

Study On Electrolyte of Low Temperature Zinc-Ion Batteries

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Abstract. With the development of science and technology, now the comprehensive use of electronic equipment, has led to the increasing demand for energy storage systems. The market requires high-performance energy storage systems, zinc-ion batteries have the merits of good energy storage performance, low cost, and high safety, thus arousing extensive attention. Because of the diversity of the environment on the earth, the aqueous zinc ion batteries should meet the requirement of sustainability and feasibility working in wide temperature environments. How to ensure that zinc-ion batteries can work in such a harsh environment has become a research topic nowadays. As the ambient temperature decreases, the energy storage performance decays, including greatly reduced cycling life, increased resistance, and inferior charge/discharge performance. Especially below zero, the electrolyte may be frozen. Therefore, the application of aqueous zinc-ion batteries in these low-temperature environments has become a further research direction. To enhance the low-temperature performance of zinc-ion batteries, many strategies have been developed, such as improving the performance of the positive and negative electrodes, optimizing the electrolyte material, and developing separators. Among them, optimizing the electrolyte is the most effective strategy. Electrolyte is an important part of the battery, which contacts with the positive and negative stages of the battery and produces chemical reactions to produce electricity. In the process of charge and discharge, the electrolyte is mainly used for mass transportation, so the electrolyte is particularly important for enhancing low-temperature performance for zinc-ion batteries. Correspondingly, many researchers focus on designing and synthesizing advanced electrolytes. This paper summarizes the state-of-art development of low-temperature zinc-ion batteries domestically and internationally and classifies and analyzes the solid, liquid, and gel electrolytes.

Keywords: low temperature; zinc-ion battery; solid electrolyte; liquid electrolyte; gel electrolyte.

1. Introduction

With the global energy crisis and environmental pollution becoming increasingly severe, people's demand for renewable energy and green transportation is becoming increasingly urgent. As the most developed new energy storage device, lithium-ion batteries (LIBs) have been widely used in portable electronic products, electric vehicles, and energy storage systems. However, the limited and uneven distribution of lithium resources limits the long-term sustainable development of LIBs. In addition, the limited and constantly rising prices of lithium resources, as well as the safety issues caused by the use of flammable organic electrolytes, greatly hinder future development. Therefore, exploring new energy storage devices that can replace LIBs is of great significance. Considering the mentioned problems, many attempts have focused on alternatives to LIBs, such as sodium-ion batteries, potassium-ion batteries, and aluminum-ion batteries. Among them, water zinc-ion batteries (ZIBs) prepared by zinc anodes, metal composite cathodes, and aqueous electrolytes have attracted widespread research interest in recent years. Compared with other metals, zinc has a lower oxidation-reduction potential of 0.76 V vs. SHE and a relatively high hydrogen evolution overpotential [1]. This makes it stable in aqueous electrolytes and has a large voltage window of around 2 V, which is highly valued for its low cost, high natural abundance, large capacity, and ease of manufacturing. ZIBs work similarly to LIBs in principle, achieving energy storage and release through the migration of zinc ions between the positive and negative electrodes[2]. However, the poor performance of ZIBs under low-temperature conditions limits their application in cold regions. To improve the performance of low-temperature ZIBs, researchers have carried out a series of studies on solid, liquid, and gel electrolytes.

Solid electrolytes have good ion transport performance in low-temperature ZIBs. Compared with liquid electrolytes, solid electrolytes have higher ion conductivity, lower viscosity, and better chemical stability. This makes the transfer speed of zinc ions faster in solid electrolytes, which is beneficial for improving the performance of low-temperature ZIBs. In addition, solid electrolytes can also avoid the solidification problem of liquid electrolytes under low-temperature conditions, thereby improving the low-temperature stability of batteries. At present, researchers have successfully developed various solid electrolyte materials, such as oxides, sulfides, and organic compounds, and have achieved good application effects in low-temperature ZIBs. For example, a solid polymer electrolyte based on polyethylene (vinylidene fluoride hexafluoropropylene) film was constructed, and an all-solid-state ZIB was constructed, which can maintain good cycling performance at $-20\text{ }^{\circ}\text{C}$ [3].

