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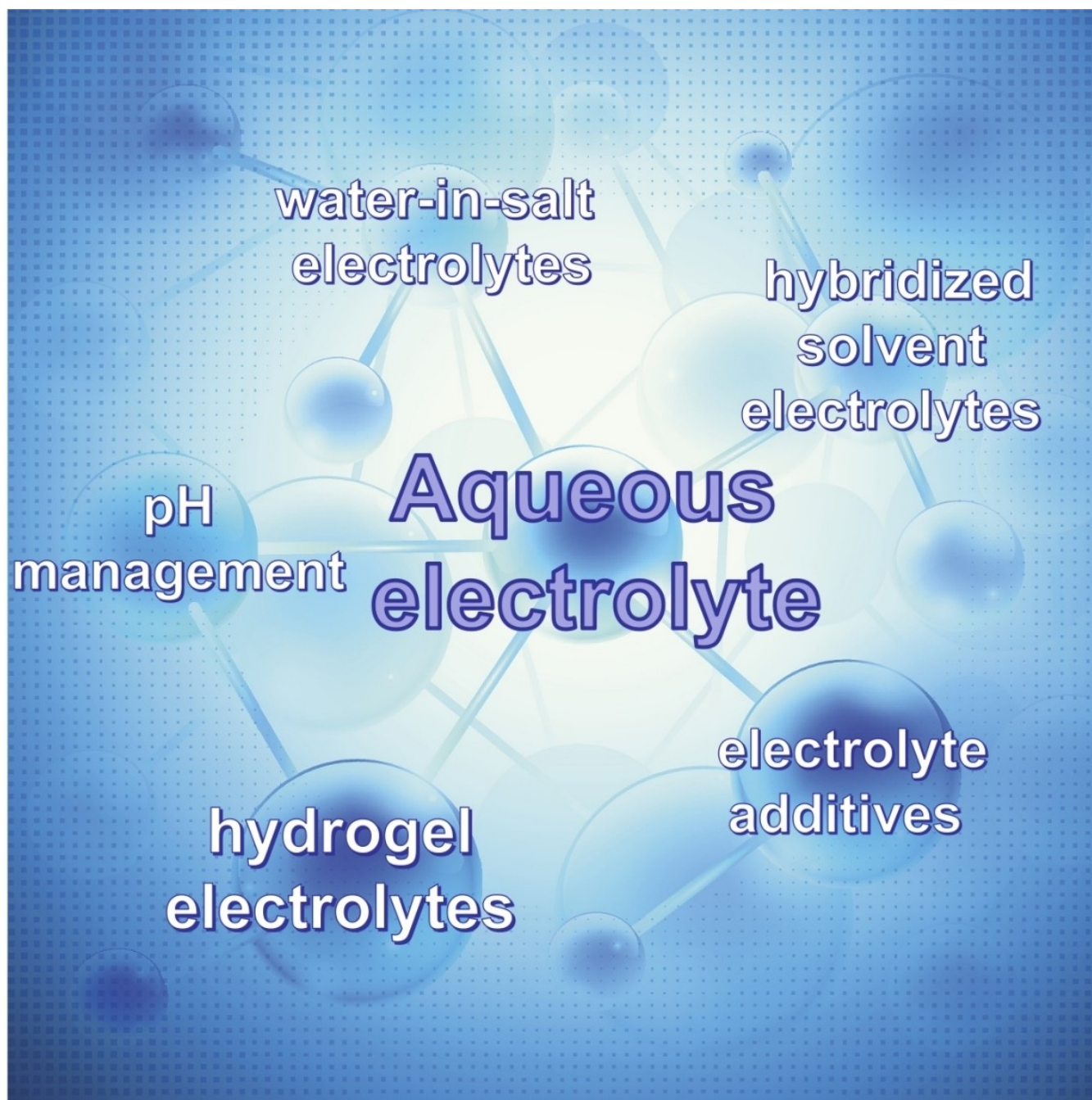European Chemical Societies Publishing

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Insight into the Improvement Strategies of Aqueous Electrolyte for Aqueous Rechargeable Batteries

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Aqueous rechargeable batteries (ARBs) have attracted wide attention due to their rich resources, environmental friendliness, and safety. The high ionic conductivity, safety and interfacial wettability of the aqueous electrolyte are essential for energy storage devices. However, the narrow electrochemical stability window (ESW) of the aqueous electrolyte and the side reactions of the electrode/electrolyte lead to the low energy density of the ARBs. In the past studies, the above problems were generally solved by improving the ion transport characteristics of the electrolyte and the electrode/electrolyte interface. Herein, we discuss the background, limitations, and key concepts for performance improvement of aqueous electrolytes, aiming to provide a comprehensive perspective and inspiration for further research on aqueous electrolytes and promote their development and application in the field of energy storage.

1. Introduction

Energy is the backbone of human social development and plays a key role in the economy. The global energy paradigm is changing rapidly, which may pose additional challenges to energy security. In the future, renewable energy sources will rapidly expand in scale and drive a profound reform of the energy system, ultimately realizing "carbon neutrality". Therefore, enhancing the utilization of renewable energy has become one of the current hotspots. Because of its intermittency and instability, it is crucial to establish a stable, flexible, and safe electric energy storage. Electrochemical energy storage devices possess the advantages of long cycling life, high energy density, and low maintenance costs. Different kinds of battery systems such as metal-ion batteries and metal-air batteries have emerged, consisting of anode, cathode, and electrolyte. The electrolyte is crucial for high energy density and high-safety batteries. Nevertheless, most batteries use flammable organic electrolytes, and the manufacturing process requires a strictly dry environment, which carries certain risks.[1] In contrast, aqueous electrolyte have the advantages of high conductivity, high safety, and low cost. Therefore, aqueous rechargeable batteries (ARBs) can be applied in electric energy storage to establish an ultra-fast charging and discharging energy storage system.[2]

Aqueous electrolytes were first proposed by Dahn and coworkers in 1994. Because of the low energy density of ARBs, it has not attracted much attention at that time.[3] Firstly, aqueous electrolytes have a narrow ESW, beyond which leading to side reactions (hydrogen evolution reaction (HER) and oxygen evolution reaction (OER)). The decomposition voltage of water is low, only 1.23 V, which limits the operating voltage of the device in practical use. It also affects the choice of electrode material and directly leads to low energy density.[2] The cathode dissolution caused by the strong polarity of water molecules and the side reactions between the electrode and water or air will change the structure of the electrode material, resulting in the decrease of the energy density.[4] Especially in lithium-ion batteries, the reaction of embedded lithium with water or air affects the stability of aqueous batteries.[5] In addition, temperature changes can cause phase transitions in water, limiting the

temperature window of aqueous electrolyte. Overall, it is significant to explore safe and cost-effective electrochemical energy storage systems. Therefore, it is essential to develop high performance aqueous electrolyte to solve the existing problems of flammability and toxicity of organic electrolyte.

