Issues and rational design of aqueous electrolyte for Zn-ion batteries

Qi Zhang¹,## | Zefang Yang¹,## | Huimin Ji¹ | Xiaohui Zeng² | Yougen Tang¹ | Dan Sun¹ | Haiyan Wang¹

¹ Hunan Provincial Key Laboratory of Chemical Power Sources, College of Chemistry and Chemical Engineering, Central South University, Changsha, P. R. China
² Institute for Superconducting and Electronic Materials (ISEM), Australian Institute for Innovative Materials (AIIM), University of Wollongong, Wollongong, New South Wales, Australia

Correspondence
Haiyan Wang, Hunan Provincial Key Laboratory of Chemical Power Sources, College of Chemistry and Chemical Engineering, Central South University, Changsha, 410083, P. R. China.
Email: wanghy419@csu.edu.cn

#Qi Zhang and Zefang Yang contributed equally to this work.

Funding information
the National Nature Science Foundation of China, Grant/Award Numbers: 21975289, U19A2019; Hunan Provincial Research and Development Plan in Key Areas, Grant/Award Number: 2019GK2033; Hunan Provincial Science and Technology Plan Project of China, Grant/Award Numbers: 2017TP1001, 2020JJ2042, 2018RS3009

Abstract
Aqueous Zn-ion batteries (AZIBs) are regarded as a promising alternative to the widely used lithium-ion batteries in large-scale energy storage systems. The researches on the development of novel aqueous electrolyte to improve battery performance have also attracted great interest since the electrolyte is a key component for Zn^{2+} migration between cathode and anode. Herein, we briefly summarized and illuminated the recent development tendency of aqueous electrolyte for AZIBs, then deeply analyzed its existing issues (water decomposition, cathode dissolution, corrosion and passivation, and dendrite growth) and discussed the corresponding optimization strategies (pH regulation, concentrated salt solution, electrolyte composition design, and functional additives). The internal mechanisms of these strategies were further revealed and the relationships between issues and solutions were clarified, which could guide the future development of aqueous electrolytes for AZIBs.

KEYWORDS
aqueous electrolyte, dendrite growth, rational design, water decomposition, Zn-ion batteries

1 | INTRODUCTION

A large-scale energy storage system (ESS) has attracted widespread research interests in recent years because it can be used as a medium to regulate the unstable power generation from renewable energy resources (e.g., solar, wind, and tide).¹ However, the widely used lithium-ion batteries are not very suitable for large-scale ESS which focuses more on low cost and high safety.² Zn is a nontoxic and high-abundance metal with high theoretical capacity (820 mAh g⁻¹) and low electrochemical potential (−0.76 V vs. standard hydrogen electrode).³ Rechargeable aqueous Zn batteries using a nonflammable aqueous electrolyte and easily available Zn anode show broad application prospects in large-scale ESS. Traditional alkaline Zn batteries (e.g., Zn-Mn and Zn-Ni batteries) are

This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

© 2021 The Authors. SusMat published by Sichuan University and John Wiley & Sons Australia, Ltd.
FIGURE 1 The increasing number of publications on aqueous Zn-ion battery searched by Web of Science with the keywords: “Aqueous Zn-ion battery,” “Aqueous Zn-ion battery + cathode,” “Aqueous Zn-ion battery + anode,” and “Aqueous Zn-ion battery + electrolyte”

based on Zn dissolution/precipitation at the anode (Zn + 4OH− ↔ Zn(OH)42− + 2e− ↔ ZnO + 2OH− + H2O + 2e−) and proton intercalation/extraction at the cathode (MnO2 + H2O + e− ↔ MnOOH + OH− or NiOOH + H2O + e− ↔ Ni(OH)2 + OH−), which were successfully commercialized and widely applied in many devices.4 However, it is hard to realize a long-term stable charge and discharge operation for these alkaline Zn batteries due to the formation of passivation layers on anode surface and the spontaneous hydrogen evolution in alkaline electrolytes.5

Aqueous Zn-ion batteries (AZIBs) worked in neutral or mildly acidic electrolytes were first proposed by Kang et al. in 2011 and have developed rapidly these years.6 Most of the cathodes of AZIBs are Mn-based oxides, V-based oxides, and Prussian blue analogs which can reversibly insert or extract Zn2+ and the common anodes are Zn foils or Zn-containing compounds which can provide reversible Zn2+ by plating and stripping.7–9 As an important component connecting the cathode and anode by ion transmission, the electrolyte has also been studied to improve the electrochemical performance of AZIBs. Figure 1 clearly shows the increasing research interests in each component of AZIBs (cathode, anode, and electrolyte).

Although AZIBs exhibit smaller hydrogen evolution and less passivation effect compared with alkaline Zn batteries, there still are some crucial issues needed to be solved for their practical applications when using aqueous Zn salt solution as the electrolyte.10 The modification approaches for electrolyte mostly belong to the following two aspects: increasing salt concentration and introducing functional additives.11–14 Up to now, there is no instructional guideline to include all of them since these researches appear to be independent or even contradictory and the internal mechanisms of the interactions between electrolytes and electrodes remain unclear. Relevant published reviews only describe the current status of the modification methods for electrolytes in AZIBs but the existing issues and their potential solutions are seldom discussed.15,16

In this review, we aim at elucidating the relationship between modification approaches and practical issues such as electrolyte decomposition, cathode dissolution, anode corrosion, hydrogen evolution, byproduct generation, and dendrite growth. We briefly review the research progress of electrolytes for AZIBs and then emphatically analyze the modification mechanisms of the current methods for solving specific issues. Finally, we summarized the remaining challenges and present several pieces of advice toward the rational design of aqueous electrolytes for Zn-ion batteries.

