

Strategies for solving hydrogen precipitation problems in aqueous zinc ion batteries

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Abstract. Aqueous zinc ion batteries have revealed many problems while solving the safety problems of conventional batteries, among which the narrow electrochemical stability window of water causes the battery to be prone to hydrogen precipitation reactions. In this paper, we summarize two strategies to solve the problem. From the electrolyte side, firstly, we use a mixture of salt-in-water electrolyte to lower the starting potential of hydrogen precipitation reaction, so that the hydrogen precipitation reaction can be inhibited. The second strategy is to use intermolecular forces to configure a high concentration electrolyte to change the presence of ions in the solution, thus reducing the free water content and the activity of water to inhibit the hydrogen precipitation reaction.

Keyword : Aqueous zinc ion Batteries;hydrogen precipitation reaction;Salt-in-water electrolyte; intermolecular forces.

1. Introduction

As the application scenario of batteries continues to extend, people have put forward new requirements for batteries, among which safety issues have received particular public attention. The organic electrolyte in traditional batteries has been a major cause of safety concerns. Organic electrolytes are highly toxic, flammable and unstable, making the safety of batteries controversial. And because of its toxicity, flammability and instability, the requirements for battery processing and production process are also very strict, which further leads to the increase of battery processing cost¹⁻³.

However, batteries with aqueous electrolytes have the safety, ruggedness, affordability and environmental friendliness required by many devices⁴. The water in the aqueous electrolyte not only provides fire protection, but also has a higher ionic conductivity than conventional organic electrolytes⁵. So these problems in conventional batteries can be solved⁶. But the electrochemical stability window (ESW) of water in aqueous electrolytes is only 1.23V⁷, this causes a side reaction to occur in the battery when the battery voltage exceeds 1.23V. Hydrogen evolution reaction (HER) will occur in the cell to produce hydrogen gas. Even a very small amount of hydrogen can have a significant impact on the safe operation of the battery. For example, the battery bulge, damage electrodes^{8, 9}, or even cause the battery hydrogen explosion. In conventional organic electrolyte cells, the decomposition products of the electrolyte are deposited to form a passivation layer called the solid electrolyte interface (SEI). This interface can effectively play a role in preventing further decomposition of electrolyte, which in turn ensures stable operation of the battery. In the aqueous battery, the electrolyte products of water cannot be deposited, so the SEI film cannot be formed on the electrode surface¹⁰. Therefore, the key to solve the hydrogen precipitation problem and improve the stability of aqueous batteries lies in the widening of the electrochemical stabilization window of water and the formation of SEI films. The common strategies can be divided into two major aspects: electrolyte and electrode.

For electrolyte, when the concentration of the electrolyte changes or when the mass or volume of the electrolyte exceeds that of the solvent, significant ionic aggregation occurs and the properties of the electrolyte will change. Khan classifies such very high concentrations of electrolytes into two categories.ⁱ) High electrolyte concentration in electrolyte solution, but still contain anadequate amount of solvent for the primary solvation sheath associated with cations. (ii) In solvent-in-salt

electrolytes, the amount of salt considerably exceeds the number of solvent molecules. In this extreme case, a primary solvation sheath around cations could not form, and no solvent molecule remained free. In this paper, we choose the second type of electrolytes mentioned above and designate the solvent as water, which is called water-in-salt electrolytes || (WISEs)¹¹. The formation of anionic and cationic aggregates in WISEs will favor the reduction of anions over the reduction of water. This will result in a broadening of the ESW of the electrolyte, which will lead to the inhibition of HER. Wang's team increased the concentration of electrolyte to form a salt-in-water structure that can increase the electrochemical stability window of water from 1.23V to 3V¹². Very high concentrations (molar concentration > 20 m) of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) dissolved in water to obtain a "salt-in-water" electrolyte will lead to changes in the Li⁺ solvated sheath, and the defluorination reaction will take precedence over the decomposition reaction of water after the addition of high concentrations of LiTFSI electrolyte. The electrode surface will produce a LiF protective film after the defluorination reaction, which is similar to the SEI film in function. And the electrolyte in very high concentration will break the hydrogen bonding network between water molecules, making the hydrogen bonding network become very small. The solute ions in high concentration also form an aggregate network and intertwine with the disrupted hydrogen bonding network, resulting in a large decrease in the free water content in the electrolyte and a decrease in the water activity¹³. Thus, the goal of expanding the electrochemical stabilization window of water is achieved.