In this review, we summary the strategies to improve electrolyte properties by broadening the ESW, improving the electrode/electrolyte interface, and inhibiting side reactions. The working principle and application of water-in-salt electrolytes (WiSE), electrolyte additives, and hydrogel electrolyte are emphasized. Finally come to the conclusion that by improving the properties of the electrolyte can be significantly increase the energy density and cycle life of it.

2. Presentation of Recent Aqueous Electrolytes

Despite the advantages of aqueous electrolytes such as safety and high ionic conductivity, water decomposition, dendrite growth of anode materials, and susceptibility to decay and passivation of cathode materials in aqueous batteries have seriously affected the capacity, cycling stability, and lifetime of aqueous batteries. In 2013, an innovative aqueous rechargeable lithium battery (ARLB) using coated lithium metal as the anode and $LiMn_2O_4$ as the cathode was established in a report by Wang et al. The average output voltage of this ARLB reached 4.0 V, with an energy density 80% higher than that of conventional lithium-ion batteries and an energy efficiency of over 90%.[6] This result provides a new perspective and a breakthrough in the study of aqueous electrolytes. Nowadays, the improved strategy of aqueous electrolytes that have recently been developed can be categorized into WiSE, electrolyte additives, gel electrolytes, etc.

2.1. Water-in-salt electrolyte

Salt concentration is one of the important factors affecting ESW, ionic conductivity and electrode/electrolyte interface in aqueous electrolytes. In 2010, Huggins et al. investigated the effects of two common salts used in aqueous lithium batteries (ALIBs) ($LiNO_3$ and Li_2SO_4) on the ESW of aqueous electrolytes.[7] The results showed that concentrated $LiNO_3$ and Li_2SO_4 showed similar stability ranges, approximately 2.3 V wide at a current density of 50 $\mu A/cm^2$, both higher than the range of pure water. In addition, Zhao et al. constructed an ARLB to verify this fact.[8] The ARLB is built up with $LiFePO_4$/C and LiV_3O_8 in 9 M $LiNO_3$

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Table 1. Effect of crystal orientation on the growth of zinc dendrites.

Crystal orientation	Zinc dendrite growth direction and zinc surface angle degrees	Affect
(002), (103), (105)	0–30°	No dendrite growth
(114), (112), (102), (101)	30–70°	favorable for dendrite growth
(100), (110)	70–90°	favorable for dendrite growth

aqueous electrolyte, delivering a capacity of 88.7 mAh g^{-1} at 10 C-rate after 100 cycles. This ARLB shows still the discharge capacity of 60 mAh g^{-1} at 50 C-rate after 500 cycles. Then, in 2015, Suo and his colleagues first proposed the water-in-salt electrolyte (WiSE), and achieved a breakthrough of 3 V ESW. In this report, WiSE is defined as a mixture where the salt weight and volumn is more than that of water.[9] Inspired by this work, WiSE has attracted wide attention, greatly promoting the development of the field. Then, several studies have shown that aqueous sodium ion battery (ASIB) and aqueous zinc ion battery (AZIB) also have good electrochemical performance. For instance, the ASIB constructed by Suo et al. still has a high coulombic efficiency of 99.2% after 350 cycles at a low rate (0.2 C). At high rate (1 C), it still has excellent cycle stability after 1200 cycles.[10] And wang et al. used 1 m Zn(TFSI)$_2$ + 20 m LiTFSI as electrolyte and LiMn$_2$O$_4$ as cathode to construct an AZIB. This AZIB provides 180 Whkg^{-1} and maintains 80% capacity after 4000 cycles.[11] With the continuous development of the research, WiSE was found to broaden the ESW by improving the stability of the electrolyte, creating a solid electrolyte interface (SEI) on the anode,[12] and inhibiting the dissolution of the cathode.[4] Next, we will introduce the development of WiSE and its application in ARBs.

2.1.1. The function of water-in-salt electrolyte

In 2015, Suo et al. first reported the use of aqueous electrolytes in salt.[9] They obtained the WiSE by dissolving lithium bis(trifluoromethane sulfonyl)imide (LiTFSI) at a very high concentration (> 21 M), this breakthrough WiSE exhibited an electrochemical stabilization window of 3 V. They constructed an all-hydrate lithium-ion battery utilizing LiMn$_2$O$_4$ and Mo$_6$S$_8$ as the cathode and anode, presenting an open-circuit voltage of 2.3 V and a high 1000-cycle times. When LiTFSI concentration is increased to 21 M, it can be predicted that an average of two TFSI$^-$ will be observed in each Li$^+$ primary solvated sheath (Figure 1a), and the high content of TFSI$^-$ leads to an interphase chemical reaction dominated by TFSI$^-$ reduction. Thus, it is conclude that this reduction process generates sufficient LiF from TFSI$^-$ to form an anode-electrolyte interphase, which prevent the reduction of water while allowing the Li$^+$ to migrate. In addition, there is insufficient free water at high concentrations (Figure 1b), which reduces the electrochemical activity of water and improves the stability of the electrode. These factors work together to expand ESW.[9]

For the purpose of further exploring the formation mechanism of the anode electrolyte interface, researchers have made continuous efforts. Dubouis et al. proved that the formation of the fluorinated solid-electrolyte interface (SEI) is catalyzed by the reaction of hydroxide produced in the process of hydrogen evolution with TFSI$^-$.[13] In another study, researchers proposed a new method of forming SEI. Researchers found that SEI formation is dynamic, meaning it does not adhere to the electrode during the cycle but breaks down/rebuilds.[14] In addition, the WiSE can availably suppress the dissolution of vanadium based cathodes.[15] In 2020, Suo et al. proposed interface concentrated-confinement to explain this phenomenon.[4] Experimental results show that the super highly concerntrated WiSE has high viscosity, low vanadium ion diffusion, low polarity of solvated water and scarce solvent-water dissolved surface. These factors observably reduce the thermodynamically controlled solubility and dissolution kinetics through the local mass interface constraints of time and physical space, and improve the cycle stability of water system batteries.