2 DEVELOPMENT OF ELECTROLYTES FOR AZIBS

The normal electrolyte for AZIBs is composed of water as the solvent and some Zn-containing salts as the solute. The low decomposition voltage of water solvent results in a narrow electrochemical window for stable operation in AZIBs, which greatly hinders the application of high-voltage cathodes and confines the energy density of batteries at a low level.17 Some researches focus on the modification of solvent to expand the electrochemical window of aqueous electrolytes such as altering acidity, introducing surfactants, or mixing the aqueous solvent with organics.18–20 It is worth noting that the pure organic solvent can eliminate water-related side reactions and simplify the electrochemical redox reactions.21–23 However, organic electrolytes show lower ionic conductivity than aqueous electrolytes, resulting in the inferior high-rate performance of batteries and the difficulty to respond quickly to the sudden change in the electricity generation from the unstable new energy resources. Besides, most organics are expensive, toxic, and flammable, which seem neither safe nor environmental friendly.24 Unless the above fatal problems in organic electrolytes are solved, aqueous electrolytes are still the most suitable choice for large-scale ESS. Pure organic electrolytes for Zn-ion batteries are outside the scope of this review.

Various Zn salts have been applied in the electrolyte of AZIBs such as Zn(NO3)2, ZnCl2, ZnSO4, Zn(CF3SO3)2, Zn(CH3COO)2, and Zn(ClO4)2, ZnF2. However, many of these solutes are not quite appropriate in a practical AZIB system. For example, the properties of both anode and cathode may be deteriorated by the strong oxidizing nitrate ions in Zn(NO3)2,25 the anodic potential window is excessively narrow in ZnCl2,26 Zn(CH3COO)2 exhibits low ionic...
conductivity due to its incomplete ionization. ZnO passivation layer formed on anode surface leads to a large polarization during cycling in Zn(ClO$_4$)$_2$ and ZnF$_2$ is limited by its low water solubility. ZnSO$_4$ and Zn(CF$_3$SO$_3$)$_2$ are considered to be feasible solutes because they can meet the basic requirements of good solubility, high ionic conductivity, low polarization, high stability, and no negative influence on the electrode performance. ZnSO$_4$ is the most widely used solute in the electrolyte for AZIBs owing to its low cost, but the electrochemical performance of AZIBs using ZnSO$_4$ electrolyte is worse in comparison with Zn(CF$_3$SO$_3$)$_2$ electrolyte which exhibits better reversibility and faster Zn$^{2+}$ transport kinetics. These improvements of Zn(CF$_3$SO$_3$)$_2$ electrolytes can be ascribed to the reduced solvation effect by the less contact between water molecules and Zn$^{2+}$. However, Zn(CF$_3$SO$_3$)$_2$ is about 15 times more expensive than ZnSO$_4$, which is a disadvantage of its application in large-scale ESS. The salt concentration is also a key factor in the properties of the aqueous electrolyte. The higher salt concentration can effectively increase the Coulombic efficiency and operating stability of the battery by reducing water activity and the meliorative transport behavior of both cations and anions. A novel ultra-concentrated electrolyte named “water-in-salt” with Zn salt as the main component was proposed recently. In this electrolyte, the Zn$^{2+}$ solvation sheath is composed of the anions in the Zn salt instead of water molecules. Besides, the gel electrolyte with a unique crosslink polymer structure can confine the free water in the network, which is a promising alternative to the liquid aqueous electrolyte. Both “water-in-salt” electrolyte and gel electrolyte can reduce the activity of water to mitigate some water-related side reactions. Their special properties offer a new direction for the development of aqueous electrolyte.

Electrolytes can also affect the electrode interface in direct contact. The main issues are as follows: (1) Cathode dissolution. Some slightly water-soluble cathode materials suffer from the rapid capacity fading by their continuous dissolution. (2) Corrosion, hydrogen evolution, and by-product generation. The hydrogen evolution easily occurs in the weakly acidic Zn aqueous solutions and the increase of pH value can induce the by-product generation during the discharge process. (3) Dendrite growth. The uneven distribution of electrons and ions tends to promote dendrite growth on the anode surface. A series of functional additives (e.g., surfactants, inorganic salt, and Zn-oriented organics) have been developed to address these issues related to the electrodes. These additives can alter the electrochemical behavior of water or Zn$^{2+}$ at the solid-liquid interface to stabilize the electrodes and avoid side reactions.

### 3. ISSUES, SOLUTIONS, AND MECHANISMS

The current issues and corresponding solutions of AZIBs are shown in Figure 2. Note that one problem usually corresponds to multiple solutions and one strategy can also solve multiple problems. Different issues and methods are interrelated, which needs to be further clarified. In this part, these electrolyte modification methods and their internal mechanisms will be classified and analyzed in detail from the review of solving specific issues.

#### 3.1 Water decomposition

The thermodynamic decomposition voltage of water is only 1.23 V corresponding to the hydrogen and oxygen evolution reactions (OERs) (2H$_2$O $\rightarrow$ 2H$_2$↑ + O$_2$↑). When the AZIBs work at excessive voltage, the continuous gas generation increases the internal pressure and eventually bursts the sealed battery from inside. Water decomposition occurs at about 2 V in practice due to the overpotential caused by the slow reaction kinetics of oxygen evolution involving the multielectron transfer process. Nevertheless, the operating voltage is still limited and the energy density of AZIBs is insufficient which is far lower than that of non-aqueous batteries. The specific water decomposition voltage which can achieve enough gas generation rate to affect the battery performance depends on the pH value and the composition of electrolytes. These are also the two main aspects of current researches to expand the voltage range for water stabilization.

