

Low-Temperature Aqueous Batteries

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Abstract. Although aqueous rechargeable metal-ion batteries (ARMBs) have become one of the current research frontiers due to their low cost, high safety, and other unique characteristics, traditional lithium-ion batteries (LIBs) lose most of their capacity and power at ultra-low temperatures (below -40°C), which largely limits their application in high-tech fields such as new energy vehicles, national defense security, space exploration, and deep-sea operations. For ARMB to become a more practical device, technology must be developed to make lithium-ion batteries adaptable to a variety of environments, especially cold weather. Although organic electrolyte lithium-ion batteries have made some achievements in low-temperature applications, research in low-temperature ARMBs is still in its infancy. The reason for this difficulty is the freezing of water at low temperatures, which leads to a sharp delay in kinetics. This paper reviews the problems faced by low-temperature aqueous batteries at this stage and proposes strategies to solve the problems and optimize the performance of low-temperature aqueous batteries.

Keywords: Microtherm, aqueous batteries, water freezes.

1. Introduction

With the growing demand for energy storage and the emergence of various application scenarios, the requirements for batteries to adapt to extreme weather are getting higher and higher [1]. For example, devices such as electrochemical energy storage devices (EES) have been widely used in smart home appliances, portable computers, production, and electric vehicles [2-3], but the performance of widely used EES devices will rapidly decline due to development and mining activities at low temperatures such as high altitudes and high latitudes [4]. In this regard, researchers began to improve the temperature range of the battery and expand the low-temperature range of the battery, which is of great significance for the development of batteries in submarines, aircraft, and drones.

At present, most of the batteries in the energy storage market are organic electrolyte batteries, so many researchers are also working on the development of low-temperature organic electrolyte batteries. However, compared with non-aqueous batteries, aqueous rechargeable metal-ion batteries (ARMBs) are safer, less costly, and easier to assemble, and can be used in some specific application scenarios [5-6]. When water is used as an electrolyte solvent, it has the following advantages: (1) strong operability, (2) convenient industrialization, (3) aqueous electrolyte is flame retardant, (4) high ionic conductivity, (5) environmental friendliness. Although aqueous batteries have made great progress at room temperature, the low decomposition voltage and high freezing point of water lead to a narrow electrochemical window for aqueous electrolytes, which greatly limits the energy density and temperature range of aqueous energy storage systems. For example, in the case of water freezing, the performance of ARMB is degraded due to the lower ionic conductivity of the electrolyte at sub-zero temperatures, the reduced rate of chemical reactions, and the slower charge transfer kinetics. To improve the low-temperature performance of ARMB, researchers optimized the electrolyte composition and designed a suitable interface structure based on the above findings, but there is still a gap between the actual needs and the actual needs.

From the perspective of electrolyte structure and ion transport, there are many reasons why the development of low-temperature electrolytes is difficult. From an electrolyte point of view, the biggest challenge is to lower the freezing point of the electrolyte, because only electrolytes with a low freezing point can remain liquid at lower ambient temperatures, ensuring stable electrochemical performance. Another difficulty is that some conventional electrolytes solidify at low temperatures,

forming a solid structure, and resulting in a decrease in conductivity. In addition, at low temperatures, the interfacial kinetics of the electrolyte are slow, which reduces the reaction rate and interfacial processes inside the battery, and reduces the charge-discharge efficiency of the battery. From the perspective of ion transport, the capacity decay of electrochemical energy storage devices in low-temperature environments is due to the reduction of the solubility and ion transport capacity of the electrolyte under low-temperature conditions, which reduces the usable battery capacity [7]. Therefore, to solve the problem of low-temperature electrolyte development and bridge the gap with actual needs, researchers strive to reduce the freezing point of electrolytes, optimize electrolyte composition and additives, and improve conductivity and interfacial dynamics.