In general, extremely high salt concentrations may sacrifice the ionic conductivity and viscosity of the electrolyte. But studies have shown that a three-dimensional network is formed at 21 M LITFSI, facilitating the conduction of lithium ions.[16]

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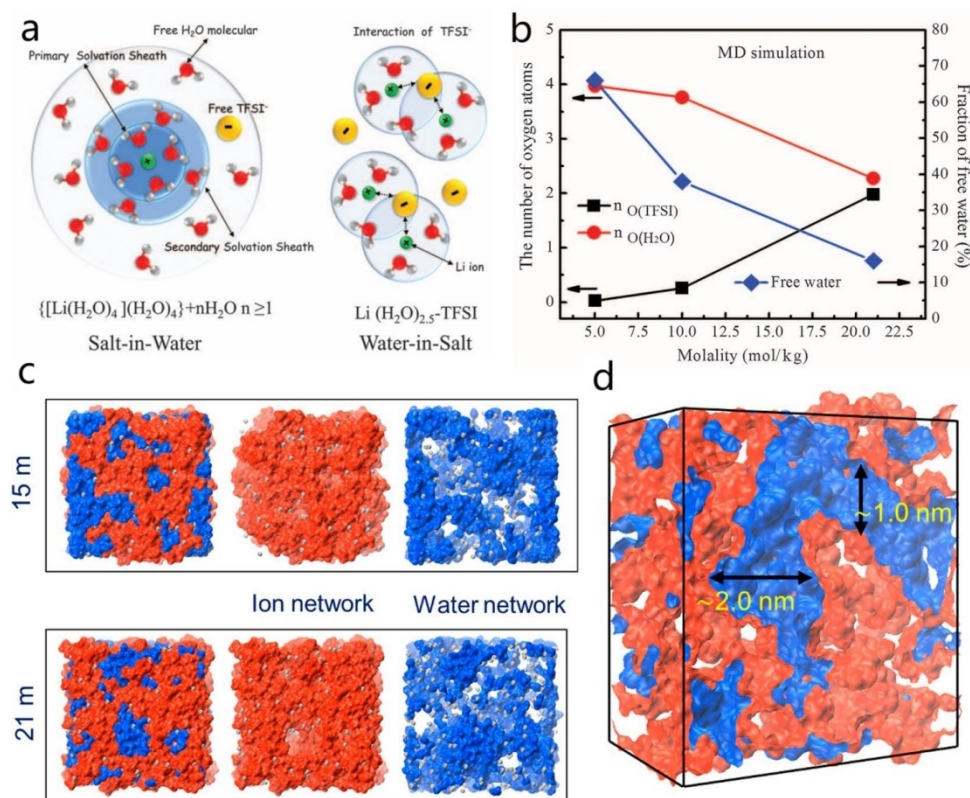
Figure 1. (a) Difference of lithium ion solvated sheath in salt-in-water electrolyte and water-in-salt electrolyte.[10] (b) Plot of the number of oxygen atoms as a function of concentration in water and TFSI⁻ in the main solvation sheath of Li⁺, and changes in the content of free water.[10] (c) MD-simulated structures of 15 M and 21 M LiTFSI electrolyte solution structure.[17] (d) Simulated structure of the 21 M LiTFSI electrolyte solution, where the blue and red regions correspond to water and ionic aggregates, respectively.[17]

(Figure 1c) Therefore, it is reasonable to explain that the WiSE can still reach high lithium ion conductivity.[9]

2.1.2. The challenges and application

At present, the research on WiSE has made significant gains, but it still faces some challenges. A major challenge with WiSE is their limited operating temperature range. WiSE usually reaches the salt solubility limitation, and with the decrease of temperature, the solubility of the aqueous electrolyte is significantly reduced, and crystallization occurs, which greatly affect the performance of the battery.[17] An effective strategy is that WiSE based on lithium (pentafluoroethanesulfonyl)-(tri-fluoromethanesulfonyl) imide remain thermodynamically in the liquid state down to at least −10 °C.[18] They propose a novel lithium salt based on the asymmetric (pentafluoroethanesulfo-nyl)(trifluoromethanesulfonyl) imide (PTFSI) anion. Owing to the absence of a S–F bond, it exhibits good chemical stability. Moreover, its 20 M binary mixtures with LiOTf have particularly low liquidus temperatures as low as −14°C, surmounting the low-temperature challenge of WiSE. In addition, preparing WiSE heavily uses expensive organic salts, raising battery costs. To reduce costs, several research groups have focused on finding cost-effective salt alternatives.[19] For example, Maria R. Lukat-skaya et al. used potassium acetate with high solubility to prepare WiSE with a water-cationic ratio as low as 1.3, which has a fairly high conductivity and an ESW of 3 V.[20]

Considering the cost and resource issues, sodium salts, which are more abundant in natural resources and lower cost, have attracted attention compared with lithium salts. However, the sodium salt has a lower solubility in water, resulting in a narrower ESW. Compared with the most representative lithium salt WiSE (21 M LiTFSI), the maximum solubility of NaTFSI is only 8 M.[21] However, despite the lower solubility of NaTFSI, NaOTF is sufficient to form SEI because of more intense ion aggregation between the sodium cation and the OTF anion.[10] In the sodium-ion water-in-salt electrolyte (NaWiSE) system, the most representative research is a full aqueous Na-ion battery (ANIBs) employing $Na_{0.66}[Mn_{0.66}Ti_{0.34}]O_2$ and $NaTi_2(PO_4)_3$ as cathode and anode in 9.26 M NaOTF electrolyte.[10] The sodium-ion battery has more than 350 cycles at 0.2 ° C and a long cycle life of more than 1,200 cycles at 1 °C. In addition, to solve the problem of low solubility, a new class of the inert-cation-assisted WiSE (IC-WiSE) containing the tetraethylammonium (TEA⁺) inert cation is reported.[22] The complete ANIB has an average voltage of 1.74 V and a high energy density of 71 Wh kg⁻¹ and also exhibits good cycling performance.

