

# Electrolyte Solvation Structure for Aqueous Zinc Ion Batteries

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Zinc as an anode, with low potential ( $-0.762$  V vs. SHE) and high theoretical capacity ( $820$  mAh  $g^{-1}$  or  $5854$  mAh  $L^{-1}$ ), shows great promise for energy storage devices. The aqueous zinc ion battery (ZIB) is known as a prospective candidate for large-scale application in the future due to its high safety, environmental friendliness, abundant zinc resources on earth, and low-cost advantages. However, the existence of zinc dendrites and side reactions limit the practical application of ZIBs. Therefore, a lot of effort has been made to improve the performance from aspects including the structure design and surface modification of zinc anodes, regulation of the electrolyte solvation structure, and design of the functional separator.

aqueous zinc ion batteries

electrolyte

solvation structure

## 1. Introduction

The depletion of fossil energy and deterioration of the environment have led to the rapid development of sustainable clean energy, such as wind and solar energy. Thus, their proportion in the energy consumption structure has increased yearly. Due to the discontinuous and regional characteristics of clean energy, the development of energy storage devices has been driven [\[1\]\[2\]\[3\]](#). The aqueous zinc ion battery (ZIB) with metal zinc as the anode exhibiting a high theoretical capacity and low reduction potential has attracted much attention. Meanwhile, ZIBs show the advantages of low cost with rich and cheap zinc resources, high energy density, and high safety, which has been regarded as one of the most favorable candidate systems for broad application prospects [\[4\]\[5\]\[6\]](#).

As early as 1986, Yamamoto et al. [\[7\]](#) made a preliminary exploration of the neutral secondary zinc manganese battery. In 2012, Kang et al. [\[8\]](#) proposed an environment-friendly and safe power battery structure consisting of  $MnO_2$  as the cathode with zinc metal as the anode, and  $ZnSO_4$  as the neutral electrolyte solution, which is called a "zinc ion battery" with the working principle of reversible intercalation/stripping of  $Zn^{2+}$  in  $MnO_2$ . These works opened the prelude to the research of ZIBs. Since then, researchers have invested a lot of effort in studying the energy storage mechanism of ZIBs and have proposed many feasible strategies, for example,  $Zn^{2+}$  insertion/extraction,  $H^+/Zn^{2+}$  insertion/extraction, and chemical conversion reaction.

## 2. High-Concentration "Water-in-Salt" Strategy

Conventional aqueous electrolytes, influenced by the voltage of water decomposition, show a narrow electrochemical window ( $\sim 1.23$  V) [9]. The water activity will decrease and the electrochemical stability window will enlarge in aqueous electrolytes with the increase in salt concentration [10][11]. Meanwhile, the coordination environment of metal ions can be tuned and the number of solvation water molecules of metal cations can be reduced by employing high-concentration salt. The solvent sheath layer of metal ions is occupied by anions, which reduces the required energy for the desolvation of metal ions. The active water molecules reaching the electrode and electrolyte surface are reduced, which is able to prohibit the evolution of  $H_2$  and the corrosion phenomenon, and inhibit the occurrence of side reactions of the metal anode, effectively promoting the cycle life of ZIBs [12][13].

Given the advantages of low cost, non-toxicity, good solubility, and stable electrochemical properties of zinc sulfate ( $ZnSO_4$ ) in an aqueous solution, it is regarded as one of the common zinc salts at this stage and widely used in aqueous ZIBs. In the mixed electrolyte ( $ZnSO_4+MnSO_4$ ), Raman spectra show that the broad peaks indicating free water molecules are gradually suppressed, and  $Zn^{2+}$ -coordinated ambient water molecules are reduced as the electrolyte concentration of  $ZnSO_4$  increases from 2 M to 4.2 M. It is able to restrain side reactions and improve the cyclic stability of zinc metal anodes. A half-cell of  $Zn||Cu$  showed low polarization in dilute electrolyte (2 M  $ZnSO_4$  + 0.1 M  $MnSO_4$ ) with Zn plating/stripping cycles over 1000 h at  $0.2\text{ mA cm}^{-2}$  current density [14]; the average coulombic efficiency (ACE) for cycling  $>120$  was 97.54%; while in 4.2 M  $ZnSO_4$  and 0.1 M  $MnSO_4$  mixed electrolyte, it was able to reach 99.21%. Another full cell of  $Zn||MnO_2$  showed advanced long-cycle behavior under a measurement of more than 1200 cycles at  $938\text{ mA g}^{-1}$ , with an ACE close to 100% and 88.7% capacity retention. The dissolution of the cathode material would be inhibited via addition of  $MnSO_4$  and a synergistic effect with its solvation structure was created to achieve a stable, reversible, and high-performing  $Zn||MnO_2$  full cell [15]. The Zn anode in 3 M  $ZnSO_4$  electrolyte exhibited an impressively advanced coulombic efficiency ( $>99\%$ ) [16], excellent reversibility, as well as good rate capability, achieving  $>8000$  cycles, which significantly prolonged the cycle life of Zn with increasing current density.

