Supporting Information for

Design of Cellulosic Poly(Ionic Liquid)s with Hydrogen Bond/Ion Dual Regulation Mechanism for Highly Reversible Zn Anode

Kui Chen,^{ab} Yongzhen Xu,^{ab} Hebang Li,^{ab} Yue Li,^{ab} Lihua Zhang,^{ab} Yuanlong Guo,^{ab} Qinqin Xu,^{ab} Yunqi Li,^{ab} Haibo Xie*^{ab}

K. Chen, Y. Xu, H. Li, Y. Li, L. Zhang, Y. Guo. Q. Xu, Y. Li, H. Xie
^aDepartment of Polymeric Materials & Engineering, Guizhou University, West Campus, Guizhou University, Huaxi District, Guiyang, P.R. China, 550025
Email: hbxie@gzu.edu.cn
^bTechnology Innovation Center for High-Efficiency Utilization of Bamboo-Based Biomass in Guizhou Province, Guiyang 550025, China.

Experimental Section

Chemicals and materials: Microcrystalline cellulose (MCC) with a degree of polymerization of 220 was supplied from Aladdin Reagents Co., Ltd (Shanghai, China). Carbon dioxide (CO₂) with a purity of 99.99% was supplied by Guiyang Sanhe Gas Company. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU), 1-methylimidazole (Mim), triethylamine (Et₃N), methyl bromoacetate ($C_3H_5BrO_2$) were purchased from Aladdin Commerce Reagent Co. Ltd. Dimethyl sulfoxide (DMSO) was purchased from Tianjin Kai Xin Chemical Industry Co., Ltd and dried by 4Å molecular sieves. D₂O and DMSO-d6 were purchased from Sigma-Aldrich Co. Ltd. Acetonitrile (AR), ethyl acetate (AR), dichloromethane (AR) and ethanol (AR) were obtained from Tianjin Kemiou Chemical Reagent Co., Ltd. All reagents were of analytical grade and used without further purification. Zinc trifluoromethanesulfonate (98%, Zn(OTf)₂), ammonium vanadate (99.9%, NH₄VO₃) and oxalic acid dihydrate (C₂H₂O₄·2H₂O) were purchased from Aladdin Reagents Co., Ltd (Shanghai, China). Acetylene black (AB), 1-methyl-2-pyrrolidone (NMP) and poly-(vinylidene fluoride) (PVDF) were purchased from Japan KURARAY (Shanghai, China). Stainless steel mesh (304, 250 mesh) was supplied by Kelude Technology Co., Ltd. Zn foil (100 µm and 30 µm, 99.9%), copper foil (90 µm, 99.99%) were supplied by Canrd Co., Ltd. Glass fiber separator (GF/A2916, 0.029 ± 0.01 mm) was supplied by Olegee technology.

Synthesis of small-molecule ILs precursors ($[Et_3N][Br]$ and [Mim][Br]): The synthesis procedure of [Mim][Br] as follows: a solution of 1-methylimidazole (20.7 g, 253 mmol) and methyl bromoacetate (42.4 g, 277 mmol) in acetonitrile (300 mL) were heated to 50 °C for 24 h. After the reaction, the white powder was precipitated with ethyl acetate and vacuum dried overnight (yield: 87.6%). The synthesis procedure of $[Et_3N][Br]$ has a slight change. Triethylamine (20 g, 198 mmol) and methyl bromoacetate (33.3 g, 217 mmol) were added to 300 ml acetonitrile and reacted at 50 °C for 24 h. After the reaction, a small amount of

dichloromethane was added and evaporated at 85 °C to remove solvent. Finally, the oily product was washed with ethyl acetate to obtain a white solid (yield: 73.2%). The synthetic routes are as follows:



Scheme 1. Synthetic routes of (a) [Et₃N][Br] and (b) [Mim][Br].

Synthesis mechanism: The N atoms on triethylamine and 1-methylimidazole have lone pair electrons, enabling them to act as nucleophiles. The Br atom in methyl bromoacetate, due to its strong electronegativity, is highly susceptible to nucleophilic attack. Consequently, the N atoms in triethylamine and 1-methylimidazole attack the Br atom in methyl bromoacetate, leading to the formation of an intermediate. In this process, the Br atom is substituted by triethylamine and 1-methylimidazole, resulting in the production of triethylamine- and 1-methylimidazole-substituted methyl acetate.

Cellulose dissolution: Cellulose was dissolved according to previous publications.¹ Typically, 2.0 g (12.34 mmol -OH) of MCC, 5.6 g (37.2 mmol) of DBU, and 30.8 g of DMSO were added into a high-pressure reactor, and 2.0 MPa of CO₂ was then introduced into the system for 5 min until the pressure of CO₂ was stabilized. The solution was then heated to 50 °C and maintained for 3 h under magnetic stirring. After the temperature decreased to room temperature, the CO₂ was released slowly to obtain a cellulose solution (5 wt%).

Synthesis of cellulosic poly(ionic liquid)s ([CellEt₃N][Br] and [CellMim][Br]): 10 g 5 wt% MCC solution was placed in a two-neck flask, to which 7.06 g of [Et₃N][Br] (in 20 mL DMSO) or 6.53 g of [Mim][Br] (in 20 mL DMSO) were added, and the reaction was carried out at 120

°C for 24 h. After the reaction, the product was precipitated with ethyl acetate, washed three times with ethanol, filtered to obtain flocculent product, and finally dissolved in ultrapure water for freeze-drying. The reaction mechanism of cellulose dissolution and *in situ* transesterification reaction as follows:



Scheme 2. The reaction mechanism of cellulose dissolution and *in situ* transesterification reaction.

