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Recent Advances on Electrolyte Additives Regulating the Electrode/electrolyte Interface to Stabilize the Zinc Anode

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Abstract: Energy and environment are the two most serious problems in todays social development. With the depletion of fossil resources such as coal and oil and the deterioration of the environment, the development of renewable energy has become a new trend. As an emerging energy storage technology, aqueous zinc-ion batteries (AZIBs) have attracted widespread attention due to their low cost, high safety, good environmental sustainability, and high energy density. However, problems such as dendrite growth in zinc anode, electrolyte decomposition and cathode dissolution limit its commercial application. In order to overcome these challenges, the research of electrolyte additives has become a hot field. Electrolyte additives can improve the cycle stability and efficiency of aqueous zinc-ion batteries by regulating the electrode/electrolyte interface, stabilizing the zinc anode, and improving the overall performance of the battery.

Keywords: Electrolyte additive, Electrode/electrolyte interface, Aqueous zinc ion battery, Zinc anode.

1. Introduction

Energy and environment are the two most serious problems in todays social development. With the depletion of fossil resources such as coal and oil and the deterioration of the environment, it is urgent to develop renewable energy. However, traditional lead-acid batteries will cause environmental pollution, so it is very important to study new environmentally friendly energy storage systems. Nowadays, as one of the mainstream electrochemical energy storage devices, batteries have been widely favored by scientific researchers. Among them, aqueous zinc-ion batteries have attracted much attention because of their intrinsic environmental protection, safety, low cost and high energy density. Aqueous zinc-ion batteries make full use of the resource abundance and safety of metallic zinc, and at the same time show efficient electrochemical performance in aqueous electrolytes. They are expected to significantly reduce manufacturing costs and improve safety by replacing traditional organic electrolyte systems, thus showing great potential in the field of large-scale energy storage.

At present, many researchers have studied the electrochemical performance and reaction mechanism of zinc-ion batteries, as well as the future development trend by analyzing the structure and properties of electrode materials. Although aqueous zinc-ion batteries have many advantages, problems such as dendrite growth, electrolyte decomposition and cathode dissolution of zinc anodes limit their commercial application. In this paper, the research progress of the effect of electrolyte modification on the performance of zinc anode is mainly reviewed. Firstly, the problems and challenges encountered in the anode of zinc ion batteries are introduced, including dendrite growth, side reactions and synergistic reactions between them. Secondly, the mechanism of action of electrolyte additives on zinc anodes is summarized, and prospects for electrolyte additive strategies to improve the electrochemical performance of zinc anodes to achieve their high cycle stability and reversibility are put forward. Finally, further research and development of high-performance and long-life AZIBs provide theoretical guidance and reference.

2. Problems and Challenges of Aqueous Zinc-ion Batteries at The Anode

2.1. Dendrite growth

Similar to lithium-ion batteries, due to the uneven distribution of electrons and ions at the interface, Zn^{2+}During the electrodeposition process, heterogeneous nucleation will occur, resulting in the formation of dendritic dendrites, which will lead to cell failure. Specifically, because the electrode surface cannot reach atomic level flatness, the surface charge distribution is uneven and nucleation is hindered, so the Zn at the interface Zn^{2+} It will be preferentially deposited at positions with higher degree of defects and active sites, which leads to uneven growth of zinc nuclei during the initial nucleation process, and the deposition of the formed protrusions further aggravates the electric field and ions at the interface. Uneven distribution, leading to subsequent Zn^{2+}The deposition always tends to agglomerate at the tip, eventually leading to the formation of dendrites. Typically, high electric fields and Zn^{2+}The "tip effect" caused by distribution protrusions can exacerbate the growth of dendrites. The growth of dendrites will affect the cycle life and performance stability of the battery. Even when the dendrites grow to a certain extent, due to the high mechanical strength and Youngs modulus of Zn, the sharp needle-like tip will increase the risk of penetrating the separator, resulting in internal short circuit and battery failure [2, 14]. Therefore, uniform surface energy, electric field and ion flux are effective methods to alleviate zinc dendrites [1].