2. Electrolytes

The biggest problem in aqueous batteries is that the electrochemical stability window of water is only 1.23V²², which will lead to the limitation of the application scenarios of aqueous batteries. When the operating voltage of the battery exceeds 1.23V, the water in the battery electrolyte will decompose and precipitate hydrogen, so the problem of suppressing hydrogen precipitation in aqueous batteries can also be understood as extending the electrochemical stability window of water further. In order to achieve the purpose of expanding the electrochemical window of water, the electrolyte is usually used to improve the aqueous battery, and the strategy is usually divided into two kinds, one is to use high concentration of electrolyte decomposition precipitation, so that the high concentration of electrolyte at the beginning of the reaction to form a solid protective film on the electrode surface, and make the battery work in the electrolyte ions preferential redox, so as to achieve the inhibition of water decomposition. The second is to use the intermolecular interaction force - hydrogen bonding to inhibit the decomposition of water and induce the formation of a solid electrolyte interface, thus making the electrochemical stabilization window of water wider¹³.

2.1 water-in-salt electrolytes

Liumin Suo's team at the University of Maryland has focused on the strategy of mixing salt-in-water electrolytes to solve the problem of negative electrode hydrogen precipitation. Salt-in-water means that a high concentration of electrolyte salt is added to water, causing the water and electrolyte salt to interact to form a hydrate. In a highly concentrated electrolyte, a limited number of solvent molecules are bound by too many electrolyte ions. In contrast to the traditional "electrolyte salt in solvent", highly concentrated electrolytes tend to form polymers-in-salt²³ or solution salinization²⁴.

According to Bockris and Reddy, solution kinetics will deviate from the ideal state in high salt solutions, and this change can be monitored by measuring the activity coefficients of the ions. The increase in activity coefficients at high salt concentrations reflects the decrease in free water in solution and the enhanced anion/cation interactions²⁵. When such polymers in salt are formed in aqueous electrolytes, the weight and volume of the electrolyte salt in solution exceeds that of the solvent. As a result, the number of water molecules available in solution for solvation of each

ion will be much less than the number of water molecules available for association with ions in a conventional electrolyte.

The addition of a high concentration of electrolyte brings two benefits, the first being that the polymer in the salt formed reduces the amount of free water in solution, making it harder for water to undergo redox reactions, thus having the effect of widening the electrochemical window of stability of water. In testing LiTFSI, the reactions at both electrodes were monitored, and it was found that as the electrolyte concentration increased, the potential for hydrogen precipitation at both electrodes was well above 1.23 V. Most of this reduction occurred at 2.7-2.8 V, and the team also found that as the electrolyte concentration increased, the plateau current decreased by more than an order of magnitude, i.e., passivation occurred. The electrochemical stability window of the stainless steel electrode was measured using cyclic voltammetry, and the cathode and anode were examined, and the results are shown in Figure 1. This passivation, in turn, would inhibit the hydrogen precipitation reaction¹². Secondly, an increase in concentration causes a change in the relationship between the solution structure and the electrochemical properties of the solution. For dilute solutions (concentrations below 5 mol), the cation remains well hydrated in its primary solvation sheath and there is sufficient free water in the electrolyte. In this case, the reduction potential of water is higher than the lithiation potential, resulting in the priority of reduction of the free water in the electrolyte and the continuous precipitation of hydrogen in the cell. When the concentration of LiTFSI is greater than 20 mol, there are two TFSIs in each primary solvation sheath, and in this case the TFSI at the interface reacts preferentially. The reduction process of TFSI⁻ can form an electrolyte interface at the anode, which has the same effect as the SEI membrane formed in the non-aqueous electrolyte.

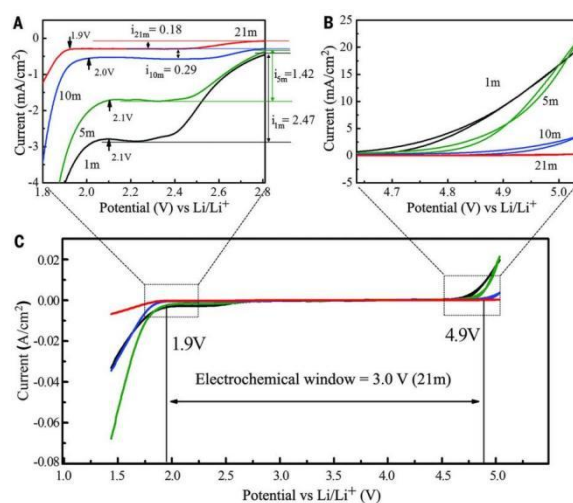


Figure 1 The electrochemical stability win-dow of LiTFSI-H₂O electrolytes on nonac-tive electrodes.