Reaction mechanism: To functionalize cellulose, we employ a novel DBU/DMSO/CO₂ solvent system, which facilitates a transesterification reaction without the need for additional catalysts. 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), a strong base, effectively activates the hydroxyl groups on cellulose, enabling efficient esterification with ionic liquid precursors. The transesterification reaction avoids the use of toxic catalysts, simplifies the reaction process, and enhances the incorporation of ionic liquid functionalities into the cellulosic backbone in a highly efficient manner.

Preparation of 3 M Zn(OTf)₂, **Zn(OTf)**₂/[CellEt₃N]⁺ and **Zn(OTf)**₂/[CellMim]⁺ electrolytes: 21.8 g Zn(OTf)₂ was added to 20 ml deionied water to obtain 3 M Zn(OTf)₂ electrolyte. Zn(OTf)₂ with [CellEt₃N]⁺ and Zn(OTf)₂ with [CellMim]⁺ electrolytes were obtained by adding [CellEt₃N][Br] and [CellMim][Br] to 3 M Zn(OTf)₂ electrolyte solution, denoted as with [CellEt₃N]⁺, and with [CellMim]⁺ respectively. Zn(OTf)₂ containing different concentrations of [CellEt₃N]⁺ or [CellMim]⁺ electrolytes were labeled as with [CellEt₃N]⁺_x and with [CellMim]⁺_x, respectively, where x represents the concentration of [CellEt₃N]⁺ or [CellMim]⁺ and x = 0.5, 1.0 and 2.0 g·L⁻¹).

Preparation of NH₄**V**₄**O**₁₀ (**NVO**) **cathode material:** The NVO was prepared with a facile hydrothermal reaction. In a typical procedure, 2.74 mmol NH₄VO₃ is dissolved into 40 mL deionized water, and the solution is stirred for 10 minutes at room temperature. Subsequently, 4.6 mmol H₂C₂O₄·2H₂O solid powder is directly added in the above-mentioned solution, followed by magnetically stirring for 30 minutes until a black-green solution is obtained. The obtained solution is then transferred to a 60 mL Teflon-lined stainless autoclave and keep at 180 °C for 3 h. After cooling naturally to room temperature, the dark blue precipitate was collected *via* centrifugation. Finally, the precipitate was washed thoroughly with distilled water and absolute ethanol, then dried in a vacuum oven at 60 °C overnight to obtain the NVO product. To prepare the electrode, the NVO powder was mixed with AB and PVDF in a weight ratio of 7:2:1 to form a homogeneous mixture. NMP was added to the mixture to create a slurry, which was subsequently coated onto a stainless steel mesh and dried at 70 °C overnight.

Characterizations: Nuclear magnetic resonance spectra (NMR) (Varian INOVA 400 MHz) and fourier transform infrared spectroscopy (FTIR) (Bruker ALPHA) were performed to characterize the structures of [CellEt₃N][Br] and [CellMim][Br]. Contact angle instrument (DSA25, Germany) was analyzed the Zn affinity of electrolytes. The fluorescence emission spectrum was measured on Agilent Cary Eclipse fluorescence spectrometer (USA) with a slit width of 5 nm under 353 nm excitation light. Field-emission scanning emission scanning electron microscopy (SEM) (JEOL JSM-7500F) and transmission electron microscopy (TEM) (JEOL JEM-F200) were applied to investigate the surface morphology. The TEM sample was

prepared by collecting the solid deposited on the Zn electrode surface of a symmetric cell, cycled 30 times at 5 mA cm⁻² and 2 mA cm⁻². The collected solid was then ultrasonically dispersed in ultrapure water and subsequently loaded onto a copper grid for testing. *In situ* observations of Zn deposition behaviors were detected on optical microscopy (UB200i, UPO Photoelectric). X-ray diffraction (XRD) (D/teX Ultra 250) and X-ray photoelectron spectroscopy (XPS) (Thermo SCIENTIFIC Nexsa) were used to analyze the structure and the chemical bonding environments. Confocal laser scanning microscope images (CLSM) (Olympus OLS3000) was applied to analyzed the morphology of the Zn electrode.

The degree of substitution (DS) of [CellEt₃N][Br] and [CellMim][Br] were evaluated by the following equation according to ¹H-NMR spectrum.

$$DS = \frac{I_{methylene} \times 7}{I_{AGU} \times 2} \tag{1}$$

where $I_{methylene}$ and I_{AGU} are the integral of the methylene group and the anhydroglucose unit (AGU), respectively.

Electrochemical measurements: Zn foil and Cu foil were applied as anode and cathode for the Zn||Cu cell, respectively. The CEs of Zn²⁺ plating/stripping in different electrolytes were measured using asymmetric Zn||Cu cells with a cut-off charging potential of 0.5 V. CR2032 coin cells were assembled in an open-air environment by using a glass fiber separator with 100 μ l electrolytes and tested on Neware (CT-4800) battery cycling system. Cyclic voltammetry (CV) curves, electrochemical impedance spectra (EIS) and Tafel tests were conducted on a CHI660E electrochemical workstation, where Tafel tests was performed in a three-electrode setup (platinum as both working electrode and counter electrode, and Ag/AgCl as the reference electrode). The hydrogen evolution reaction was recorded using the linear sweep voltammetry method in Zn||Ti cell at a scan rate of 1 mV s⁻¹. The potentiostatic current time transient curves were measured at a fixed overpotential of -150 mV. The differential capacitance–potential curve of Zn||Ti cell was obtained from Alternating current (AC) voltammetry test at the amplitude of 5 mV and frequency of 6 Hz, the voltage range is from 0.1 V to 0.9 V.

