergoes a larger current response compared to the hybrid electrolytes. This result means that the HER is significantly suppressed by DMF addition, further confirming the reformation of HB arising from the strong interaction between DMF and H_2O . Therefore, the DMF is expected to positively influence the electrodeposition behavior of Zn metal, which further enables a new interface chemistry induced by DMF, as discussed below.

High Zn/Zn^{2+} reversibility and uniform Zn deposits:

The stability and reversibility of the Zn anode in $\text{ZnSO}_4\text{-H}_2\text{O}$ electrolyte with and without DMF were evaluated at a current of 1 mA cm^{-2} and a capacity of 1 mA h cm^{-2} using symmetrical $\text{Zn}||\text{Zn}$ cells (**Figure 3a** and **Supplementary Figure 7**). After the initial activation, the symmetric $\text{Zn}||\text{Zn}$ cells in $\text{ZnSO}_4\text{-H}_2\text{O}$ -DMF ($\text{H}_2\text{O}:\text{DMF} = 5:1$ and 4:2) electrolytes exhibited steady charge/discharge process over 1780 and 2500 h, respectively. By contrast, the $\text{Zn}||\text{Zn}$ cell using $\text{ZnSO}_4\text{-H}_2\text{O}$ electrolyte failed in doing after 92 h of cycling process due to an internal short circuit arising from Zn dendrites. The larger overpotential in hybrid electrolytes than that in $\text{ZnSO}_4\text{-H}_2\text{O}$ electrolyte is attributed to the lower ion conductivity (15.0 mS cm^{-1}) of the former compared to 48.7 mS cm^{-1} of the latter (**Supplementary Figure 8**). $\text{ZnSO}_4\text{-H}_2\text{O}$ -DMF (4:2) was chosen to evaluate the electrochemical performance at higher

current densities due to the longer cycle life of the Zn||Zn cell than that with ZnSO₄-H₂O-DMF (5:1). As shown in **Supplementary Figure 9** and **Figure 3b**, the Zn||Zn cell in ZnSO₄-H₂O-DMF (4:2) electrolyte achieved a stable operating status of over 1400 h at 2 mA cm⁻² and 1000 h at 4 mA cm⁻², respectively, with the specific capacity of 1 mA h cm⁻². As compared to the cycling performances of symmetrical cells plotting the cumulative capacities of Zn||Zn cells as shown in **Figure 3c** (based on the data summarized in **Supplementary Table 4**), ZnSO₄-H₂O-DMF (4:2) electrolyte surpasses the values of most of the previous works at different current densities using the electrolyte optimization strategies^{12, 13, 16–20, 27–41}. **Figure 3d** and **Supplementary Figure 10** exhibit the rate capability of the symmetric cells in hybrid and ZnSO₄-H₂O electrolytes at an area capacity of 1 mA h cm⁻². Although the overpotential of the cells using ZnSO₄-H₂O-DMF electrolyte was slightly larger than that in ZnSO₄-H₂O electrolyte, the former showed a superior rate capability up to 10 mA cm⁻² and a stable cycle life of over 1000 h when the current was changed back to 1 mA cm⁻², whereas the latter revealed short circuits at 4 mA cm⁻² after cycling at 1 and 2 mA cm⁻². In addition, Zn||Cu asymmetrical cells were employed to evaluate the Coulombic efficiency (CE) of Zn plating/stripping (**Figure 3e**). The Zn||Cu cells in hybrid electrolytes exhibit a high average CE of 99.6%, which is enhanced from 99.0% within initial cycles due to the formation of robust SEI. Stable voltage curves for Zn plating/stripping, where the separation of charge and discharge potentials decreases initially and is stabilized at ~40 mV after 50 cycles, are observed in ZnSO₄-H₂O-DMF electrolyte (**Figure 3f**). On the other hand, the fluctuated values for CE and unstable stripping profiles after 80 cycles were found in ZnSO₄-H₂O electrolyte due to dendrite formation, H₂ generation, and the corrosion of Zn (**Supplementary Figure 11**).

The greatly improved performance of Zn anodes is strongly influenced by the suppression of the corrosion reaction of Zn in the hybrid electrolyte. The Zn metal in ZnSO₄-H₂O-DMF electrolytes shows more positive corrosion potential and decreased corrosion current compared to those in ZnSO₄-H₂O electrolyte, indicating a less tendency of corrosion reactions and a lower corrosion rate of the Zn electrode in the hybrid electrolyte (**Supplementary Figure 12**). When Zn foil was immersed in different electrolytes for 5 days, no discernible change was observed in ZnSO₄-H₂O-DMF electrolyte, while numerous scattered flakes were seen in ZnSO₄-H₂O electrolyte (**Supplementary Figures 13–14**). As shown in the XRD patterns of the immersed Zn foils in different electrolytes (**Supplementary**

