Electronic Supplementary Information

Choline chloride enhances the electrochemical stability of zinc plating/stripping

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EXPERIMENTAL PROCEDURES

Preparation of electrolytes

The control electrolyte was 0.5 M zinc chloride (Acros). The modified electrolytes were dissolved 0.5, 1.5, 2.5 and 3.5 M choline chloride (CC, Innochem) and 0.5 M zinc chloride into deionized water, which were marked as 0.5 M CC-$ZnCl_2$, 1.5 M CC-$ZnCl_2$, 2.5 M CC-$ZnCl_2$, and 3.5 M CC-$ZnCl_2$.

Assembly of cells

CR2032-type coin cells of the symmetric Zn‖Zn cells and Zn‖Cu half cells were assembled in the air. Glass fiber based separator from Whatman was adopted (thickness 260 μm). The thickness of zinc foil was approximately 80 μm.

Materials Characterizations

The morphology and microstructure on the electrode surface were characterized via scanning electron microscopy (SEM, HITACHI SU8010, Japan). X-ray diffraction (XRD, D8 Advance, Germany) with Cu-$K_{\alpha 1}$ radiation (λ=1.5405 Å) was implemented to detect the crystalline information of the electrode surface. In order to analyze the change of phase-transition temperature in different electrolytes, differential scanning calorimetry (DSC, Mettler Toledo, Swiss) was performed in N_2 atmosphere between -50–30 °C at a ramping rate of 5 °C min^{-1}. The attenuated total reflectance (ATR) infrared spectrum was obtained by a Fourier transform infrared spectrometer (Nicolet IS50, America) from 400 to 4000 cm^{-1}. Nuclear magnetic resonance spectroscopy

(NMR, Bruker AVANCEIII400, Germany) was applied to qualitatively analyze the interactions between the electrolyte components. Conductivity meter (METTLER TOLEDO FE38, Swiss) and rotational viscometer (NDJ-79, China) were adopted to investigate the physicochemical properties of different electrolytes.

Electrochemical measurements

Linear scanning voltammetry (LSV) was tested in a three-electrode system by an electrochemical working station (CHI660E). Ti foil (thickness 10 μm) was used as working electrode and counter electrode. Ag/AgCl electrode was used as reference electrode. The electrolytes were 0.5 M $ZnCl_2$ and 2.5 M CC-$ZnCl_2$, respectively. The range of potential was from 1.0 to -0.2 V (versus Zn/Zn^{2+}) and the scanning rate was 10 mV s^{-1}. A LAND battery measurement system was applied to test the galvanostatic and long cycling performance.

Calculation of average Coulombic efficiency (CE)

In Zn‖Cu half cells, the process of CE measurements followed the reported method. Firstly, Cu foil (approximately 10 μm) was preconditioned with one cycle at the capacity of 5 mAh cm^{-2} to eliminate the oxidants of the substrate surface. Then a given amount of charge (Q_r, 5 mAh cm^{-2}) was employed to deposit Zn onto the Cu foil. Next, a smaller capacity (Q_C, 0.5 mAh cm^{-2}) was used to cycle between the Cu foil working electrode and the Zn counter electrode for ten cycles (n=10). Finally, the remaining Zn reservoir was exhaustively stripped to the cut-off potential, obtaining the final stripping

charge capacity of Q_S. Thus, the average CE can be calculated by:

