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ZnCl₂ Water-in-Salt Electrolyte for Reversible Zn Metal Anode

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We report a low-cost water-in-salt electrolyte of 30 m ZnCl₂ that enables dendrite-free Zn metal anode with high Coulombic efficiency (CE). In asymmetric Zn||Zn cells with the limited mass of plated Zn as the working electrode, the ZnCl₂ WiSE improves the average CE of Zn anode to 95.4% from 73.2% in 5 m ZnCl₂.

Rechargeable Zn-metal battery is one of few aqueous electrochemical devices that could potentially rival the energy density of non-aqueous metal-ion batteries. Recently, remarkable progress has been made on the cathode materials that can reversibly host Zn²⁺ ions such as MnO₂ and V₂O₅.¹⁻⁵ As for the anode, Zn metal anode (ZMA) is known for its irreversible stripping/plating behavior, i.e., low CE as well as the dendrite-formation problem.²⁻¹⁰ Recently, Wang et al. discovered that a mixture water-in-salt electrolyte (WiSE) comprising 20 m lithium bistrifluoromethanesulfonimide (LiTFSI) and 1 m Zn(TFSI)₂ delivers extremely high CE of 99.7% on a platinum current collector.^{5,11} The challenge for the costly fluorinated-salt-based electrolytes is that its practical viability relies on the industry to employ the economy of scale in their manufacturing. Herein, we introduce a new WiSE based on inexpensive ZnCl₂, which can reach a very high concentration of 31 m at room temperature.¹² In this study, our results demonstrate that 30 m ZnCl₂ WiSE facilitates high reversibility of ZMA, which may serve as a most promising electrolyte for ZMA-based energy storage devices.

We first tested ZMA's stability in Zn||Zn symmetric cells with excessive Zn on both electrodes by plating/stripping for 10 minutes at 0.2 mA cm⁻² (Figure 1A). The Zn electrode in 30 m ZnCl₂ electrolyte (ZnCl₂ WiSE) shows highly stable galvanostatic charge-discharge (GCD) profiles over 600 hours without any significant overpotential fluctuation, whereas the overpotential for the Zn electrode in 5m ZnCl₂ increases by 4 times over 580 hours. The

transference number of Zn²⁺ in the 30 m ZnCl₂ electrolyte is slightly higher than that in the 5 m ZnCl₂ electrolyte (Figure S1A). The Zn plating/stripping in the 30 m ZnCl₂ exhibits smaller overpotentials than in the 5 m ZnCl₂ electrolyte (Figure S1B & C), despite the fact that the 30 m ZnCl₂ electrolyte shows higher viscosity (Figure S1D) and lower conductivity (Figure S2) than the 5 m ZnCl₂ electrolyte. Moreover, the pH values of ZnCl₂ electrolytes increase with the concentration (Figure S2), indicating that the hydrolysis of Zn²⁺ is depressed by a higher concentration. Thus, the less extent of hydrolysis could mitigate the formation of Zn(OH)₂/ZnO, benefiting high reversibility of the Zn metal anode. Furthermore, in the ZnCl₂ WiSE the plated Zn metal exhibits dense and smooth morphology after 75 cycles at a high current rate of 1 mA cm⁻² with a sweep duration of 1 hour; however, in the 5 m electrolyte, the Zn electrode cycled under the same conditions is of undesirable fluffy morphology comprising nano-flakes (Figure 1B, C).

The CE of ZMA ultimately depends on whether the plated phase is metallic zinc metal. After cycling in ZnCl₂ WiSE, ZMA displays nearly the same XRD pattern as the pristine Zn metal, revealing the reversibility; however, in 5 m ZnCl₂ electrolyte, the XRD pattern of the cycled ZMA shows the significant presence of surface Zn(OH)₂ and ZnO phases (Figure 1D).

We further measured the average CE of ZMA by GCD measurements in asymmetric Zn||Zn cells with a titanium foil as the current collector to support Zn plating/stripping at a current density of 1 mA cm⁻². Note that we did not employ aluminum current collectors in this study because electrolyte-born Zn²⁺ ions can be reduced by Al metal. The CE measurements follow the recently reported protocol for lithium metal anode by Zhang et al.¹³ Briefly, we first deposit Zn with the capacity of 4 mAh cm⁻² (Q₇). In the following cycles, we then strip and plate 0.4 mAh cm⁻² (Q_c) from and to the initially plated Zn, respectively, for 100 cycles. The capacity observed in the last stripping sweep is named Q_s. Thus, the average CE is calculated based on the following equation:

$$CE = \frac{100 * Q_c + Q_s}{100 * Q_c + Q_T} \quad (1)$$

In this asymmetric cell, the plating/stripping in 30 m ZnCl₂ demonstrates a much higher average CE of 95.4% than 72.3% in 5 m ZnCl₂ (Figure 1E & F).