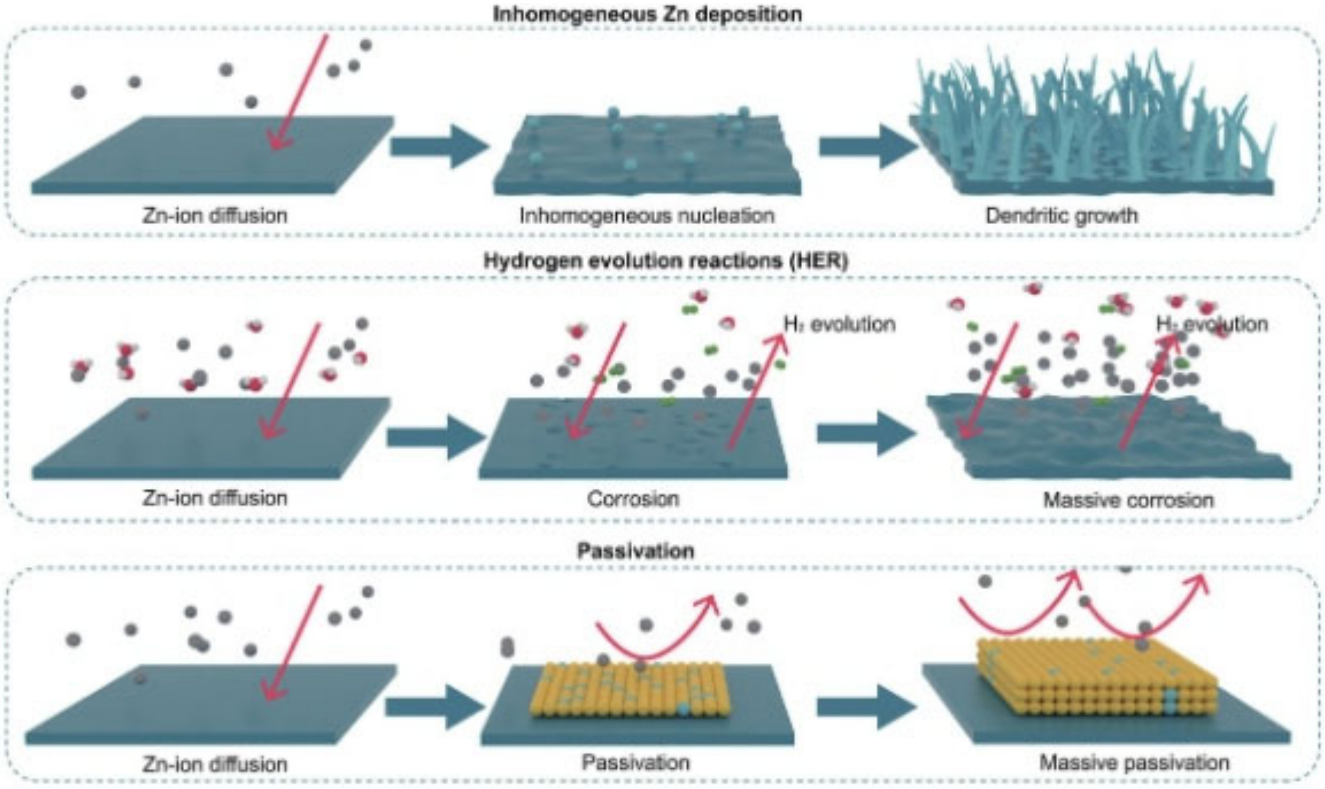

Figure 1. Issues of zinc metal anode/electrolyte interface: dendrite growth and side reactions [1]

2.2. Side reactions

With the growth of dendrites, a series of side reactions will occur at the interface between zinc anode and electrolyte during the working process of AZIBs. When the active water molecules are ionized and decomposed on the surface of the zinc anode, H^+ is generated and OH^-H^+Under the action of current, hydrogen is reduced to form, which leads to high OH concentration, local pH changes and side reactions on the surface of zinc anode [1]. It has been proved that the side reactions mainly include hydrogen evolution, corrosion and passivation [2c]. The occurrence of side reaction will seriously affect the cycle life of zinc anode, and cause the electrochemical performance of AZIBs to be greatly reduced, which will become one of the biggest obstacles in its further development and application.