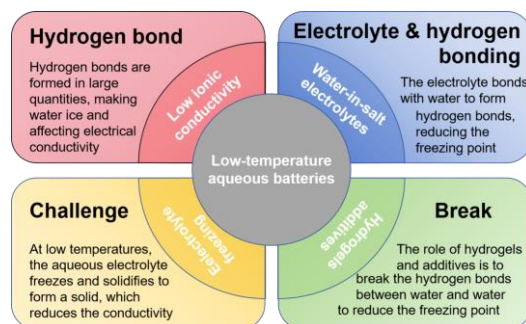


Figure 1. Challenges in low-temperature aqueous batteries and optimization strategies for this problem

In this paper, the influencing factors of aqueous solution at low temperatures on batteries are introduced, and the optimization strategies of aqueous low-temperature electrolytes are systematically summarized (Figure 1), to provide new insights for the development of low-temperature electrolytes.

2. Low temperature aqueous solution

The degradation of battery performance at low temperatures is mainly due to the freezing of the electrolyte in the water at low temperatures, which reduces the conductivity. While aqueous solutions are generally considered excellent conductors of electrolysis, the physical and chemical properties of water that occur at sub-zero temperatures can change dramatically. The change of water from a liquid state to a solid state is a very complex phase change behavior with different results under different conditions. To better understand the effect of water on electrolytes at low temperatures, let's start with the freezing mechanism of water. There are a large number of hydrogen bonds present in water, which is the basic structure of water. In hydrogen bonding, hydrogen atoms are shared in hydrogen bonds, and a network is gradually formed between hydrogen bonds, which are constantly broken and reunited. But regardless of their physical state in a liquid or solid. A fully hydrogen-bonded water molecule will be surrounded by four water molecules to form a tetrahedral structure, i.e., with a DDAA (D: proton donor, A: proton acceptor) configuration [8]. When the temperature gradually decreases, the formation and breaking of hydrogen bonds accelerate, and after less than 4°C, the rate of hydrogen bond formation is much greater than the speed of breaking, and ice is formed in this state.

After understanding the principle of how water turns into ice, the question that needs to be solved is the freezing point of water and how hydrogen bonding is affected in the aqueous solution. Many factors affect the freezing point of water, such as salt solutions, types of electrolytes, co-solvents, and additives. The principle of these things affecting the freezing point is to affect the hydrogen bonds in the aqueous solution, and by adding different kinds of additives to make the electrolyte form stronger bonds with water molecules, to reduce the formation of hydrogen bonds between water and water, and inhibit the formation of ice lattices. Or it can be done by breaking the hydrogen bonds of water to water to achieve the same purpose. In a saline solution in practical applications, the ionic conductivity decreases with a decrease in temperature because the decrease in temperature slows

down the movement of the carrier in the solution. At the same time, the viscosity of the electrolyte increases at low temperatures, which affects the ion mobility.

In general, the freezing process of water is understood, and the solution is reasonably specified according to the influencing factors of the freezing point at low temperatures, and the hydrogen bond structure in the aqueous electrolyte is changed, to inhibit the formation of ice grids.

3. Resolution strategy

This section mainly introduces the antifreeze strategy developed based on the principle of the influence of low-temperature aqueous solution. The aqueous electrolyte is modified and transformed, and the properties of the electrolyte in the aqueous solution are optimized in different ways to enhance the performance of the battery at low temperatures. These strategies include the use of co-solvents, additives, water-in-salt electrolytes, and hydrogels.

3.1. Co-solvents and additives

Organic matter is often used as a co-solvent to inhibit the formation of ice trays. The addition of these substances can promote the diffusion rate of the electrolyte in the aqueous solution and ensure that the ionic conductivity has a high value. The principle that co-solvents can lower the freezing point in solution is that the organic matter forms new hydrogen bonds with water molecules, which promotes the reduction of hydrogen bonds between water molecules. Unlike co-solvents, additives can be organic or salt additives. Salt additives are added directly to water by soluble salts, which can break hydrogen bonds and inhibit the formation of ice grids. In practice, there is usually no distinction between co-solvents and additives, and the commonly used additives are ethylene glycol (EG) and dimethyl sulfoxide (DMSO).