The theoretical decomposition voltage of water is independent of pH value but the decrease in pH value of the electrolyte positively shifts the potentials of both hydrogen evolution reaction (HER) (1), and oxygen evolution reaction (OER) (2). HER is insensitive to pH change because it can easily occur when the impressed voltage is slightly higher than the theoretical decomposition voltage of water due to its simple reaction process and low thermodynamic cost. However, the positive shift in potential results in the higher OER overpotential, thus, increases the actual water decomposition voltage. The water decomposition voltage at different pH values is shown in Figure 3A. Qiao et al. investigated the impact of pH value on the electrochemical properties of Zn-MnO$_2$ cells. The potentials of HER and OER are significantly suppressed to ≈1.06 and 1.35 V (vs. Ag/AgCl) when 0.1 M H$_2$SO$_4$ was added to the electrolyte, corresponding to a maximum stable operating voltage of 2.41 V (Figure 3B). The higher OER potential in the weakly acidic electrolyte can also ensure the full oxidation...
The current issues and the corresponding solutions using electrolyte engineering of AZIBs

**Figure 2**

The expanded electrochemical window. (A) The comparison of the electrochemical window in the neutral electrolyte (1 M K$_2$SO$_4$), acid electrolyte (0.5 M K$_2$SO$_4$ + 0.5 M H$_2$SO$_4$), and alkaline electrolyte (2 M KOH). Reproduced with permission from Ref. [44] Copyright 2019, Elsevier. (B) The expanded operating voltage of the Zn-MnO$_2$ battery with the addition of 0.1 M H$_2$SO$_4$. (C) Electrochemical performance of Zn-Zn symmetric cells cycled in the electrolytes with 0.10, 0.15, and 0.30 M H$_2$SO$_4$ at 20 mA/cm$^2$. Reproduced with permission from Ref. [18] Copyright 2019, John Wiley and Sons Ltd

of the MnO$_2$ cathode. It is found that the symmetric cell displays poor reversibility in the excessive acidic electrolyte (Figure 3C) since the non-negligible HER is accompanied during the Zn electrodeposition. HER even occurs spontaneously in the acidic AZIBs and the excessive acidic environment can accelerate the Zn dissolution, which is the limitation of expanding the electrochemical window by pH alteration.

\[
2H^+ + 2e^- \rightarrow H_2 \uparrow \tag{1}
\]

\[
2H_2O - 4e^- \rightarrow O_2 \uparrow + 4H^+ \tag{2}
\]

The other way to expand the electrochemical window of electrolytes is by reducing the activity of water molecules. In the low-concentration normal electrolyte, most of the water molecules are dissociative and only a small portion integrates with ions to form the solvation sheath. When increasing salt concentration, more water molecules can participate in the solvation process, which can decrease the activity and increase the overpotential of water decomposition. Taking the concentrated NaClO$_4$/Zn(CF$_3$SO$_3$)$_2$ electrolyte as an example (Figure 4A), the electrochemical window can be significantly expanded in the Zn(CF$_3$SO$_3$)$_2$ electrolyte with high NaClO$_4$ concentration owing to the higher kinetic barrier of water molecules in solution sheath compared with free water molecules. The wide electrochemical window in the above method is achieved by reducing the activity of water molecules in the electrolyte. However, the additional demand for large amounts of salt will increase the cost and the resulting higher electrolyte density will also reduce the overall energy density of the battery. Some oxygen-containing chemical bond organic compounds can be employed as electrolyte additives to inhibit water reaction by constructing H-bond with water molecule, which can form strong and robust H-bond with water to reduce free water molecules, thus, suppressing hydrogen evolution in the wide voltage window. 1,2-dimethoxyethane (DME) additive with hydrophilic hydration ether oxygen was proposed to restrict HER in the Zn-salt electrolyte caused by dissociative solvent water molecules through Cui and coworkers (Figure 4B). As shown in Figure 4C, by virtue of the optimal concentration of DME in the aqueous electrolyte, the onset potential for HER in the weakly acidic electrolyte with 5 vol% DME additives was reduced to −1.20 V (vs. Ag/AgCl) in comparison with blank
The water decomposition performances. (A) CV curves were measured in the electrolytes containing NaClO₄ and Zn(CF₃SO₃)₂ with different concentrations. Reproduced with permission from Ref. [48] Copyright 2018, American Chemical Society. (B) Schematic illustration of suppressing water reactivity via constructing H-bonding with free water by adding low-concentration DME. (C) Electrochemical windows in 2 M ZnSO₄ solution with various volume fractions of DME. Reproduced with permission from Ref. [49] Copyright 2020, Elsevier. (D) The electrochemical window of blank electrolyte and the modified electrolyte with the addition of sodium dodecyl sulfate (SDS) at the critical micelle concentration (CMC). Reproduced with permission from Ref. [19] Copyright 2017, Royal Society of Chemistry.

electrolyte (−1.09 V). These results can be ascribed to the intensive connection between ether oxygen in DME additive and free water in aqueous electrolyte by H-bond. Plenty of water molecules can be bundled on the surroundings of DME to decrease active water participating in HER, which enables wide electrochemical window in the weakly acidic electrolyte for AZIBs. It is only necessary to limit the contact between water molecules and electrodes since the water decomposition occurs at the solid-liquid interface. Qian et al. proposed that the stable voltage window of the aqueous electrolyte could be extended to 2.5 V (Figure 4D) with the addition of sodium dodecyl sulfate (SDS) when its concentration reached the critical micelle concentration (CMC).¹⁹ SDS is a common surfactant whose hydrophilic groups tend to adsorb at the electrode surface and alkyl chains are vertically distributed to form a hydrophobic layer. It becomes more difficult for water molecules to contact the electrolyte because extra energy is required to allow the water molecules to penetrate the hydrophobic layer, which contributes to the extra overpotential for the evolution of hydrogen or oxygen.⁵⁰