Because of the excellent stability of Zn in water, aqueous zinc-based batteries (AZIBs) also have been extensively studied. Zinc batteries have the following advantages: (1) Two-electro-

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n transfer, (2) high safety and simple installation environment, (3) high abundance and low cost, (4) high theoretical capacity.

On account of the unique electrochemical properties of WiSE, it greatly promotes the application of water system lithium ion battery. The WiSE overcomes some of the challenges of aqueous batteries, such as (1) the limitation of using low potential anode material due to narrow ESW, (2) the dissolution of cathode material, and (3) the narrow temperature window.[9] Since the thermodynamic stability window of water has been significantly extended from 1.5 V to 3.0 V by increasing salt concentration,[9] there are more options for electrode materials. For example, $LiFePO_4$[22] and $LiCoO_2$[23] are used as cathode materials, and TiS_2[24] is replaced as anode material. These full cells, Mo_6S_8//$LiFePO_4$, TiS_2/$LiMn_2O_4$, Mo_6S_8//$LiCoO_2$ all show high discharge voltage (1.2 V, 1.7 V, 2.5 V) and high energy density as well as satisfactory rate performance.

2.2. Electrolyte additives

Electrolyte additives are an innovative energy storage technology that has been used in the past to enhance the functionality of traditional lithium-ion batteries(LIBs). The report shows that these additives can (1) improve the performance of the SEI layer on the electrode surface, (2) improve the ionic conductivity of the electrolyte, and (3) enhance the stability of $LiPF_6$.[25] Consequently, the electrolyte additives improve battery safety, avoiding the dissolution of the positive electrode material and overcharging, reducing irreversible capacity and gas generation. In the past few years, with the rise of ARBs research, electrolyte additives have been used to improve the performance of aqueous batteries, especially AZIBs. Usually, the amount of an additive in the electrolyte is no more than 5% either by weight or by volume, while its presence significantly improves the cycle ability and cycle life of LIBs.[26] These additives are mainly ions, organics, inorganic salts and metals. Electrolyte additives improve electrolyte, cathode, and anode performance, and their effects on each component are detailed below.

2.2.1. Improvement of electrolyte properties by electrolyte additives

The aqueous electrolyte, as one of the important components of the ARBs, provides the basic operating environment to ensure the transport of Zn^{2+} ions between the two electrodes during charging and discharging and determines the ESW. The ion transport characteristics and ESW of the electrolyte are crucial elements in determining the multiplicity performance and energy density of the battery, so the study of the electrolyte is necessary. Electrolyte additives improved electrolyte properties can mainly be attributed to the following aspects: (1) enhance ion transport properties, (2) widen the ESW, (3) form a solid electrolyte interfacial film.[27]

Ion transport characteristic is a primeval characteristic of the electrolyte, and the conductivity of the electrolyte reflects the ability to transport ions in solution, which directly affects the

multiplication performance of the ARBs. The conductivity of the electrolyte is relevant to the type of solution, and the type and number of solute ions. In a strong electrolyte solution, according to Kohlrausch's Law, the equation can be introduced.

$$\kappa = c(v_+ \lambda_+^0 + v_- \lambda_-^0) \tag{1}$$

The v_+ and v_- are the number of moles of cation and anion dissociated by dissolving 1 mole of electrolyte respectively, λ_+^0 and λ_-^0 are the limiting molar conductivity of cations and anions, from which it can be seen that electrolyte additives can strengthen ion transport performance by changing ion concentration, cation and anion types to improve ion conductivity.[27] For example, the ionic conductivity can be enhanced by adding Mn^{2+} additives. The classic case reported by Chen et al. in 2017 confirmed that the addition of Mn^{2+} improves the initial coulombic efficiency and ionic conductivity of the electrolyte.[28] They selected $Mn(CF_3SO_3)_2$ as the electrolyte additive and found that the optimized electrolyte composition was 3 M $Zn(CF_3SO_4)_2$ + 0.1 M $Mn(CFO_3)_2$, which had high coulombic efficiency and ionic conductivity. The results of Zn-MnO_2 cells with different electrolytes were also investigated by using 3 M $Zn(CF_3SO_3)_2$ + 0. 1 M $MnSO_4$ electrolyte. The initial discharge capacity (205 mAh g^{-1}) of battery was higher than that in 3 M $ZnSO_4$ + 0.1 M $MnSO_4$ electrolyte (110 mAh g^{-1}). This shows that changing the ionic species also changes the battery capacity. Based on the above theory and research, it can be seen that ionic additives can improve ionic conductivity by changing the ion type and number, such as Na^+[29], Mg^{2+}[30], Co^{3+}.[31]

Aqueous electrolyte have limitations in their application, mainly in terms of their narrow ESW(1.23 V), which constrain the operating voltage and leads to lower energy storage density. Exceeding this ESW cause water decompose and produce hydrogen and oxygen, further causing battery expansion, structural damage, and affecting cycle life. For this reason, increasing the oxygen evolution potential and decreasing the hydrogen evolution potential has become one of the main avenues for improvement. For example, the addition of ionic additives with redox-competing properties can inhibit the oxygen evolution reaction (OER) and widen the ESW. In 2019, Qiao et al. successfully fabricated a novel Zn-MnO_2 battery using the unique two-electron redox reaction of Mn^{4+}/Mn^{2+}, which has a high output voltage of 1.95 V, and an imposing gravimetric capacity of about 570 mAh g^{-1}.[32] The second approach is altering the interface between the electrode and the electrolyte with additives that form a hydrophobic layer to reduce the contact between water and the electrode, thereby expanding the electrochemical stabilization window. For example, Hou and his team added sodium dodecyl sulfate (SDS) to a full cell assembled with a zinc anode and a $Na_2MnFe(CN)_6$ cathode in 2017.[33] Experimental results showed that this full cell had a highly efficient coulombic efficiency and a low self-discharge rate, allowing the electrolyte's ESW to be expanded to ~2.5 V. According to the measured wetting Angle of the electrode, SDS is adsorbed on the surface of the electrode by electrostatic adsorption, and its hydrophilic group faces the electrode and its hydrophobic group faces the medium. It