The ionic conductivity (σ , S m⁻¹) of the electrolytes was calculated though the equation according to EIS tests with a frequency range from 0.01 Hz to 1×10^5 Hz.

$$\sigma = \frac{L}{R \times A} \qquad (2)$$

where L, A, and R are the thickness (1 cm), electrode contact area (1 cm²), and bulk resistance, respectively.

The electric double layer capacitance (C_{EDL}) was calculated as follows:

$$C_{EDL} = \frac{i}{v} \qquad (3)$$

Where *i* denotes the capacitive current, *v* represents the scan rate, C_{EDL} is the capacitance of electric double layer which can be calculated from the slope for *i* versus *v* curves.

The exchange current density by Zn stripping/plating process was characterized by

$$i = i_0 \frac{F \eta}{RT2} \qquad (4)$$

Where i_0 represents exchange current density, *i* represents actual current density, η represents overpotential, *F* represents faraday constant (\approx 96485.3 C/mol), *R* represents gas constant (8.314 J/(mol·K)), *T* represents temperature in Kelvin.

The transfer kinetics of Zn^{2+} ions at the interface are quantitatively compared by calculating the activation energy using arrhenius equation:

$$\frac{1}{R_{ct}} = Aexp\left(\frac{-E_a}{RT}\right) \tag{5}$$

Here, R_{ct} represents the charge transfer resistance, E_a denotes the activation energy, A stands for the frequency factor, R is the ideal gas constant, and T represents the temperature in Kelvin.

The cumulative capacity (CC) of Zn||Zn symmetric cells were defined as follows:

$$CC = J \cdot t \qquad (6)$$

Where J is current density (mA cm⁻²), t is duration time (h), CC is cumulative capacity (mAh cm⁻²).

The Zn utilization rate (ZUR) was calculated as follows:

$$ZUR = \frac{AC}{C_{Zn, volume} \times L} \times 100\%$$
(7)

Here, AC represents actual area capacity (mAh cm⁻²), $C_{Zn, volume}$ is the theoretical volume capacity of Zn metal (5855 mAh cm⁻³), L stands for the thickness of Zn metal.

According to Luo's method,² to more comprehensive and reasonable evaluation of the symmetric cell performance, the "life factor" was defined as follows:

life factor =
$$\frac{CC}{AC} \times ZUR$$
 (8)

Where *CC* is cumulative capacity (mAh cm⁻²), *AC* is actual area capacity (mAh cm⁻²), *ZUR* is Zn utilization rate.

Computational Method: The feasibility simulation of the inferred chemical composition was carried out using the powerful Gaussian 16 package. To ensure accurate results, very tight convergence criteria and ultrafine integration grids were employed in all molecule structure optimizations. The calculations of analytical frequencies on converged constrained molecules were deemed valid, as the molecule plus its infinitely-compliant constraining potential is a stationary point.³ For the optimization of all molecules, the hybrid B3LYP-D3 (BJ) combined with the 6-311G (d) basis set was utilized.^{4, 5} In order to simplify the calculation model, the repeating units of [CellMim]⁺ and [CellEt₃N]⁺ were selected as the polymer matrix model respectively. The molecular electrostatic potential (MESP) of the H₂O and [CellMim]⁺ molecules were calculated using the advanced Multiwfn3.8 software.⁶ The visually stunning MESP maps were expertly rendered using the cutting-edge VMD1.9.3 program.⁷ To calculate the frequencies of the stable configurations of the H₂O, [CellEt₃N]⁺ and [CellMim]⁺, the M06-2X/def2-TZVP method in Gaussian 16 program was employed. The interaction energy was calculated using the following equation:

$$E_{b}(H_{2}O - H_{2}O) = E_{(H_{2}O + H_{2}O)} - 2E_{(H_{2}O)} \qquad (9)$$

$$E_{b}([CellEt_{3}N]^{+} - H_{2}O) = E_{([CellEt_{3}N]^{+} + H_{2}O)} - \left[E_{([CellEt_{3}N]^{+})} + E_{(H_{2}O)}\right] \qquad (10)$$

$$E_{b}([CellMim]^{+} - H_{2}O) = E_{([CellMim]^{+} + H_{2}O)} - \left[E_{([CellMim]^{+})} + E_{(H_{2}O)}\right] \qquad (11)$$

Where ${}^{E}(H_{2}O + H_{2}O)$, ${}^{E}([CellEt_{3}N]^{+} + H_{2}O)$ and ${}^{E}([CellMim]^{+} + H_{2}O)$ represents the total energy of H₂O-

H₂O, [CellEt₃N]⁺-H₂O and [CellMim]⁺-H₂O complex, respectively. $E_{(H_2O)}$, $E_{(ICellEt_3N]^+}$) and $E_{(ICellMim]^+}$) are the total energies of H₂O, [CellEt₃N]⁺ and [CellMim]⁺, respectively. This allows for a comprehensive understanding of the energetics of the system, providing valuable insights into the underlying chemical processes at play. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) were calculated by Multiwfn 3.8 whose snapshots were presented by VMD 1.9.3, in which the Gaussian format checkpoint file was used as the input file.