In this section, we have discussed some promising methods to avoid water decomposition in the aqueous electrolyte. The expanding electrochemical window of AZIBs using electrolyte engineering is summarized in Table 1. A wide voltage window to maintain the inherent stability of aqueous solvent during the electrochemical process is a prerequisite for high-performance AZIBs. Some other issues caused by the interaction between electrolyte and electrode are more fatal, which may decrease the Coulombic efficiency and even induce battery failure. Therefore, suitable modification of electrolytes to match the cathode and anode is another key factor to achieve the long-term stability of AZIBs.
3.2 Cathode dissolution

Most of the cathodes or their intermediates generated during charge-discharge cycling are soluble in weakly acidic electrolytes of AZIBs, which may rapidly deteriorate the electrochemical performance due to the disorder of electrode structure. A common strategy for the inhibition of cathode dissolution in published literature is introducing some inorganic salts with the same element as cathodes into electrolytes in advance to adjust the dissolution equilibrium. For MnO₂ cathode, soluble Mn²⁺ is generated by the equilibrium reaction (3).

\[
\text{MnO}_2 + 2\text{H}_2\text{O} + 2\text{e}^- \leftrightarrow \text{Mn}^{2+} + 4\text{OH}^- \quad (3)
\]

For the above reversible reaction, its equilibrium constant at a certain temperature is expressed as Equation (4).

\[
K = \frac{a_{\text{Mn}^{2+}} \cdot a_{4\text{OH}^-}}{a_{\text{MnO}_2} \cdot a_{2\text{H}_2\text{O}}} \quad (4)
\]

where \(K\), \(a_{\text{Mn}^{2+}}\), \(a_{\text{OH}^-}\), \(a_{\text{MnO}_2}\), and \(a_{\text{H}_2\text{O}}\) represent chemical equilibrium constant, Mn²⁺ activity, OH⁻ activity, MnO₂ activity, and H₂O activity (10⁻⁵). Accordingly, the preaddition of MnSO₄ in the ZnSO₄ electrolyte can not only make the electrolyte reach the Mn²⁺ dissolution equilibrium before the electrochemical reaction to suppress MnO₂ dissolution but also prevent the formation of Zn²⁺ vacancies for Zn²⁺ insertion since excessive Zn²⁺ insertion may result in the unstable crystal structure. The redox behavior of MnO₂ cathode in ZnSO₄ electrolyte remains unchanged in comparison with the bare ZnSO₄ electrolyte, which indicates that no extra side reactions are introduced after the addition of MnSO₄ in the electrolyte (Figure 5A). The theoretical equilibrium concentration of Mn²⁺ is calculated to be 0.089 M. Therefore, the slightly excessive concentration (0.1 M) can effectively prevent MnO₂ dissolution and inhibit the capacity fading of the batteries (Figure 5B). Similar strategies can be also applied in the electrolyte modification to suppress the dissolution of V-based cathode. For example, Niu et al. reported that NaV₂O₅ could maintain a long-term stability when Na₂SO₄ was added into the ZnSO₄ electrolyte (Figure 5C). This improved performance can be ascribed to the altered dissolution equilibrium of NaV₂O₅ (Figure 5D).

“Water-in-salt” electrolyte is another strategy to inhibit cathode dissolution. As we discussed in the previous section, in the high-concentration salt solution, all the water molecules participate in the formation of the solvation sheath and bind firmly with ions so that there are no free water molecules to dissolve soluble intermediates from the cathode. It is considered that cathode dissolution can be more effectively suppressed by combining these two methods to simultaneously adjust the solubility equilibrium and reduce the activity of water molecules. Sun et al. developed the aqueous electrolyte containing 13 M ZnCl₂ and 0.8 M H₃PO₄ to prevent the dissolution of the VOPO₄ cathode. The result shows that the supernate is still colorless (Figure 5E) in the mixture of VOPO₄ powder and modified electrolyte and the P/V ratio (Figure 5F) of the residue remains unchanged after 3 days of maintenance, indicating that the cathode dissolution was completely inhibited.

A novel strategy to hinder anode dissolution is to transform dissolved ions into compounds suitable for Zn ion intercalation by pH regulation. It is well known that the dissolution of crystalline V₂O₅ in water strongly depends on the pH value and the content of V⁵⁺ species. As shown in Figure 5G, the dissolution reactions associated with different acidity and V⁵⁺ species are occurring as follows.

\[
\text{V}_2\text{O}_5 + 2\text{H}^+ \rightarrow 2\text{VO}_2^+ + \text{H}_2\text{O} \quad (5)
\]

\[
\text{V}_2\text{O}_5 + 3\text{H}_2\text{O} \rightarrow 2\text{VO}_2(\text{OH})_2^+ + 2\text{H}^+ \quad (6)
\]

The further reaction can happen in an aqueous solution with Zn salt.

\[
2\text{VO}_2(\text{OH})_2^- + 3\text{Zn}^+ + 3\text{H}_2\text{O} \rightarrow 2\text{Zn}_3\text{V}_2\text{O}_7(\text{OH})_2 \cdot 2\text{H}_2\text{O} + 4\text{H}^+ \quad (7)
\]