Another example of zinc salt is  $Zn(TFSI)_2$  with high electrochemical stability and ionic conductivity. Wang and coworkers [17] introduced the concept of "water-in-salt" in ZIBs for the first time by using the electrolyte with high concentration (20 m  $LiTFSI$  + 1 m  $Zn(TFSI)_2$ ), resulting in an electrolyte pH of 7. According to the FTIR and  $^{17}O$ -NMR spectra, it can be found that with increase in the concentration of Li ions, the water molecules tend to form solvent sheaths with Li ions more. When the concentration of  $LiTFSI \geq 20$  m, the water molecules are strictly confined to the Li ions' solvation structure, and such a solvent sheath layer of Zn ions is changed from the original partition to be occupied by anions, and  $TFSI^-$  surrounds  $Zn^{2+}$ . The altered solvation structure of zinc ions avoids direct contact between the zinc metal anode and the water molecules of the solvent sheath layer, thus significantly inhibiting the HER phenomenon and the formation of by-products. The metallic Zn cathode exhibits superb electrochemical stability and deposition/stripping reversibility. The highly concentrated electrolyte results in dendrite-free zinc plating/stripping of about 100% coulombic efficiency with no observed by-product formation throughout the application. As for another highly concentrated solution with 20 m  $LiTFSI$ + 1 m  $Zn(OTf)_2$  [18],  $Zn^{2+}$  prefers to combine with  $O(TFSI^-)$  compared to  $O(\text{water})$ . Compared with low-concentration electrolytes, it shows good reversibility of galvanizing/zinc stripping, less polarization in long cycles, and long cycle life. It can form a stable SEI film, which makes the galvanized Cu surface uniform and flat. The capacity retention of the  $Zn||LiMn_2O_4$

full cell is 92% with an average CE about 99.62% after 300 cycles. A Zn||P(4VC<sub>86</sub>-stat-SS<sub>14</sub>) full cell exhibited an ultra-long lifetime in 4 M Zn(TFSI)<sub>2</sub> electrolyte [19]. A high reversible capacity about 184 mAh g<sup>-1</sup> was maintained with a capacity retention rate of 83% after 48,000 continuous cycles.

ZnCl<sub>2</sub> with significant solubility is often chosen as a high-concentration electrolyte. A highly reversible full cell of V<sub>2</sub>O<sub>5</sub>||Zn was fabricated by Tang et al. [20] with a ZnCl<sub>2</sub> “water-in-salt” electrolyte (WISE) to extend its life at high-temperature storage. V<sub>2</sub>O<sub>5</sub> cathodes in dilute electrolytes experience severe lattice swelling from 4.4 to 13.9 Å (319%) due to the co-insertion of hydrated zinc ions, with reduced active material, resulting in capacity loss and reduced cycling performance. An ultrahigh capacity of about 302 mAh g<sup>-1</sup> can be achieved by a V<sub>2</sub>O<sub>5</sub>||Zn full cell with conventional electrolyte (1 M ZnSO<sub>4</sub>), and the capacity decreases rapidly. In contrast, cycling in 30 m ZnCl<sub>2</sub> exhibits a maximum capacity of 341 mAh g<sup>-1</sup>, which shows about a 9.5% decay after 300 cycles, demonstrating ultra-high cycling stability within 1000 cycles. The ZnCl<sub>2</sub> WISE (30 m) can prevent co-insertion of water molecules, and inhibit dissolution of vanadium-based materials, resulting in an expanded electrochemical window, which inhibits the protrusion of zinc dendrites, and improves electrochemical performance. A mixed electrolyte was formed by adding 5 m LiCl to 30 m ZnCl<sub>2</sub>, in which hydrogen bonds between H<sub>2</sub>O can be broken by Li salt, reduce the free water molecules around Zn<sup>2+</sup>, and limit the solvation process of Zn<sup>2+</sup> ions to achieve a higher CE of the mixed double-ion (5 m LiCl + 30 m ZnCl<sub>2</sub>) WISE than that of a single salt (30 m ZnCl<sub>2</sub>) [21]. Zhang and coworkers [22] found that the solubility of ZnCl<sub>2</sub> was able to reach 31 m at room temperature and proposed using a 30 m ZnCl<sub>2</sub> solution as an electrolyte for ZIBs to enhance the reversibility of the Zn anode. Distinct from 5 m ZnCl<sub>2</sub>, a symmetric cell of Zn||Zn exhibited excellent cycle stability when plating/stripping at 0.2 mA cm<sup>-2</sup> for 10 min in a 30 m ZnCl<sub>2</sub> electrolyte solution. The viscosity of the electrolyte solution increases with concentration increases and electrical conductivity decreases. However, the ion migration number of Zn<sup>2+</sup> is higher in the highly concentrated electrolyte than that in the lowly concentrated one. A lower degree of hydrolysis slows down Zn(OH)<sub>2</sub>/ZnO formation, and the electrochemical window and pH also increase with concentration, indicating that the hydrolysis of Zn<sup>2+</sup> is inhibited and inhibits the HER, which brings higher reversibility of the zinc metal anode as well as tunes the uniform deposition of Zn<sup>2+</sup>.

