

Short Communication

Effect of Electrolyte Additives on the Performance of Zinc Ion Batteries

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The zinc dendrite growth and by-products formation of rechargeable zinc metal batteries hinder their rapid development as promising energy storage equipment. Herein, we use a composite additive composed of leveling agent and surfactant to improve the ZnSO₄ electrolyte system to obtain a zinc anode with reversible electroplating/stripping for high-performance aqueous zinc ion batteries (ZIBs). Benzylidene acetone leveling agent can be adsorbed on the crystal nucleation sites to promote homogeneous nucleation in the zinc deposition process, thus inhibiting the zinc dendrites growth, zinc corrosion, and by-products formation. Alkylphenol ethoxylate can improve the crystallinity of the zinc anode surface and increase the nucleation sites, thus reducing the potential nucleation barrier in the zinc deposition process. In addition, alkylphenol ethoxylate is the carrier of benzylidene acetone, which can cooperate with benzylidene acetone, and further enhance the leveling effect of benzylidene ketone. As a result, the Zn/Zn symmetric battery with ZSO+additive electrolyte displays a small overpotential and good cycle stability for 1000 hours. With the increase in current density, the voltage hysteresis does not severely fluctuate. The Zn/MnO₂ battery with ZSO+additive electrolyte can provide a higher capacity (179.7 mAh g⁻¹) and longer cycle life (76.6% capacity retention after 200 cycles), which proves that the additives can improve the performance of ZIBs. The composite additive proposed in this work provides a new way to develop high-performance zinc ion batteries.

Keywords: Leveling agent; Benzylidene acetone; Alkylphenol ethoxylate; Zinc ion batteries

1. INTRODUCTION

Energy shortage and environmental pollution push the world towards new technologies in energy storage [1,2]. Commercial lithium-ion batteries (LIBs) have brought great convenience to our lives, but

there are still some problems, including high economic cost and low security [3]. In contrast, aqueous-based metal ion batteries, especially zinc ion batteries (ZIBs), are promising alternatives because of their higher capacity, lower material and assembly costs, and safer operation [4]. The main obstacle to developing advanced ZIBs with long cycle life is the zinc dendrites growth, zinc corrosion, and by-products formation during zinc deposition[5,6]. Researchers have adopted many effective strategies to mitigate or inhibit zinc dendrites, such as controlling specific crystal planes [7], coating a protective layer on the zinc anode surface [8], depositing zinc nanostructures on the 3D skeleton [9], and adjusting the electrolyte structure [10]. Injecting some additives (including solutes or solvents) into the original electrolyte is a simple and affordable solution to solve the problems of ZIBs. Previously, researchers added a small number of solutes to ZnSO₄ electrolytes, such as polyacrylamide or tetrabutylammonium sulfate, which can be absorbed on the zinc anode surface to ensure uniform deposition of the zinc layer [11]. In addition, various solvents, such as succinonitrile [12], dimethyl sulfoxide [13], and antisolvent in pure aqueous-electrolyte [14], help to adjust the solvation structure of the zinc hydrate layer, thus inhibiting the formation of by-products. Therefore, additives should be a fascinating way to optimize the solvation structure around zinc ions in the electrolyte and simultaneously control the environment on the electrode-electrolyte interface to achieve uniform nucleation on the zinc anode. Adding leveling agent to the electrolyte is a pretty mature technology in the electroplating industry, which can improve the quality of zinc film deposited in traditional electroplating. The storage of zinc in ZIBs and the electroplating industry are almost the same, except for the slight difference in the electrolyte system. Therefore, introducing a leveling agent into the electrolyte solution should be an effective way to improve the performance of ZIBs.