All the DFT calculations were conducted based on the Vienna Ab initio Simulation Package (VASP).^{8, 9} The exchange-correlation potential was described by the Perdew-Burke-Ernzerhof (PBE) generalized gradient approach (GGA).¹⁰ The electron-ion interactions were accounted by the projector augmented wave (PAW).¹¹ All DFT calculations were performed with a cutoff energy of 400 eV, and the Brillouin zone was sampled using a $3\times3\times1$ k-point grid. The energy and force convergence criteria of the self-consistent iteration were set to 10^{-4} eV and 0.02 eV Å⁻¹, respectively. DFT-D3 method was used to describe van der Waals (vdW) interactions.¹²

The adsorption energies (E_{ads}) of adsorbate A molecule were defined as

$$E_{ads} = E_{*A} - E_A - E_{sub} \qquad (12)$$

where E_{*A} represent the energy of A molecule adsorbed on the surface. E_{sub} is the energy of clean surface, E_A represent the energies of A molecule.

Model building: The computational domain can be divided into two regions of electrolyte and Zn anode. During the battery reaction, Zn^{2+} ions are driven by the electric field and finally deposited on the Zn anode surface to form Zn dendrites. Since the phase field method can accurately describe the complex changes of the phase interface in the two-phase flow calculation, the phase field equation is used to simulate the growth of Zn dendrites. The ion diffusion coefficient at the anode interface can be adjusted to change the dendrite morphology. In this model, the phase field order parameter is a non-conservative quantity, so the Allan-Cahn form of the phase field equation is used.

$$\frac{\partial\varphi}{\partial t} = -L_i \left[\frac{\partial g(\varphi)}{\partial \varphi} - \kappa \nabla^2 \varphi \right] - L_m h'(\varphi) \left\{ e^{\left[\frac{(1-\alpha)nFP}{RT} \right]} - \frac{c_+}{c_0} e^{\left[\frac{-\alpha nFP}{RT} \right]} \right\}$$
(13)

Where φ is the phase field sequence parameter, φ value is 1 in the electrode phase, φ in the electrolyte phase is 0, φ varies continuously from 0 to 1 in the electrode-electrolyte intermediate phase. L_i and L_m are interface mobility and reaction coefficient respectively. $g(\varphi) = W\varphi^2(1-\varphi)^2$ is a double well function, where W is the barrier height. κ is the gradient energy coefficient. $h(\varphi)$ is an interpolation function that can be expressed as $h(\varphi) = \varphi^3(6\varphi^2 - 15\varphi + 10)$. R, T, n, and F are the gas constant, absolute temperature, number of transferred electrons, and Faraday constant, respectively.

Phase-field simulation: The phase field simulations were performed on COMSOL. In the phase-field equation, φ is coupled with Zn²⁺ concentration (c) and overpotential (P). To simulate the spatial and temporal distribution of Zn²⁺ ions concentration, the Nernst-Planck equation is followed:

$$\frac{\partial c^{+}}{\partial t} = \nabla \cdot (D_{eff} \nabla c^{+} - \frac{D_{eff} nF}{RT} \nabla P) - c \frac{\partial \varphi}{\partial t}$$
(14)

Where D_{eff} represents effective diffusivity, which can be expressed as $D_e * h(\varphi) + D_1 * [1 - h(\varphi)]$, here, D_e and D_1 are the diffusion rates of Zn^{2+} ions in electrode and electrolyte, respectively.

In addition, the Poisson equation is used to ensure the electrical neutrality of the calculation system and the distribution and evolution of the overpotential as follow:

$$\nabla \cdot \sigma_{eff} \nabla P = nFc \frac{\partial \varphi}{\partial t} \qquad (15)$$

Where σ_{eff} represents effective conductivity, which can be expressed as $\sigma_e * h(\varphi) + \sigma_1 * [1 - h(\varphi)]$, here, σ_e and σ_1 are the conductivity of Zn^{2+} in electrode and electrolyte, respectively.

Note 1: All parameters in the model have been normalized.

Note 2: In the phase field, all boundary conditions are insulation boundary conditions. In an electric field, the upper boundary is the Dirichlet boundary condition, specifying a voltage of 0.1 V. In the concentration field, the upper boundary is the Dirichlet boundary condition, specifying a concentration of 3 mol L⁻¹.

Note 3: In the phase field, the initial value of the electrode phase is 1, and the initial value of the electrolyte phase is 0. In the electric field, the initial value of the electrode phase is 0, and the initial value of the electrolyte phase is 0.1 V. In the concentration field, the initial value of the electrode phase is 0 and the initial value of the electrolyte phase is 3 mol L⁻¹.



Figure S1. (a) ¹H-NMR and (b) ¹³C-NMR spectra of [Et₃N][Br].



Figure S2. (a) ¹H-NMR and (b) ¹³C-NMR spectra of [Mim][Br].



Figure S3. (a) ¹H-NMR and (b) ¹³C-NMR spectra of [CellEt₃N][Br] (DS = 1.00).

In the ¹H-NMR spectrum, the chemical shift at 1.37, 3.64 and 4.35 ppm in [CellEt₃N][Br] were assigned to the H protons within three terminal methyl ($-CH_3$), three methylene ($-CH_2-$) and one methylene ($-CH_2-$) near ester group, respectively. In the ¹³C-NMR spectrum, the clear C peak signals at 164.96, 58.39, 54.71 and 7.16 ppm were attributed to C atoms of the ester group and triethylamine, respectively. And the chemical shifts of C1-C6 on the cellulose skeleton are obviously in the range of 59-103 ppm.



Figure S4. (a) ¹H-NMR and (b) ¹³C-NMR spectra of [CellMim][Br] (DS = 0.48).

In the ¹H-NMR spectrum, the chemical shifts observed at 8.82, 7.51, 7.48 and 3.90 ppm in [CellMim][Br] were ascribed to the H protons within the methylimidazole. Also, the H protons of methylene ($-CH_2-$) near ester group were detected at 5.23 ppm. In the ¹³C-NMR spectrum, the clear C peak signals at 167.78, 137.51, 123.53, 49.75 and 35.95 ppm were attributed to C atoms of the ester group and methylimidazole, respectively. And the chemical shifts of C1-C6 on the cellulose skeleton are also in the range of 59-103 ppm.