2.2.1. Hydrogen evolution reaction

Although zinc metal can be used as the anode of AZIBs due to its relative stability, if the battery system Zn^{2+}/Zn (− 0. 76 V vs SHE) has a lower equilibrium potential than H_2O/H_2 (0V vs SHE), will result in Zn and H_2O reacts spontaneously and releases hydrogen [1, 3], and its reaction process is: anode: $Zn \leftrightarrow Zn^{2+}+2e^-$Cathode: $2H_2O+2e^-\leftrightarrow 2OH^-+ H_2\uparrow$ This allows the hydrogen evolution reaction (HER) to irreversibly consume the electrode and electrolyte, thereby reducing the lifetime and coulombic efficiency of AZIBs. In addition, with the gradual accumulation of hydrogen, the battery expands due to the increase of internal pressure until it ruptures, eventually leading to the leakage of electrolyte. In addition, the continuous release of hydrogen will lead to the local pH change of the electrolyte, which will be accompanied by the occurrence of corrosion and aggravate the damage to the battery [2c, 4].

2.2.2. Corrosion

During the repeated charging and discharging process of AZIBs, the zinc anode irreversibly consumes the electrode and electrolyzes and generates inert by-products. Due to the loose structure of these by-products, it cannot act as a solid electrolyte layer (SEI), but breaks away from the electrode surface and enters the solution, forming corrosion. Corrosion will cause the zinc anode to gradually dissolve, resulting in the decrease of Coulomb efficiency and battery capacity, which in turn leads to the failure and life shortening of AZIBs. In addition, since the by-product layer increases the interface impedance and limits the diffusion of electrons/ions, Zn will be triggered Zn^{2+}The deposited high energy barrier seriously reduces the electrochemical performance of AZIBs [2c ~ e, 5].

2.2.3. Passivation

In alkaline environment, ZnO passivation layer will be formed on the surface of zinc anode. Although it can be insulated from zinc anode to some extent and reduce HER and other side reactions, the thick passivation layer covers the electrode/electrolyte interface layer, causing Zn^{2+}The reaction sites deposited/exfoliated at the interface are greatly reduced and the electrochemical reaction fails. At the same time, when neutral or weakly acidic solution is used as the electrolyte, the passivation reaction is greatly reduced due to the reduction of OH-, and the passivator $Zn_4SO_4(OH)_6\bullet xH_2O$ is still present in $ZnSO_4$On the cathode and anode of the electrolyte, and leads to the slowdown of the electrochemical reaction [1, 5, 6]. Therefore, even under neutral or weakly acidic conditions, the passivation of zinc anode still needs attention. Passivation will adversely affect battery performance, mainly in two aspects: on the one hand, passivation reduces Coulomb efficiency [11-13] and durability by consuming active materials in the battery; On the other hand, by-products covering the anode increase the internal impedance and hinder the rapid transport of electrons and ions [2c ~ e].