Here we use a composite additive composed of leveling agent and surfactant to improve the ZnSO₄ electrolyte system to obtain a zinc anode with reversible electroplating/stripping for high-performance aqueous ZIBs. Benzylidene acetone leveling agent can be adsorbed on the crystal nucleation sites to promote homogeneous nucleation in the zinc deposition process, thus inhibiting the zinc dendrites growth, zinc corrosion, and by-products formation. Alkylphenol ethoxylate can improve the crystallinity of the zinc anode surface and increase the nucleation sites, thus reducing the potential nucleation barrier in the zinc deposition process. In addition, alkylphenol ethoxylate is the carrier of benzylidene acetone, which can cooperate with benzylidene acetone, and further enhance the leveling effect of benzylidene ketone. As a result, the Zn/Zn symmetric battery with ZSO+additive electrolyte displays a small overpotential and good cycle stability for 1000 hours. With the increase in current density, the voltage hysteresis does not severely fluctuate. The Zn/MnO₂ battery with ZSO+additive electrolyte can provide a higher capacity (179.7 mAh g⁻¹) and longer cycle life (76.6% capacity retention after 200 cycles), which proves that the additives can improve the performance of ZIB. The composite additive proposed in this work provides a new way to develop high-performance zinc ion batteries.

2. EXPERIMENT

2.1 Materials

The chemicals in this work were commercially available, and directly used without further

purification. Benzylidene acetone was purchased from Shanghai Macklin ($C_{10}H_{10}O$, >99.5%). Alkylphenol ethoxylate was purchased from Nantong Hai'an Petroleum Chemical Plant ($C_8H_{17}C_6H_4O(CH_2CH_2O)_{10}H$, >99%). Zinc sulfate ($ZnSO_4$, >99.5%), manganese acetate ($Mn(CH_3COO)_2 \cdot 4H_2O$, >99%), and potassium permanganate ($KMnO_4$, >99%) were purchased from Sigma Aldrich. Zinc and titanium foils were purchased from Sinopharm Chemical Reagent Co., Ltd. Deionized water was used to prepare all aqueous electrolytes.

2.2 Preparation of electrolytes and electrodes

0.375 g of benzylidene acetone was added into 3.75 g of alkylphenol ethoxylate and then continued stirring until the benzylidene acetone was completely dissolved. The above solution was added drop by drop into 50 mL of 2 M zinc sulfate solution. And then, the mixture was stirred until a uniform and transparent solution (ZSO+additive) was formed. The reference sample was a 2 M zinc sulfate electrolyte without additives (ZSO).

The cathode material was prepared by a one-step hydrothermal method. 11 mmol of manganese acetate was dissolved in deionized water with stirring for 0.5 h. 8 mmol of potassium permanganate was dissolved in 80 mL of deionized water. Then, the above solution was added drop by drop into the manganese acetate solution. After stirring for 0.5 hours, the mixture was poured into a 100 mL teflon-lined stainless autoclave and heated to 120 °C. The reaction was maintained for 12 hours. After the system cooling down to room temperature, the product was washed with deionized water and ethanol three times, respectively, and dried in a vacuum drying oven for 8 hours to obtain the manganese dioxide.

To obtain the cathode, the synthesized manganese dioxide, conductive carbon black, and polyvinylidene fluoride (PVDF) were mixed at a mass ratio of 7:2:1. Then, N-methyl-2-pyrrolidone was added into the above mixture. After grinding for 20 minutes, a slurry was obtained and then evenly coated on a clean titanium foil. After drying at 70 °C for 12 hours in a vacuum drying oven, the product was cut into a round piece with a diameter of 12 mm to obtain the cathode. Commercial zinc foil was used as the anode. The zinc foil was polished with 1200 mesh sandpaper and then cut into a circular disc with a diameter of 12 mm. Finally, the zinc foil was cleaned with anhydrous ethanol by ultrasonic cleaning and dried at room temperature.

2.3 Battery assembly

The battery assembly process was carried out in the air. Glass fiber (GF/A, Whatman) was used as the separator. ZSO+additive and ZSO were used as the electrolytes. After putting them aside for 2 hours, the batteries were activated for several cycles at a low current density of 0.1 A g^{-1} .