### 3. Functional Additives

As mentioned above, side reactions and Zn dendrites are the main issues that need to be addressed in ZIBs, which can result in corrosion, HER, and passivation. Different types of functional electrolyte additives can inhibit side reactions and growth of zinc dendrites by different mechanisms. In recent years, the role of additive engineering has been extensively studied in ZIBs.

Tetrabutylammonium sulfate (TBA<sub>2</sub>SO<sub>4</sub>) is an effective, low-cost, non-toxic cationic surface-activator-type electrolyte additive. Zhu et al. [23] proposed to add TBA<sub>2</sub>SO<sub>4</sub> to the 2 M ZnSO<sub>4</sub> electrolyte with a small amount about 0.029 g L<sup>-1</sup>, and the positively charged TBA<sup>+</sup> gathered at the negatively charged zinc “bulge” by electrostatic adsorption, forming an electrostatic shield and limiting the tip effect. TBA<sup>+</sup> causes Zn<sup>2+</sup> deposition in adjacent flat areas, inducing uniform zinc deposition through a unique zincophobic repulsion mechanism. A full cell of Zn||MnO<sub>2</sub> with TBA<sub>2</sub>SO<sub>4</sub> exhibits a cycle stability of about 300 times at 1 A g<sup>-1</sup> with a 94% capacity retention. Wang et al. [24]

found that by adding 2 v.% of diethyl ether ( $\text{Et}_2\text{O}$ ),  $\text{Zn}^{2+}$  will shift to other regions during zinc deposition.  $\text{Zn}||\text{MnO}_2$  cells in 0.1 M  $\text{Mn}(\text{CF}_3\text{SO}_3)_2$  and 3 M  $\text{Zn}(\text{CF}_3\text{SO}_3)_2$  mixed aqueous solution with  $\text{Et}_2\text{O}$  as an additive were able to cycle 4000 times at  $5 \text{ A g}^{-1}$  with a 97.7% capacity retention rate, showing excellent cycling performance. Because  $\text{Et}_2\text{O}$  molecules can preferentially adsorb on the prominent tip, eliminating the “tip effect” and flattening the zinc anode surface, it can largely restrain growth of zinc dendrites. Guo et al. [25] added a small amount ( $25 \times 10^{-3} \text{ M}$ ) of  $\text{Zn}(\text{H}_2\text{PO}_4)_2$  salt to 1 M  $\text{Zn}(\text{CF}_3\text{SO}_3)_2$  electrolyte. From the Raman spectrum, it can be seen that SEI-Zn has bonds between Zn and O, and P and O, compared with bare-Zn, which demonstrates the formation of the SEI.

The abovementioned additives can be broadly classified as ionic and nonionic, capable of achieving dendrite-free zinc deposition by electrostatic shielding or by forming SEI films. Improving the performance of ZIBs also requires avoiding side reactions. In the aqueous electrolyte, the stable form of  $\text{Zn}^{2+}$  is  $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$  requires high energy for desolvation during the deposition process. Researchers have found that additives can adjust the solvation structure. Replacing  $\text{H}_2\text{O}$  molecules in  $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$  with other ions or molecules with weaker solvation structure effects can reduce the desolvation energy as well as prevent the side reactions [26].