Figure 15), the byproduct of corrosion ($\text{Zn}_4\text{SO}_4(\text{OH})_6 \cdot 3\text{H}_2\text{O}$) is detected in $\text{ZnSO}_4\text{-H}_2\text{O}$ electrolyte. Pure Zn phase is solely captured in hybrid electrolytes, confirming their anti-corrosion effect. Moreover, the $\text{Zn}||\text{Zn}$ symmetrical cell cycled in the hybrid electrolyte exhibited a more stable interface, as supported by the electrochemical impedance spectroscopy (EIS) evolution during cycles (**Figures 3g and 3h**). Consequently, the charge transfer resistance (R_{ct}) of the $\text{Zn}||\text{Zn}$ cells, which is derived from the semicircles in the high-frequency region, is lower in the $\text{ZnSO}_4\text{-H}_2\text{O-DMF}$ electrolyte than that in $\text{ZnSO}_4\text{-H}_2\text{O}$ electrolyte (**Supplementary Table 5**). In particular, the initial R_{ct} values of the symmetric cells after 30 minutes are gradually reduced after 10 and 20 cycles at 1 mA cm^{-2} and 1 mA h cm^{-2} in both electrolytes, which is attributed to the better contact between Zn anodes and electrolyte as cycled (**Figures 3g and 3h**). The enhanced wettability of Zn foil in the hybrid electrolyte is beneficial for facilitating the Zn^{2+} flux to the Zn surface, reducing the charge transfer resistance as well as the Gibbs free energy of the nucleation during the repeat Zn stripping/plating processes (insets of **Figures 3g and 3h**)²⁷.

In order to confirm the inhibition effect for Zn dendrite growth of the hybrid electrolyte, the Zn deposition morphologies and cross-sectional views in different electrolyte were analyzed using scanning electron microscopy (SEM) and atomic force microscopy (AFM). The Zn surface in $\text{ZnSO}_4\text{-H}_2\text{O}$ electrolyte becomes rough with numerous protrusions (dendrites) and scattered flakes (corrosion products) along with a contact angle of 48.4° after 20 cycles at 1 mA cm^{-2} and 1 mA h cm^{-2} (**Figures 4a and 4b** and inset of **Figure 3g**). Obviously, the smooth dendrite-free morphology and contact angle of $\sim 0^\circ$ was obtained for the Zn cycled in $\text{ZnSO}_4\text{-H}_2\text{O-DMF}$ electrolyte (**Figures 4d and 4e** and inset of **Figure 3h**). Particularly, the AFM altitude intercept of Zn foil cycled in $\text{ZnSO}_4\text{-H}_2\text{O-DMF}$ electrolyte (621.4 nm) is much lower than that in $\text{ZnSO}_4\text{-H}_2\text{O}$ electrolyte (3164.4 nm), which is consistent with the SEM results (**Figures 4c and 4f**). The direct evidence of regulating Zn plating by DMF addition was obtained from the *in situ* optical visualization observation (**Supplementary Movies 1-2**). At 10 mA cm^{-2} , the relatively flat Zn foil in $\text{ZnSO}_4\text{-H}_2\text{O}$ electrolyte in the initial state became uneven and odd after 10 min of deposition, along with discernible gas bubble on the surface (**Figure 4g**). On the other hand, the Zn foil in $\text{ZnSO}_4\text{-H}_2\text{O-DMF}$ electrolyte achieved uniform and compact Zn deposition without the dendrite formation over time interval of 60 min under the same evaluation condition (**Figure 4h**). To further understand the Zn deposition behaviors in different electrolytes,

cyclic voltammetry (CV) and chronoamperometry (CA) characterizations were conducted in Zn||Ti and Zn||Zn symmetric cells, respectively. The nucleation overpotential in ZnSO₄-H₂O-DMF electrolyte is ~120 mV, which is higher than that in ZnSO₄-H₂O electrolyte (**Supplementary Figure 16**). The increased nucleation overpotential is attributed to the strong solvation of Zn²⁺ in the hybrid electrolyte as revealed by the DFT calculation (**Figure 2e**). As derived from the Arrhenius equation, the activation energy in ZnSO₄-H₂O is 58.0 kJ mol⁻¹, lower than 66.0 kJ mol⁻¹ in ZnSO₄-H₂O-DMF, indicating a higher energy barrier of Zn²⁺ deposition in the hybrid electrolyte in accordance with the theoretical calculations (**Supplementary Figure 17**)⁴². Considering that high nucleation overpotential is associated with the fine-grained Zn deposits⁴³, smaller critical nucleus size for Zn deposition is predicted in the hybrid electrolyte, as being herewith confirmed experimentally and theoretically. As verified by the CA test, the deposition model in ZnSO₄-H₂O electrolyte corresponds to a long and rampant 2D ion diffusion process and rough deposition propagation, showing the continuous increase in current density for more than 800 s at a constant potential of -150 mV (**Supplementary Figure 18**). On the other hand, the CA profile in ZnSO₄-H₂O-DMF electrolyte is fitted with a relatively stable 3D diffusion process after 200 s of planar diffusion and nucleation process, indicating a short and placid diffusion and smooth deposition⁴³.

