

High Performance Electrolyte for Iron-Ion batteries

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Abstract: Aqueous rechargeable batteries have received widespread attention due to their excellent power density, simple manufacturing process, and inexpensive electrolyte. Iron-ion batteries are expected to meet the goals of high safety, low cost, and non-toxicity pursued in the field of rechargeable batteries. However, passivation, parasitic hydrogen evolution reaction (HER), and low electroplating efficiency (50%-70%) limit the improvement of electrochemical performance, which greatly restricts their practical application. In this study, a high-performance electrolyte for iron-ion batteries was prepared, and the effect of zinc chloride (ZnCl_2) additives on inhibiting HER and the improvement of coulomb efficiency in ferrous chloride (FeCl_2) electrolyte was explored. Additionally, the effect of the addition of complexing agents in the electrolyte on the coulomb efficiency of the electrodes was studied. It's demonstrated that the electrode can still obtain a coulomb efficiency of nearly 100% after 20 hours cycling in the electrolyte containing ZnCl_2 additive and FeCl_2 , while in FeCl_2 electrolyte, its coulomb efficiency after 20 hours of cycling is only 65%.

Keywords: Coulomb efficiency, Aqueous batteries, Electrolyte, HER.

1. Introduction

With the increasing demand for renewable energy and clean energy, energy conversion technologies based on solar, wind, and tidal energy have developed rapidly. However, most renewable energy sources are intermittent. Therefore, it is necessary to develop efficient and low-cost energy storage systems. Rechargeable batteries are one of the most potential energy storage devices. In addition, with the large-scale popularization of new energy vehicles and portable electronic products, it is particularly urgent to develop high-performance and low-cost rechargeable batteries. So far, the field of rechargeable batteries has been committed to using lithium, sodium, and potassium ions as charging carriers, as well as non-aqueous electrolyte batteries. However, lithium resources are relatively scarce and expensive, while sodium-ion batteries and potassium-ion batteries require a large amount of battery additives to achieve the expected energy density. On the other hand, the organic electrolytes used in these alkali metal ion batteries are expensive and toxic, which has a negative impact on the environment.

Among the alternatives to lithium-ion batteries, zinc-ion batteries (with a theoretical mass specific capacity of 820 mAh g^{-1} and a theoretical volume specific capacity of 5851 mAh cm^{-3})^[1] are undoubtedly the focus of attention. However, the content of zinc in the earth's crust is not high, resulting in high costs for zinc-based batteries. In addition, zinc-ion batteries also suffer serious zinc dendrites during the cycling. Therefore, the research on aqueous batteries with other metal anodes has received increasing attention. Among the few candidates, iron-ion batteries present great potential. As the second metal in the earth's crust, iron has a price of about 1/40 of zinc, and its theoretical energy density (theoretical mass specific capacity of 960 mAh g^{-1} , theoretical volume specific capacity of 7557 mAh cm^{-3})^[1] is significantly higher than the theoretical energy density of zinc. In addition, there is no obvious preferred crystal orientation in the growth of iron, which means that there is no serious dendritic growth in the

iron anode. However, at present, there are few relevant reports and research work in this field, and there are many problems to be solved. In a few reported research achievements, Fe-I^[2], Fe-Prussian blue^[1], Fe-S^[3] batteries, and Fe-LiFePO₄^[1] dual ion batteries have been developed. Fe-S batteries have achieved an energy density of 1050 mAh g^{-1} and a coulomb efficiency of 90.7%. Moreover, due to the insolubility of iron sulfides, they can also inhibit the shuttle effect of polysulfides. Due to the low price of iron salts, the cost of this type of battery (less than $\$20 \text{ KWH}^{-1}$)^[4] is far lower than that of other batteries.

In this paper, the modification of its electrolyte was studied to improve the electrochemical performance of iron-ion batteries, especially for the improvement of their coulomb efficiency. ZnCl_2 is used as an additive in the electrolyte of iron-ion batteries. During the working process of the battery, Fe and Zn will co-deposit, forming a Fe-Zn alloy layer on the electrode surface. This alloy layer can effectively inhibit the occurrence of HER, which improves the coulombic efficiency.

2. Materials and Methods

2.1. Preparation of mixed electrolytes with different ZnCl_2 concentrations

Firstly, introduce 1 M FeCl_2 powder and $x \text{ ml}$ ZnCl_2 ($x=5,10,15,20,25$) saturated solution into a beaker, and then add deionized water. After sufficient stirring and constant volume, 30 ml electrolyte was obtained.