$$CE_{ave} = \frac{nQ_c + Q_s}{nQ_c + Q_r}$$
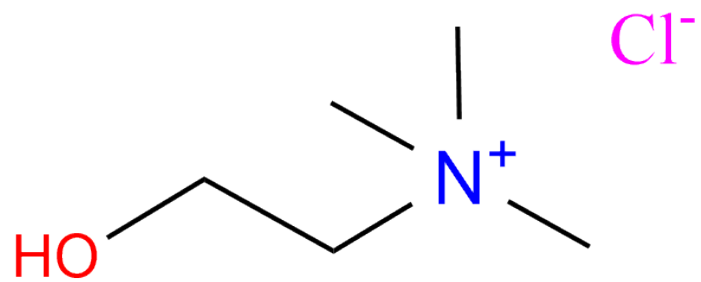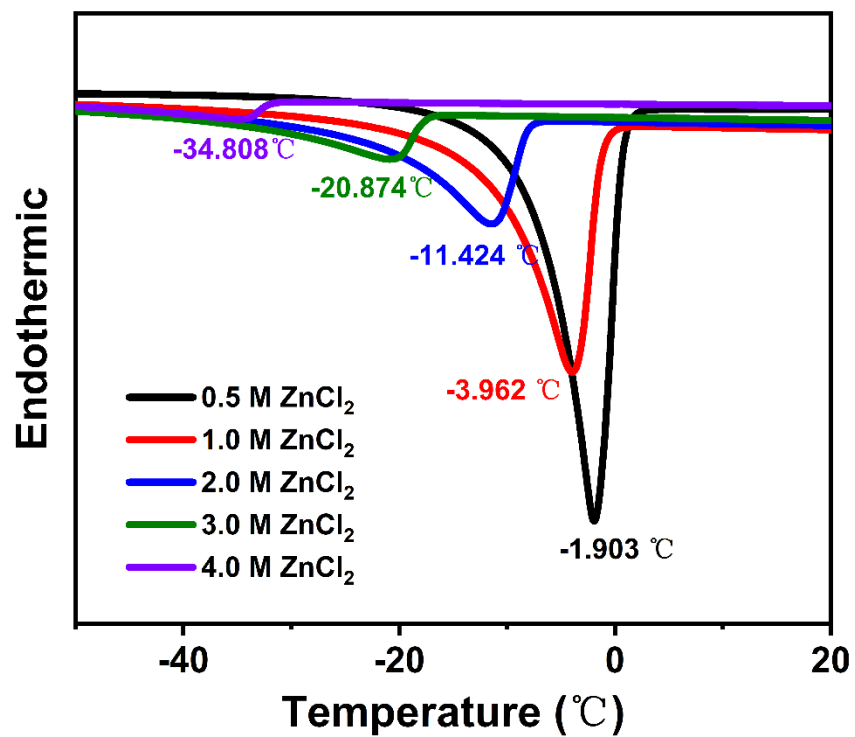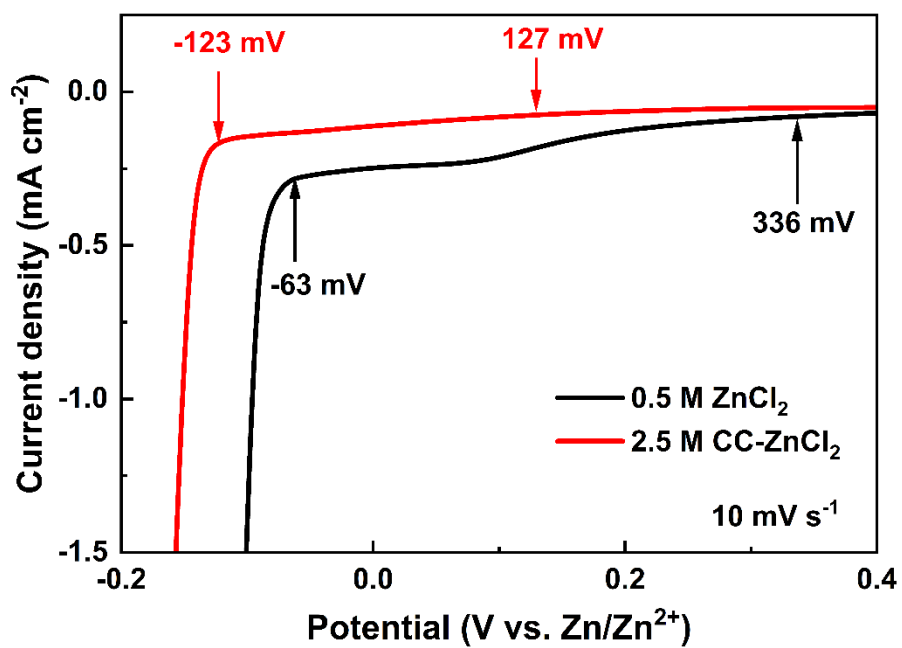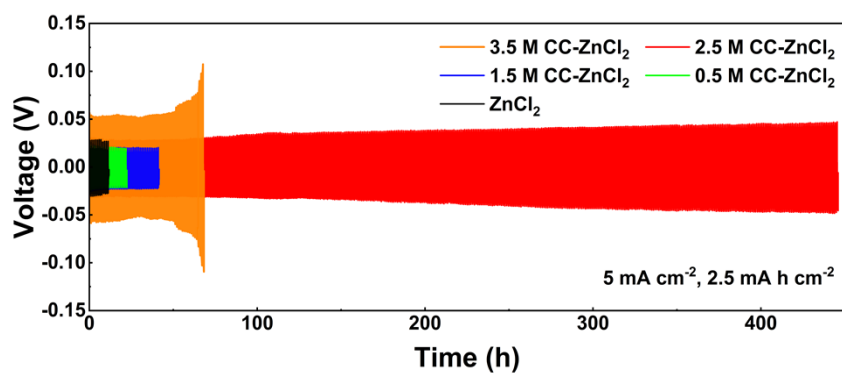
Fig. S1. Structural formula of choline chloride.

