Electronic Supplementary Information

A Corrosion-Free Zinc Metal Battery with Ultra-Thin Zinc Anode and High Depth of Discharge

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Experimental

Preparation of Electrolytes

Zinc triflate $(Zn(OTF)_2)$ was purchased from Innochem without further purification. The baseline electrolyte was prepared by dissolving 0.75 M $Zn(OTF)_2$ into the deionized water, which was marked as H₂O for short. The modified electrolytes were prepared by dissolving 0.75 M $Zn(OTF)_2$ into the 1,3-dimethyl-2imidazolidinone solvent, marked as DMI for short. The pure deionized water was marked as pure H₂O for short. The pure 1,3dimethyl-2-imidazolidinone solvent was marked as pure DMI for short.

Preparation of Cathodes

The polyaniline (PANI) doped by sulfonic acid was purchased from Macklin without further purification. The PANI cathode was fabricated by mixing the PANI active materials with Super P and polytetrafluoroethylene (PTFE) with the weight ratio of 6:3:1. The above mixture was mixed with a certain dose of anhydrous ethanol to form a slurry. The slurry was rolled onto a titanium mesh as the electrode. Then it was dried in a vacuum oven at 60°C overnight. The mass loading of PANI cathodes after drying ranged from 4.0 to 18.0 mg cm⁻², whose specific loading was explicitly marked in the diagrams.

Fabrication of Cells

Zinc foil with a thickness of 10 μ m and copper foil with a thickness of 10 μ m were adopted as electrodes. Whatman glass fiber (GF/D) was adopted as the separator for electrochemical tests. Titanium mesh was adopted as the current collector. Zinc foil with a thickness of 80 μ m was adopted in the test of in-situ optical images. CR2032-type coin cells and single-layer pouch cells were adopted for evaluating the electrochemical performance. Both cells were assembled in the air atmosphere. The sizes of positive and negative electrodes in pouch cells were 43 mm*56 mm and 45 mm*58 mm.

Electrochemical Tests

The cyclic voltammetry (CV), linear scanning voltammetry (LSV), electrochemical impedance spectroscopy (EIS), transfer number (TN) test, and linear polarization curves (LPC) were conducted using a Bio-Logic electrochemical workstation (VMP-300). Galvanostatic cycling and rate capability were tested with the LAND testing system. Three electrodes were performed in the atmosphere, and a 50 mL electrolytic cell was used as the testing

vessel. Specific testing conditions were explicitly marked in diagrams. The de-solvation energy test was performed using a Princeton Applied Research electrochemical workstation (PARSTAT 4000A). The tested Zn||Zn symmetric cells were precycled 30 times at the current density of 1 mA cm⁻² and the areal capacity of 0.5 mAh cm⁻². Then, their electrochemical impedance spectroscopies were collected from 100 mHz to 100 kHz at different temperatures. Finally, the interfacial resistances at different temperatures were fitted using the Arrhenius equation to obtain the de-solvation energy.

Material Characterizations

Scanning electron microscopy (SEM, Hitachi SU8010, Japan) was performed to observe the morphology of the metallic zinc. X-ray diffraction (XRD, D8 Advance, Germany) with Cu-K_{α 1} radiation was performed to identify the components of the metallic zinc. The conductivity meter (Mettler Toledo FE38, Switzerland) and rotational viscometer (NDJ-79, China) were adopted to measure the physicochemical properties of electrolytes. Differential scanning calorimetry (DSC, Mettler Toledo, Switzerland) and thermal gravimetric analysis (TGA) were adopted to test the phase-transition temperature of electrolytes. Attenuated total reflectance infrared

spectrometer (ATR, Nicolet IS50, U.S.A.) and Raman spectrometer (Horiba Lab RAM HR800, U.S.A.) were adopted to obtain changes in characteristic functional groups. Nuclear magnetic resonance spectrum (NMR, Bruker Avance III 400, Germany) was adopted to analyze interactions between electrolyte components. Highresolution mass spectroscopy (HRMS, Q exactive Focus, U.S.A.) was adopted to confirm electrolyte components.

DFT Calculation

The spin-polarized density functional theory (DFT) computations with the local meta–GGA exchange correlation functional M06-2x were carried out by using the Gaussian 16 program. In this work, all geometry optimizations were fully relaxed, and energy calculations were obtained with 6-311G(d) basis sets for main elements and SDD for Zn element. The bulk solvent effect of water media was considered by the self-consistent reaction field (SCRF) method using the SMD solvent model with M05-2x/6-31G(d) method¹. The electrostatic distribution was visualized and analyzed by Multiwfn² and VMD³ software.