These organic additives can be mixed with water in any proportion, and experiments have shown that the reduction of the freezing point has a V-shaped relationship with the proportion of additives. Ethylene glycol is often used as an additive in electronic devices. When only ethylene glycol is in the device, the freezing point is at -13°C . When ethylene glycol is mixed with water, the lowest freezing point can reach -33°C . For example, in Li_2SO_4 batteries, the addition of ethylene glycol can effectively reduce the freezing point, from -4.6°C to -24.6°C . Similarly, the addition of ethylene glycol to the ZnSO_4 battery inhibits the hydrogen bonding between the ethylene glycol and water molecules, which greatly reduces the freezing point to -33°C while maintaining a high electrical conductivity. Dimethyl sulfoxide (DMSO) forms stronger hydrogen bonds with water when mixed with water. For example, when the molar ratio of DMSO is 30% water, the freezing point drops sharply to -130°C , which is much lower than pure DMSO (18.9°C). In NaClO_4 cells, the DMSO-water-hydrogen bond formed is fairly stable, and $1\text{DMSO}-2\text{H}_2\text{O}$ is the basic bonding unit in this electrolyte, which prevents the mixture from producing an ordered crystal structure (ice) at low temperatures, thus reducing the freezing point.

3.2. High concentration of electrolytes

The high concentration of aqueous electrolyte is very beneficial for batteries to work at sub-zero temperatures. At present, they have been applied to aqueous lithium-ion batteries (ALIBs), aqueous zinc-ion batteries (AZIBs), and metal-air batteries, and the corresponding systems contain different components, such as LiCl , ZnCl , and cation. Although these electrolytes have been often used in the use and manufacturing of organic electrolyte batteries, there are not many electrolytes used in the direction of low-temperature aqueous batteries.

Normally, water freezes when the temperature reaches 0°C , and when an electrolyte is added to the water to become an electrolyte, the freezing point of the whole system decreases, and it freezes when the temperature reaches below 0°C . The principle of electrolyte lowering freezing point is that in the electrolyte. The electrolyte is divided into anions and cations, and the cations will interact with the water molecules in the water, causing the cations to interact with the dipoles in the water

molecules, robbing the reaction between the water molecules and the water molecules, and reducing the formation of hydrogen bonds. The whole process can be referred to as salt hydrolysis and hydration, and in the electrolyte, when the electrolyte concentration is high enough, a concentrated electrolyte (often referred to as the water-in-salt electrolyte WiSE) is formed. WiSE plays an important role in practical applications, as it means that aqueous electrolytes are more stable in the electrolyte and can react in a wider range. For example, in aqueous lithium-ion batteries (ALIBs), LiCl saturated solution is used as the electrolyte, which can still have excellent performance at temperatures of -45°C , and in this regard, LiCl works better than organic electrolytes. Similarly, Tang et al. improved the performance of aqueous zinc-ion batteries (AZIBs) by using ZnCl. The use of ZnCl saturated solution as the electrolyte to construct the battery with Zn/V₂O₅ not only stabilized the performance of the battery at low temperatures, ensure the overall chemical stability, but also extended the service life of the battery.

To optimize the performance of the battery, a suitable high concentration of electrolyte can be selected, although the ionic conductivity will still be low at sub-zero temperatures, this can be solved by a composite strategy. The compounding strategy is to add other additives at the same time as a high concentration of electrolytes and use the characteristics of the additives to promote the reduction of the freezing point. For example, Cheng et al. combined electrolytes and methanol additives to prepare batteries. Taking advantage of the fact that methanol can be anti-freezing, the addition of methanol successfully reduces the freezing point, so that the battery still has stable performance at -30°C . At the same time, the addition of high-concentration electrolytes can reduce the corrosion of the electrode, ensure the stability of the reaction, and also avoid the danger of battery combustion and explosion. Although these features allow the ARMB to operate in cold environments. However, fundamentally speaking, the application range of high-concentration electrolytes is still relatively small, and because of their high cost, it is difficult to popularize them, so more research should be invested in this area to optimize the application of high-concentration electrolytes.

3.3. Hydrogel

Hydrogel is an environmentally friendly and safe product, so the battery made with hydrogel is also safe enough. Generally speaking, the components in hydrogels mostly contain hydrophilic groups, which can be better connected to water through chemical and physical changes, which can destroy the interaction between water molecules in free water, enhance the interaction between ions and water, and reduce the freezing point of the whole system. Attention should be paid to the proportion when adding hydrogels so that the appropriate amount can reduce the freezing point without affecting the ionic conductivity of the whole system.