Much research related to organic substances as common additives already exists. Li et al. [27] added ethylene glycol (EG) to the  $\text{ZnSO}_4$  electrolyte and found that it is effective in improving  $\text{Zn}^{2+}$  reversible deposition. The red-shift in the OH stretches  $\text{H}_2\text{O}$  ( $3200\text{--}3400 \text{ cm}^{-1}$ ), and OH stretched bending of C-OH ( $1460\text{--}1465 \text{ cm}^{-1}$ ) shows a blue shift and can be noted from the Raman spectrum, indicating that the electron density of OH in  $\text{H}_2\text{O}$  is lower and the electron density of C-OH in EG is higher, and the hydroxyl group of EG has a solid force to generate hydrogen bonds with  $\text{H}_2\text{O}$ , which can effectively weaken the force between  $\text{Zn}^{2+}$  and  $\text{H}_2\text{O}$ . Experiments and theoretical calculations show that with the increase in EG content, the OH stretching vibration range from  $3000$  to  $3500 \text{ cm}^{-1}$  can lead to a significant redshift, and  $\text{H}_2\text{O}$  bending vibration in the range of  $1600\text{--}1700 \text{ cm}^{-1}$  is slightly blueshifted in the FTIR spectrum [28][29]. Pan et al. [30] used ab initio calculations to analyze the solvation energy of different  $\text{Zn}^{2+}$  solvation sheaths in ethylene glycol/water solutions. They found that the solvation energy was ranked as  $[\text{Zn}(\text{H}_2\text{O})_m (\text{EG})_n]^{2+} < [\text{Zn}(\text{H}_2\text{O})_6]^{2+} < [\text{Zn}(\text{EG})_3]^{2+}$ , indicating that the interaction force between EG and zinc ions was greater than that between  $\text{Zn}^{2+}$  and water, disrupting the solvation of  $\text{Zn}^{2+}$  and effectively inhibiting the occurrence of the HER.  $\text{H}_2\text{O}$  in a zinc ion solvation sheath can be replaced by DMSO because of its (29.8) higher Gutmann donor number and larger dielectric constant than that of  $\text{H}_2\text{O}$  (18), and O had a smaller electron density in DMSO [31][32]. With the addition of DMSO, interaction between solvation water and  $\text{Zn}^{2+}$  can be weakened, which facilitates the desolvation process of zinc ions and can suppress the decomposition of active  $\text{H}_2\text{O}$ , improving the zinc plating and stripping coulombic efficiency. The solvation DMSO can lead to SEI layer formation in situ on the anode surface, which allows passage of zinc ions and hinders the passage of water molecules. The  $\text{Zn}||\text{Zn}$  symmetric cell in such a mixed electrolyte exhibited a cycle life of more than 1000 h. The cycle life was improved by a factor of 2.5 compared to that of the  $\text{ZnCl}_2\text{--H}_2\text{O}$  symmetric cell.  $\text{Zn}||\text{Ti}$  half-cells increased the CE to 99.0% and finally 100% within 30 cycles, exhibiting a stable over potential of  $\sim 24 \text{ mV}$ , confirming the ability of the DMSO additive in improving the CE of plating/stripping. Qiao et al. [33] added 50 v.% methanol to the  $\text{ZnSO}_4$  electrolyte. They found that methanol can insert into the internal  $\text{Zn}^{2+}$  solvation sheath owing to the high dielectric constant and small size (37.2) [34][35] and can disrupt the coordination equilibrium of  $\text{Zn}^{2+}$  by adjusting the amount of methanol addition. The methanol molecules will first interact with  $\text{H}_2\text{O}$  in the first layer of the  $\text{Zn}^{2+}$  solvated sheath

layer and form hydrogen bonds. In addition, the high wettability between methanol and the Zn metal anode makes it easier for methanol molecules to adsorb on the surface of Zn metal than solvent water, inducing the realization of dendrite-free  $\text{Zn}^{2+}$  uniform deposition. When the size of methanol molecules becomes larger, they will eventually insert into the inner layer of the  $\text{Zn}^{2+}$  solvent sheath, the activity of water will decrease, and both hydrogen precipitation reactions and side reactions will be inhibited. Yang et al. [36] demonstrated by introducing N-methyl-2-pyrrolidone (NMP) polar additives to  $\text{ZnSO}_4$  that the addition of organic solvents containing carbonyl groups contributes to stabilizing the hydrogen bonding network of water and the structural remodeling of  $\text{Zn}^{2+}$ -solvation, and such a synergistic effect helps to inhibit dendrite formation and water-induced parasitic reactions.

