Solvation Structure Design for Aqueous Zn Metal Batteries

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ABSTRACT: Aqueous Zn batteries are promising energy storage devices for large-scale energy-storage due to low cost and high energy density. However, their lifespan is limited by the water decomposition and Zn dendrite growth. Here, we suppress water reduction and Zn dendrite growth in dilute aqueous electrolyte by adding dimethyl sulfoxide (DMSO) into ZnCl₂·H₂O, in which DMSO replaces the H₂O in Zn⁺⁺ solvation sheath due to a higher Gutmann donor number (29.8) of DMSO than that (18) of H₂O. The preferential solvation of DMSO with Zn⁺⁺ and strong H₂O–DMSO interaction inhibit the decomposition of solvated H₂O. In addition, the decomposition of solvated DMSO forms Zn₂(SO₄)Cl₂(OH)₁₅·SH₂O, ZnSO₃, and ZnS enriched-solid electrolyte interphase (SEI) preventing Zn dendrite and further suppressing water decomposition. The ZnCl₂–H₂O–DMSO electrolyte enables Zn anodes in Zn/Ti half-cell to achieve a high average Coulombic efficiency of 99.5% for 400 cycles (400 h), and the Zn/MnO₂ full cell with a low capacity ratio of Zn:MnO₂ at 2:1 to deliver a high energy density of 212 Wh/kg (based on both cathode and anode) and maintain 95.3% of the capacity over 500 cycles at 8 C.

INTRODUCTION

Metallic zinc (Zn) is an ideal anode material for aqueous batteries because of its high theoretical capacity (5851 mAh mL⁻¹ and 820 mA h g⁻¹), low redox potential (−0.76 V versus the standard hydrogen electrode), high abundance, water compatibility, and intrinsic safety. However, the reaction of Zn anodes with water in aqueous electrolytes reduces Coulombic efficiency (CE), consumes water and Zn, and promotes Zn dendrite growth.²⁻¹⁰

Parasitic water reduction during Zn deposition is accelerated by the high overpotential associated with strong Coulombic interactions between the solvated Zn⁺⁺ ion and its surrounding H₂O shell.⁹⁻¹¹ The increase in local pH environment due to H₂ evolution promotes the formation of Zn⁺⁺-insulating passive layer (such as Zn hydroxides) on the Zn surface,²⁻¹⁵ reducing the Zn utilization and cycle life, and promoting Zn dendrite growth.¹⁴⁻¹⁵ To suppress the water reduction and Zn dendrite, the bonding strength between Zn⁺⁺ ion and solvated H₂O should be weakened, and a uniform Zn-ion conductive solid electrolyte interphase (SEI) has to be constructed, which allows Zn⁺⁺ transport while preventing H₂O from penetration to Zn anode surface. To weaken the bonding strength between Zn⁺⁺ ion and H₂O, Wang et al. developed a 21 m LiTFSI–H₂O–1 m Zn(TFSI)₂ water-in-salt, where the support Li⁺ strongly bonds with H₂O, while Zn⁺⁺ ions are closely coordinated with TFSI⁻ rather than H₂O, thus significantly reducing the H₂O activity in the electrolyte. Ji et al. developed a 30 m ZnCl₂·H₂O–5 m LiCl water-in-salt, where the hydrogen bonding network of water is interrupted and Zn⁺⁺ ions are closely coordinated with Cl⁻ rather than H₂O, thus strengthening O–H covalent bonds and decreasing H₂O activity in the electrolyte. Chen et al. reported a 7.5 m ZnCl₂ electrolyte with interrupted hydrogen bonding network of water and decreased H₂O activity at −70 °C. Adding salt concentration can effectively weaken the bonding between Zn⁺⁺ and H₂O, thus suppressing the water decomposition during Zn deposition. However, the high cost and high viscosity of the water-in-salt electrolytes remain unsolved.¹⁸⁻¹⁹ Alternatively, the H₂O reduction on Zn can also be prevented by forming a ZnF₂–Zn₃(PO₄)₂ SEI through a hydrophobic organic electrolyte surface coating.²⁰ However, the complex surface coating of the organic layer electrolyte limits its large-scale application. It is highly desired to form SEI and reduce the H₂O activity by simply adding additives into aqueous electrolytes. Liu and Pan et al. added poly(ethylene oxide) polymer (PEO) as additive into ZnSO₄, where ether groups of PEO interact strongly with Zn²⁺ ions and PEO molecules adsorbed onto Zn anodes. However, Zn²⁺ ion transfer kinetics and power density are seriously reduced, although H₂ generation on Zn metal anode is suppressed. The electrolyte additive should satisfy three stringent requirements: (1) The solvent additive should have a...
higher Gutmann donor number than H₂O enabling it to replace the H₂O in the Zn²⁺ solvation sheath without seriously sacrificing Zn²⁺ ion transfer kinetics. 