Fig. S2. DSC in pure ZnCl$_2$ solutions without CC.

Fig. S3. LSV curves measured using polarization scanning at 10 mV s^{-1} on Ti electrodes between -0.2 V and 0.4 V versus Zn/Zn^{2+}.

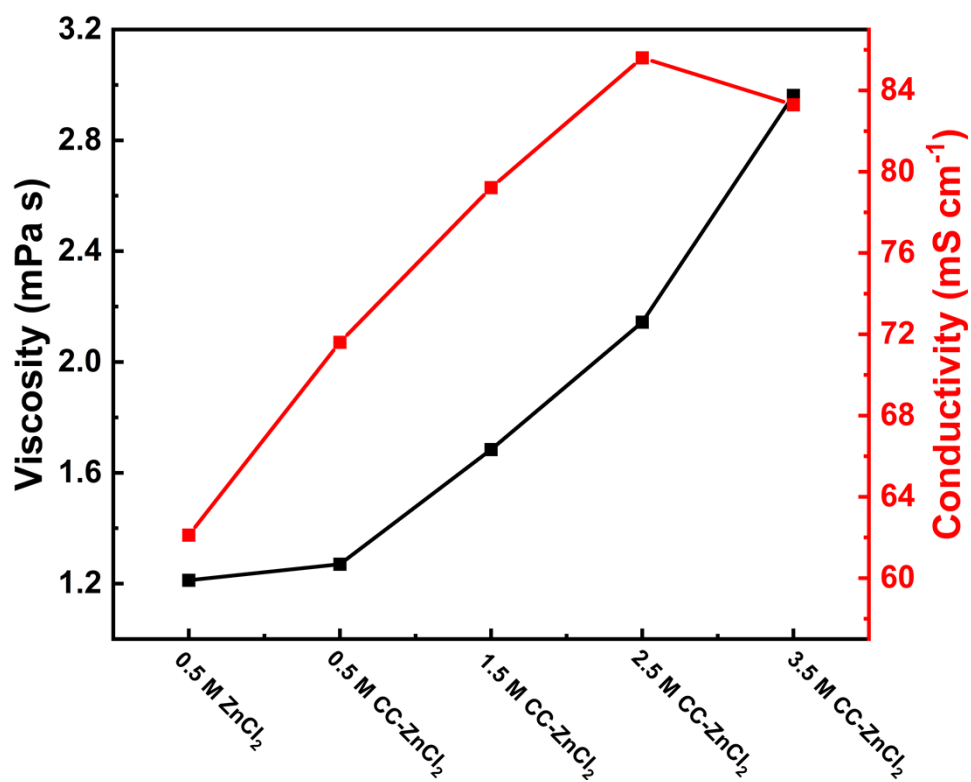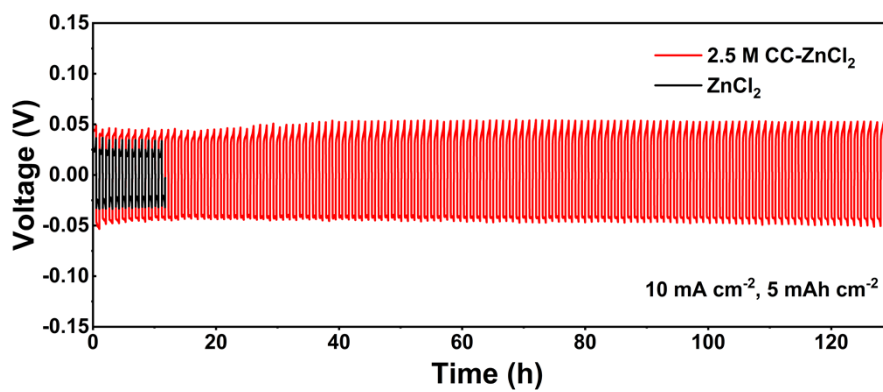**Fig. S4.** Galvanostatic zinc plating/stripping in different electrolytes.
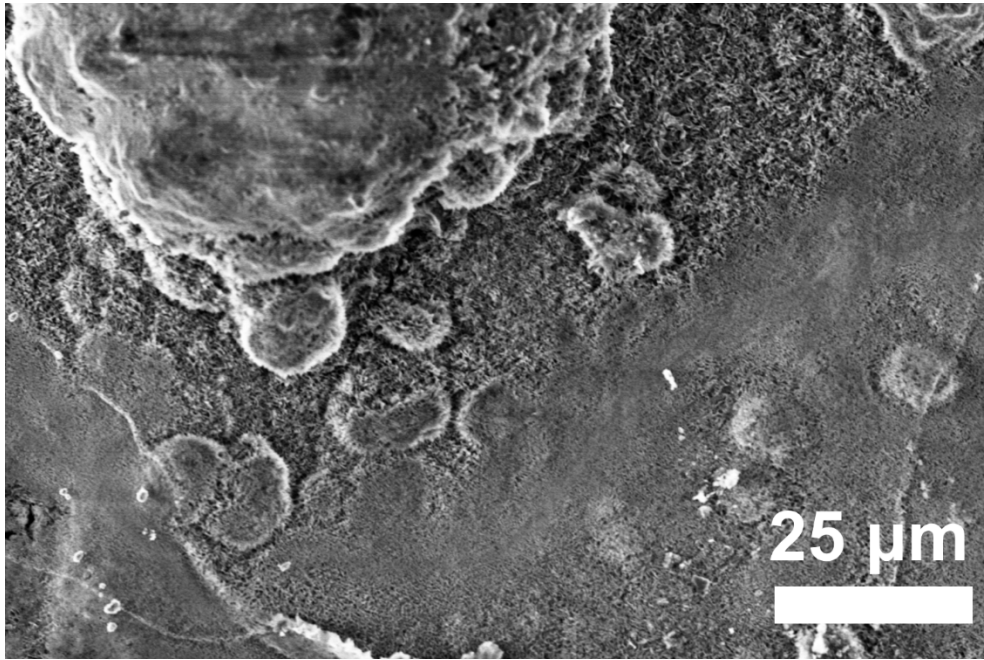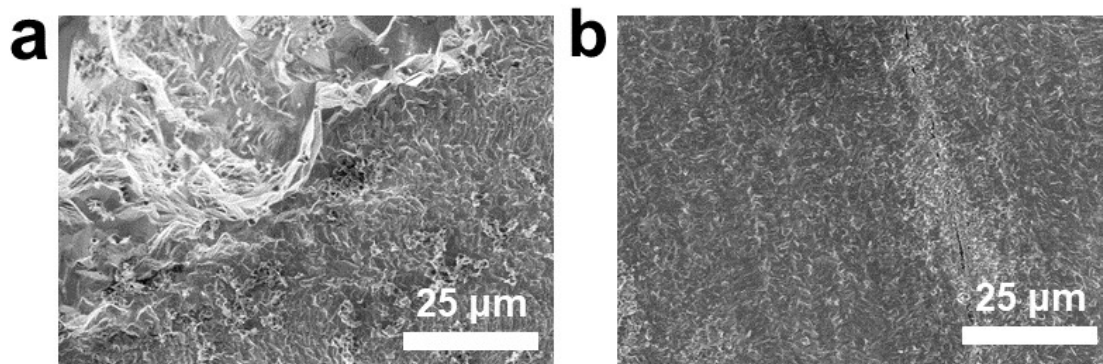
Fig. S5. Viscosity and conductivity of the five electrolytes.