Figure S5. FTIR spectra of MCC, [CellEt₃N]⁺ and [CellMim]⁺.



Figure S6. (a) FTIR spectra of different electrolytes. (b) The stretching vibration peaks of $CF_3SO_3^{-}$.



Figure S7. FTIR spectra of (a) $Zn(OTf)_2$ electrolyte and (b) $Zn(OTf)_2$ with $[CellEt_3N]^+_{1.0}$ electrolyte with typically fitted profiles.



Figure S8. Optical photographs of $3M Zn(OTf)_2$ electrolytes with different concentration of (a) [CellEt₃N]⁺ and (b) [CellMim]⁺.



Figure S9. ¹H-NMR spectra of pure H₂O and Zn(OTf)₂ electrolytes with different fractions of

(a) $[CellEt_3N]^+$ and (b) $[CellMim]^+$.



Figure S10. (a) EIS spectra and (b) ionic conductivity of $Zn(OTf)_2$ electrolytes containing cellulosic PILs with different structures characteristics at room temperature.



Figure S11. Linear polarization curves of $Zn(OTf)_2$ electrolyte and $Zn(OTf)_2$ electrolytes containing cellulosic PILs with different structures characteristics.



Figure S12. (a) The CEs of the Zn||Cu cells using different electrolytes at 5 mA cm⁻². The voltage capacity curves of Zn||Cu cells using (b) Zn(OTf)₂, (c) Zn(OTf)₂ with [CellEt₃N]⁺_{1.0} and (d) Zn(OTf)₂ with [CellMim]⁺_{1.0} electrolytes at 5 mA cm⁻².



Figure S13. The local amplification diagrams of Zn||Zn cells using $Zn(OTf)_2$ electrolyte, $Zn(OTf)_2$ with $[CellEt_3N]^+_{1.0}$ and $Zn(OTf)_2$ with $[CellMim]^+_{1.0}$ at 1 mA cm⁻² and 1 mAh cm⁻².



Figure S14. The CEs of the Zn||Cu cells using $Zn(OTf)_2$ electrolytes containing different fractions of $[CellMim]^+$ at 0.5 mA cm⁻² and 0.5 mAh cm⁻².



Figure S15. (a) The voltage capacity curves of Zn||Cu cells using (a) $Zn(OTf)_2$, (b) $Zn(OTf)_2$ with [CellMim]⁺_{1.0} and, (d) $Zn(OTf)_2$ with [CellMim]⁺_{2.0} electrolytes.



Figure S16. The selected voltage time curves of Zn ||Cu cells using $Zn(OTf)_2$ electrolytes with different fractions of [CellMim]⁺.



Figure S17. Zn plating/stripping voltage profiles of Zn||Zn cells using $Zn(OTf)_2$ electrolytes containing different fractions of [CellMim]⁺ at 1 mA cm⁻² and 1 mAh cm⁻².



Figure S18. Voltage profiles local amplification diagrams of Zn||Zn symmetric cells using (a) $Zn(OTf)_2$, (b) $Zn(OTf)_2$ with [CellMim]⁺_{0.5}, (c) $Zn(OTf)_2$ with [CellMim]⁺_{1.0} and (d) $Zn(OTf)_2$ with [CellMim]⁺_{2.0} electrolytes in different cycle stages.



Figure S19. Adsorption energies of the configurations of Zn (002) plane with (a) H_2O and (b) [CellMim]⁺.



Figure S20. Charge density difference of Zn (002) plane with (a) H_2O and (b) [CellMim]⁺.



Figure S21. Cyclic voltammetry curves of Zn||Zn symmetric cells with (a) $Zn(OTf)_2$ and (c) $Zn(OTf)_2$ with [CellMim]⁺ electrolytes at different scan rates from 10 to 20 mV s⁻¹ in a voltage range of -0.015 to 0.015 V. (b, d) Plots of capacitive currents *versus* scan rates resulting from the corresponding CV curves.



Figure S22. LUMO and HOMO iso-surface of H₂O and [CellMim]⁺.



Figure S23. SEM images of Zn foil after immersion in the (a, b) Zn(OTf)₂ electrolyte and (c, d) Zn(OTf)₂ with [CellMim]⁺ electrolyte for 10 days.



Figure S24. XRD patterns of Zn foils after immersion in different electrolytes for 10 days.



Figure S25. (a) XPS survey and fine spectrum of (b) C1s, (c) N1s, (d) O1s, (e) F1s and (f) S2p of Zn foils after immersion in different electrolytes for 10 days.



Figure S26. Photographs of (a) self-assembly *in-situ* optical microscope and (b) homemade dendritic observation electrochemical cell.



Figure S27. (a) HER curves of Zn||Ti half cells at 1 mV s⁻¹. (b) CV curves of Zn||Cu cells using $Zn(OTf)_2$ and $Zn(OTf)_2$ with [CellMim]⁺ electrolytes at 0.5 mV s⁻¹.



Figure S28. The surface and cross-section SEM images of Zn anode after Zn deposition for 60 min at 10 mA cm⁻² in (a-c) $Zn(OTf)_2$ and (d-f) $Zn(OTf)_2$ with [CellMim]⁺ electrolytes.



Figure S29. The 2D CLSM images and roughness profiles after Zn deposition for 60 min at 10 mA cm⁻² in (a, b) $Zn(OTf)_2$ and (c, d) $Zn(OTf)_2$ with [CellMim]⁺ electrolytes.