Chemical composition analysis and formation mechanism of the SEI layer on Zn anode:

SEI formed by the addition of DMF was investigated, using focused ion beam transmission electron microscopy (FIB-TEM), XRD, and FTIR. Herein, all the Zn samples were obtained after 20 cycles at 1 mA cm⁻² and 1 mA h cm⁻². As shown in **Figure 5a**, obvious interphase with a thickness of 60~70 nm was created on the Zn surface in ZnSO₄-H₂O-DMF electrolyte, which serves as an electronically insulating barrier restricting the water decomposition and an ionically conducting layer for the uniform Zn²⁺ flux. As expected, such interphase was absent from ZnSO₄-H₂O electrolyte (**Supplementary Figure 19**). XRD analysis of cycled Zn foil in ZnSO₄-H₂O electrolyte demonstrated that Zn₄SO₄(OH)₆·3H₂O byproduct was formed on the Zn surface (**Figure 5b** and **Supplementary Figure 20**). In addition to the peaks of this byproduct, the characteristic peaks of Zn₅(OH)₆(CO₃)₂ could be detected on the Zn foil in ZnSO₄-H₂O-DMF electrolyte (**Figure 5b**). In addition, the FTIR spectra in **Figure 5c** shows that large amount of CO₃²⁻ (~1500 cm⁻¹) and OH⁻ (~3800 cm⁻¹) exists in the SEI for

the Zn foil cycled in the ZnSO₄-H₂O-DMF electrolyte, which is convincing evidence of the presence of Zn₅(OH)₆(CO₃)₂⁴⁴.

The detailed structure of SEI formed in the ZnSO₄-H₂O-DMF electrolyte was characterized by the time-of-flight secondary ion mass spectrometry (TOF-SIMS) and in-depth X-ray photoelectron spectroscopy (XPS). As shown in **Figure 5d**, in the negative mode, obvious OH⁻ (*m/e*=17), CO₃²⁻ (*m/e*=60), and C⁻ (*m/e*=12, originating from the decomposition of CO₃²⁻) signals were found at various sputtering depths, which implies the existence of Zn₅(OH)₆(CO₃)₂ in the SEI. Furthermore, XPS with argon sputtering was conducted to further probe the chemical composition and element depth distribution in SEI. The C atom signal, as an indicator of CO₃²⁻, is stronger than that of S atom (an indicator of SO₄²⁻) at various etching times (**Figure 5e**). On the surface (before etching) of SEI in ZnSO₄-H₂O-DMF electrolyte, minor CO₃²⁻ specie (12.3%) was detected as evidenced by the C 1s spectra in **Figure 5f**. After etching the surface with Ar⁺ bombardment, the ratio of CO₃²⁻ increased to 17.2% at 10 min and remained saturated up to 15 min, implying the formation of a CO₃²⁻ contained interphase. Such resistance against etching might be attributed to a very dense surface interphase. The formation of CO₃²⁻ was further confirmed by O-C/O-S signal in the O 1s spectra at different etching stages (O 1s spectrum in **Figure 5f**). Besides, the SEI contains large amount of Zn-OH and slight Zn-O as observed in the Zn 2p_{3/2} spectrum, which is consistent with the distribution of OH and O²⁻_{lat} signals in O 1s spectrum.

The formation process of Zn₅(OH)₆(CO₃)₂ could be proposed in **Figure 5g**. As CO₃²⁻ was absent in the electrolyte salt (ZnSO₄), the CO₃²⁻ species were formed from the dissolved CO₂ in electrolyte, contributing to the formation of Zn₅(OH)₆(CO₃)₂. In the ZnSO₄-H₂O-DMF electrolyte, the dissolved CO₂ and H₂O reaches the equilibrium in stage i⁴⁵. Then, the hydrolysis of DMF in stage ii can easily occur due to the acid nature of the electrolyte, thereby producing formic acid (HCOOH) and dimethylamine ((CH₃)₂NH) while increasing pH value (**Supplementary Figure 21**)⁴⁶. In stage iii, the dimethylamine spontaneously reacts with HCO₃⁻ under aqueous environment, leading to the production of CO₃²⁻ species as previously demonstrated⁴⁷.

As proven by XRD, FT-IR, TOF-SIMS, and in-depth XPS analyses, Zn₅(OH)₆(CO₃)₂ is formed in SEI through the chemical reaction between CO₃²⁻, OH⁻, and Zn²⁺. Given by that Zn₅(OH)₆(CO₃)₂ is a Zn²⁺ conductor^{33,41}, the fast transport of Zn²⁺ is guided by interfacial layer as confirmed by the

decreased R_{ct} in hybrid electrolyte (**Supplementary Table 6**). Hence, this newly formed SEI allows Zn^{2+} to be quickly transported while preventing the Zn surface from water and preventing side reactions (**Figure 5h**). Based on the above results, the proposed Zn-plating induction mechanism is schematically illustrated in **Figure 1**. In different manner to $ZnSO_4$ - H_2O electrolyte provoking corrosion, HER, and dendrite formation, the $ZnSO_4$ - H_2O -DMF electrolyte allows the Zn anode to achieve uniform and dense Zn deposition for the greatly improved performance, which is attributed to the combined effect of modified solvation structure and interfacial regulation.