By investigating the influence of different organic additives on the  $\text{Zn}^{2+}$  solvation structure, researchers have provided an electrolyte regulation approach to achieve highly reversible Zn anodes and cells. Except for organic additives, salt additives are considered as another effective way to promote the electrochemical performance of Zn anode. Zhang et al. [37] used trifluoromethanesulfonate ( $\text{OTf}^-$ ) anions and ethylenediaminetetraacetic acid ( $\text{Y}^{4-}$ ) anions to form a mixed electrolyte (BE + 100 mM) consisting of 1 M  $\text{Zn}(\text{OTf})_2$  + 100 mM  $\text{Na}_4\text{Y}$ , and the double anion can change the  $\text{Zn}^{2+}$  solvation sheath to stabilize the Zn anode. In addition, this solvation structure allows decomposition of ligand anions to generate an in situ organic-inorganic SEI on the Zn surface. The resulting  $\text{Zn}^{2+}$  conducting SEI layer can lead to separation between Zn and the electrolyte, thereby inhibiting side reactions derived from  $\text{H}_2\text{O}$ . As a result, the Zn||Zn cell has a coulomb efficiency of 99.7% at  $1.0 \text{ mA cm}^{-2}$  and  $1.0 \text{ mAh cm}^{-2}$  for more than 1600 h, demonstrating excellent long-term stability. The Zn||Cu cell is highly reversible, possessing a coulomb efficiency of 99.7% at more than 400 cycles at  $1.0 \text{ mA cm}^{-2}$ . Chen et al. [38] demonstrated that via adding halogen ions to the  $\text{Zn}^{2+}$  solvation structure, the issues of dendrite growth and hydrogen precipitation reactions could be overcome. Through electrolyte regulation consisting of ammonium halide and zinc acetate,  $\text{I}^-$  can combine with  $\text{Zn}^{2+}$  to convert the conventional  $\text{Zn}(\text{H}_2\text{O})_6^{2+}$  to  $\text{ZnI}(\text{H}_2\text{O})_5^+$ , where  $\text{I}^-$  can transfer electrons to  $\text{H}_2\text{O}$ , and water molecules in the solvation structure would be reduced by inhibiting the reduction in the lowest unoccupied molecular orbital (LUMO) energy level and reducing the electron loss, thus improving the reduction stability and, thus, inhibiting HER. The formation of a dynamic electrostatic shielding layer accompanied with  $\text{NH}_4^+$  can inhibit the growth of dendrites.

In summary, electrolyte additives have obvious effects inhibiting side reactions and dendrites of ZIBs. Significantly, the selection of additives should consider three aspects: (1) Gutmann donor number of solvent additives, which can replace  $\text{H}_2\text{O}$  in the solvation sheath of  $\text{Zn}^{2+}$  when the donor number is larger than  $\text{H}_2\text{O}$  and can maintain  $\text{Zn}^{2+}$  ion transfer kinetics to some extent [39]. (2) Interaction with  $\text{H}_2\text{O}$ , which can form hydrogen bonds with  $\text{H}_2\text{O}$ , reduce  $\text{H}_2\text{O}$  activity, and inhibit  $\text{H}_2\text{O}$  reduction. (3) In situ formation of SEI film, which should form a dense, self-healing  $\text{Zn}^{2+}$ -conducting SEI film to prevent water penetration into the zinc anode. Furthermore, the electrolyte additives also have a vital effect on the cathode material. For example, the addition of triethyl phosphate (TEP) in the  $\text{Zn}(\text{OTf})_2\text{-H}_2\text{O}$  electrolyte in Zn|| $\text{V}_2\text{O}_5$  batteries can keep the pH of the electrolyte solution stable and hinder the dissolution of  $\text{V}_2\text{O}_5$  to some extent, which has strong interactions with  $\text{Zn}^{2+}$  and  $\text{H}_2\text{O}$  molecules. The TEP will enter the inner layer of the solvation sheath of  $\text{Zn}^{2+}$  and break the hydrogen bonding network between water molecules, thus reducing the activity of  $\text{H}_2\text{O}$  and avoiding the reaction between  $\text{V}_2\text{O}_5$  and  $\text{H}_2\text{O}$  [40]. Another report mentioned that introducing polyethylene glycol (PEG) into the electrolyte can reduce the content of free water molecules and

inhibit the H<sup>+</sup> insertion to the LiV<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> (LVP) cathode through the strong interaction between PEG and H<sub>2</sub>O, which is beneficial for suppressing the phase change of LVP. Significantly, much attention should also be paid to the cathode materials for the development of water-based ZIBs.

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