Figure S30. The photographs of Zn||Zn symmetric cells using (a) $Zn(OTf)_2$ and (b) $Zn(OTf)_2$ with [CellMim]⁺ electrolytes after cumulative plating test.

The cumulative plating test uses a standard symmetric cell system, which differs from the

multiple charge/discharge cycles in long-term cycling by performing a single extended charging (anode deposition) process until cell failure occurs, typically indicated by a disordered voltage profile. As a battery operates for longer periods, the internal conditions become increasingly complex, making it difficult to fully understand the underlying mechanisms. This short-term method enables effective evaluation of dendrite growth conditions while minimizing interference from hydrogen evolution reactions (HER) and corrosion. The zinc electrode has a thickness of 30 μ m and a weight of approximately 20.7 mg, corresponding to a theoretical capacity of 16.97 mAh. Zinc utilization is defined as the actual plating capacity in the Zn||Zn cell divided by the theoretical capacity of the zinc anode. After the cumulative plating test, the zinc electrode, indicated by the arrow, disappears completely.



Figure S31. Photographs and SEM images of the deposited Zn in a quartz cell using Zn(OTf)₂ with [CellMim]⁺ after one charge-discharge cycle at 10 mA cm⁻² and 15 mAh cm⁻² (A electrode: stripping first, then plating; B electrode: plating first, then stripping).



Figure S32 Photographs and SEM images of the deposited Zn in a quartz cell with $Zn(OTf)_2$ electrolyte after one charge-discharge cycle at 10 mA cm⁻² and 15 mAh cm⁻² (A electrode: stripping first, then plating; B electrode: plating first, then stripping).



Figure S33. Chronoamperograms of Zn||Zn symmetric cells in $Zn(OTf)_2$ and $Zn(OTf)_2$ with [CellMim]⁺ electrolytes at a -150 mV overpotential.



Figure S34. Time-voltage profiles of Zn||Cu cells using $Zn(OTf)_2$ and $Zn(OTf)_2$ with [CellMim]⁺ electrolytes using the one cycle pre-activation mode.



Figure S35. The XRD patterns of Cu electrodes after 100 cycles at 1 mA cm⁻² and 1 mAh cm⁻² in Zn||Cu cells using Zn(OTf)₂ and Zn(OTf)₂ with [CellMim]⁺ electrolytes.



Figure S36. The SEM images of Cu electrodes after 100 cycles at 1 mA cm⁻² and 1 mAh cm⁻² in Zn $\|$ Cu cells using (a, b) Zn(OTf)₂ and (c, d) Zn(OTf)₂ with [CellMim]⁺ electrolytes.



Figure S37. (a) Voltage profiles of Zn||Zn symmetric cells using $Zn(OTf)_2$ and $Zn(OTf)_2$ with [CellMim]⁺ electrolytes at various current density. (b) Plot the overpotential at each current density.



Figure S38. Cycling performance of Zn||Zn symmetric cells using $Zn(OTf)_2$ and $Zn(OTf)_2$ with [CellMim]⁺ electrolytes at 3 mA cm⁻² and 3 mAh cm⁻².



Figure S39. Cycling performance of Zn||Zn symmetric cells using $Zn(OTf)_2$ and $Zn(OTf)_2$ with [CellMim]⁺ electrolytes at 5 mA cm⁻² and 1 mAh cm⁻².



Figure S40. XRD patterns of Zn anode in Zn||Zn symmetric cells using (a) $Zn(OTf)_2$ and (b) $Zn(OTf)_2$ with [CellMim]⁺ electrolytes as a function of cycle time at 5 mA cm⁻² and 1 mAh cm⁻².

Table S1. The intensity obtained from textured sample $I_{(hkl)}$ and the intensity of the standard oriented sample $I_{0(hkl)}$ of pristine Zn foil.

Intensity		002	100	101	102	103	110	004	112	200	201	104
Pristine Zn foil	I I ₀	1702	626	2610	766	854	188	136	436	120	250	38
Zn(OTf) ₂	I I _{1-50h}	826	588	2808	682	814	322	72	394	92	410	36
	I _{1-100h}	802	588	2056	596	600	284	60	364	102	300	34
	I_1-200h	720	736	2544	664	688	318	_56	428	72	314	34
With [CellMim] ⁺	I I _{2-50h}	1636	792	4230	1010	1096	360	114	694	102	430	32
	I _{2-100h}	1740	658	3056	734	884	358	130	608	88	286	42
	I I _{2-200h}	1834	626	3154	850	948	398	140	540	82	334	40

The relative texture coefficients (RTCs) of each Zn lattice plane were calculated using the following formula:

$$RTCs_{(hkl)} = \frac{I_{(hkl)}/I_{0(hkl)}}{\sum I_{(hkl)}/I_{0(hkl)}} \times 100\%$$

where $I_{(hkl)}$ is the intensity obtained from the textured sample, and $I_{0(hkl)}$ is the intensity of the standard oriented sample (Table S1).



Figure S41. SEM images of Zn anode in Zn||Zn symmetric cells using (a, b) $Zn(OTf)_2$ and (c, d) $Zn(OTf)_2$ with [CellMim]⁺ electrolyte after 200 h cycle at 5 mA cm⁻² and 1 mAh cm⁻².



Figure S42. Cycling performance of Zn||Zn symmetric cells using $Zn(OTf)_2$ and $Zn(OTf)_2$ with [CellMim]⁺ electrolytes at 10 mA cm⁻² and 1 mAh cm⁻².