Lu et al. compared the change of pH value of several electrolytes after soaking with V₂O₅ powder such
FIGURE 5  The cathode dissolution tests. Comparison of CV (A) curves and (B) cycling performances of Zn-MnO$_2$ cells using normal ZnSO$_4$ electrolyte and ZnSO$_4$ electrolyte with MnSO$_4$ additive. Reproduced with permission from Ref. [36] Copyright 2016, Springer Nature. (C) The electrochemical performance of Zn-NaV$_3$O$_8$ cells cycled in ZnSO$_4$ and ZnSO$_4$/Na$_2$SO$_4$ electrolytes. (D) Change in color of ZnSO$_4$ and ZnSO$_4$/Na$_2$SO$_4$ electrolytes with NaV$_3$O$_8$ cathodes immersed. Reproduced with permission from Ref. [53] Copyright 2018, Springer Nature. (E) Digital photograph of supernate of the liquid mixed with VOPO$_4$ powder and different electrolytes after three days. (F) P/V ratios of the remaining VOPO$_4$ powder (A: 3 M Zn(OTf)$_2$, B: 3 m Zn(OTf)$_2$/0.8 M H$_3$PO$_4$, C: 13 M ZnCl$_2$/0.8 M H$_3$PO$_4$). Reproduced with permission from Ref. [54] Copyright 2019, John Wiley and Sons Ltd. (G) The pH-log[V$^{5+}$] plot in the V$_2$O$_5$-H$_2$O system. (H) Variation of pH value before and after V$_2$O$_5$ powder soaking in Zn(CF$_3$SO$_3$)$_2$, ZnSO$_4$, ZnCl$_2$, and Zn(CF$_3$SO$_3$)$_2$ electrolytes for 20 days. Reproduced with permission from Ref. [55] Copyright 2020, Springer Nature.

as 3 M Zn(NO$_3$)$_2$, 3 M ZnSO$_4$, 3 M ZnCl$_2$, and 3 M Zn(CF$_3$SO$_3$)$_2$ (Figure 5H). It is found that 3 M Zn(CF$_3$SO$_3$)$_2$ electrolyte with an initial pH = 3.95 is favorable to Equation (6). The bulky singly charged (CF$_3$SO$_3$)$^-$ with reducing solvation effect can activate Zn$^{2+}$ ions to react with VO$_2$(OH)$_2^-$. Hence, an in-situ transformation of V$_2$O$_5$ into Zn$_3$V$_2$O$_7$(OH)$_2$-2H$_2$O (ZVO) nanosheet clusters was achieved in the 3 M Zn(CF$_3$SO$_3$)$_2$ electrolyte. It is worth noting that V$_2$O$_5$ can be completely converted to ZVO for co-Zn$^{2+}$/H$^+$ intercalation/extraction owing to the continuous intercalation of H$^+$ ions into ZVO during the electrochemical discharge process. In the subsequent electrochemical cycling, ZVO is the only host for Zn$^{2+}$/H$^+$ storage, which accelerates ionic transport and promotes the optimal utilization of the active material. The integrated utilization of dissolved ions through an in-situ transformation mechanism provides a novel insight for suppressing cathode dissolution.

Recently, the solvation sheath structure with Zn$^{2+}$ ions and six water molecules was pointed out to be able
3.3 Corrosion and passivation

Some unexpected reactions may occur during battery storage or operation due to the active interface between electrode and electrolyte. Equation (8) shows the probable corrosion and hydrogen evolution at the Zn anode surface in the commonly used 1 M ZnSO$_4$ electrolyte with the pH value of about 5.

$$Zn + 2H^+ \rightarrow Zn^{2+} + H_2 \uparrow \quad (8)$$

Electromotive force ($E$) calculated by Nernst Equation (9) can be used to judge whether this reaction is theoretically feasible.

$$E = E^\circ - \frac{RT}{2F} \ln \frac{a_{Zn^{2+}}}{a_{H^+}} \quad (9)$$

where $E^\circ$, $R$, $T$, $F$, $a_{Zn^{2+}}$, and $a_{H^+}$ represent standard electromotive force (0.76 V), thermodynamic constant (8.31 J·mol$^{-1}$·K$^{-1}$), temperature (298 K), Faraday constant (96,500 C·mol$^{-1}$), $Zn^{2+}$ activity (1), and $H^+$ activity ($10^{-5}$). The calculated positive $E$ (0.46 V) indicates that the corrosion reaction is spontaneous in thermodynamics. This reaction exhibits slow kinetics due to its high hydrogen overpotential, whose hydrogen production is much less compared to the battery charge process under the high impressed voltage. Figure 6A shows the slow gas generation process at the interface between Zn anode and weakly acidic electrolyte. However, the accumulation of hydrogen cannot be neglected because of the potential risk of battery failure by the continuously increased internal pressure during the long-time battery storage process (Figure 6B).