3. Electrolyte Additive

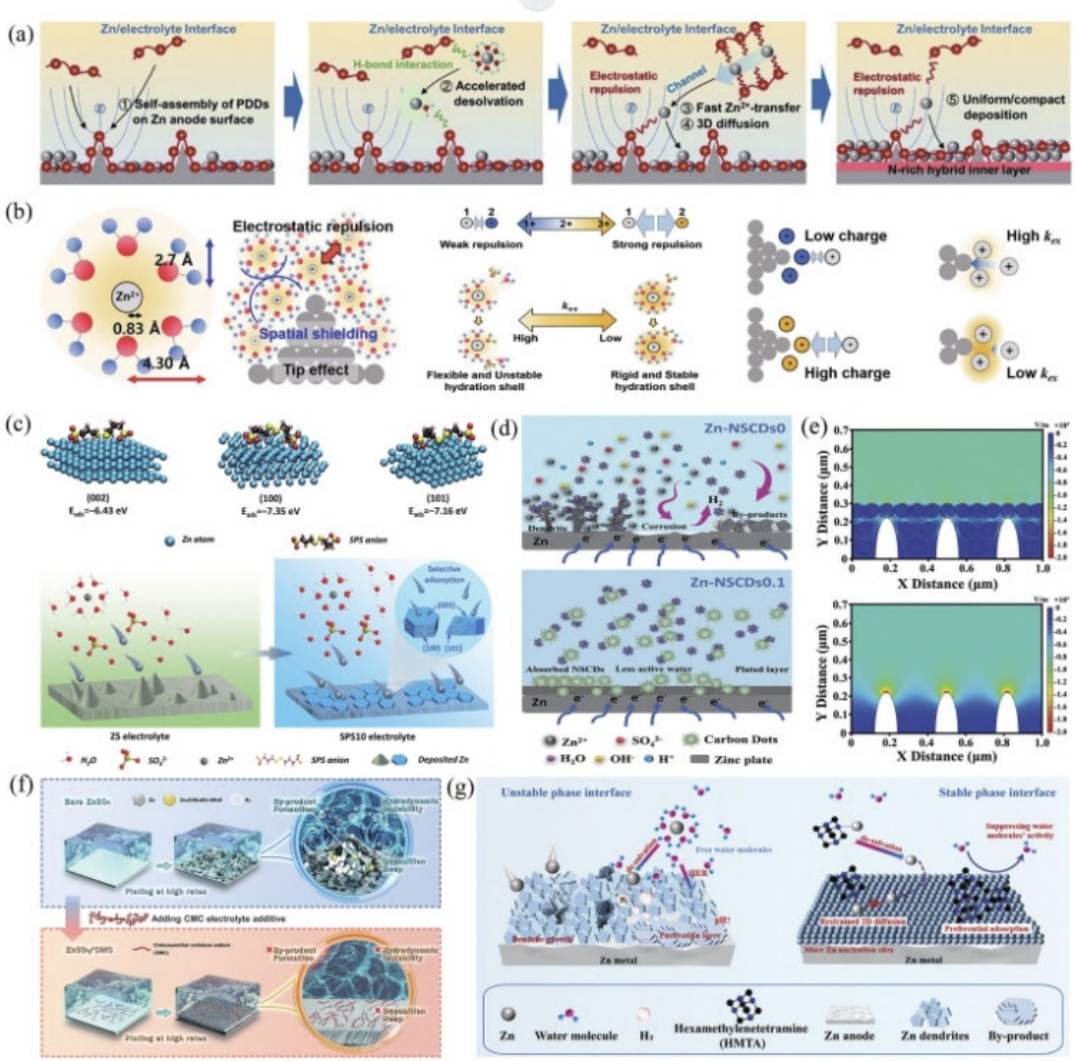

Figure 2. Mechanisms of ionic, inorganic and organic additives: (a) Polycationic electrolyte additives to modulate the electric fieldto improve the electrochemical performance of zinc metal anodes [15]; (b) Scandium ion additives to achieveve tip-blocking effect byintroducing scandium ions into the electrolyte to induce homogeneous Zn^{2+}deposition [16]; (c) Anionic surfactant additives toinduce homogeneous deposition of Zn^{2+} for high-performance zinc metal anodes[17] ; (d) N-doped sulfonated carbon dotsadditive regulates the solvation structure and reduces the ionization of reactive water to protect the zinc metal anode[18] ;(e) Silica nanoparticle additive homogenizes the surface charge and induces the formation of zinc-free dendritic anodes[19] ;(f) Sodium carboxymethyl cellulose additive protects the zinc metal anode by a multifunctional mechanism [20] ;(g) Trace hexamethylenetetetramine additive modulates the coordination environment and interfacialreaction of $Zn^{2+}$to achieve uniform and directional deposition of Zn^{2+}[21]

3.1. Ionic additive

In AZIBs, ion additives attract much attention due to their versatility, controllability, and good compatibility. Related additives in the Ni^{2+}、Bi^{3+}、Pb^{2+}Equipositive potential metal ions can have some influence on zinc anode deposition and dissolution, while Mn^{2+}、Na^{+}、Mg^{2+}Equinegative potential metal ions will form a layer of cationic electrostatic shielding at the zinc tip that favors uniform deposition. In terms of cathode reversibility, stability and reversible capacity improvement, the role of ion additives cannot be ignored. For example, the additive MnSO in the electrolyte$_4$When, it can promote the MnO_2 Enhancement of stability while ensuring uniform deposition. Lius research group tried to analyze the electrolyte ZnSO $_4$Medium Mn $^{2+}$The effect of concentration change was verified, and the result showed that the increase of surface concentration would inhibit the dissolution of cathodic manganese [7]. By adding Na to the electrolyte$_2SO_4$, Ling et al. successfully suppressed the dissolution of Zn-Na0. 56V2O5 cathode material and improved the cycle stability and long-term stability of the battery. Na^{+}Compared to Zn^{2+}In other words, the reduction potential is lower, and it can inhibit the growth of zinc dendrites under the support of electrostatic shielding effect. $[Zn(H_2O)_6]^{2+}$ Is Zn in aqueous electrolyte^{2+} The main existing form, but in water molecules with Zn^{2+}During the binding process, due to the existence of electrochemical reactions, reduction and decomposition reactions may occur. The reduction decomposition reaction will lead to the formation of some corrosive by-products, which will adhere to the surface of the zinc anode, thus affecting the performance and stability of the battery. At the same time, side reactions may lead to corrosion of the zinc anode, reducing the cycle stability and reversibility of the battery. In order to inhibit these side reactions, researchers