Figure S43. Cycling performance of Zn||Zn symmetric cells using $Zn(OTf)_2$ and $Zn(OTf)_2$ with [CellMim]⁺ electrolytes at 5 mA cm⁻² and 5 mAh cm⁻².



Figure S44. (a) Cycling performance of Zn||Zn symmetric cells using $Zn(OTf)_2$ and $Zn(OTf)_2$ with [CellMim]⁺ electrolytes at 10 mA cm⁻² and 5 mAh cm⁻². (b) The corresponding local amplification diagrams.

Table S2. Comparison of life factor of Zn||Zn symmetric cells with recently reported works under harsh conditions.

Additive	Areal capacity (mAh cm ⁻²)	Zn utilizationCumulative capacityrate (ZUR)(mAh cm ⁻²)		Life factor	Refs.	
[CellMim]+	5	28.5%	4220	240.5	This work	
	10	56.9%	3700	210.5		
MACC	2	11.4%	1400	79.5		
	10	56.9%	5500	31.3	13	
GSH	1	1.7%	3000	51.3	3 9	
	3	5.1%	4800	81.9		
PNM	1	1.7%	5800	99.2		
PNM	1	1.7%	7500	128.3	15	
IS4	2.95	50%	1180	200	16	

Additive	Areal capacity (mAh cm ⁻²)	Zn utilization rate (ZUR)	Cumulative capacity (mAh cm ⁻²)	Life factor	Refs.	
F127	7	50%	800	57.1	47	
	10	72%	600	43.2	17	
SSE	0.5	0.9%	2500	21.3		
	3	5.1%	6000	102.4	18	
	4	68.9%	200	34.5		
HPA	0.5	1.2%	1500	36.6	19	
	5	12.2%	6000	146.4		
2F-07A	15	25.6%	11130	190.1	20	



Figure S45. Calendar life of Zn||Zn symmetric cells using $Zn(OTf)_2$ and $Zn(OTf)_2$ with [CellMim]⁺ electrolytes under 3 mA cm⁻² and 3 mAh cm⁻².



Figure S46. (a) Long cycling performance of Zn||Zn pouch cells at 1 mA cm⁻² and 1 mAh cm⁻². (b, c) The corresponding local amplification diagrams in different cycle stages.



Figure S47. (a) Long cycling performance of Zn||Zn pouch cells at 5 mA cm⁻² and 1 mAh cm⁻². (b) The corresponding local amplification diagrams.



Figure S48. Voltage profiles local amplification diagrams of Zn||Zn pouch cells at 8 mA cm⁻² and 4 mAh cm⁻² in different cycle stages.



Figure S49. Nyquist plots of the Zn||Zn symmetric cells using (a) $Zn(OTf)_2$ and (c) $Zn(OTf)_2$ with [CellMim]⁺ electrolytes at different temperatures. Arrhenius plots and the corresponding activation energies obtained in (b) $Zn(OTf)_2$ and (d) $Zn(OTf)_2$ with [CellMim]⁺ electrolytes.

Intensity	Symbol	Real value
Interfacial mobility	L_{i}	$2.5 \times 10^{-6} \text{m}^3 \text{J}^{-1} \text{s}^{-1}$
Barrier height	W	$3.75 \times 10^5 \text{J m}^{-3}$
Reaction coefficient	L_m	$1 s^{-1}$
Gradient energy coefficient	$\kappa_0^{}$	$2.5 \times 10^{-5} \text{J m}^{-1}$
Diffusivity of electrode	De	$7.5 \times 10^{-13} \text{m}^2 \text{s}^{-1}$
Diffusivity of electrolyte	D_l	$2.5 \times 10^{-10} \text{m}^2 \text{s}^{-1}$
Conductivity of electrode	S_{e}	10^7S m^{-1}
Conductivity of electrolyte	S_{l}	1 Sm^{-1}
Symmetrical factors	α, β	0.5
Strength of the anisotropy	ω	4
Mode of anisotropy	δ	0.05
Temperature	Т	298.15 K

Table S3. The important coefficients of related phase field simulation equations.



Figure S50. (a) 2D map of the Zn^{2+} concentration and (b) 2D distribution of the local electric field as a function of time based on $Zn(OTf)_2$ electrolyte.



Figure S51. (a) 2D map of the Zn^{2+} concentration and (b) 2D distribution of the local electric field as a function of time based on $Zn(OTf)_2$ with [CellMim]⁺ electrolyte.



Figure S52. 1D evolutions of electric field profile along the dendrite growth direction based on (a) Zn(OTf)₂ and (b) Zn(OTf)₂ with [CellMim]⁺ electrolytes.

The dendrite growth rate (v) was calculated by the following formula: $v = \frac{x_2 - x_1}{400 - 100}$. Thus, $v_{Zn(OTf)_2} = \frac{3.85 - 1.13}{400 - 100} = 0.009 \ \mu m s_{-1}$; $v_{Zn(OTf)_2 + [CellMim]} + = \frac{1.20 - 0.60}{400 - 100} = 0.002 \ \mu m s_{-1}$.



Figure S53. (a) *In situ* EIS test procedure. *In situ* EIS curves of the Zn||Zn symmetric cells using (b) Zn(OTf)₂ and (c) Zn(OTf)₂ with [CellMim]⁺ electrolytes.



Figure S54. The XPS depth surveys of Zn anode tested in symmetric cell using $Zn(OTf)_2$ with [CellMim]⁺ electrolyte for 30 cycles at 5 mA cm⁻² and 2 mAh cm⁻².



Figure S55. The XPS depth spectra for O1s, S2p and Zn2p of Zn anode tested in symmetric cell using $Zn(OTf)_2$ with [CellMim]⁺ electrolyte for 30 cycles at 5 mA cm⁻² and 2 mAh cm⁻².