Liquid electrolytes have a high ion transport rate under low-temperature conditions. Compared with solid electrolytes, liquid electrolytes have a faster diffusion rate of zinc ions and higher conductivity. This makes liquid electrolytes have better performance in low-temperature ZIBs. However, liquid electrolytes are prone to freeze, and the solidification problems under low-temperature conditions lead to a decrease in battery performance. To solve this problem, researchers have improved the adaptability effect of liquid electrolytes in low-temperature ZIBs by adding additives, improving electrolyte formulations, and selecting low melting point electrolytes [4].

Gel electrolyte is an electrolyte with both solid and liquid advantages. Natural polymer hydrogel is an ideal candidate material for solid electrolytes in ZIBs. They are safe, biocompatible, and mechanically sturdy. It has also received widespread attention in low-temperature ZIBs. Gel electrolyte has high ionic conductivity and low viscosity, and can maintain stability at low temperatures [5]. This makes zinc ions have better transport performance in gel electrolytes. At present, researchers have successfully developed a variety of gel electrolyte materials, such as polymer gel, inorganic gel, and composite gel, and have achieved good application results in low-temperature ZIBs.

In conclusion, solid, liquid, and gel electrolytes have different application advantages in low-temperature ZIBs. The research and optimization of these electrolyte materials are expected to solve the performance problems of ZIBs under low-temperature conditions, thereby expanding their application scope in cold regions. In addition, considering environmental friendliness, cost, and resource utilization, low-temperature ZIBs have high research and application value. In this paper, the solid, liquid, and gel electrolytes of low-temperature ZIBs will be classified and discussed, the related research progress will be reviewed, and the existing problems and future development directions will be discussed, to provide theoretical guidance and reference for the wide application of low-temperature ZIBs (Figure 1).

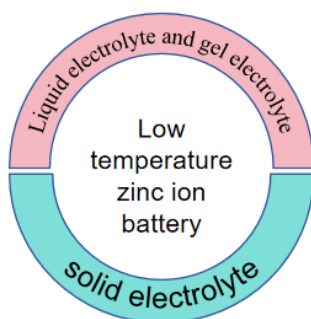


Figure 1. Classification of low-temperature zinc ion batteries

2. Modification of ZIBs electrolyte in low-temperature environment

2.1. Liquid electrolyte

The freezing of liquid electrolytes severely limits the performance of water-based ZIBs under low-temperature conditions. Therefore, researchers modified the liquid electrolyte by adding it to maintain its original performance at low temperatures.

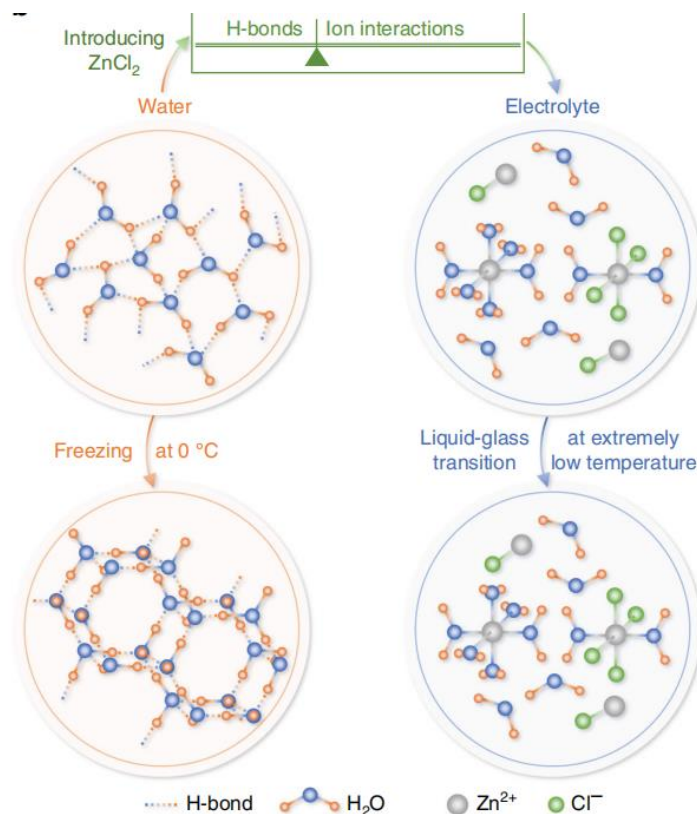


Figure 2. Hydrogen bond breaking mechanism [6]