(2) It should be able to form a strong bond with H₂O to reduce H₂O activity and suppress H₂O reduction. 

(3) It should be able to form a dense and self-repairable solid–electrolyte interphase (SEI) to prevent water penetration onto Zn anode.

Dimethyl sulfoxide (DMSO) has high dielectric constant, high donor number (29.8), and low cost, which can preferentially solvate with Zn ions and exclude water from Zn²⁺ solvation sheath. Besides, DMSO also has a strong interaction to water, reducing the water activity. DMSO has been added into alkaline, organic, and ionic liquid electrolyte forming a 1.3 m ZnCl₂/H₂O electrolyte. Since the donor number (29.8) of DMSO is much higher than that (18) of H₂O, and preferential consipation of cosolvents in the structure of the solvation sheath of Li ions, the H₂O solvated Zn²⁺ sheath was altered by preferential solvation of DMSO (Figure 1). The preference reduction of DMSO during Zn plating/stripping process, inhibiting H₂O reduction and hence increasing Zn plating/stripping CE (Figure S1). At −0.02 V vs Zn/Zn²⁺, the reduction current reduced from −16 μA (Zn + H₂) to −13 μA (Zn plating), as confirmed by almost 100% Coulombic efficiency of Zn plating/stripping in ZnCl₂−H₂O−DMSO due to the formation of Zn₁₂(SO₄)₁₃(OH)₁₅·SH₂O−ZnSO₃−ZnS SEI. In addition, oxidative decomposition of the electrolytes has been expanded from 2.0 to 2.2 V versus Zn/Zn²⁺ after adding DMSO into ZnCl₂−H₂O electrolytes.

DMSO additive reduces the bonding between Zn²⁺ and H₂O as demonstrated by X-ray absorption spectroscopy (XAS) and ft-EXAFS analysis. The edge position (when the normalized absorption coefficient is 0.5) in XAS is a good indicator of the effective charge on the atom being probed, which is Zn in this case. Edge position at higher energy indicates more effective charge. Zn XANES spectra in Figure 2a shows that the edge position obviously shifts to lower energy upon the introduction of DMSO. This indicates that the addition of DMSO leads to less electron transfer between Zn and O in H₂O or DMSO, thereby weakening the bonding strength between Zn²⁺ and H₂O in the Zn²⁺ solvation sheath. More solvation structure information is also revealed by the ft-EXAFS shown in Figure 2b, indicating that the solvation structure is mostly limited to the first shell, which corresponds to the first and the strongest peak (Zn−O bond). With the addition of DMSO, the Zn−O bond length increases, suggesting weakened interaction between Zn and the solvents. The decreased bonding strength between Zn²⁺ ions and H₂O is beneficial for the H₂O desolvation of Zn²⁺ during the Zn plating process, inhibiting H₂O reduction and hence increasing Zn plating/stripping Coulombic efficiency.

6Zn NMR spectroscopy demonstrated that DMSO participates in Zn²⁺ solvation sheath. Even with a small

\[ \text{Zn}^2+ \text{ solvation was altered by preferential solvation of DMSO interactions. The combination of reducing H}_2\text{O activity and suppression of H}_2\text{O reduction.} \]

\[ \text{DMSO also has a strong interaction to water, reducing the water activity.} \]

\[ \text{DMSO forms a dense Zn}_{12}(\text{SO}_4)_{13}(\text{OH})_{15} \cdot \text{SH}_2\text{O} \cdot \text{ZnSO}_3 \cdot \text{ZnS solid electrolyte interphase, inhibiting the decomposition of solvated H}_2\text{O.} \]

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DMSO: H2O molar ratio of 1:17, the 67Zn chemical shift of ZnCl2−H2O−DMSO (106 ppm) is significantly larger than that of ZnCl2−H2O electrolyte (83 ppm) (Figure 2c), indicating the deshielding effect of the solvation sheath on Zn2+ ions. This is because that DMSO is involved in solvation sheath to replace some H2O due to the higher donor number of DMSO (29.8) than that of H2O (18).27 and lower electron density of O in DMSO than in H2O (Figure S2). This result is consistent with the increased Zn−O bond length and decreased Zn−H2O bonding strength mentioned previously.