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effectively restricts the water molecules in contact with the electrode, thus inhibiting the generation of oxygen and hydrogen. During charging, this surfactant prevents zinc corrosion and dendritic crystal formation, preventing serious short-circuits. At the same time, this additive inhibited the dissolution of manganese and maintained the stable structure of $Na_2MnFe(CN)_6$, improving the battery cycle life. Additional studies have shown that changing the solvation structure of the electrolyte can similarly extend the ESW of water. For example, by adding Al^{3+} to AZIBs, Al^{3+} reacts with H_2O to form layered Al_xMnO_2-nH_2O, which prevents the production of oxygen and hydrogen.[34] This substance prevents the production of oxygen and hydrogen, enlarges the ESW from 1.5 V to 1.9 V, helps to obtain higher discharge voltage and higher energy density, and improves cycle stability. In summary, additives can broaden the ESW in three ways, competing for electrons through their redox reactions; changing the electrode/electrolyte boundary; and changing the electrolyte solvation structure.

Many side reactions occur during battery charging and discharging: cathode dissolution, anode passivation and electrolyte decomposition. At present, several research teams have developed additives that can form solid electrolyte interfaces(SEI) to inhibit side reactions, such as SO_4^{2-},[35] KPF_6,[36] $Zn(H_2PO_4)_2^-$,[37] trimethylethyl ammonium trifluoro-methanesulfonate ($Me_3EtNOTF$).[38]

2.2.2. Improvement of anode

Despite zinc metal as an anode material have many advantages in ARBs, several side reactions of zinc seriously affect the cell's coulombic efficiency, capacity, and lifetime. The main problems that need to be addressed are zinc dendrite growth, hydrogen evolution reactions (HER), zinc corrosion and passivation.[27] Therefore, it is essential to modify zinc anode materials with additives to alleviate these problems and obtain better-performing AZIBs.

2.2.2.1. Modulation of zinc dendrite formation

In aqueous zinc ion batteries, the anode has a Zn/Zn^{2+} ion pair, and during charging, Zn^{2+} receives two electrons to convert into Zn deposits on the anode. While under discharging, Zn releases two electrons to convert into soluble Zn^{2+}. During battery operation, with uneven Zn deposition, dendrites grow in the high deposition region, which not only result in low coulombic efficiency, poor cycle performance, and even battery short-circuiting, but also promotes the occurrence of side reactions due to the increase in anode surface area.[39] In the past, protective layers such as ultrathin TiO_2 film[40] and nanoporous $CaCO_3$ coatings[41] have often been introduced to not only avoid direct contact between the zinc plate and the electrolyte but also inhibit gas precipitation and the formation of the less conductive $Zn(OH)_2$.

The anode was later protected by introducing polar ions or molecules to form an electrostatic shielding effect, such as

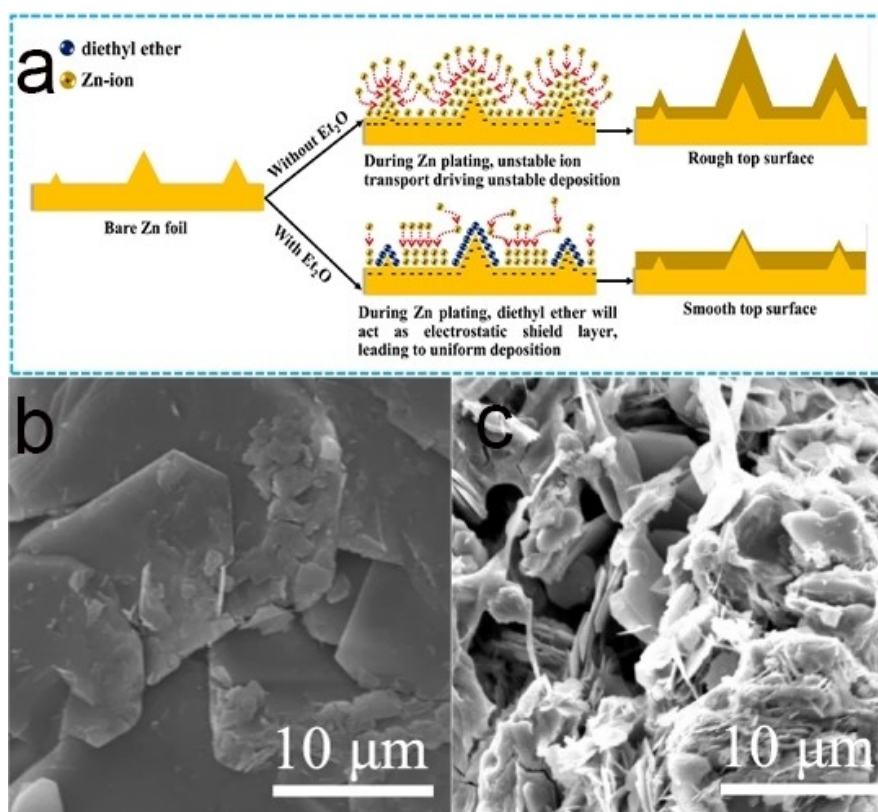Na^+,[29] diethyl ether,[42] eco-friendly silk peptide additive.[43] Before Zn^{2+} deposition, the surface of the zinc plate has a certain roughness. After starting deposition, protruding tips inevitably appear and these tips exhibit higher electric field strength, leading to the fastest ion deposition, which is the principle of dendrite growth. As schematically shown in Figure 2a, by adding a small amount of polar ions or molecules to the electrolyte, highly polarized polar molecules will be preferentially adsorbed to the tip surface under the action of the electric field to form a positively charged protective shell. Through the electrostatic shielding effect, Zn^{2+} can be prevented from further deposition to the tip area, which inhibits the dendrite growth, promotes the transfer of Zn^{2+} deposition to the uncovered area, and keeps the surface of the zinc plate flat.[42] Obviously, the smoothness of the zinc plate affects the electron transfer on the anode surface, so the addition of polar ions or molecules plays an important role in improving the coulombic efficiency and capacity.