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Generally, ZnCl_2 aqueous solution contains ionic species such as $[\text{Zn}(\text{OH})_2]^{2+}$ and $[\text{Zn}(\text{OH})_2\text{Cl}_4]^{2-}$.¹⁴ However, in 30 m ZnCl_2 , the stoichiometry of $\text{ZnCl}_2 \cdot 1.8\text{H}_2\text{O}$ cannot form the octahedral coordination for all Zn^{2+} ions.¹² As a result, there are few free water molecules, and a WiSE is essentially an ionic liquid.¹² To understand the speciation of ions in ZnCl_2 WiSE, we conducted femtosecond stimulated Raman spectroscopy (FSRS) measurements on ZnCl_2 solutions of different concentrations (Figure 1G).¹⁵ FSRS has high sensitivity and spectral resolution to detect molecular conformational states in the solution phase, particularly extending into the low-frequency region.¹⁶ The main peak at around 290 cm^{-1}

30 m ZnCl_2 solution, a new peak at 245 cm^{-1} is observed and can be assigned to $[\text{ZnCl}_4]^{2-}$ with the tetrahedral coordination. This means that with the ZnCl_2 concentration increasing, the concentration of $[\text{Zn}(\text{OH})_2\text{Cl}_4]^{2-}$ falls whereas more $[\text{ZnCl}_4]^{2-}$ ions appear. Importantly, the peak at around 390 cm^{-1} that is assigned to $[\text{Zn}(\text{OH})_2]^{2+}$ exhibits much weaker intensity than that for the anions of $[\text{Zn}(\text{OH})_2\text{Cl}_4]^{2-}$ and $[\text{ZnCl}_4]^{2-}$ at 290 and 245 cm^{-1} , respectively (Figure 1G & S3). This indicates the minor presence of $[\text{Zn}(\text{OH})_2]^{2+}$ in ZnCl_2 WiSE and the incomplete hydration shells of Zn^{2+} , which suppresses the formation of electrochemical non-active $\text{Zn}(\text{OH})_2$

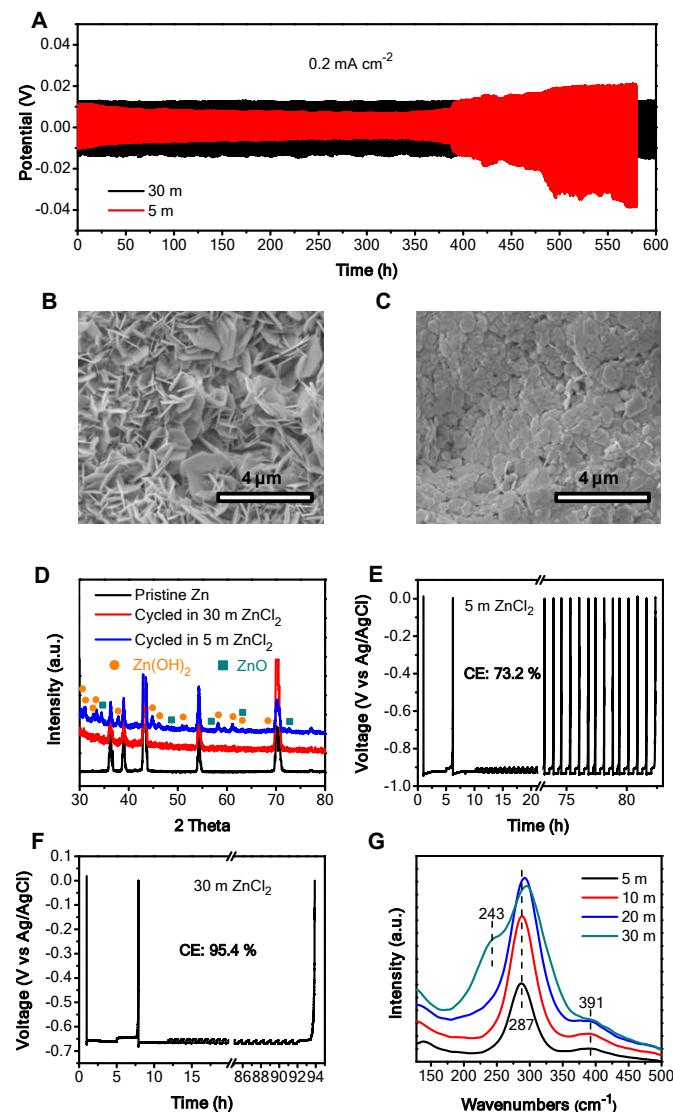


Figure 1. Characterization of the Zn metal electrode and the ZnCl_2 electrolytes. (A) The plating/stripping of Zn in 30 m ZnCl_2 in a $\text{Zn}|\text{Zn}$ symmetric cell at 0.2 mA cm^{-2} with a sweep duration of 10 minutes over 580 to 600 hours. (B, C) SEM images of Zn electrodes cycled for 75 times in beaker cells at 1 mA cm^{-2} with a sweep duration of 1 hour in 5 m and 30 m ZnCl_2 . (D) XRD patterns of pristine Zn metal and Zn electrodes cycled in 5 and 30 m ZnCl_2 electrolytes at 0.2 mA cm^{-2} with a sweep duration of 10 minutes after 580 to 600 hours. CE measurements of Zn plating/stripping in asymmetric $\text{Zn}|\text{Zn}$ cells in (E) 5 m and (F) 30 m ZnCl_2 electrolytes. (G) Raman spectra of ZnCl_2 solutions of different concentrations.