The involvement of DMSO in the solvation structure of Zn2+ was also confirmed by the high-resolution mass spectra (HRMS) of ZnCl2−H2O−DMSO electrolyte. As displayed in Figure 2d, distinct signals of various DMSO-containing [Zn(H2O)6(OH)2(DMSO)]− complexes at m/z = 265, 267, 269 are detected. The peak position and intensity differences of m/z for the same chemical structure are caused by the isotope pattern of Zn, including 48.6% abundance of Zn(64) in nature, 27.9% abundance of Zn(66), and 18.8% abundance of Zn(68). It should be noted that the test result is from a dilute solution in which H2O to the ZnCl2−H2O−DMSO electrolyte volume ratio is 10:1. The strong persistence of DMSO in the Zn2+ solvation shell from such a dilute solution further confirms the preferential solvation effect of DMSO with Zn2+ compared to that of H2O.

The strong interaction between DMSO and H2O without interference of Zn2+ was confirmed using FTIR and Raman. Figure S3 indicates that the DMSO solvent displays unique stretching modes of the sulfoxide (S=O) group at around 1050 cm−1. In the DMSO−H2O mixture where the DMSO: H2O molar ratio is 1:17, the spectral band (red line) shifts to lower wavenumbers (red shift), compared with that in pure DMSO (blue line). The red shift is attributed to the interaction between H of the O−H bond in water molecules and O of the S=O double bond in DMSO (S=O⋯H−O). Strong interaction between DMSO and H2O was also confirmed by the difference in thermal stabilities of ZnCl2−H2O−DMSO and ZnCl2−H2O electrolytes. As shown in thermal gravimetric analysis (TGA) curves (Figure S4), the addition of DMSO into ZnCl2−H2O electrolyte shows a fluctuant voltage signals with a low average CE of ~90.7% (Figure 3b, Figure S8). In contrast, the Zn/Ti cell without DMSO additive showed a low CE (90.7%) and poor cycling stability. The zinc plating/stripping CE improves to 99.0% within 30 cycles due to the formation of robust SEI and ultimately reached a high CE of ~100% with a steady overpotential of ~24 mV (Figure 3b,c, which is one of the best performances among all reported Zn anodes.7,16,17,21 The universality of DMSO additives for enhancing the CE of Zn plating/stripping was further confirmed using 1.0 m Zn(OTF)2 aqueous electrolyte. The Zn/Ti cell without DMSO additive showed a low CE (~93%) and short-circuit occurred after only 25 cycles. In contrast, adding 20 wt % of DMSO additive into 1.0 m Zn(OTF)2 aqueous electrolyte increased the CE to 99.3% for more than 250 cycles (Figure S9).

The zinc electrode surface morphologies after 50 plating/stripping cycles are characterized using SEM (Figure 4). After 50 cycles, the Zn surface in ZnCl2−H2O electrolyte becomes rough with flake-like dendrites (Figure 4a−c) due to continuous reactions between Zn and aqueous electrolyte, as evidenced by a low CE (~90.7%) and poor cycling stability. In contrast, the Zn deposited in ZnCl2−H2O−DMSO electrolyte shows a dense and smooth morphology (Figure 4d−f), confirmed by the uniform S and Cl elements distribution (Figure S10). The thickness of the cycled Zn in ZnCl2−H2O
electrolyte is 10.9 μm, and was reduced to 6.5 μm when it was cycled in ZnCl₂−H₂O−DMSO (white lines in Figure 4c and f). Therefore, DMSO addition effectively suppressed water reaction with Zn anode, which suppressed Zn dendrite growth. Here, the preference reduction of solvated DMSO and suppression of H₂O reduction promote formation of a dense SEI layer on Zn surface (Figure 4f) as demonstrated by XPS and XRD below, which can further prevent water from reacting with Zn.