The consumption of $H^+$ at the corrosion region increases the OH$^-$ concentration and further leads to the formation of insoluble zinc hydroxide sulfate ($Zn_4(\text{OH})_6\text{SO}_4\cdot n\text{H}_2\text{O}$, ZHS), which is the main component of the passivation layer (Figure 6C and D). Accordingly, it can be considered that the corrosion and passivation occur simultaneously based on Equation (10).

$$3Zn + (6 + n)\text{H}_2\text{O} + Zn\text{SO}_4 \rightarrow Zn_4(\text{OH})_6\text{SO}_4\cdot n\text{H}_2\text{O} + 3H_2 \quad (10)$$

Anode passivation can be also caused by electrostatic interaction during battery operation. At the stripping process, Zn$^{2+}$ is transferred from Zn metal and the anode surface is occupied by positive charges. Anions (SO$_4^{2-}$ and OH$^-$) tend to aggregate at the interface and coordinate with Zn$^{2+}$ to form ZHS, which is easily supersaturated in the electrolyte and precipitates on the anode surface. The insulating passivation layer and continuous water consumption are detrimental to the
FIGURE 6  The characterization of corrosion and passivation. (A) In situ optical microscopic images of the hydrogen evolution on Zn anode surface. Reproduced with permission Ref. [14] Copyright 2019, Elsevier BV. (B) The gas evolution in an aluminum laminated battery. XRD patterns (C) and top-view SEM images (D) of the Zn metal electrode maintained in the ZnSO₄ electrolyte for different times. Reproduced with permission from Ref. [61] Copyright 2020, Elsevier. (E) XRD patterns and (F) photograph observations of Zn foil with liquid and hydrogel electrolytes in Zn-Zn cell after 500 discharge and charge processes. Reproduced with permission from Ref. [66] Copyright 2021, Wiley-Blackwell

reversible Zn plating/stripping on the anode surface due to the increased interfacial impedance and insufficient electrolyte.

Cathode passivation is another side reaction in AZIBs. Taking MnO₂ cathode as an example, H⁺/Zn²⁺ coinsertion Equations (11 and 12) is its energy storage mechanism in weakly acidic electrolytes.

\[
\text{MnO}_2 + \text{H}^+ + \text{e}^- \leftrightarrow \text{MnOOH}
\]  

(11)

\[
\text{MnO}_2 + x\text{Zn}^{2+} + 2xe^- \leftrightarrow \text{Zn}_x\text{MnO}_2
\]  

(12)

H⁺ is preferentially inserted into MnO₂ owing to the faster H⁺ diffusion and weaker electrostatic interaction with the host lattice. Similar to anode passivation, the resulting pH increase of electrolyte leads to the formation of ZHS (Equation [13]).

\[
3\text{Zn}^{2+} + 6\text{OH}^- + \text{ZnSO}_4 + \text{nH}_2\text{O} \leftrightarrow \text{Zn}_4(\text{OH})_6\text{SO}_4 \cdot \text{nH}_2\text{O}
\]  

(13)

The ion transportation in cathode may be blocked by the gradually accumulated ZHS layer, leading to an increase of electrochemical impedance. However, cathode passivation is not as severe as anode passivation because this conversion reaction is generally reversible and ZHS can dissolve into electrolyte when H⁺ is extracted from the cathode.

Based on the above analysis, the detrimental anode corrosion is ineluctable in the common aqueous electrolyte because of the production of H⁺ from the ionization of water. The shifted ionization equilibrium of water by corrosion or electrochemical reaction may further lead to the passivation of electrodes. Some previous researches proposed functional interfacial layers to modify the surface activity of Zn anode, which could exhibit enhanced corrosion resistance during the battery shelving or cycling with a small specific capacity. However, the interfacial layer may lose contact with Zn anode when a large amount of Zn is stripped and the resulting void space between the anode and layer may deactivate its corrosion prevention. It is more effective to modify the inherent characteristics of electrolyte to avoid anode corrosion and maintain continuous anode protection during the dynamical plating/stripping process. There are two main methods of side reaction prevention by electrolyte modification: reducing the activity of water to inhibit its ionization and increasing the reaction overpotential to retard the corrosion. The increase of salt concentration or the introduction of organic solvent in the aqueous electrolyte can decrease the activity of ionizable free water. Cui et al. proposed a novel water-in-deep eutectic solvent (Water-in-DES) electrolyte consisting of water in urea/LiTFSI/Zn(TFSI)₂. The water content is extremely low (6 wt%) in this highly concentrated aqueous electrolyte. Thus, the water molecules are all coordinated with the eutectic solvent network and the reactivity of hydrogen evolution is restrained by the less chance of
3.4 | Dendrite growth

Zn dendrite grows when the electric field and concentration gradient are nonuniform on the deposition interface according to our previous work. The uncontrolled dendrite growth may puncture separators and cause battery failure due to the resulting short circuit. There have been many anode modification strategies to uniformize electron and ion distribution such as current collectors with three-dimensional porous structure and zincophilic decoration. However, they can only guide the Zn nucleation process and the growth of few Zn layers, which may be useless when a large amount of Zn is plated on the substrate because the Zn dendrites may still grow inside the anode. The electrolyte modification not only influences the interfacial ion behavior but also can participate in the Zn reduction reaction to continuously control the Zn deposition from the nucleation process to the subsequent growth process.

contact with Zn (Figure 7A). There have been a great number of researches on gel electrolyte with high ion conductivity and adhesion to hamper contact between aqueous solution and Zn anode. Recently, Chen and coworkers fabricated a versatile hydrogel electrolyte for dendrite-free, noncorrosive, and long-life AZIBs. The as-prepared CT3G30 hydrogel composed of cotton as the raw material of polymeric framework and tetraethyl orthosilicate as the crosslinker shows excellent adhesion with Zn electrodes and successfully limits free water molecules to induce side reaction. After 500 cycles, Zn foil against hydrogel remains smooth and unchanged on the color and no ZHS peak was identified in XRD analysis (Figure 6E and F). Gelatin microgels have been studied as a potential corrosion inhibitor in self-healing coatings. Liu et al. investigated the influence of the gelatin electrolyte additive on Zn corrosion in the mildly acidic aqueous solution. It is found that the gelatin additive with the selected concentration is capable of effectively suppressing Zn corrosion. Linear polarization curves show that the corrosion current of 2 M ZnSO₄ electrolyte with 5% gelatin additive is reduced to approximately 42 times compared with pristine electrolyte.