Figure S1. Schematic of the conventional and the weaklycoordinated aprotic electrolytes. (a) H⁺ derived from the hydrolysis of zinc salts will continuously consume metallic zinc and form harmful corrosion products; Meanwhile, due to the instability of water molecules in $[Zn(H_2O)_6]^{2+}$, serious parasitic reactions will occur during zinc plating/stripping. (b) The adoption of DMI essentially prevents the generation of H⁺, which fundamentally suppresses the corrosion reactions. Meanwhile, the distinctive weakly-coordinated solvation structures in DMI (*i.e.*, $[Zn(DMI)_3]^{2+}$, $[[Zn(DMI)_4]^{2+}$) endows the zinc metal battery with superior electrochemical performance.



Figure S2. Optical image of electrolytes.

From left to right, 0.25 M $Zn(OTF)_2$ -DMI, 0.50 M $Zn(OTF)_2$ -DMI, 0.75 M $Zn(OTF)_2$ -DMI, 1.00 M $Zn(OTF)_2$ -DMI, 2.00 M $Zn(OTF)_2$ -DMI, and 0.75 M $Zn(OTF)_2$ -H₂O.

The design principle of the current strategy can be concluded as follows. (1) Aprotic: Avoiding the generation of free H⁺ during the dissolution of zinc salts and preventing the metallic zinc from irreversible losses induced by the corrosion; (2) High polar: Ensuring excellent zinc salts solubility in electrolytes; (3) High chemical stability: Remaining stable at room temperature, normal pressure, and light conditions; (4) High electrochemical stability: Preventing from hydrogen and oxygen evolution. (5) Low viscosity: Providing fast ionic transport in the electrolyte and minimizing the polarization voltage; (6) High boiling point: Ensuring the operation of zinc metal batteries at high temperature; (7) Low toxicity: Maintaining the advantage of environmental-benignity of zinc metal batteries;



Figure S3. Average Coulombic efficiency tested by the protocol of "reservoir half-cell".

Zn||Cu half-cells with 0.75 M OTF-H₂O were repeatedly tested by many times, and there were still fluctuations in the charge and discharge curves.



Figure S4. Electrochemical impedance spectroscopies of Zn||Zn symmetric cells with (a) H₂O and (b) DMI at different temperatures.

In aqueous electrolytes, the binding energies of modified solvation structures usually are higher than $[Zn(H_2O)_6]^{2+}$ so that they can replace the original solvated structure. In this case, side reactions induced by the instability of solvated water molecules can be mitigated. However, the higher binding energies increases the difficulty of the de-solvation process. In this work, the distinctive solvation structures are formed in DMI (*i.e.*, $[Zn(DMI)_3]^{2+}$ and $[Zn(DMI)_4]^{2+}$). Their binding energies are lower than $[Zn(H_2O)_6]^{2+}$ in H₂O and some modified solvation structures in reported work⁴⁻⁷ while preventing the side reactions induced by the solvated water molecules. Therefore, it presents excellent electrochemical performance of metallic zinc anode.



Figure S5. Ionic conductivity and viscosity of both electrolytes.



Figure S6. Thermal gravimetric analysis of both electrolytes.

As shown in **Figure S6**, the mass of the H_2O electrolyte started to gradually decrease around 50°C. The mass of the DMI electrolyte started to gradually decrease around 100°C, which was consistent with the results of differential scanning calorimetry. It indicates that the thermal stability of the DMI electrolyte is superior to that of the H_2O electrolyte, which has the potential for stable operation of zinc metal batteries at high temperatures. The specific results of high-temperature storing and cycling tests will be discussed in the next section.



Figure S7. A photographic image of zinc foils. (From left to right: zinc foil being soaked in H_2O after two weeks, zinc foil being soaked in DMI after two weeks, and zinc foil without soaking; their thickness is 10 μ m and the width is about 1 cm)

The above results showed that the adoption of DMI electrolyte avoids the generation of H^+ , and thus mitigates the corrosion reactions of the metallic zinc in electrolytes, which paves the way for the practical application of ultra-thin metallic zinc. However, the complete elimination of H^+ poses a challenge to the H^+ co-insertion typed cathode active materials, whose discharge capacity greatly decreases. By combining aprotic solvents like DMI and water, a tradeoff might be found between cathode and zinc anode, which deserves to be explored in the future.



Figure S8. Magnified SEM images of zinc foil soaked in H_2O and (b) DMI.



Figure S9. Energy dispersive spectroscopy mapping of zinc foil cycled in (a) H₂O and (b) DMI.



Figure S10. Galvanostatic pre-cycling of Zn||Zn symmetric cells.



Figure S11. Cyclic voltammetry curves of Zn||Cu half cells.



Figure S12. Galvanostatic cycling of $Zn \|Cu$ half cells.



Figure S13. Charge and discharge curves of Zn||Cu half cells at the current density of 1.0 mA cm⁻² and the areal capacity of 0.5 mAh cm⁻².



Figure S14. Galvanostatic cycling of Zn||Cu half cells.



Figure S15. Charge and discharge curves of Zn||Cu half cells at the current density of 0.50 mA cm⁻² and the areal capacity of 0.25 mAh cm⁻².