**SEI on Zn Anode.** The SEI composition on the Zn anode was analyzed using X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) with an Ar⁺ sputtering depth profiling characterization. XRD (Figure 5a) and optical image analysis (Figure S11) of cycled Zn anodes in ZnCl₂−H₂O electrolyte demonstrated that random platelet-shape Zn₂⁺-insulating Zn₉(OH)₆Cl₂·H₂O byproducts were formed on the cycled Zn electrode surface. However, Zn₂⁺ conductive SEI layer was formed on Zn that cycled in ZnCl₂−H₂O−DMSO electrolyte as evidenced by well-identified characteristic peak of the Zn₁₂(SO₄)₃Cl₃(OH)₁₅·5H₂O and Zn₉(OH)₆(CO₃)₂ crystals in XRD and smooth surface in optical image (Figure S11). The detail composition distribution in SEI was also further analyzed using X-ray photoelectron spectroscopy (XPS) with an Ar⁺ sputtering depth profiling (Figure 5b, Figures S12, S13, S14). S 2p spectrum in Figure 5b demonstrated that the top surface (before sputtering) of SEI formed in ZnCl₂−H₂O−DMSO electrolyte mainly contains inorganic ZnSO₄ (46%), ZnSO₃ (30%), and ZnS (8%) with minor organic S−C species (16%), referring to the XPS binding energy database of National Institute of Standard and Technology (NIST). During Ar⁺ sputtering, the organic S−C species reduce while inorganic ZnS increase after 600 s of sputtering due to reduction of DMSO molecular decomposition during Zn deposition. Upon further sputtering to 1200 s on the Zn anode surface, the ZnSO₄ peak disappeared; meanwhile, the ZnSO₃ content plunged to ~5%, and inorganic ZnS dominated with the signal reaching ~75% of all the S signals. After 1800 s of sputtering, the inorganic ZnS content further increased to 88%. The inorganic ZnCO₃ signal detected from the C 1s and O 1s spectra (Figure S13), consistent with XRD spectra (Figure 5a), further confirmed the decomposition of DMSO molecules. In addition, the Cl 2p spectrum arises from two major components: inorganic chlorine from ZnCl₂ salt and organic chlorine from C−Cl species.28,29 The organic chlorine could arise from reaction products between ZnCl₂ and DMSO, while inorganic chlorine from ZnCl₂ originate from the precipitation of electrolyte. The inorganic ZnCl₂ content increased from 77.2% at 1200 s to 93.1% at 1800 s. XPS analysis demonstrated that Zn₁₂(SO₄)₃Cl₃(OH)₁₅·5H₂O−ZnSO₄−ZnS SEI was formed on the Zn surface in ZnCl₂−H₂O−DMSO electrolyte, which allows Zn²⁺ to diffuse through but block the water. The contribution from DMSO to form the Zn₁₂(SO₄)₃Cl₃(OH)₁₅·5H₂O−ZnSO₄−ZnS SEI are strongly associated with the solvation structure of Zn²⁺ ion in electrolytes.