Inhibiting the growth of zinc dendrites can also increase the nucleation rate by increasing the deposition overpotential of Zn and inhibiting the two-dimensional diffusion of Zn^{2+} on the anode surface. Although increasing Zn^{2+} deposition potential is not conducive to Zn^{2+} deposition, it actually has less of an effect and instead facilitates the increase in the number and rate of nucleation thereby inhibiting dendrite growth. For example, surfactants(FC-170 C, CTAB, tetramethylammonium sulfate hydrate (TMA_2SO_4),[44] and ionic liquids (imidazolium ionic liquids (ILs))[45] can increase the deposition potential.

In addition, several additives have been used to inhibit the two-dimensional diffusion of Zn^{2+} at the anode, such as $PEG200$,[46] TBA_2SO_4,[47] and acrylamide (AM).[36] A recent report found that acrylamide monomers absorbed on the surface of zinc foils catalyzed by zinc can polymerize into a cross-linked polyacrylamide (PAM) polymer layer before zinc deposition. The PAM polymer layer with abundant polar amide groups was strongly coordinated with the zinc ions, limiting the free movement of the zinc ions, inhibiting dendrite growth, and improving the coulombic efficiency and long-term cycling stability of the cell.[36]

However, in the past research on how to inhibit dendrite growth, the focus is often placed on the plating process, and the stripping process of zinc metal anodes is usually not considered. Recently, a work has demonstrated that the stability of Zn anodes is not only affected by the operating conditions but also by the initial stripping/plating. Zn electrodes that were initially plated in the first cycle exhibited a more uniform morphology in subsequent cycles. On the contrary, for the initially stripped Zn electrodes, severe dendrites were formed at the pit locations. After 1000 h cycling that of at 5 mA cm^{-2}, the PD–Zn electrode shows a uniform morphology with blocks of hexagonal lamellae (Figure 2b). However, the non-predeposited Zn electrode shows a dendritic morphology (Figure 2c). Based on the above analysis, a pre-deposited zinc anode (PD–Zn) is proposed to induce uniform zinc plating/stripping, e.g., by adding 0.05 M KPF_6 to the electrolyte, and the cell shows an extended life of more than 1000 h.[48]

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Figure 2. (a) During Zn plating, morphologic evolution of zinc anodes in mild aqueous electrolytes with and without Et_2O additives.[43] (b) The Pd—Zn electrodes showed a homogeneous morphology after 1000 h cycling. (c) The dendritic morphology of the non-predeposited zinc electrode after 360 h cycling.[49]

The modulation of surface texture is also a factor affecting zinc deposition, and zinc surface texture has a vital impact on the surface morphology of the zinc anode, which determines the direction of dendrite growth and corrosion resistance. The effect of crystal orientation on zinc dendrite growth can be summarized according to Chen et al.'s report and is summarized in Table 1.[49] Since the (002) surface is the lowest energy close-packed crystal surface, increasing the ratio of the (002) crystal surface can successfully inhibit the occurrence of side reactions such as dendrites, and typical additives are indium sulfate, tin oxide, and boric acid, at which time the zinc anode has higher corrosion resistance.

In general, the main methods of using additives to modulate zinc deposition include the introduction of a protective layer, the use of electrostatic shielding mechanisms, the enhancement of the nucleation rate, pre-deposition, and the modulation of the surface weave, which all provide effective ideas for improving zinc anodic deposition.

2.2.2.2. Inhibit the occurrence of side effects

Zinc anode side reactions are mainly corrosion, passivation and HER. At present, several research teams have developed additives that can form solid electrolyte interfaces(SEI) to inhibit side reactions, such as SO_4^{2-},[35] KPF_6,[50] $Zn(H_2PO_4)_2$,[37] trimethy-

lethyl ammonium trifluoro-methanesulfonate ($Me_3EtNOTF$).[38] The most representative of these is the innovation of Zeng and colleagues to simply add a small amount of Zn ($H_2PO_4)_2$ to a conventional aqueous electrolyte (1 M Zn ($CF_3SO_3)_2$).[37] By utilizing the local pH changes caused by hydrogen evolution, a compact Zn^{2+} conductive film ($Zn_3(PO_4)_2 \cdot 4H_2O$) can be formed on the Zn surface. Zeng's team have demonstrated that the SEI layer stabilizes the Zn-electrolyte interface through guiding dendrite-free Zn plating/stripping and inhibiting continuous consumption of both Zn and aqueous electrolyte during cycling. The new in situ interfacial design provides an innovative strategy for implementing practical high-performance AZIBs. Passivation of the zinc anode mainly inhibits the stripping of Zn^{2+} from the zinc negative electrode, thus limiting the discharge capacity. Classic additives such as ethanol molecules and sodium dodecylbenzene sulfonate (SDBS) can make a big difference in this regard. Ethanol additives enhance the dissolution of zinc and impede the passivation of the zinc negative electrode, thus increasing the discharge capacity,[51] while SDBS additives cause a porous structure on the zinc surface, thus inhibiting the passivation.[52]

In addition, the HER also has a significant impact on battery life, hydrogen release leads to battery expansion, causing electrolyte leakage or even battery failure.