have taken a series of measures, one of which is to modify the water molecules in the solvated structure to reduce the possibility of reduction and decomposition reactions. Fan et al. confirmed that Zn^{2+}In Mg^{2+}Under the action of additives, the surrounding H_2The number of molecules will decrease, so the solvation effect will also be weakened, and the side reaction of the battery can be effectively controlled [8]. Meanwhile, Mg^{2+}Compared to Zn^{2+}In other words, its reduction potential is lower, and it plays an important role in promoting uniform zinc deposition and the formation of electrostatic shielding layer, which is conducive to the realization of dendrite-free deposition. By observing the electron probe microanalysis (EPMA) map, it can be found that containing Mg^{2+}In the ZnMg-0. 1 electrolyte, Zn^{2+}Better deposition can be achieved, and the corrosive byproducts produced will also be greatly reduced.

3.2. Inorganic additives

In AZIBs electrolyte studies, inorganic additives are usually difficult to reach high concentrations due to the limitation of their solubility, and the order is usually in mmol/L or lower, or even insoluble in water. Therefore, few studies focus on inorganic additives. Based on the existing research results, it is not difficult to find that in terms of battery electrochemical performance, the influence of such additives cannot be underestimated. Vanadium pentoxide (V_2O_5), lead oxide (PbO), zinc oxide (ZnO), tin oxide (SnO_2) isooxides and phosphoric acid (H_3PO_4), boric acid [B $(OH)_3$] and other inorganic acids are the main representatives of inorganic additives in research. These additives are gradually becoming a research hotspot by affecting the electrochemical reaction mechanism of batteries and improving the performance of batteries. Qin and colleagues conducted an innovative study. They chose Graphene Oxide (GO) as an additive. GO is a single-layer two-dimensional carbon material with high polarity and abundant oxygen-containing groups. These properties make it well dispersed in electrolytes. When GO is added to $ZnSO_4$In the electrolyte and dispersed, the oxygen-containing groups of GO can be interacted with Zn^{2+}Ions form stable complexes such that Zn^{2+}Enriched on the surface of GO particles. In addition, the polar groups on the surface of GO particles will also affect Zn^{2+}Ions generate attractive forces such that Zn^{2+}The ions migrate along the GO particles to the reaction interface. This migration process contributes to the increase of nucleation sites and consequently the nucleation rate, a characteristic that allows GO to develop in electroplating/exfoliating Zn^{2+}Excellent performance in the process and uniform deposition of zinc was achieved [10]. The results of Niu et al. showed that MXene (Ti_3C_2Tx) after adding electrolyte, a battery with stronger electrochemical performance can be formed. In this system, under the action of electrostatic adsorption, Zn^{2+}It can combine with MXene, and a solid electrolyte interface (SEI) will be formed on the anode surface, which can achieve ion flux and promote the uniformity of nucleation. The electrochemical test results showed that the current density was 2mA/cm^2After introducing MXen additive into symmetrical Zn//Zn battery, the cycle stability reaches more than 1100 times. It should be noted that although the improvement effect of MXene additive in terms of cycle stability is quite outstanding, under the condition of current density of 1A/g, the assembled full battery shows a specific capacity of 192 mAh/g after 300 cycles, but it only has a capacity retention rate of 59%.