Highly stable HZICs operated at wide-range temperature:

To clarify the superiority of our hybrid electrolyte for practical application, HZICs were fabricated by coupling Zn anodes with commercial active carbon (AC) cathodes (**Figure 6**). For comparison, the electrochemical performance of HZICs with $ZnSO_4$ - H_2O electrolyte was evaluated under the same condition. CV curves and galvanostatic charge-discharge (GCD) profiles show that both HZICs in two electrolytes exhibit typical Faradaic features originating from the stripping/plating process of Zn/Zn^{2+} (**Figures 6a and 6b and Supplementary Figure 22**). The specific capacity and IR drop of HZICs in $ZnSO_4$ - H_2O -DMF were nearly comparable to those of $ZnSO_4$ - H_2O at 0.2 A g^{-1} despite the lower ion conductivity (**Figure 6c and Supplementary Figure 8**). Nonetheless, the cycling performance was dramatically improved in hybrid electrolytes. As shown in **Figure 6d**, the HZICs in $ZnSO_4$ - H_2O -DMF demonstrates a long-term stability over 14000 cycles with a CE of nearly 100% at a high current density of 2 A g^{-1} . On the other hand, the capacity decay was severe in $ZnSO_4$ - H_2O , and the CEs are quickly dropped after 3000 cycles indicating the formation of dead Zn. As demonstrated by the morphology of the Zn anodes after 500 cycles in SEM (**Supplementary Figure 23**), massive protrusions were observed on the Zn anode cycled in $ZnSO_4$ - H_2O , while a smooth dendrite- or void-free surface was seen in $ZnSO_4$ - H_2O -DMF.

In comparison to other solvent additives such as dimethyl sulfoxide and acetonitrile, DMF shows a relatively lower freezing point of $-61\text{ }^{\circ}\text{C}^{22}$. Considering that the HBs in $ZnSO_4$ - H_2O -DMF were destroyed by DMF, hybrid electrolyte is expected to provide an anti-freezing nature at low temperatures⁴⁸. $ZnSO_4$ - H_2O starts to be frozen at $-11\text{ }^{\circ}\text{C}$, while the freezing points of the hybrid electrolytes decrease down to $-18\text{ }^{\circ}\text{C}$ and $-32\text{ }^{\circ}\text{C}$ for $ZnSO_4$ - H_2O -DMF (5:1 and 4:2), respectively (**Supplementary Figure 24**). As verified by the temperature-dependent ionic conductivities, the

conductivity values of ZnSO₄-H₂O-DMF (2.8 mS cm⁻¹) and ZnSO₄-H₂O (1.5 mS cm⁻¹) are reversed at -20 °C (**Supplementary Figure 25**). The digital photos in **Figure 6e** support that the freezing of ZnSO₄-H₂O at -20 °C is attributed to the sudden drop of ionic conductivity. By contrast, liquid state was preserved for ZnSO₄-H₂O-DMF with high ionic conductivity. Accordingly, voltage profiles for Zn||Zn symmetrical cells in ZnSO₄-H₂O-DMF were very stable over 2000 h at -20 °C (**Figure 6f**). Even at -20 °C, the HZICs reached a high capacity retention of 99% after 10000 cycles along with high CEs of nearly 100% (**Figure 6g**).

In addition to low temperature operation, the high temperature operation in ZnSO₄-H₂O-DMF needs to be considered for wide range applications. The thermal stability of ZnSO₄-H₂O is strengthened by the addition of DMF due to the inhibited evaporation of H₂O associated with the strong interaction between DMF and H₂O as confirmed by the DSC test from 25 to 150 °C (**Supplementary Figure 26**). At 60 °C, the HZICs using hybrid electrolyte exhibits a much higher reversible capacity of 38.4 mA h g⁻¹ after 1000 cycles at 2 A g⁻¹, while the cells cycled in ZnSO₄-H₂O failed after 570 cycles (**Supplementary Figure 27**). Even at a high temperature of 70 °C, the HZICs could be well operated in ZnSO₄-H₂O-DMF over 600 cycles, but the capacity in ZnSO₄-H₂O was abruptly dropped to near zero after 20 cycles (**Supplementary Figure 28**). When the water in ZnSO₄-H₂O electrolyte is evaporated at high temperatures, solubility in the electrolyte is lowered for the salt precipitation and chemical activity increases causing undesirable reaction, resulting in degrading cyclic stability and capacity of HZICs¹⁰. Moreover, the HZICs with ZnSO₄-H₂O-DMF electrolyte are very tolerant of operating a wide range of temperatures from -30 to 70 °C (**Figures 6h** and **6i**). In the course of the temperature fluctuation, the capacities of HZICs in ZnSO₄-H₂O were suddenly dropped at -20 to 70 °C while those in hybrid electrolytes became much higher. The CEs of the HZICs in hybrid electrolytes were ≈100%, while cell failure was observed in DMF-free electrolyte when cycled at -30 °C and 70 °C (**Figure 6i** and **Supplementary Figure 29**). To the best of our knowledge, this is the first record of Zn metal anode in liquid electrolytes to achieve the outstanding performances and stabilities in a wide-range extreme temperature range.