The reaction can be inhibited by increasing the HER potential, so the commonly used additives are tartaric acid,

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succinic acid, phosphoric acid, citric acid, and other acid additives.[53] In addition, hydrogen evolution can be inhibited by additives such as glycine to reduce the content of solvated water.[54]

2.2.3. Improvement of cathode

The commonly used cathode materials for AZIBs are vanadium oxide (V_2O_5) and manganese dioxide (MnO_2). However, the unstable cathode materials due to the dissolution of V and Mn cause a poor rate capacity and poor cycling stability of AZIBs. The dissolution of Mn can be inhibited by adjusting the equilibrium reaction and film forming mechanism between cathode and electrolyte with additives. Studies have shown that the 0.1 M Mn^{2+} additive can maintain the dissolution/oxidation balance, so that the active substance is difficulty dissolved in the electrolyte, protecting the cathode and reducing capacity loss. Based on scientific experiments and equation calculations, the content of Mn^{2+} additive also affects the stability level. For example, in 2 M $ZnSO_4$ electrolyte, the increase of Mn^{2+} concentration will improve the capacity and stability of MnO_2/C—Zn battery, and the best performance will be achieved when the concentration of $MnSO_4$ reaches 0.5 M.[55]

The protection mechanism of vanadium-based cathode in aqueous zinc ion batteries is discussed next. Some additives inhibit cathode dissolution by altering the dissolution equilibrium of the cathode material. For example, adding $MgSO_4$ additive to $Mg_xV_2O_5 \cdot nH_2O$ cathode can not only inhibit the dissolution of $Mg_xV_2O_5 \cdot nH_2O$ by changing the Mg^{2+} dissolution equilibrium of $MgxV_2O_5 \cdot nH_2O$ cathode, but also can insert Mg^{2+} into the vanadium oxide layer to play a "pillar effect", which maintain the stability of $Mg_xV_2O_5 \cdot nH_2O$ structure.[30] In addition, the solvation structure also affects the stability of the cathode. Strong ligand additives (such as urea) reduce the intercalation of water molecules and reduce the damage degree of the cathode structure.[56]

The application of electrolyte additives is not only of great significance in AZIBs but also has a wide range of application prospects in other types of batteries. Through continuous research and innovation, we believe that electrolyte additives can make a greater contribution to the future development of energy storage technology and contribute to the success of promoting the development of the clean energy industry.

2.3. Hydrogel electrolytes

Gel electrolytes are formed by colloidal particles or polymers solidifying in sol or solution under specific conditions, maintaining a spatial reticular structure, a state that allows them to maintain their original structure even when absorbing liquid solutions. The gel electrolyte, which is between liquid and solid, has the characteristics of high ion mobility, good flexibility, lightness and superior adhesion. Hydrogels are typical of these, synthesized by cross-linking, dual network cross-linking and self-assembly. Depending on the source, they are categorized

into synthetic polymer hydrogels and natural polymer hydrogels. Natural sources have good biocompatibility and abundant reserves, but usually have poor mechanical properties and are unstable.[57] In contrast, synthetic polymer hydrogels exhibit good stability and designability due to controlled physical or chemical processes. Hydrogels have excellent salt solubility and flowability, which stems from their excellent water absorption. Synthesis methods include physical and chemical cross-linking. Physical cross-linking forms clusters with homogeneity defects, while chemical cross-linking forms stable covalent bonds with thermal stability. These properties are important in electrolyte design. Gelatin-based hydrogel electrolyte (GHE) is classical gel electrolytes utilizing physical cross-linking. In the gelatin hydrogel system, the physical crosslinking points are provided by the hydrogen bonds present between the -OH, -CO and -NH groups. Due to their special shape and structure, GHEs are effective in avoiding electrolyte leakage and preventing short circuits in AZIBs.[58]

However, hydrogel electrolytes through physical cross-linking show poor thermal stability, so the development of hydrogel electrolytes with chemical cross-linking is more promising. Polyacrylamide (PAM)-based chemically cross-linked hydrogels are the most promising electrolytes. In the PAM hydrogel matrix, cross-linking points are present between all chain segments, resulting in a highly porous framework (Figure 3a).[59] Due to the backbone structure connected by chain segments, PAM hydrogel electrolytes exhibit excellent mechanical properties. In addition, the electrochemical properties of hydrogel electrolytes can be improved by modifying the functional groups on the framework. For example, the hydroxyl groups in nanofibrillated cellulose (NFC) readily form hydrogen bonds with water molecules, which enhances the water retention in NFC/PAM hydrogel electrolytes, resulting in a more porous backbone structure.[60]

It is possible to improve the ionic conductivity of electrolytes by incorporating hydrogels with a three-dimensional mesh structure which contain many adsorption sites and a large amount of water (typically 300%).[61] However, since hydrogels containing a large amount of liquid electrolyte (typically 300w%) are only considered as quasi-solid electrolytes, they tend to dehydrate easily when exposed to the environment and have poor mechanical strength. Batteries are prone to failure under dehydration and severe external deformation. In order to improve its mechanical strength, a functional dual-network hydrogel electrolyte (FDHE) was developed, where the unique poly-2-acrylamide-2-methylpropanesulfonic acid/polyacrylamide (PAMPS/PAAM) structure provides strong mechanical properties. Meanwhile, dimethyl sulfoxide additives as H-acceptor and solvation modifier were incorporated during the synthesis of FDHE, which not only inhibited the side reactions by decreasing the activity of free water but also reduced the desolvation energy barriers by modulating the solvation structure of Zn^{2+}.[62]