An anticorrosive coating similar to the interfacial protective layer can be formed on the anode surface by chemical or electrochemical reactions. Zn(ClO₄)₂ aqueous solution is mildly acidic with a pH value of 4.9. When using Zn(ClO₄)₂ as the salt in aqueous electrolyte, the Zn plating and stripping process is also based on the typical Zn²⁺/Zn redox reaction. Lower intensity of ZHS peak was detected in the Zn anode cycled in Zn(ClO₄)₂ electrolyte compared with ZnSO₄ and Zn(CH₃COO)₂ electrolytes (Figure 7B), which indicates the suppressed passivation reaction at the interface between Zn anode and electrolyte by the controlled formation of a Cl⁻ containing protective layer on anode surface (Figure 7C). Various other inorganic or organic additives have been proposed based on these methods, such as fumed silica, sodium dodecyl sulfate, and thiourea, which also show a great effect to inhibit the corrosion and passivation for the stable Zn anodes.

There is an easily overlooked issue that oxygen from the air dissolved in the aqueous electrolyte may be detrimental to the electrodes. When the oxygen is removed from the electrolyte, the corrosion potential is positively shifted (Figure 7D) and the anode surface maintains smooth (Figure 7E), indicating that the removal of dissolved O₂ can alleviate the serious corrosion. This discovery brings a new viewpoint that researchers cannot just focus on improving the electrolyte performance by additive but also cannot neglect the influence of substances inherently existed in the electrolyte such as the dissolved salt and gas.
An electric double-layer structure can be used to simulate the ion transmission from the electrolyte to anode surface (Figure 8A). Hydrated Zn$^{2+}$ is first transferred near the anode surface by the electric field, then desolvated in the compact layer, and finally deposited on the anode surface. The energy consumption of Zn$^{2+}$ desolvation in the compact layer has an important influence on the quality of Zn deposition. A low energy consumption indicates the fast transfer kinetics in the electric double-layer, which can provide abundant nucleation sites and uniformize Zn deposition to reduce the risk of dendrite formation. Besides, the Zn$^{2+}$ adsorbed on the anode surface can diffuse laterally along the surface and be reduced to Zn at the low-energy-barrier site, resulting in the aggregation of Zn deposited at the previous Zn particles to minimize the surface area exposed to the electrolyte. This uneven Zn deposition may eventually lead to dendrite growth (Figure 8B). Therefore, the modification method to suppress Zn dendrites should focus on optimizing the desolvation process in an electric double layer to reduce the charge transfer resistance and restraining the interfacial two-dimensional Zn$^{2+}$ diffusion to prevent Zn aggregation. The TBA$_2$SO$_4$ (Figure 8C) additives can be adsorbed on the Zn electrode surface to hinder Zn-ion migration and aggregation, enabling the formation of numerous tiny nucleation centers to induce uniform Zn deposition by limiting 2D Zn$^{2+}$ ions diffusion on the anode surface.

The electric field is relatively high at the tips of small Zn particles formed at the beginning of Zn deposition on the anode surface. The highly polarized diethyl ether shows a “self-healing electrostatic shield” effect which can preferentially attach to Zn tips to avoid the two-dimensional Zn$^{2+}$ diffusion to the high-electric-field region (Figure 9A). The Zn deposition is transferred to the flat regions with fewer diethyl ether molecules, which induces the smooth surface of Zn anodes (Figure 9B).
According to the electrostatic shield mechanism, a positive ions additive with low reduction potential (vs. Zn/Zn$^{2+}$) can preferentially be reduced on the Zn tips to avoid dendrite growth. Na$_2$SO$_4$ additive with low reduction potential introducing ZnSO$_4$ electrolyte not only suppresses Zn dendrite extension but also prevents cathode dissolution when NaV$_3$O$_8$·1.5H$_2$O cathode was coupled with Zn to assemble full batteries. $^{53}$ Besides, some organics (such as sodium dodecylbenzene sulfonate and polyacrylamide) can be served as anchors to forcibly guide the Zn$^{2+}$ transfer on the limited position of anode surface and the modified electrolytes with these organic additives also exhibit the dendrite-free Zn deposition behavior. $^{51,78}$ In the mild aqueous electrolyte, Zn$^{2+}$ with fast reaction kinetics on the Zn anode surface may facilitate the inhomogeneous Zn deposition. A long-chain polyethylene oxide polymer (PEO) additive in ZnSO$_4$ electrolyte can effectively slow down Zn$^{2+}$ transfer to regulate concentration distribution and electrolyte flux through interactions between Zn$^{2+}$ and ether group in PEO, which ensures homogeneous Zn$^{2+}$ distribution on the interface between Zn anode and electrolyte to achieve a uniform deposition/dissolution process. $^{79}$ Some organics additives introduced in the aqueous electrolyte remain in the anode surface and participate in the interfacial reactions, which may complicate the continuous Zn plating/stripping processes. A different Zn$^{2+}$ solvation sheath can be obtained through electrolyte composition design, which can further affect the desolvation process of Zn deposition. Wang et al. proposed a novel concentrated water-in-salt electrolyte containing 1 M Zn(TFSI)$_2$ and 21 M LiTFSI for AZIBs. $^{80}$ The Zn$^{2+}$ solvation sheath is composed of TFSI$^-$ in this unique electrolyte and Zn$^{2+}$ is desolvated from TFSI$^-$ sheath instead of water sheath during Zn deposition because of the strong interaction between Li$^+$ and water molecules (Figure 9C). The optimized energy barrier for the Zn$^{2+}$ desolvation endows the Zn anode with enhanced cycle stability and uniform Zn deposition (Figure 9D). Gel electrolytes can also reduce the activity of water by the strong hydrogen-bonding interactions to restrict water molecules (Figure 9E). $^{81}$ This mechanism to induce uniform Zn deposition and suppress water-related reactions is similar to the water-in-salt electrolyte.
**TABLE 2** Summary of recently reported electrolyte engineering for dendrite-zinc anode in AZIBs