In order to investigate the stability of the Zn anode-electrolyte interphase at low and high temperatures, the EIS test was conducted for the Zn||Zn symmetrical cells after 20 cycles at -20 °C and 70 °C with a current of 1 mA cm⁻² and a capacity of 1 mA h cm⁻² (**Supplementary Figure 30** and

Supplementary Table 6). It notes that the first semicircle (R_{int}) is associated with ion adsorption and desorption on the SEI at the high-frequency region, and the other is attributed to the R_{ct} at the medium-frequency region¹⁸. The R_{int} can be fitted with 3077 (at $-20\text{ }^{\circ}\text{C}$) and $8.9\text{ }\Omega$ (at $70\text{ }^{\circ}\text{C}$), corresponding to an ion conductivity of $1.1\sim 1.3\times 10^{-6}$ and $3.8\sim 4.4\times 10^{-4}\text{ mS cm}^{-1}$, respectively, which results in guiding uniform Zn flux and deposition through SEI layers. In order to evaluate the thermal stability of SEI, we synthesized the sheet-like $\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$ compounds *via* a facile precipitation method⁴⁹, as characterized by SEM and XRD (**Supplementary Figure 31**). As shown in TGA (**Supplementary Figure 32**), the weight loss at below $200\text{ }^{\circ}\text{C}$ occurs due to the evaporation of adsorbed water, then one endothermic peak is captured at about $250\text{ }^{\circ}\text{C}$, indicating the thermal decomposition of $\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$ ($\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2 \rightarrow 5\text{ZnO} + 2\text{CO}_2 + 3\text{H}_2\text{O}$ ⁴⁹). This decomposition temperature is far beyond the operating temperature of the HZIC at $70\text{ }^{\circ}\text{C}$, confirming an outstanding interfacial thermal stability. Therefore, the wide-range temperature tolerant electrochemical performances of HZIC cells in hybrid electrolytes are attributed to the following aspects: The modified solvated structure and the newly formed $\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$ SEIs of the hybrid electrolyte leads to achieve its thermal stability at high temperatures and high ion conductivity at low temperatures.

Discussion

In summary, we developed a new electrolyte chemistry for Zn metal batteries by adding DMF as a co-solvent in the electrolyte, thus manipulating the solvation structure of Zn^{2+} and the formation of SEI. Both of experimental and simulation analysis results indicated that the intensified HB of DMF- H_2O and weakened solvation interaction of Zn^{2+} with H_2O were realized by the strong solvation effect between DMF and Zn^{2+} . This unique Zn^{2+} solvation structure promotes the *in situ* formation of a Zn^{2+} -conducting and robust $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ SEI, which is confirmed by comprehensive characterizations. As a result, this hybrid electrolyte could effectively suppress the parasitic reactions, which enables highly reversible and dendrite-free Zn plating/stripping performance of over 2500 h (1 mA cm^{-2} and 1 mA h cm^{-2}) and 1000 h (4 mA cm^{-2} and 1 mA h cm^{-2}) in the Zn||Zn symmetric cells. Furthermore, the DMF-contained hybrid electrolyte allows a greatly extended cycling stability in HZICs that couple Zn anode and AC cathode when they are operated at a wide operating temperature range from -30 to $70\text{ }^{\circ}\text{C}$. Thus, this work not only proposes a simple but effective electrolyte modification approach to achieve dendrite-free Zn anodes for high-performance aqueous zinc-based energy storage devices

operated at wide-range temperature, but also shows a new electrolyte chemistry which can also guide the design and development of other aqueous electrochemical energy storage systems.

Methods

Chemical Reagents. Zn foil (250 μm in thickness, 99.9% trace metals basis, Sigma-Aldrich) was polished with sandpapers and then washed by ethanol before use. $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (99.5%, Junsei Chemical Co.,Ltd.), N, N-Dimethylformamide (DMF, 99.9%, DAEJUNG), and active carbon (YP-50F, Kuraray) were directly used without any further purification.

Preparation of Electrolytes. Firstly, DMF was mixed with deionized water in different volume ratios (1:5, 2:4, 3:3, 4:2, and 5:1). And then stoichiometric amount of 2M $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ was dissolved in the above solvents by stirring for 12 h. For comparison, the solutions of 2M $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ in pure DMF and H_2O were also prepared. If without any other special emphasis, $\text{ZnSO}_4\text{-H}_2\text{O-DMF}$ represents the electrolyte of 2M ZnSO_4 in $\text{H}_2\text{O/DMF}$ (4:2 in volume ratio).