To improve the working performance of hydrogels at low temperatures, researchers have conducted a lot of research, and generally speaking, the following methods can be used to improve frost resistance. These include the use of organic solvents, the use of concentrated solutions, the addition of more hydrophilic groups, and the modification of terminal groups. Common organic antifreeze solvents include EG and glycerol, which are both polyols, that can form strong hydrogen bonds with water molecules, inhibit the formation of ice grids, and ensure that the whole system still has high ionic conductivity at low temperatures. Concentrated ionic compounds, such as concentrated calcium chloride (CaCl₂) solutions, can also be used to inhibit ice crystallization in the aqueous phase. The introduction of hydrophilic groups is to reduce the freezing point by their strong interaction with water, such as amino groups ($-\text{NH}_2$) and hydroxyl groups ($-\text{OH}$), these groups are extremely hydrophilic, and the ionic conductivity is still within an acceptable range after the addition. For example, in polyacrylic acid (PAA) hydrogels, the polarity of the terminal hydroxyl group can be modified to enhance the interaction with water molecules, which can significantly reduce the freezing point to -25°C .

All in all, hydrogels are usually composed of a variety of polymers, and they are usually not used alone but are used together with other components such as co-solvents, to better stabilize the performance of the battery and ensure the stable operation of the battery at low temperatures.

3.4. Other influencing factors and solutions

The previous strategies were based on electrolyte modification to improve performance, and while these methods were effective, they did not take into account factors other than the electrolyte, such as whether the electrolyte was compatible with the electrode, whether the transport mechanism was considered, and some physical issues.

In addition, the electrode will also change at low temperatures, and the performance will change, so it is necessary to select the electrode material with better performance at low temperatures to ensure that the ionic conductivity is sufficient. The problem that needs to be solved is how to increase the diffusion rate of ions inside the electrode material, and the electrode material that can diffuse quickly at low temperatures can exert better low-temperature performance. The effect of the transport mechanism is also significant, as the ion diffusion rate of the carrier mechanism is slow, which is exacerbated when some additives are used, which seriously affects the electrochemical performance at low temperatures. At the physical level, the surface tension of the water increases at low temperatures, and the contact angle of the electrode-electrolyte increases, which reduces the performance of the battery. These problems are not related to electrolyte modification, and reasonable solutions need to be found in the future.

At present, the possible solution is to adopt the physical constraint method, because the hydrogen bond is highly directional and non-flexible, and the physical constraint is used to affect the structure of the hydrogen bond and limit the configuration between water molecules, to achieve the purpose of inhibiting the generation of ice grid and reducing the freezing point.

4. Summary and outlook

The research on low-temperature aqueous batteries is still in its infancy, and due to the easy-to-freeze characteristics of aqueous electrolytes, there is still a long way to go in the research and development of low-temperature aqueous batteries in order to solve this problem. However, it is undeniable that many studies on improving the low-temperature operating performance of aqueous batteries are steadily progressing, whether it is adding additives adding high-concentration salt solutions, or using hydrogels to prepare batteries, these methods have the same purpose, to reduce the freezing point. These strategies are to add another substance that can have strong interaction with water molecules to the system, to reduce the number of hydrogen bonds between water molecules, inhibit the formation of ice grids, and reduce the freezing point. Although many achievements have been made in low-temperature batteries, the capacity retention rate of ARMBs is lower than that of organic batteries under the same low-temperature conditions because the freezing point of water is higher than that of most organic materials, which is still a problem that needs to be solved.

If you want to improve the low-temperature performance of ARMBs, there are also practical factors to consider. For example, the cost of some electrolytes is very high, which means the cost of the entire battery will be raised after its industrial mass production, which is not conducive to the wide application of batteries. To avoid such a situation, the preparation of low-temperature aqueous batteries with easily available salts such as LiCl and ZnCl can effectively reduce costs and make the development prospects of batteries better.

In short, the current research on low-temperature aqueous batteries is still in its infancy. In the future, the requirements for batteries may not only be low-temperature performance requirements, but also stable operation in special environments (such as corrosive environments). The current research on low-temperature aqueous batteries requires further understanding of the anti-freeze mechanism, reasonable optimization of anti-freeze strategies, designing batteries taking into account both physical and chemical factors, and promoting the development of the battery industry based on actual needs.

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