2.4 Material characterization and electrochemical characterization

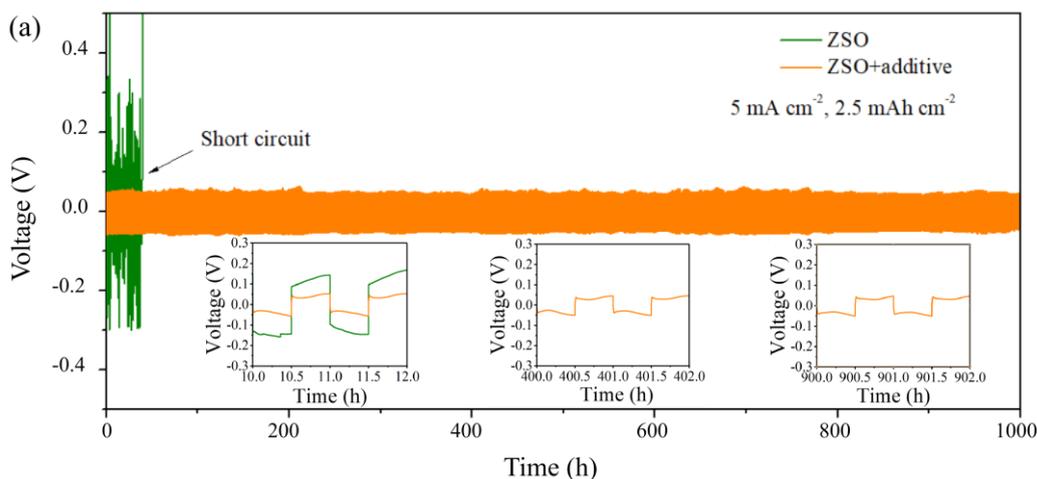
The surface morphology and microstructure of the anode before and after cycling were observed by scanning electron microscopy (SEM, SU8010). The charge/discharge processes were performed on

the Neware battery tester (CT4008). The CV voltage range was 0.5~2.0 V, and the scanning speed was 0.1 mV s^{-1} . The electrochemical impedance spectroscopy (EIS) tests were performed from 100 kHz to 10 MHz, and the amplitude was 5 mV.

3. RESULTS AND DISCUSSION

3.1 Effect of additives on electrochemical performance of Zn/Zn battery

To understand the dynamic stability of the zinc/electrolyte interface, the voltage response curves of Zn/Zn symmetric batteries were studied. The current density is 5.0 mA cm^{-2} . For ZSO electrolyte, the plating/stripping processes last only 39 hours, and the overpotential is large. On the contrary, the ZSO+additive electrolyte displays good cycle stability with 1000 hours, and the overpotential is low (Fig. 1a). Compared with the previous literature [15], the ZSO+additive electrolyte can provide better cycle performance. Improved cycle stability means accelerating ion migration during plating/stripping processes, which can be further confirmed by the charge transfer resistance of the battery (Fig. 1b). Compared with the ZSO electrolyte, the charge transfer resistance of the ZSO+additive electrolyte is much smaller before and after cycling. The surface morphology can also verify the deposition mode. As shown in Fig. 2, compared with the ZSO electrolyte, the anode surface of the battery with ZSO+additive electrolyte is smoother, and the zinc coating surface is visible. Even after 20 cycles, only a few zinc dendrites are on the surface. These results indicate that the introduction of additives can inhibit zinc dendrites growth and reduce the overpotential.