2.2. Preparation of mixed electrolytes with different FeCl_2 concentrations

Firstly, introduce $x \text{ M}$ FeCl_2 ($x=0.1,0.2,0.4,0.5,1,2,3$) powder and $x \text{ ml}$ ZnCl_2 ($x=5,10,15,20,25$) saturated solution into a beaker, and then add deionized water. After sufficient stirring and constant volume, 30 ml electrolyte was obtained.

2.3. Preparation of mixed electrolytes with different trisodium citrate concentrations

Firstly, introduce 0.5 M FeCl₂ powder, 5 ml ZnCl₂ saturated solution and *x* M trisodium citrate (C₆H₅O₇Na₃) (*x*=0.005,0.01,0.02,0.05) into a beaker, and then add deionized water. After sufficient stirring and constant volume, 30 ml electrolyte was obtained.

2.4. Preparation of electrolytes with different ZnCl₂ concentrations

Introduce *x* ml ZnCl₂ saturated solution into a beaker and then add deionized water. After sufficient stirring and constant volume, 30 ml electrolyte was obtained.

2.5. Electrochemical measurements

The electrochemical performance of the electrode in the prepared electrolyte was evaluated by the CV curve tested at

CHI760E and the cycling test at CT3001A 1U with three electrode system. In detail, Pt is served as the counter and working electrode, and Ag/AgCl is applied as the reference electrode in three electrode system.

3. Results and Discussion

As shown in Figure 1a, it could be found that after adding 25 ml of ZnCl₂ saturated solution, the coulomb efficiency of the electrode remained 98.5% after 45 cycles, while in an electrolyte without zinc chloride addition, the coulomb efficiency of the electrode was only 65% after 45 cycles. Furthermore, the coulomb efficiency of the electrode decreased to 10% during 30 cycles in 25 ml ZnCl₂ saturated solution. Notably, the function of C₆H₅O₇Na₃ was to stabilize the electrolyte as a complexing agent to prevent the oxidation of Fe²⁺, but the addition of this substance will reduce electrode coulomb efficiency (Figure 1b).

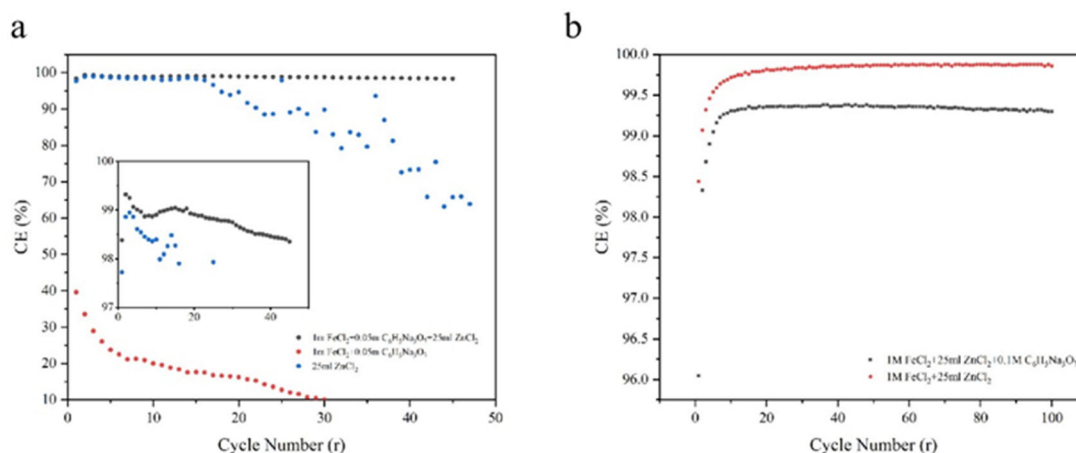


Figure 1. (a) Effect of mixed electrolyte on coulomb efficiency; (b) Effect of C₆H₅O₇Na₃ on coulomb efficiency of mixed electrolyte

It was speculated that C₆H₅O₇Na₃ will participate in the electrode reaction, which attracted some redox electrons. In addition, this side reaction will become more serious as the concentration of C₆H₅O₇Na₃ increases. As shown in Figure 2,

as the concentration of C₆H₅O₇Na₃ increases, the coulomb efficiency of the electrode gradually decreases, and this downward trend is increasingly evident.