Based on the above theory, in a zinc cell with LiMn₂O₄ as the cathode, Fei Wang calculated based on DFT theory that Zn(TFSI)₂(H₂O)₂ clusters tend to form in 1 m Zn(TFSI)₂ + 10 m LiTFSI electrolyte, and Zn(TFSI)₂(H₂O)₂ clusters at about 2.55 V relative to Li/Li⁺. The hydrogen gas precipitates in the reduction reaction at about 2.55 V relative to Li/Li⁺. This phenomenon suggests that the hydrogen precipitation reaction becomes the dominant reaction in this cell system when water is present in the Solvation-sheath of Zn²⁺²⁶. In contrast, in the concentrated electrolyte 1 m Zn(TFSI)₂ + 20 m LiTFSI, water is not present in the Solvation-sheath of Zn²⁺, but is surrounded by TFSI⁻, so that the reduction potential of Zn(TFSI)_n has an elevated reduction potential. And at high TFSI concentration, the defluorination potential of litfsi will be higher than the hydrogen precipitation reaction²⁷. LiTFSI forms a LiF solid interface on the electrode surface after the defluorination reaction, and the presence of this interface can prevent low-potential hydrogen precipitation. More surprisingly, when faced with the problem of dendrite growth during the zinc cell cycle²⁶⁻²⁸²⁷⁻²⁹, the concentrated electrolyte allows the zinc cell to achieve a reversible and dendrite growth-free electrical cycle.

2.2 Intermolecular forces

Gurney classified electrolyte ions as structure makers and structure destroyers, and different ions have different effects on water³⁰. Related theoretical studies suggest that high concentrations of electrolytes that are destructive to the structure of water will exhibit a tendency to form polymer networks with water, thus enhancing the possibility of expanding the window of electrochemical stability of water¹³. This is explained in terms of intermolecular forces. As the electrolyte content in the aqueous electrolyte gradually increases, the hydrogen bonding network between water molecules will be disrupted. As the salt concentration increases, the average number of hydrogen bonds decreases and the average bond length will become longer, which will result in less stable intermolecular interactions between water molecules. The size of the hydrogen bond network will also decrease with increasing salt concentration. Solute ions at high salt concentrations will tend to form two types of aggregate structures because of the specific nature of the ions. One is the aggregation of ions to form tightly packed clusters of molecules that exclude water molecules from the interior. The second is the formation of spatially extended network-like ionic aggregates of ions that are intertwined with a similarly extended network of water hydrogen bonds^{13, 31, 32}. And in Zhang's study, he investigated water-water and water-ion interactions in 5 mol-30 mol of ZnCl_2 ³³ and examined the data using Fourier variation infrared spectroscopy and Raman spectroscopy. In the low concentration electrolyte, typical water has two H-O stretching bands at 3200 cm^{-1} and 3400-1. The band at 3200 cm^{-1} belongs to strongly hydrogen-bonded water, which has the same degree of hydrogen bonding as in ice and is of the DDAA type. While the one at 3400 cm^{-1} is partially hydrogen bonded water, which belongs to DA and DDA³⁴. during the change of electrolyte concentration from 5 mol-30 mol, the strong molecular interaction between Zn and water molecules breaks the O-H in water, and the symmetric stretching band is enhanced and the asymmetric stretching band is weakened.

Chong Zhang tested the ZnCl_2 cell and found that as the concentration of ZnCl_2 solution increased from 5m to 20m, the electrochemical window of ZnCl_2 solution increased from 1.6v to 2.3v. The results of the variation of the electrochemical stabilization window with concentration are shown in Figure 2. The plating potential of Zn increased as the concentration increased and the starting potential of the hydrogen precipitation reaction decreased further³³. This means that as the concentration of ZnCl_2 increases, the hydrogen precipitation reaction becomes more and more difficult. A similar principle was applied by Myeong Hwan Lee's group, which successfully used a 17 mol NaClO_4 electrolyte to increase the electrochemical stability window of water. NaClO_4 at a concentration of 17 mol is mainly composed of a large number of highly aggregated ionic states with very low free water content. This finding is in agreement with previous results based on density flooding theory calculations. There is a significant increase in the number of large ionic aggregates in WiSE, which break the hydrogen bonds of water by acting as intertwined networks. This leads to a decrease in the activity of water and thus to a broadening of the electrochemical stabilization window of water¹³

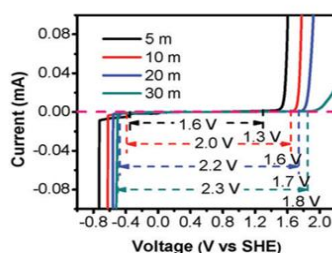


Figure 2 electrochemical stability window of the ZnCl_2 electrolyte at different concentrations

3. Conclusion

We can understand from the above that high concentration of electrolytes can be utilized to further expand the electrochemical stabilization window. And the intermolecular forces in the electrolyte are altered by the electrolyte. Through these two strategies can make the aqueous battery can realize the safe work, and provide a new result idea for the aqueous battery to solve the hydrogen precipitation problem of the aqueous battery.

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