Preparation of $\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$ compound. $\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$ were synthesized using a precipitation method. In a typical synthesis procedure, 3 M NH_4HCO_3 and 1 M NH_4OH were mixed under continuous stirring at room temperature for 10 min. Then the mixed solution was dropped into a solution of 3 M ZnSO_4 under continuous stirring at room temperature for 30 min. After that, the resulting white product was collected by filtration, thoroughly washed with deionized water several times, and then dried at 80 $^\circ\text{C}$ for 12 h.

Characterizations. The morphologies were observed on a SEM (Field-emission JEOL JSM-7500F). TEM images were taken using a Zeiss Libra 200 Cs MC TEM tool with an acceleration voltage of 200 kV. The TEM sample was prepared *via* a focused ion beam (FIB, SMI 3050TB) milling and lift-off process, and the ensuing low-kV Ar surface milling was conducted on the thin samples at 700 V (Fischione Model 1040 NanoMill) for 15 min as a post treatment to remove damaged surface layer formed on the thin samples caused by heavy Ga ion beam thinning in the FIB system. The crystal structures were identified by XRD analysis performed on an X'Pert Pro X-ray diffractometer

1 (PANalytical, Almelo, the Netherlands) device operated at 40 kV and 30 mA, using Cu-K α radiation
2 ($\lambda = 0.154$ nm) as the X-ray source. The surface chemistry was determined by XPS (ESCALAB 250
3 Xi, Thermo Fisher). The contact angles between Zn anodes and electrolyte were measured using a
4 liquid-droplet analysis tool (SmartDrop, Femtofab Co., Ltd, Korea). Atomic force microscopy (AFM)
5 test was conducted on AFM (AFM-5000, Hitachi, Tokyo, Japan). The Fourier transform infrared
6 (FTIR) spectra were measured with a Jasco FT/IR6200 spectrophotometer. ^{67}Zn and ^{17}O NMR spectra
7 of electrolyte were obtained using a Bruker Avance-NEO-600 NMR spectrometer (Bruker
8 Corporation, MA, USA). 2M $\text{Zn}(\text{NO}_3)_2$ in D_2O was used as the reference solution during the testing
9 process of ^{67}Zn NMR. The Raman experiments were conducted in a XperRam C confocal micro-
10 Raman microscope (NANOBASE Inc., Korea) using a laser excitation wavelength of 532 nm (laser
11 power for the sample was 2 mW). Time-of-flight SIMS (TOF-SIMS) experiments were conducted
12 using a TOF-SIMS 5 (ION-TOF GmbH, Münster, Germany). A pulsed 25 keV Bi^+ primary ion source
13 was employed for analysis, and the data were collected in $40\text{ }\mu\text{m}^2$ areas along the length of the
14 rectangular sample. The dried $\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$ powders were analyzed using combined
15 thermogravimetry–differential thermal analysis (TG–DTA, Hitachi STA 7300) under air atmosphere
16 with a heating rate of $5\text{ }^\circ\text{C min}^{-1}$.

17 **Electrochemical Measurements.** Corrosion test was carried on an electrochemical workstation of
18 EC-Lab (NEO Science). Linear polarization and chronoamperograms (CAs) measurements were
19 operated with a three-electrode configuration. The corrosion potential and corrosion current were
20 calculated from Tafel fit system in electrochemical workstation. Bare Zn was used as the working
21 electrode and counter electrode, and silver chloride (Ag/AgCl) electrode as the reference electrode.
22 Electrochemical impedance spectroscopy (EIS) studies were performed at a sinusoidal perturbation of
23 5 mV and in the frequency range of 1 mHz~100 kHz. Symmetric $\text{Zn}||\text{Zn}$ cells were assembled to
24 explore the long-term plating/stripping stability of Zn anodes in different electrolytes with a
25 charge/discharge areal capacity of 1 mA h cm^{-1} at different current densities. Also, similar $\text{Zn}||\text{Ti}$

asymmetric cells were carried out to analyze the Coulombic efficiency for Zn plating/stripping process. Galvanostatic cycling tests were conducted with a Maccor battery tester using CR2032-type coin cells. The separator was glass microfiber membrane (Whatman, Grade GF/A).

The ionic conductivity of the electrolytes was measured at different temperatures through EIS with cells consisted of two parallel Pt-plate electrodes (1 cm × 1 cm). The applied frequency was in the range of 1 mHz~100 kHz with a sinusoidal perturbation of 5 mV. The electrode resistance was obtained from the intercept of Nyquist plot and the ionic conductivity was calculated according to the following equation:

$$\sigma = \frac{d}{R_s S} \quad (S1)$$

where σ (S cm⁻¹) is the per unit conductivity, R_s is the electrolyte resistance, d (cm) is the interval distance (1 cm) between the two Pt-plate electrodes, S (cm²) is electrode area.