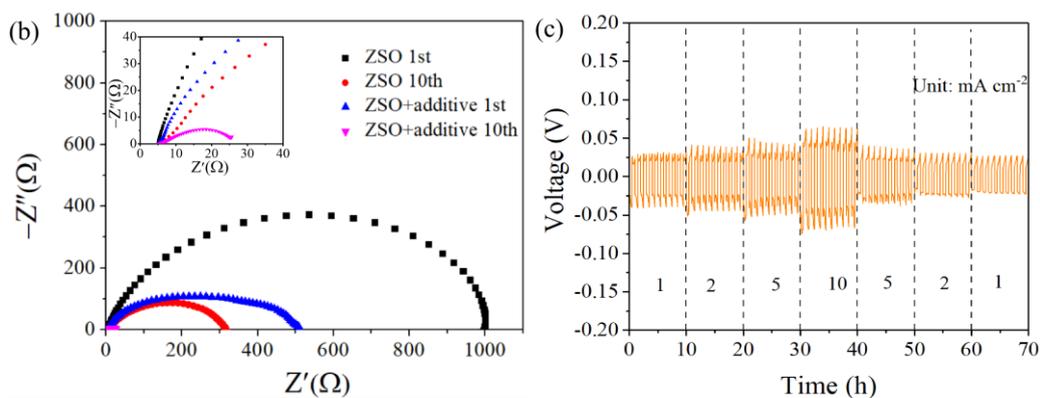


Figure 1. (a) Cycling performance of Zn/Zn symmetric batteries at 5.0 mA cm^{-2} for 2.5 mAh cm^{-2} . (b) Nyquist plots. (c) Rate performance of Zn/Zn symmetric battery with ZSO+additive electrolyte at current densities ranging from 1.0 to 10 mA cm^{-2} .

The rate performance of the Zn/Zn symmetric battery with ZSO+additive electrolyte was investigated. The current density increases from 1.0 to 10 mA cm^{-2} . With the increase in current density, the voltage hysteresis does not severely fluctuate. The battery still shows a relatively small voltage hysteresis even under a high current density of 10 mA cm^{-2} (Fig. 1c). It is worth noting that lower voltage hysteresis means better zinc affinity, more uniform zinc deposition and higher stability of zinc anode.