A common method is to adjust the structure of the electrolyte or add additives to disrupt the hydrogen bonding network in the original water molecules, to lower the freezing point of the liquid electrolyte and form an ultra-low freezing point. By adjusting the electrolyte structure, as an example in a ZIB with ZnCl₂ as the electrolyte, the viscosity between ions was increased by increasing the concentration of ZnCl₂, as shown in Figure 2. Water molecules are composed of positively charged H atoms and negatively charged O atoms. Hydrogen bonds are formed between water molecules through electrostatic interactions, with oxygen atoms adjacent to hydrogen atoms. Increasing ion concentration can disrupt hydrogen bonds in water. But as the temperature decreases, the solubility of metal salts in water will greatly decrease, which will seriously limit the temperature range. By introducing highly soluble salts and adjusting the interaction forces of ionic bonds to form weaker hydrogen bonds, the freezing point of the liquid is reduced [6,7].

Another method is to modify the liquid electrolyte by using unique liquid electrolytes to improve its ion conductivity at low temperatures. A new type of hydrated deep eutectic electrolyte (DEE) containing sulfur alkane (SL) and Zn(ClO₄)₂ · 6H₂O has been developed through research to prevent water-induced metamorphism. The strong coordination between SL and Zn²⁺ triggers the deep eutectic effect, prolonging the operating temperature window of DEE [8]. This can effectively improve the problem of electrolyte freezing at low temperatures, resulting in better electrochemical performance and longer lifespan at low temperatures.

Improving the cathode electrode of the battery can also greatly enhance the electrochemical performance of ZIBs at low temperatures. Research has found that chemically pre-inserted transition metal ions can effectively enter the intermediate layer of vanadium pentoxide cathode, which can

enhance the electrochemical properties of aqueous solutions, including high capacity, high-speed capacity, and long-term cycling stability. At the same time, they also have good adaptability to a wide range of temperatures. By improving and adjusting the internal structure of vanadium pentoxide, new metal salts are formed, effectively improving the stability of conductivity and enhancing charge-discharge efficiency, thereby enhancing electrochemical performance [9].

Overall, low-temperature ZIBs still have a wide range of development prospects, whether it is through changing the concentration of liquid electrolytes to break hydrogen bonds in aqueous solutions, thereby reducing the freezing point, or using some unique electrolytes to improve the electrochemical performance of ZIBs at low temperatures, all of which effectively improve the problems encountered by ZIBs at low temperatures. Unfortunately, applications at low temperatures still face many challenges due to high prices and viscosity. Therefore, developing new ionic electrolytes to maintain a balance between viscosity and freezing point is the main goal for future development.

2.2. Solid electrolyte

ZIBs can also improve their physical properties at low temperatures by using solid electrolytes. Solid electrolytes have excellent electrochemical performance, so there is still great development prospect for the research and development of solid electrolytes, but they also face many problems and challenges.

In current research, quasi-solid electrolytes are commonly used, which have ion conductivity: solid electrolytes can conduct electricity through the conduction of ions in their lattice. This is because there are mobile ions in solid electrolytes that can jump and transfer charges in the lattice. High ion mobility: solid electrolytes typically have high ion mobility, allowing ions to move quickly and conduct electricity. This makes solid-state electrolytes have important applications in devices such as batteries and fuel cells. Stability: solid electrolytes typically have good chemical and thermal stability, able to maintain their ion conductivity in high temperatures and extreme environments. This makes solid-state electrolytes suitable for high-temperature batteries and other high-temperature applications [10]. For example, quasi-solid electrolytes with anti-freezing properties and high capacity $\text{NH}_4\text{V}_3\text{O}_8 \cdot 1.9\text{H}_2\text{O}$ cathodes with quasi-solid ZIBs also exhibit excellent electrochemical performance at low temperatures. When cycling at 0.2 A g^{-1} , the discharge capacity of quasi-solid-state batteries at different temperatures is as follows: 283 mAh g^{-1} at 20°C , 215 mAh g^{-1} at 0°C , and 119 mAh g^{-1} at -20°C . After 800 cycles, the capacity retention rates can reach 90.3% and 90.7% at 20°C and 0°C , respectively. In addition, after 450 cycles at 0.5 A g^{-1} , the battery can still reach 83% of its initial capacity. These results indicate that quasi-solid-state batteries have relatively stable capacity retention rates at different temperatures and cycles [11].