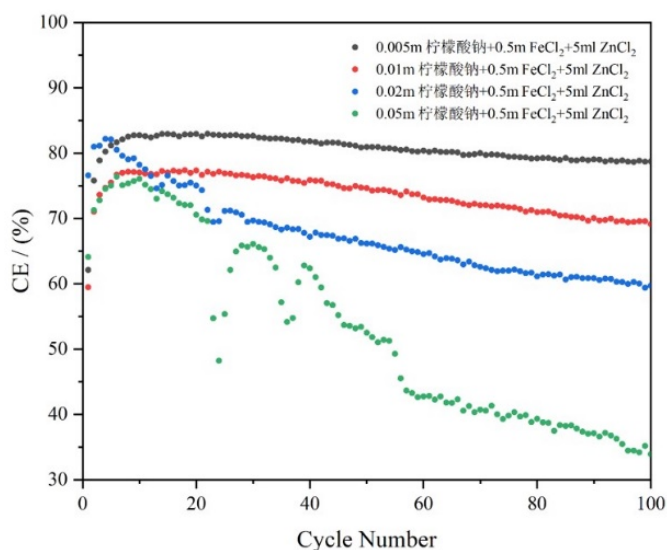


Figure 2. Effect of C₆H₅O₇Na₃ concentration on coulomb efficiency

In order to deeply explore the effect of zinc chloride additives on the performance of electrolytes, electrolytes with

different amounts of ZnCl₂ were prepared. As shown in Figure 3a, with the content of zinc chloride increasing, the

coulomb efficiency of the electrode became higher and higher. It could be speculated that “the salt in water structure” formed by high concentration of ZnCl_2 , reduced the free water molecules in the electrolyte, thereby inhibiting HER. Considering the performance and cost of the electrolyte, 5ml saturated ZnCl_2 solution was selected as the optimal addition amount [5-6]. In Figure 3b, the effect of Fe^{2+} concentration on

the performance of the electrolyte at the optimal amount of ZnCl_2 was studied. It can be observed that when the concentration of Fe^{2+} is between 0.1 M and 1 M, the coulomb efficiency of the electrode will increase with the increase of concentration, while its coulomb efficiency decreased significantly between 2 M and 3 M. Among them, 1 M of Fe^{2+} had the best coulomb efficiency performance.

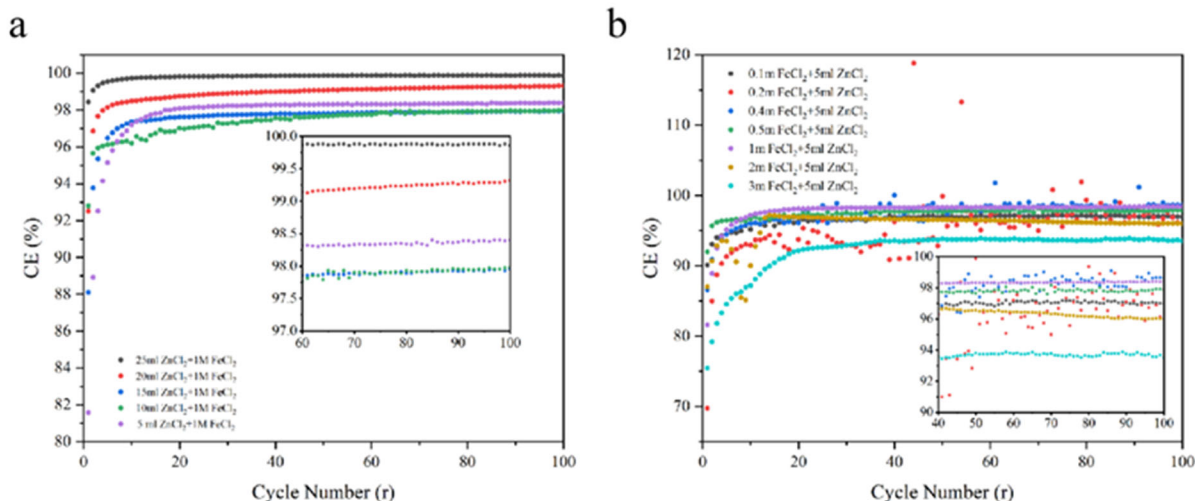


Figure 3. (a) Effect of ZnCl_2 concentration on coulomb efficiency; (b) Effect of FeCl_2 concentration on coulomb efficiency