Figure S56. (a, b) SEM images and (c) element mapping of $NH_4V_4O_{10}$.



Figure S57. XRD pattern of NH₄V₄O₁₀.



Figure S58. CV curves of Zn||NVO batteries using (a) $Zn(OTf)_2$ and (b) $Zn(OTf)_2$ with [CellMim]⁺electrolyte at 1st to 5th cycles.



Figure S59. CV curves of Zn||NVO batteries using (a) $Zn(OTf)_2$ and (b) $Zn(OTf)_2$ with [CellMim]⁺ electrolytes at various scan rates from 0.2 to 1.0 mV s⁻¹.



Figure S60. GCD profiles of Zn||NVO batteries using (a) $Zn(OTf)_2$ and (b) $Zn(OTf)_2$ with [CellMim]⁺ electrolytes at various current densities from 0.2 to 5 A g⁻¹.



Figure S61. Galvanostatic discharge/charge curves of the Zn||NVO batteries at (a) 0.2 A g^{-1} and (b) 0.5 A g^{-1} .



Figure S62. The selected GCD profiles of Zn||NVO batteries using (a) $Zn(OTf)_2$ and (b) $Zn(OTf)_2$ with [CellMim]⁺ electrolytes at 1 A g⁻¹.



Figure S63. Galvanostatic discharge/charge curves of the Zn||NVO batteries in different electrolytes at 3 A g⁻¹. The selected GCD profiles of Zn||NVO batteries using (b) $Zn(OTf)_2$ and (c) $Zn(OTf)_2$ with [CellMim]⁺ electrolytes.



Figure S64. The selected GCD profiles of Zn||NVO batteries using (a) $Zn(OTf)_2$ and (b) $Zn(OTf)_2$ with [CellMim]⁺ electrolytes at 5 A g⁻¹.

References

- M. Pei, X. Peng, Y. Shen, Y. Yang, Y. Guo, Q. Zheng, H. Xie and H. Sun, *Green Chemistry*, 2020, 22, 707-717.
- J. Luo, L. Xu, Y. Yang, S. Huang, Y. Zhou, Y. Shao, T. Wang, J. Tian, S. Guo, J. Zhao, X. Zhao, T. Cheng, Y. Shao and J. Zhang, *Nature Communications*, 2024, 15, 6471.
- 3. T. J. Kucharski and R. Boulatov, Journal of Materials Chemistry A, 2011, 21, 8237-8255.
- 4. L. Goerigk, A. Hansen, C. Bauer, S. Ehrlich, A. Najibi and S. Grimme, *Phys. Chem. Chem. Phys.*, 2017, **19**, 32184-32215.
- J. Witte, M. Goldey, J. B. Neaton and M. Head-Gordon, *J. Chem. Theory Comput.*, 2015, 11, 1481-1492.
- 6. J. Zhang and T. Lu, Phys. Chem. Chem. Phys., 2021, 23, 20323-20328.
- 7. T. Lu and F. Chen, Journal of Computational Chemistry, 2012, 33, 580-592.
- 8. G. Kresse and J. Hafner, *Physical Review B*, 1993, 47, 558-561.
- 9. G. Kresse and J. Hafner, *Physical Review B*, 1994, 49, 14251-14269.
- 10. K. J. P. Perdew, M. Burke and Ernzerhof, *Physical Review Letters*, 1996, 77, 3865-3868.
- 11. B. X. Shi, R. J. Nicholls and J. R. Yates, *Physical Review B*, 2023, **108**, 115112.
- S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *The Journal of Chemical Physics*, 2010, 132, 154104.
- L. Zheng, H. Li, X. Wang, Z. Chen, C. Hu, K. Wang, G. Guo, S. Passerini and H. Zhang, ACS Energy Letters, 2023, 8, 2086–2096.
- 14. X. Liang, R. Yang, Y. Zheng, F. Zhang, W. Zhang, C.-S. Lee and Y. Tang, *Advanced Functional Materials*, 2024, DOI: 10.1002/adfm.202403048.
- 15. D. Luo, X. Ma, P. Du, Z. Chen, Q. Lin, Y. Liu, B. Niu, X. He and X. Wang, *Angewandte Chemie International Edition*, 2024, **63**, e202401163.
- 16. L. Liu, X.-Y. Wang, Z. Hu, X. Wang, Q. Zheng, C. Han, J. Xu, X. Xu, H.-K. Liu, S.-X. Dou and W. Li, *Angewandte Chemie International Edition*, 2024, **63**, e202405209.
- X. Chen, P. Gao, W. Li, N. A. Thieu, Z. M. Grady, N. G. Akhmedov, K. A. Sierros, M. Velayutham, V. V. Khramtsov, D. M. Reed, X. Li and X. Liu, *ACS Energy Letters*, 2024, 9, 1654–1665.
- X. Yun, Y. Chen, H. Gao, D. Lu, L. Zuo, P. Gao, G. Zhou, C. Zheng and P. Xiao, Advanced Energy Materials, 2024, 14, 2304341.
- Z. Yang, Y. Sun, S. Deng, H. Tong, M. Wu, X. Nie, Y. Su, G. He, Y. Zhang, J. Li and G. Chai, *Energy & Environmental Science*, 2024, 17, 3443-3453.

R. Huang, J. Zhang, W. Wang, X. Wu, X. Liao, T. Lu, Y. Li, J. Chen, S. Chen, Y. Qiao,
 Q. Zhao and H. Wang, *Energy & Environmental Science*, 2024, 17, 3179.