3.3. Organic additives

In order to achieve high-performance AZIBs, through chemistry or physics, organic additives can be adsorbed on the electrode surface and form a protective layer that can isolate the electrode from water, and at the same time, it can have a certain change effect on the solvated structure. The electrolyte additive acrylamide-methyl acrylate (APA) is a nonionic amphiphilic polymer, and the design team is Wangs research group. The addition of APA can also affect the behavior of solvated ions in the electrolyte, which can change the structure and stability of the coordination complex, thus affecting the migration rate of lithium ions and the rate of other electrochemical reactions. During the cycling of the battery, the addition of APA helps to form a stable solid electrolyte interface (SEI), and the formation of SEI is crucial for the reversibility and cycling stability of the battery. Capacity 1mAh/cm^2And current density 1 mA/cm^2Under these conditions, the cycle life of symmetrical batteries can reach more than 8800 hours after using this additive. In addition, Zhang et al. also tried to add nonionic polymer polyvinylpyrrolidone (PVP, mass fraction 0.03%) to the electrolyte. The mechanism of action of this additive is that PVP molecules will accumulate near the protrusions through electrostatic action, forming an electrostatic shielding layer, and Zn^{2+} Ions will encounter this shielding layer during the lateral diffusion process, thus being effectively blocked. Thus, Zn^{2+} Ions cannot accumulate in large quantities on the zinc nucleus, which reduces the formation of dendrites. The experimental results show that the cycle stability of this improved zinc symmetric battery has been significantly improved. After multiple charge-discharge cycles, the performance decay is less, the capacity retention rate is higher, and the current density of the battery is 0.5 mA/cm^2When, it can stably achieve 1000 h The above run. The electric double layer plays a crucial role in the stable construction of solid electrolyte layer. According to the research results of Chens team, saccharin (Sac), an interface stabilizer, plays a role that cannot be ignored. Derived anions refer to negatively charged molecules or ions produced in the electrolyte through chemical reactions, which can interact with zinc. (Zn) active materials are strongly bound, so they will be preferentially adsorbed on the anode surface. After the derivatized anions are adsorbed on the anode surface, they form a dry electric double layer, reducing the possibility of zinc ions reacting with solvents or other components in the electrolyte [9]. The presence of the dried electric double layer can also improve the wettability of the electrode material and reduce the penetration of the electrolyte on the anode surface, thereby further inhibiting the occurrence of side reactions. This is of great significance for improving the performance and stability of the battery. Therefore, at a current density of 40 mA/cm ^{2}Under the same conditions, if Sac is added to the symmetrical battery, it can still stably achieve a running time of more than 200h. Li et al. found that in the application of zinc anode, dioxane was able to interact with Zn^{2+} The ions interact, thereby improving the stability of the zinc anode. In addition, the addition of dioxane also helps to improve the diffusion path of zinc ions, making the deposition and dissolution process of zinc ions on the electrode surface more controllable. This helps prevent heterogeneous deposition of zinc ions, which reduces the formation of dendrites and improves the cycle stability of the battery. In zinc and Zn^{2+}Aspect, the binding ability exhibited by dioxane is quite remarkable, and Zn^{2+} The solvation structure will change, the

water molecules in the solvation layer are greatly reduced, and the occurrence of side reactions will be effectively controlled. More importantly, the dioxane ring can tightly adsorb on the zinc surface, forming a dry double electric layer, which provides a stable and reversible working environment for the zinc anode. In AZIBs, organic chelators are widely used as electrolyte additives, because they can form stable complexes with Zn^{2+}, the nucleation overpotential is therefore enhanced, and the hydration degree of zinc ions in the electrolyte will be reduced. Jiang et al. attempted to verify the effect of 2-double (2-hydroxyethyl) amino-2- (hydroxyethyl) -1,3-propylene glycol (BIS-TRIS) when using electrolyte additives in AZIBs. It is found that the additive can change the molecular weight of water contained in the inner Helmholtz plane, and the formation of corrosion by-products and the hydrogen evolution reaction will be inhibited to a certain extent.

4. Conclusion

As a new energy storage technology, aqueous zinc-ion battery is regarded as the most promising substitute for lithium-ion battery because of its environmental friendliness, abundant resources and high safety. Researchers have successfully improved the overall performance of aqueous zinc-ion batteries by designing new additives, exploring the mechanism of action of additives, and optimizing the dosage and ratio of additives. Although electrolyte additives can significantly improve the performance of aqueous zinc-ion batteries, the addition process may also bring some problems, such as increased costs and increased complexity of battery systems. Therefore, how to minimize the use of electrolyte additives and reduce the cost and complexity of batteries while ensuring performance improvement will also be an important direction of future research.

5. Declaration of Competing Interest

The authors declare no competing financial interests.