Fig. S6. Galvanostatic zinc plating/stripping in symmetric Zn‖Zn cells in 0.5 M $ZnCl_2$ and 2.5 M CC-$ZnCl_2$ electrolytes.

Fig. S7. SEM image of Ti foil after zinc plating at a current density of 5 mA cm^{-2} and a capacity of 5 mAh cm^{-2} in 0.5 M ZnCl$_2$

Fig. S8. SEM image of Cu foil after zinc plating at a current density of 5 mA cm^{-2} and a capacity of 5 mAh cm^{-2} in (a) 0.5 M ZnCl$_2$ and (b) 2.5 M CC-ZnCl$_2$.

Table S1. CE in different electrolytes based on standardized Zn CE protocol

Electrolyte	CE	Ref.
$Zn(TFSI)_2$/acetamide (1/7 by mol)	75.8%	1
1 M $Zn(OTf)_2$ in H_2O	80.5%	1
$Zn(OTf)_2$/LiTFSI/acetamide (10/20/70 by mol)	89.0%	1
30 M $ZnCl_2$	95.4%	2
2.5 M CC-$ZnCl_2$	96.2%	Our work

References

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2. C. Zhang, J. Holoubek, X. Wu, A. Daniyar, L. Zhu, C. Chen, D. P. Leonard, I. A. Rodríguez-Pérez, J.-X. Jiang, C. Fang and X. Ji, *Chemical Communications*, 2018, **54**, 14097-14099.