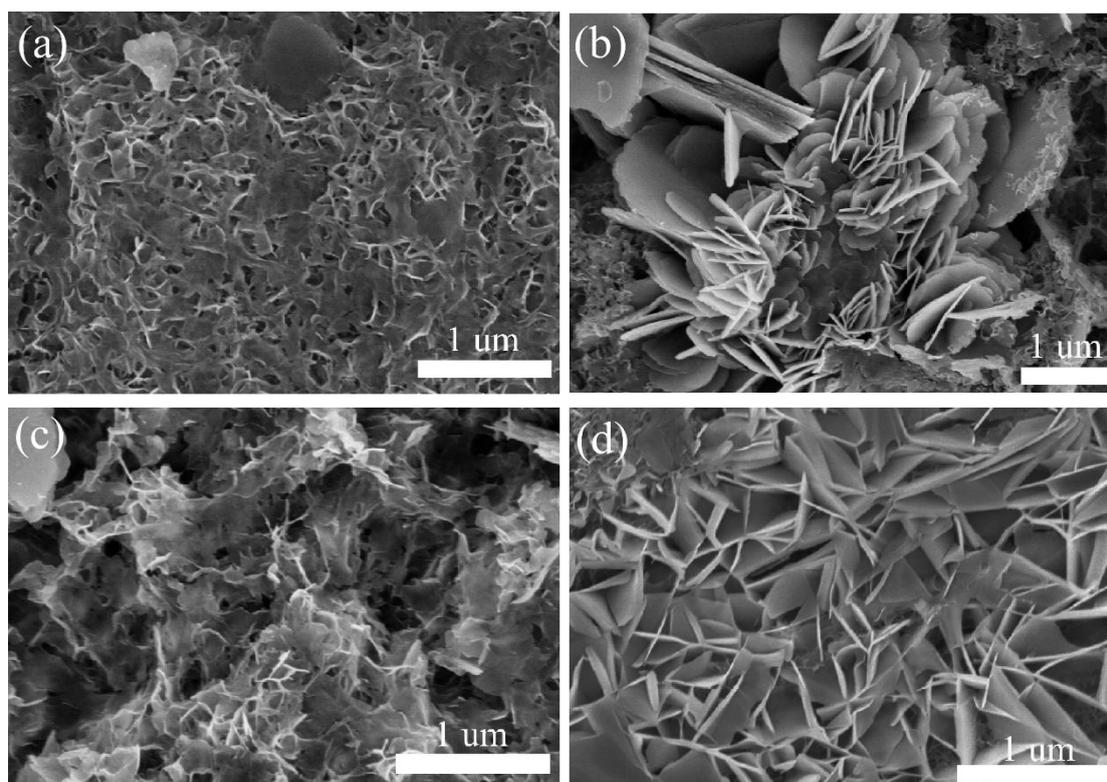


Figure 2. SEM images of morphological evolutions of Zn anodes with (a, c) ZSO+additive electrolyte and (b, d) ZSO electrolyte at (a, b) 1 cycle and (c, d) 20 cycles.

3.2 Effect of additives on electrochemical performance of Zn/MnO₂ battery

The electrochemical performance of Zn/MnO₂ batteries with ZSO+additive and ZSO electrolytes was studied. As shown in Fig. 3a, both of the cyclic voltammetry (CV) curves exhibit two pairs of redox peaks, corresponding to the two-step reverse oxidation/reduction reaction between MnO₂ and MnOOH. For the Zn/MnO₂ battery with ZSO+additive electrolyte, the two reduction peaks at 1.33 and 1.20 V can be attributed to the insertion of H⁺ and Zn²⁺, respectively [16]. It is worth noting that the polarization of the battery with the ZSO+additive electrolyte is smaller than that of the battery with the ZSO electrolyte, which means that the battery with the ZSO+additive electrolyte has a faster charge transfer rate [17]. This result is consistent with the EIS results of the Zn/Zn symmetric battery. Fig. 3b shows the cycling performance of the Zn/MnO₂ batteries at a current density of 0.2 A g⁻¹. The battery with the ZSO+additive electrolyte exhibits a higher capacity and longer cycle life. Even after 200 cycles, the battery still achieved a capacity of 137.7 mAh g⁻¹, corresponding to a capacity retention rate of 76.6%. On the contrary, the battery with ZSO electrolyte has a high capacity decay rate. After 100 cycles, the capacity is only about 70 mAh g⁻¹. These results show that the additives are conducive to improving the capacity and cycling stability of the battery.