**Electrochemical Performance of MnO₂ Cathodes and Zn||MnO₂ Full Cells.** The ZnCl₂−H₂O−DMSO electrolyte was evaluated in a Zn||MnO₂ full cell using β−MnO₂ with a tunnel structure, one of the most promising cathodes with a high theoretical capacity of 308 mAh/g for aqueous Zn batteries, and compared with that using ZnCl₂−H₂O aqueous electrolyte. We first evaluated the electrochemical performance of the MnO₂ cathode in two electrolytes using Zn||MnO₂ cells with excess Zn anode to reflect MnO₂ behavior. Figure 6a shows the CV response of the Zn||MnO₂ half-cell at a scan rate of 0.1 mV/s. MnO₂ in both electrolytes showed similar behavior with distinct Mn-ion redox peaks, consistent with the previous work.30 Besides, the reduction peak at 1.15 V in the ZnCl₂−H₂O−DMSO electrolyte is lower than 1.22 V in ZnCl₂−H₂O electrolyte. This peak was evaluated in a Zn||MnO₂ full cell using β−MnO₂ with a tunnel structure, one of the most promising cathodes with a high theoretical capacity of 308 mAh/g for aqueous Zn batteries, and compared with that using ZnCl₂−H₂O aqueous electrolyte. We first evaluated the electrochemical performance of the MnO₂ cathode in two electrolytes using Zn||MnO₂ cells with excess Zn anode to reflect MnO₂ behavior. Figure 6a shows the CV response of the Zn||MnO₂ half-cell at a scan rate of 0.1 mV/s. MnO₂ in both electrolytes showed similar behavior with distinct Mn-ion redox peaks, consistent with the previous work.30 Besides, the reduction peak at 1.15 V in the ZnCl₂−H₂O−DMSO electrolyte is lower than 1.22 V in ZnCl₂−H₂O electrolyte. This peak was evaluated in a Zn||MnO₂ full cell using β−MnO₂ with a tunnel structure, one of the most promising cathodes with a high theoretical capacity of 308 mAh/g for aqueous Zn batteries, and compared with that using ZnCl₂−H₂O aqueous electrolyte. We first evaluated the electrochemical performance of the MnO₂ cathode in two electrolytes using Zn||MnO₂ cells with excess Zn anode to reflect MnO₂ behavior. Figure 6a shows the CV response of the Zn||MnO₂ half-cell at a scan rate of 0.1 mV/s. MnO₂ in both electrolytes showed similar behavior with distinct Mn-ion redox peaks, consistent with the previous work.30
limited Zn anode enable a high energy density of 212 Wh kg$^{-1}$ (based on the weight of the cathode and anode; Figure S15). The long-term cycling stability of the ZnlMnO$_2$ cell was evaluated at 8 C in both electrolytes with the capacity ratio of Zn:MnO$_2$ at 2:1 (Figure 6b,c). The ZnlMnO$_2$ cells in two electrolytes show a charge/discharge behavior (Figure 6b). However, the capacity of ZnlMnO$_2$ cells in ZnCl$_2$–H$_2$O electrolyte decays rapidly in 150 cycles, while the capacity of ZnlMnO$_2$ cells in ZnCl$_2$–H$_2$O–DMSO electrolyte remain stable for 500 cycles (Figure 6c). The capacity decay of Znl MnO$_2$ cells in ZnCl$_2$–H$_2$O electrolyte is mainly attributed to the capacity decay of Zn anodes (Figure S16) and drying out of electrolytes. The ZnlMnO$_2$ full cell after 500 cycles in ZnCl$_2$–H$_2$O–DMSO electrolyte still maintained $\sim 150.3$ mAh g$^{-1}$, which was 95.3% of the initial capacity with CE approaching 100%, which is one of the best performances reported to date for Zn/MnO$_2$ with similar P/N ratio. In contrast, the capacity of the ZnlMnO$_2$ cell in the ZnCl$_2$–H$_2$O reference electrolyte quickly dropped to 51.5% of initial capacity due to low CE for Zn plating/stripping.

**CONCLUSIONS**

The strong H$_2$O–DMSO interaction decreases the activity of solvated water and suppresses the decomposition of solvated H$_2$O. In addition, DMSO replaces solvated H$_2$O in the solvation structure of Zn$^{2+}$ due to a high Gutmann donor number of DMSO, resulting in preferential reduction of solvated DMSO to in situ form a dense and self-repaired Zn$_{12}$(SO$_4$)$_3$Cl$_6$(OH)$_6$5H$_2$O–ZnSO$_4$–ZnS SEI on Zn anodes. The SEI allows Zn$^{2+}$ transport but blocks H$_2$O penetration, which further inhibits the water reduction and suppresses Zn dendrite growth. Addition of multifunctional DMSO into ZnCl$_2$–H$_2$O electrolytes enhances Zn plating/stripping CE to $\sim 100\%$ enabling ZnlMnO$_2$ cells with a low capacity ratio of 2:1 to achieve a capacity retention of 95.3% of the initial capacity after 500 cycles.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/10.1021/jacs.0c09794. Chemicals, detailed experimental methods, characterizations, and additional figures (PDF)

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**Author Contributions**

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**Notes**

The authors declare no competing financial interest.

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