The activation energy (E_a) is calculated based on the Arrhenius equation:

$$\frac{1}{R_{ct}} = Ae^{(-\frac{E_a}{RT})} \quad (S2)$$

where R_{ct} is the charge transfer resistance, A is the preexponential constant, T is the absolute temperature, R is the standard gas constant.

The ion conductivity (δ) is calculated based on the following equation:

$$\delta = \frac{L}{R_{int} S} \quad (S3)$$

where δ (S cm⁻¹) is the per unit conductivity, R_{int} is the interfacial resistance, L (cm) is the thickness of the SEI (60~70 nm), S (cm²) is electrode area.

Hybrid zinc-ion capacitors were fabricated by using bare Zn foil as anode, active carbon as cathode, and the above prepared aqueous solution as electrolyte. The active carbon (80 wt%) were mixed with acetylene black (10 wt%) and polyvinylidene fluoride (10 wt%) in N-methyl-2-pyrrolidone. The obtained slurry was then casted on Ti foil and dried at 80 °C in vacuum for 12 h. The mass loading of active material was ~5 mg cm⁻². The galvanostatic cycling tests was tested on a

Maccor battery tester in the voltage range of 0.2~1.8 V (Zn^{2+}/Zn). Cyclic voltammetry tests were carried on an electrochemical workstation of EC-Lab (NEO Science).

Molecular Dynamics Simulations. Molecular dynamics (MD) simulations were conducted using the Large Scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) code and Optimized Potential for Liquid Simulations-all atom (OPLS-AA) force field. Three models were constructed to model the electrolytes with different DMF/ H_2O ratios as listed in **Supplementary Table 1**. The number of ions and solvent molecules in each model are listed in **Supplementary Table 2**. The initial atomic coordinates were generated with Packing Optimization for Molecular Dynamics Simulations (Packmol) program and the final constructions were visualized by VESTA.

For all the molecular dynamics simulations, the time step was fixed to be 1 fs. The temperature was set to be 293 or 263 K with Nose–Hoover thermostat with a time constant of 1 ps. The electrolyte systems were first equilibrated in NPT ensemble using the Parrinello–Rahman barostat to maintain the pressure of 1 atm with a decay constant of 0.1 ps for 500 ps. After that, a 7-ns production run in NVT ensemble was conducted. Only the final 5-ns was sampled for mean square displacement and radial distribution function (RDF) analyses.

Density Functional Theory Calculations. The density functional theory calculations were conducted in Gaussian (G09) program with parameter hybrid method using the Lee–Yang–Parr correlation functional (B3LYP). The basis was set to 6-311G++G(d, p). The solvation effect was considered with integral equation formalism variant of the Polarizable Continuum (IEFPCM) model. The binding energy (E_b) between solvents and Zn ion was defined as following:

$$E_b = E_{\text{total}} - E_{\text{Zn}} - E_{\text{solvent/ion}} \quad (\text{S4})$$

where E_{total} , E_{Zn} , and $E_{\text{solvent/ion}}$ are the total energy of the Zn^{2+} - H_2O (DMF or SO_4^{2-}) complex, Zn ion, and solvent/ SO_4^{2-} , respectively.

The dissociation energy (E_d) of the $\text{Zn}[\text{DMF}]_x[\text{H}_2\text{O}]_y[\text{SO}_4^{2-}]_z$ was calculated by using the following equation:

$$E_d(\text{Zn}[\text{DMF}]_x[\text{H}_2\text{O}]_y[\text{SO}_4^{2-}]_z) = E_{\text{Zn}^{2+}} + xE_{\text{H}_2\text{O}} + yE_{\text{DMF}} + zE_{\text{SO}_4^{2-}} - E_{\text{Zn}[\text{DMF}]_x[\text{H}_2\text{O}]_y[\text{SO}_4^{2-}]_z} \quad (\text{S5})$$

where $E_{\text{Zn}^{2+}}$, $x E_{\text{H}_2\text{O}}$, $y E_{\text{DMF}}$, $z E_{\text{SO}_4^{2-}}$, and $E_{\text{Zn}[\text{DMF}]_x[\text{H}_2\text{O}]_y[\text{SO}_4^{2-}]_z}$ are the total energies of the Zn^{2+} cation, the H_2O molecule, the DMF molecule, the SO_4^{2-} anion, and the $\text{Zn}[\text{DMF}]_x[\text{H}_2\text{O}]_y[\text{SO}_4^{2-}]_z$ complexes, respectively.

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request

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Acknowledgement

This research was supported by the financial support from the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT) (NRF-2020R1A3B2079803), Republic of Korea.

Author Contributions

P. X. designed the experiments and analyzed data. Y. Kang, L. Zeng, Q. Dou, X. Han, R. Harpalsinh, Z. Tian, J. H. Park assisted with the material synthesis and characterizations. N. Yao, X. Chen, Q. Zhang conducted the calculations. H. S. P. conceived and supervised the project. All authors contributed to interpretation of the results.