In addition, gel electrolytes is instrumental in the fabrication of flexible batteries due to their excellent physical flexibility, superior electrochemical properties, and complete mechanical properties. Typical examples are quasi-solid-state fibrous zinc-
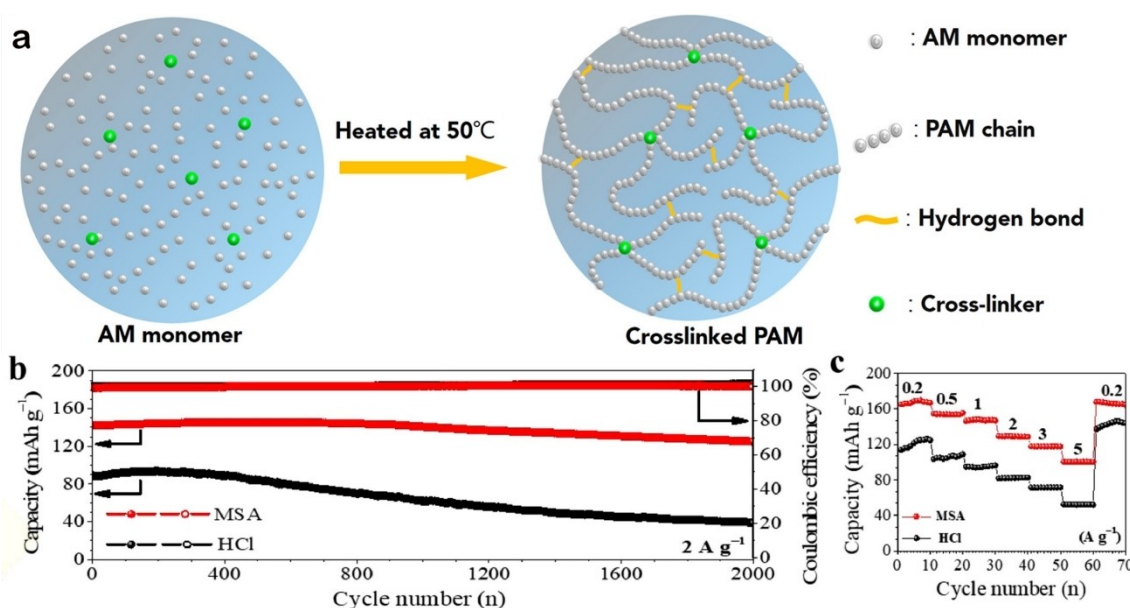
Figure 3. (a)The formation of the cross-linked PAM-based electrolyte.[60] (b) and (c) show the difference between cycling performance of Fs-ZPB$_{MSA}$ and Fs-ZPB$_{HCl}$.

polyaniline batteries(Fs-ZPBs) with methanesulfonic acid-filled poly(vinyl alcohol)-based gel-type electrolytes.[63] Fs-ZPBs with methylsulfonic acid (Fs-ZPB$_{MSA}$)showed a high initial discharge capacity of 141.9 mAh g^{-1} and a high capacity retention rate of 88% for 2000 cycles(Figure 3b). On the contrary, the Fs-ZPB with HCl (Fs-ZPB$_{HCl}$) exhibit a low initial discharge capacity of 89.0 mAh g^{-1} and exhibit a rapid capacity decay (capacity retention rate = 43%). Moreover, Fs-ZPB$_{MSA}$ have a higher power density. Because at a current of 5 A g^{-1}, Fs-ZPB$_{MSA}$ delivered high capacity of 100.3 mAh g^{-1}(Figure 3c). The methanesulfonic acid connects the polyvinyl alcohol chains through intermolecular hydrogen bonding, forming an effective connection to the polyaniline surface and the electrolyte. As a result of this connection, the electrolyte is more ionic conductive and facilitates charge transfer between the polyaniline and electrolyte. The larger size of the methanesulfonic acid molecule prevents the entry of water into the active materials (polyaniline and Zn) but allows for doping of the Cl$^-$ anion. This dual anion doping and water trapping inhibited the degradation of polyaniline and corrosion of Zn, leading to excellent cell performance. According to flexural testing, capacity remained at 88.1% after 2000 cycles and capacitance remained at 92.7% after 500 cycles.[63] This study provides a new avenue for innovation in flexible energy storage systems.

2.4. Other ways to improve electrolyte

In addition to the three new electrolyte concepts discussed above, there are a number of ways to improve the performance of electrolytes, such as pH management, hybridized solvent electrolytes, and interface tuning. The pH of aqueous electrolytes affects the redox potential and even the reaction mechanism of the electrodes, thus affecting the stability and

operating voltage of the whole battery, which is an important step to overcome the drawbacks of ARBs. Therefore, people have improved these problems by modulating the pH to inhibit anodic oxidation and influence the electrode working potential, or using double PH decoupling electrolytes.[64] In addition, to improve the battery cycling stability, people also improve the formation of electrode/electrolyte interface by mixing solvents, respectively, LiTFSI WiSE and organic (non protonic) solvents, ionic liquids, and low freezing point solvents.[65]

For example, a mixed electrolyte is prepared by mixing 7 M NaOTf in water and 8 M NaOTF in propylidene carbonate (PC). This hybrid electrolyte provides a wide ESW of up to 2.8 V at 20 °C stainless steel, from -1.25 to 1.55 V compared to Ag/AgClKCl.[66] Aqueous electrolytes present superior interfacial dynamics and wettability but are deficient in chemical and thermal stability, so it is crucial to address this issue by modulating the solid electrolyte interface and the cathode electrolyte interface. According to the study, it was found that it can be solved by regulating the solid electrolyte interface and cathode electrolyte interface. Examples include in-situ construction of SEI, pre-coating of SEI/protective layer (HFE-PEO protective gel), and formation of in-situ CEI coating on the surface.[67] The in-depth understanding of electrolyte properties and further development of interface modulation techniques will drive innovation in electrochemical energy storage, improve the energy density and stability of batteries, and promote their application in fields such as renewable energy and portable devices.

3. Summary and Outlook

Aqueous energy storage systems have attracted the attention and research of many scientists as a potential energy storage

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solution. However, its narrow ESW, frequent side reactions, and restricted temperature range of use have become key challenges that limit its large-scale application. To cope with these problems, scientists have proposed a variety of improvement methods, including electrolyte additives, WiSE, and gel electrolytes. The principles of these methods mostly focus on regulating the redox potential, forming an interfacial protective film, and adjusting the solvation structure. By these means, the performance of aqueous batteries, such as cycle stability, energy density, and coulombic efficiency, has been significantly improved. However, despite the success achieved in the laboratory stage, there are limitations in the theoretical research, while the practical application will face a more complicated situation. Considering the production cost, manufacturing difficulty, and other practical factors, aqueous energy storage systems still need to overcome a series of challenges before large-scale application. Among them, the commercial feasibility and stability of electrolyte additives and new electrolyte concepts still need to be further verified. Meanwhile, technical challenges in the preparation process and production scale-up also need to be addressed.

Nevertheless, through the continuous development of novel electrolyte concepts, aqueous energy storage systems have taken an important step forward. In the future, we can expect more research results on material design, process improvement, and environmentally friendly aqueous batteries. With the advancement of technology and innovation, we believe that these challenges will be gradually overcome, paving the way for the widespread application of aqueous energy storage systems.

Acknowledgements

Conflict of Interests

The authors declare no conflict of interest.

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