There are also all solid-state ZIBs, which have better electrochemical performance. Compared to liquid electrolytes, ZIBs in all solid-state electrolytes do not form dendritic structures due to zinc ion deposition, effectively suppressing the occurrence of side reactions and battery short circuits. This makes the battery more long-lasting and has better cycling ability. A solid-state zinc ion battery was constructed using polyethylene (vinylidene fluoride hexafluoropropylene) thin film solid polymer electrolyte. All solid-state ZIBs exhibit good cycling stability after 30000 cycles of testing at room temperature. In addition, the battery can still maintain reliable operation under high-temperature conditions (70°C) and operate normally under low-temperature conditions (-20°C). In addition, after 100 cycles of 150° bending deformation abuse tests and 8 cuts, the battery can still maintain its performance [12]. This battery has good electrochemical performance at both high and low temperatures, laying a certain foundation for future development.

In summary, solid electrolytes also have good ion conductivity in extreme environments, which can avoid the formation of dendritic deposits due to electrolyte deposition problems, leading to short circuit problems in batteries. But so far, there is still a lack of usable and stable solid electrolytes. Therefore, how to invent a good solid electrolyte is a major problem that we will face in the future.

2.3. Gel electrolyte

Gel electrolytes should also have excellent flexibility, high toughness, high strength, excellent elasticity, good self-healing ability, and high adhesion, which is a good choice for ZIBs. The gel electrolyte with high water content at low temperatures will also have the effect of freezing and performance degradation, so overcoming the problem of gel electrolytes at low temperatures is the main direction of research and development today [13]. There are also two ways to improve the performance of gel electrolytes at low temperatures: the electrochemical performance of gel electrolytes at low temperatures can also be improved by changing the ion concentration of the liquid, and the main performance of the electrolyte at low temperatures can also be improved by adding antifreeze. However, these methods can not improve the performance of gel electrolytes.

However, by mixing some natural gel materials, gel electrolytes with superior electrochemical performance can be formed. For example, guar gum (GG) and sodium alginate (SA) are mixed to form a gel electrolyte with high electrochemical performance, which plays a significant role in zinc ion batteries. To improve the effect of GG/SA gel electrolyte at low temperatures, ethylene glycol (EG) was added to form GG/SA/EG antifreeze hydrogel electrolyte. It also has good electrochemical performance at -20 °C. GG/SA/EG hydrogel maintains high ionic conductivity (6.19 mm cm^{-1}). The zinc ion battery made of GG/SA/EG hydrogel electrolyte has excellent discharge performance at low temperatures, and the specific capacity at 0.1 A g^{-1} is 181.5 mAh g^{-1} [14].

There is also a borax cross-linked polyvinyl alcohol (PVA)/glycerol gel electrolyte, in which glycerol can strongly interact with the PVA chain, thus effectively preventing the formation of ice crystals in the entire gel network. Therefore, the freezing point of this gel electrolyte is extremely low, making it work at -35 °C. Even at -35 °C, it still exhibits good performance with a high ionic conductivity of 10.1 mS cm^{-1} and excellent mechanical properties. And it has good durability and retention value, with a high energy density at -35 °C. It has played a good reference role in the development of gel electrolytes in the future [15].

In general, no matter which method is used to improve the gel electrolyte, as long as the product that can help human development can be developed, it is worthy of researchers to develop and research. Therefore, finding and developing a reasonable gel electrolyte is the main direction of future research and development. It can also improve the original gel electrolyte, reduce the production cost and R&D cost, and improve the electrochemical performance at low temperatures, which can contribute a research achievement to the development of ZIBs in the future and provide suitable products for the low-temperature working environment.

3. Conclusion

The development of low-temperature ZIBs has attracted extensive attention and discussion. Whether in liquid, solid, or gel electrolyte, ZIBs are the development direction. However, nowadays, there are still many opportunities and challenges for ZIBs at low temperatures, and researchers still need to research and develop them in practical applications. It is worth noting that the most serious problem at low temperatures is the freezing of the electrolyte, which affects ion conduction in the electrolyte. Solid electrolytes have the advantage of having no liquid or a small amount of liquid, making them less affected by low temperatures. The ion conductivity can be maintained within a good range, which is a very favorable development direction for the future. However, there is currently limited research on ZIBs solid electrolytes, and there is still a very broad development prospect in this direction. For liquid electrolytes and colloidal electrolytes, overcoming the problem at low temperatures is still a top priority for future development.

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