Competing Interests Statement

The authors declare that they have no competing interests.

Additional Information

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4

Figures

Figure 1. Schemes illustrating different reaction processes of Zn^{2+} solvation structure and corresponding interfacial interaction between Zn anode surface and electrolyte under (a) $\text{ZnSO}_4\text{-H}_2\text{O}$ and (b) $\text{ZnSO}_4\text{-H}_2\text{O-DMF}$ electrolytes.

Figure 2. Snapshots of (a) ZnSO₄-H₂O and (c) ZnSO₄-H₂O-DMF electrolytes during MD simulations. Radial distribution functions (RDFs) and coordination number distribution functions obtained from MD simulations for (b) ZnSO₄-H₂O and (d) ZnSO₄-H₂O-DMF electrolytes. (e) Dissociation energy of different Zn²⁺[DMF]_x[H₂O]_y[SO₄²⁻]_z complexes. (f) Relative binding energy for Zn²⁺ with different species obtained from DFT calculations. (g) ⁶⁷Zn NMR spectra of ZnSO₄-H₂O and ZnSO₄-H₂O-DMF electrolytes. (h) Raman (left) and FTIR (right) spectra of H₂O, DMF, and different electrolytes. (i) LSV response curves of different electrolytes at 0.5 mV s⁻¹.

Figure 3. Cycling performance of Zn||Zn symmetric cells in different electrolytes at (a) 1 mA cm⁻² and (b) 4 mA cm⁻² for 1 mA h cm⁻². The voltage increase in (a) at around 700 h is caused by the temperature drop due to power failure of the temperature-controlled equipment. (c) Comparison of the cumulative capacity with recently reported Zn anodes using optimization strategies. (d) Rate performance of Zn||Zn symmetric cell in ZnSO₄-H₂O-DMF at various current densities. (e) CE of Zn plating/stripping on Cu foil in different electrolytes and (f) the corresponding charge-discharge profiles in ZnSO₄-H₂O-DMF electrolyte at 1 mA cm⁻² for 1 mA h cm⁻². EIS of Zn||Zn symmetric cells in (g) ZnSO₄-H₂O and (h) ZnSO₄-H₂O-DMF before cycle, rest 30 min, and after cycling (insertion are the contact angles before and after 20 cycles).

Figure 4. SEM images of Zn anodes after 20 cycles in (a-b) $\text{ZnSO}_4\text{-H}_2\text{O}$ and (d-e) $\text{ZnSO}_4\text{-H}_2\text{O-DMF}$. AFM images of Zn anodes after 20 cycles in (c) $\text{ZnSO}_4\text{-H}_2\text{O}$ and (f) $\text{ZnSO}_4\text{-H}_2\text{O-DMF}$. Operando optical images of Zn anodes in (g) $\text{ZnSO}_4\text{-H}_2\text{O}$ and (h) $\text{ZnSO}_4\text{-H}_2\text{O-DMF}$ observed in symmetric transparent cells cycled at 10 mA cm^{-2} (the scale bar is $200 \mu\text{m}$ in each image).

Figure 5. (a) TEM image of Zn anode surface after 20 cycles in ZnSO₄-H₂O-DMF. (b) XRD patterns and (c) FTIR spectra of Zn anodes after 20 cycles in ZnSO₄-H₂O and ZnSO₄-H₂O-DMF. (d) TOF-SIMS analysis of Zn anode surface after 20 cycles in ZnSO₄-H₂O-DMF. (e) Atomic composition of the SEI on Zn anode surface after 20 cycles in ZnSO₄-H₂O-DMF. (f) XPS spectra of C 1s, O 1s, and Zn 2p_{3/2} after Ar⁺ sputtering with different times. (g) Formation mechanism and (h) schematic diagram of proposed Zn₅(OH)₆(CO₃)₂-contained SEI.

Figure 6. Electrochemical performances of HZICs with different electrolytes using the AC electrodes as a working electrode and the Zn foil as the counter electrode at wide operating temperatures. (a) CV curves of HZICs in ZnSO₄-H₂O-DMF at different scan rate. (b) Galvanostatic charge-discharge profiles of HZICs in ZnSO₄-H₂O-DMF at various current densities. (c) Galvanostatic charge-discharge profiles of HZICs in different electrolytes at 0.2 A g⁻¹. (d) Cycling performance of HZICs with different electrolytes at 2 A g⁻¹. (e) The physical state of ZnSO₄-H₂O and ZnSO₄-H₂O-DMF electrolytes at -20 °C. cycling performance of (f) Zn||Zn symmetric cell at 0.5 mA cm⁻² and 0.5 mA h cm⁻² and (g) HZICs at 0.5 A g⁻¹ in ZnSO₄-H₂O-DMF. (h) Galvanostatic charge-discharge profiles in ZnSO₄-H₂O-DMF tested at 0.5 A g⁻¹ and various temperatures. (i) The temperature fluctuation test for HZICs at 0.5 A g⁻¹.

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