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References

[1] Liu Y, Lu X, Lai F, et al. Joule, 2021, 5: 2845-2903.

[2] (a) Wang T, Sun J, Hua Y, et al. Energy Storage Mater. ,2022, 53: 273 ~ 304; (b) Li R, Du Y, Li Y, et al. ACSEnergy Lett. , 2022, 8: 457 ~ 476; (c) Yin J, Feng X, GanZ, et al. Energy Storage Mater. , 2023, 54: 623 ~ 640; (d)Zou Y, Yang X, Shen L, et al. Energy Environ. Sci. ,2022, 15: 5017 ~ 5038; (e) Yang J, Yin B, Sun Y, et al.Nanomicro Lett. , 2022, 14: 42; (f) Zuo Y, Wang K, PeiP , et al. Mater. Today Energy, 2021, 20: 100692.

[3] (a) Hao J, Li X, Zhang S, et al. Adv. Funct. Mater. ,2020, 30: 1909469; (b) Zhao J, Zhang J, Yang W, et al.Nano Energy, 2019, 57: 625 ~ 634; (c) Zhao Z, Zhao J,Hu Z, et al. Energy Environ. Sci., 2019, 12: 1938 ~ 1949; (d) Guo X, Zhang Z, Li J, et al. ACS Energy Lett., 2021,6: 395 ~ 403.

[4] (a) Trócoli R, La Mantia F. ChemSusChem, 2015, 8: 481~ 485; (b) Chen J, Zhao W, Jiang J, et al. Energy StorageMater. 2023, 59: 102767.

[5] Li Y, Yao H, Liu X, et al. Nano Res., 2023, 16: 9179~ 9194.

[6] Jayakumar R, Harrison D M, Xu J, et al. J. Mater. Chem.A, 2023, 11: 8470 ~ 8496.

[7] Jin Mingzhe, Wang Chen, Wang Tan, et al. Research progress of electrolyte additives of drainage zinc ion battery [J]. Journal of Shanghai University (Natural Science Edition), 2023,29 (5): 900-914.

[8] Shen Qibin, Chen Taiqiang. Research progress of electrolyte additive of drainage zinc ion battery [J]. Guangzhou Chemical, 2023,48 (4): 26-30.

[9] Xie Zhiying, Zheng Xinhua, Wang Mingming, etc. Water system zinc ion battery [J]. Chemical Progress, 2023,35 (11): 1701-1726.

[10] Ma Chenhui. Regulation of zinc cathode interface stability in drainage zinc ion battery [D]. Changchun: Jilin University, 2023.

[11] Kim Y, Park Y, Kim M, et al. Corrosion as the origin of limited lifetime of vanadiumoxide-based aqueous zinc ion batteries[J]. Nature Communication, 2022, 13(1): 2371.

[12] Zhou W, Chen M, Tian Q, et al. Cotton-derived cellulose film as a dendrite-inhibitingseparator to stabilize the zinc metal anode of aqueous zinc ion batteries [J]. Energy StorageMaterials, 2022, 44: 57-65.

[13] Li H, Guo C, Zhang T, et al. Hierarchical confinement effect with zincophilic and spatialtraps stabilized Zn-based aqueous battery[J]. Nano Letters, 2022, 22(10): 4223-4231.

[14] Wang D, Li Q, Zhao Y, et al. Insight on organic molecules in aqueous Zn-ion batteries with anemphasis on the Zn anode regulation[J]. Advanced Energy Materials, 2022, 12(9): 2102707.

[15] Peng M, Tang X, Xiao K, et al. Angew. Chem. Int. Ed. ,2023, 62: e202302701.

[16] Kim M, Shin S J, Lee J, et al. Angew. Chem. Int. Ed., 2022, 61: e202211589.

[17] Lin Y, Mai Z, Liang H, et al. Energy Environ. Sci., 2023, 16: 687-697.

[18] Song T B, Huang Z H, Zhang X R, et al. Small, 2023, 19: e2205558.

[19] Wu H, Yan W, Xing Y, et al. Adv. Funct. Mater. 2023, 34 (5): 2213882.

[20] Huang H, Yun J, Feng H, et al. Energy Storage Mater., 2023, 55: 857 ~ 866.

[21] Yu H, Chen D, Li Q, et al. Adv. Energy Mater. 2023,13: 2300550.