exists in all the spectra of ZnCl_2 solutions, corresponding to $[\text{Zn}(\text{OH})_2\text{Cl}_4]^{2-}$, which becomes broader and continuously shifts from 287 to 295 cm^{-1} with higher ZnCl_2 concentrations.^{14,17} For the

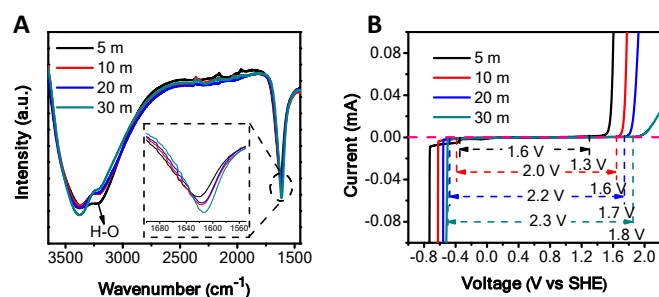


Figure 2. (A) FTIR spectra and (B) electrochemical stability window of ZnCl_2 electrolyte with different concentrations.

and ZnO .^{5,12} Therefore, the higher CE can be achieved in ZnCl_2 WiSE.

The incomplete hydration shells of Zn^{2+} would render water molecules tightly bound, restricting them from reacting with ZMA. Fourier transform infrared (FTIR) reveals the strong interaction between Zn^{2+} and water molecules (Figure 2A). When the concentration of ZnCl_2 increases from 5 to 30 m, the H-O-H bending vibration red-shifts from 1623 to 1612 cm^{-1} , likely corresponding to increased viscosity. Meanwhile, in the O-H stretching band, symmetric stretch (3200 cm^{-1}) decreases and asymmetric stretch (3400 cm^{-1}) increases, reflecting a disturbed O...H hydrogen bonding network due to water's strong binding with Zn^{2+} .¹² These spectral results explain the lack of presence and the significant presence of the undesirable side reaction products of $\text{Zn}(\text{OH})_2$ and ZnO when 30 m ZnCl_2 WiSE and 5 m ZnCl_2 are employed as electrolytes, respectively.⁵

The electrochemical stability window of ZnCl_2 electrolytes was measured with linear sweep voltammetry on a titanium foil as the working electrode in three-electrode cells at a scan rate of 0.2 mV s^{-1} (Figure 2B). In the three-electrode cells, an excess mass of activated carbon (AC) and Ag/AgCl (saturated KCl) function as the counter electrode and reference electrode, respectively. From 5 to 30 m, the electrochemical window of the ZnCl_2 solutions is widened from 1.6 to 2.3 V. As the concentration increases, the Zn plating potential rises, and the onset potential of H_2 evolution reaction (HER) is pushed to a lower potential, where both factors may help improve the CE of Zn plating/stripping in WiSE.

In summary, we for the first time investigate reversibility of Zn metal anode in the 30 m ZnCl_2 WiSE. In ZnCl_2 WiSE, plating/stripping processes of ZMA give rise to densely plated Zn metal. In dilute ZnCl_2 , ZMA suffers fluffy morphology of the plated Zn and the pronounced side reactions that lead to the formation of $\text{Zn}(\text{OH})_2$ and ZnO . In asymmetric $\text{Zn}|\text{Zn}$ cells, ZnCl_2 WiSE helps ZMA exhibit a CE of 95.4% vs. 73.2% in 5 m ZnCl_2 .

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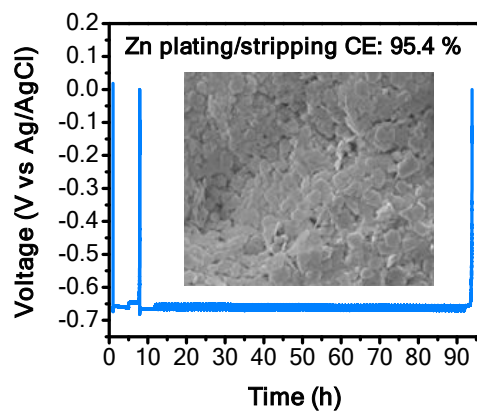
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Conflicts of interest

There are no conflicts to declare.

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