Eventually, to explore the working mechanism of electrodes in mixed electrolyte, CV tests were carried out at different Fe^{2+} concentrations (Figure 4). In Figure 4a, it could be clearly observed that as the concentration of Fe^{2+} increases, the oxidation peak of the electrode shifts towards a higher potential. This could be due to the increasing concentration of Fe^{2+} in the electrolyte, that resulted in a decrease of Fe-Zn alloy deposition resistance, thereby reducing its deposition potential. Even when the concentration of Fe^{2+} exceeded 3 M, this trend was most obvious. Combined with Figure 4b, it could be found that when the concentration of Fe^{2+} was between 0.1 M and 2 M, the concentration of Fe^{2+} in the electrolyte became lower than the concentration of Zn^{2+} ,

making the deposition behavior of the electrode closer to the Zn^{2+} deposition behavior. But, while the concentration of Fe^{2+} was up to 3 M in the electrolyte, which was higher than that of Zn^{2+} , the deposition behavior of the electrode got closer to that of Fe^{2+} . In addition, it was worth noting that the higher the concentration of Fe^{2+} , the greater the probability of oxidation reaction occurring. This could also explain that when the concentration of Fe^{2+} exceeded 2 M, the coulomb efficiency of the electrode decreased with the Fe^{2+} concentration increasing. Thus, considering cost and performance, a mixed electrolyte of 1 M FeCl_2 and 5 ml saturated ZnCl_2 was the best electrolyte for iron-ion batteries.

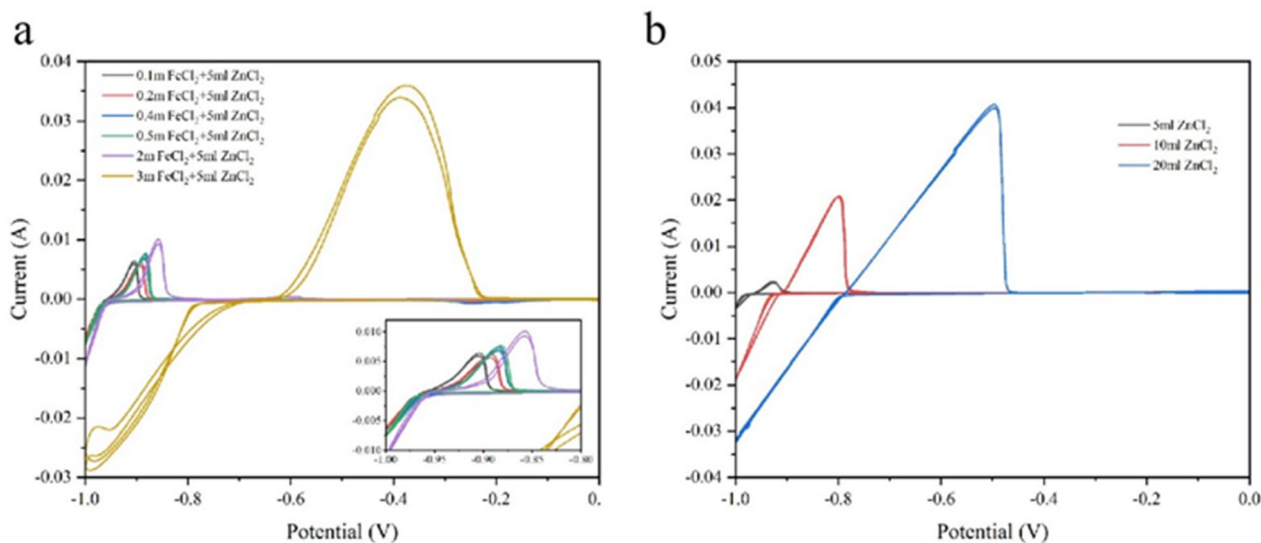


Figure 4. (a) CV curves at different concentrations of FeCl_2 in mixed electrolytes; (b) CV curves in ZnCl_2 electrolytes with different concentrations

4. Conclusion

In this paper, a high-performance mixed electrolyte for iron-ion batteries was prepared by adding ZnCl_2 to the electrolyte of commonly used iron-ion batteries. Due to the co-deposition phenomenon of zinc and iron ions, this will change the deposition behavior of iron ions. The deposition potential barrier of co deposited Fe-Zn alloy is lower, which is more conducive to the deposition of metal ions. Moreover, the high concentration of ions in the electrolyte can inhibit the content of free water, thereby reducing HER. In summary, the high-performance mixed electrolyte for iron ion batteries prepared in this paper can effectively inhibit HER and improve the coulomb efficiency of the battery, providing a new strategy for the development of iron-ion batteries.

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