Figure S16. Galvanostatic cycling of Zn||Zn symmetric cells.



Figure S17. Magnified SEM image of the zinc foil cycled in (a) H_2O and

(b) DMI for 10 times.



Figure S18. Charge and discharge curves of Zn||PANI full cells at different current density.

Although Zn||PANI full cells with the DMI electrolyte exhibited a slightly higher discharge capacity than that with the H₂O electrolyte at 0.1 A g^{-1} , but its rate capability at high current density were still lower than that with the H₂O electrolyte limited by its inferior kinetic performance.



Figure S19. Galvanostatic cycling of Zn||PANI full cells before/after aging at 60°C.

Notably, during the electrochemical performance testing of different cathode active materials, it was found that most common cathode materials (*e.g.*, δ -MnO₂, V₂O₅, AC, unmodified PANI) except for sulfonic acid-doped PANI exhibited lower discharge capacity in DMI compared to that in H₂O. It indicates that Zn²⁺ is likely not the only energy storage medium in common cathode active materials, and H⁺ likely contributes a large proportion of discharge capacity. Namely, despite the elimination of H⁺ promotes the practical application of ultrathin metallic zinc anode, but it also leads to the absence of energy storage media H⁺ in common cathode active materials. How to balance the contradictory role of H⁺ in cathode and zinc anode might be one of the next promising research directions.



Figure S20. Charge and discharge curves of Zn||PANI full cells with H_2O

before/after aging.



Figure S21. Charge and discharge curves of Zn||PANI full cells with DMI before/after aging.

Types	Reaction Equations		
Main Reaction:	$Zn+6H_2O \rightleftharpoons [Zn(H_2O)_6]^{2+}+2e^{-}$		
Thermodynamic Instability:	$4Zn+2H^{+}+SO_{4}^{2-}+11H_{2}O \rightarrow$		
	$Zn_4(OH)_6SO_4$ ·5 H_2O +4 H_2 ↑		
Electrochemical Instability:	$4[Zn(H_2O)_6]^{2+}+SO_4^{2-}+6e^- \rightarrow$		
	$Zn_4(OH)_6SO_4{\cdot}5H_2O{+}13H_2O{+}3H_2{\uparrow}$		

Table S1. Analysis of the reaction types and equations on the metalliczinc anode in conventional aqueous electrolytes.

Taking the most common zinc salts (ZnSO₄, zinc sulfate) as an example, there are three types of reactions. Among them, the electrochemical instability receives great attention. In contrast, the thermodynamic instability has not been attracted by enough attention, which results from the active H^+ generated by the hydrolysis reaction of zinc salts in solvent water.

Current	Current	Areal	Average	Lifespan	Ref.
Collector	density	Capacity	Coulombic		
	(mA cm ⁻²)	(mAh cm ⁻²)	efficiency (%)		
Cu	0.5	0.25	99.72%	2000	This
					work
Cu	1	0.5	99.79%	1000	This
					work
Cu	3	1.5	99.94%	500	This
					work
Cu	0.5	0.25	99.20%	1000	18
Cu	2	1	99.60%	750	1 ⁸
Cu	1	0.5	99.68%	400	2 ⁹
Cu	5	1	99.70%	2000	310
Cu	5	5	98.70%	80	310
Ti	5	1	99.50%	1000	4 ¹¹
Cu	4	1	99.05%	800	5 ¹²
Cu	1	1	98 32%	300	5 12
Cu	1	1	00.60%	1600	613
Cu	1	1	99.00%	2000	013
Cu	1	0.5	99.30%	2000	714
Cu	8	8	99.50%	200	8^{15}

Table S2*. Coulombic efficiency of zinc plating/stripping comparisonwith the latest research

Cu	10	10	99.40%	100	815
Ti	2	1	99.66%	1000	9 ¹⁶
Cu	5	1	99.80%	600	1017
Cu	1	0.5	99.66%	2900	1118
Cu	5	1	99.75%	1700	1118
Cu	40	1	99.88%	400	1118
Cu	6	3	99.50%	150	1219
Cu	5	2	99.83%	1200	13 ²⁰
Cu	5	5	99.50%	80	1421
Cu	1	0.5	99.40%	200	1421
Cu	1	1	99.50%	2000	1522
Cu	1	1	99.60%	650	16 ²³
Cu	1	1	99.60%	200	1724
Cu	4	4	99.85%	100	1724
Cu	5	1	99.87%	2500	1825
Ti	0.5	0.5	99.57%	750	1926
Cu	1	1	99.00%	225	2027
Cu	3	3	98.60%	450	2128
Ti	1	1	99.30%	350	227
Cu	1	1	99.50%	600	23 ²⁹

*Note: The current density has a significant impact on the average CE of zinc plating/stripping. Although some references achieved high average

CE of zinc plating/stripping in asymmetric cells at extremely high current density, and this current density is difficult to apply to the electrochemical tests of full cells.

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