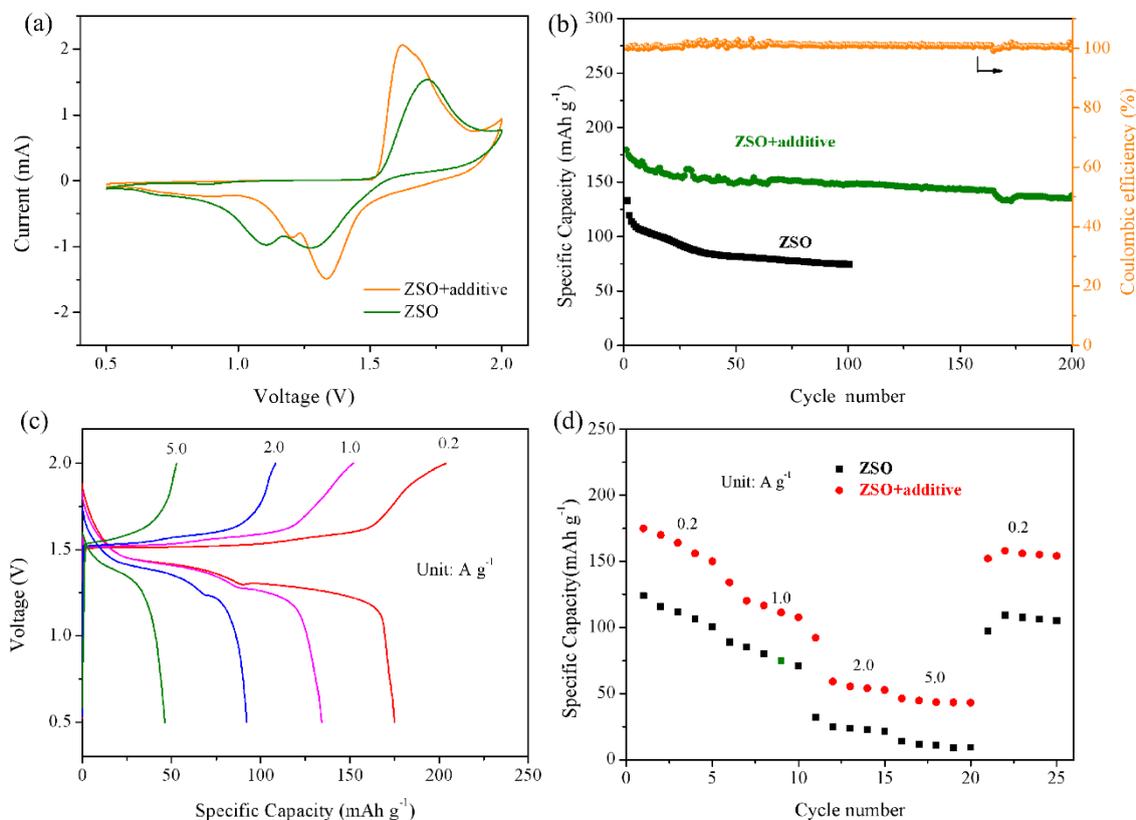


Figure 3. (a) CV at a scan rate of 0.1 mV s⁻¹. (b) Cycling performance of Zn/MnO₂ batteries at 0.2 A g⁻¹. (c) Charge/discharge curves at different current densities of Zn/MnO₂ battery with ZSO+additive electrolyte. (d) Rate performance.

Fig. 3d shows that the Zn/MnO₂ battery exhibits excellent rate performance. Even under a high current density of 5.0 A g⁻¹, a reversible capacity of 46 mAh g⁻¹ is maintained. In addition, the battery still displays a specific capacity of 152.1 mAh g⁻¹ when the current was set back to 0.2 A g⁻¹ after rate cycles, corresponding to a capacity retention of 86.9%. The excellent cycle stability and rate performance demonstrate that the additives and the synergistic effect between the additives lead to improved flatness and crystallinity of the zinc anode surface. As a result, the zinc dendrites growth, zinc corrosion, and by-products formation are effectively inhibited. Under different current densities, the voltage plateaus are detected at 1.33 and 1.20 V in the charge/discharge curves (Fig. 3c), which are in good agreement with the CV analysis results.

4. CONCLUSION

In summary, we have rationally designed a highly-reversible Zn anode by introducing a novel additives into the ZnSO₄ electrolyte. The added solutes and the synergistic effect between solutes improve the flatness and crystallinity of the zinc anode surface, and thus effectively inhibit the zinc dendrites growth, zinc corrosion, and by-products formation. As a result, the Zn/Zn symmetric battery with ZSO+additive electrolyte displays a small overpotential and good cycle stability for 1000 hours, which is much longer than that of the ZnSO₄ electrolyte. With the increase in current density, the voltage hysteresis does not severely fluctuate. The battery still shows a relatively small voltage hysteresis even under a high current density of 10 mA cm⁻². In addition, the Zn/MnO₂ battery with ZSO+additive electrolyte can provide a higher capacity (179.7 mAh g⁻¹) and longer cycle life (76.6% capacity retention after 200 cycles), which proves that the additives can improve the performance of ZIBs. The composite additive proposed in this work provides a new way to develop high-performance zinc ion batteries.

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