| Anodes             | Strategies                        | Operating condition       | Lifespan (h) | Ref. |
|--------------------|-----------------------------------|---------------------------|--------------|------|
| Zinc plated copper mesh | Polyaclrylamide additive         | 0.2 mA/cm², 1 mAh/cm²     | 350          | [11] |
| Zinc foil          | Diethyl ether additive            | 0.2 mA/cm², 0.2 mAh/cm²   | 250          | [12] |
| Zinc foil          | Hydrated eutectic electrolytes    | 0.05 mA/cm², 0.5 mAh/cm²  | 800          | [17] |
| Zinc plated copper foam | Tetrabutylammonium sulfate additive | 2 mA/cm², 2 mAh/cm²       | 300          | [77] |
| Zinc foil          | Sodium dodecyl benzene sulfonate additive | 0.5 mA/cm², 0.25 mAh/cm²  | 1500         | [78] |
| Zinc foil          | High concentration Zn(TFSI)₂+Li(TFSI) | 0.2 mA/cm², 0.032 mAh/cm³ | 170          | [80] |
| Zinc foil          | PVA/Zn(CF₃SO₃)₂ hydrogels         | 0.1 mA/cm²                | 800          | [89] |

Gel electrolyte makes flexible AZIBs possible (Figure 9F), which can be applied to the emerging portable and wearable electronic products.

The enhanced electrochemical performances of AZIBs with dendrite-free zinc anode using the electrolytes engineering are summarized in Table 2. Highly concentrated salt aqueous electrolytes and gel electrolytes can greatly promote the uniformity of Zn anode by reducing the solvation and desolvation effect. However, their increased viscosity results in a lower ionic conductivity, which is detrimental to the battery performance at the high current density.\(^\text{82}\) Besides, some additives can block grain growth to achieve a uniform and denser Zn deposition through increasing Zn growing overpotential. High overpotential is not conducive to develop high energy density AZIBs.\(^\text{83}\) It is essential to develop new strategies to balance all related issues to enhance the overall performance of Zn anodes.

4 | SUMMARY AND OUTLOOK

AZIBs have been considered as promising candidates for large-scale EES owing to their plentiful impressive advantages. The aqueous electrolyte, as an important component of AZIBs, is meanwhile developed rapidly and the related modification strategies have also been proposed to solve the existing issues. It should be noted that there are still many remaining challenges although some significant progresses have been achieved on the modification of electrolytes in AZIBs. Herein, we propose some suggestions for the rational design of aqueous electrolytes for AZIBs based on our best understanding of the electrochemical mechanisms:

1. In situ methods to dynamically monitor interfacial reactions between electrolyte and electrode. Unlike the formation of stable solid electrolyte interphase in the alkali metal (Li and Na) batteries operated in the organic electrolyte, the interfacial reaction products in AZIBs are more complex and may even tend to restrict ionic migration.\(^\text{84}\) At present, there is still no mature theoretical model to describe the relationship between interfacial reaction and electrochemical properties. In situ observation techniques show the potential to closely monitor the interfacial reaction and achieve the key information during some transient processes such as the Zn\(^{2+}\) insertion into the cathode and Zn nucleation at the anode surface.\(^\text{85}\)

2. Further development of advanced gel electrolyte. Gel electrolyte is safer than traditional liquid electrolytes because liquid leakage is avoided and it can be used as the separator, which can simplify the battery fabrication process. The current problems facing the advanced gel electrolyte are its poor mechanical strength and unstable interface.\(^\text{86}\) The polymer network determines the mechanical property of the gel electrolyte. Typical polymers used in the gel electrolyte mainly include polyvinyl alcohol, gelatin, and polyacrylamide.\(^\text{87-89}\) However, their mechanical strength is insufficient to meet the requirements of practical application. Besides, the gel electrolyte/electrode interface is difficult in full contact, which leads to a sharp increase in internal resistance. Only after solving the above problems, the gel electrolyte can be applied to AZIBs to replace the traditional liquid electrolyte.

3. The exploitation of localized supersaturated electrolyte. The organic electrolyte can eliminate parasitic reaction related to water and simplify the electrochemical redox reactions in comparison with aqueous electrolyte. Also, the high concentration electrolyte can decrease the activity of ionizable free water and inhibit corrosion and passivation of anode. However, both the organic and high concentration electrolytes are expensive, which is contradictory to low-cost large-scale ESS.\(^\text{90}\) The compromised strategies are to construct a composite electrolyte system composed of a trace amount of supersaturated electrolyte on the surface of zinc anode and salt-in-water electrolyte close to cathode, which not only
alleviates the corrosion and passivation caused by water but also obtains a moderate cost.

4. Integrated design for the practical batteries. The electrolyte optimization to address one specific issue may generally aggravate other issues. For example, the pH regulation can broaden the electrochemical window of the aqueous electrolyte but the side reactions in the cathode and anode may become more violent, resulting in the inferior reversibility of the Zn anode. And the concentrated electrolyte can improve the ability of uniform electroplating while it is also possible to decrease ionic conductivity, which may reduce the performance of the electrode under high current density. For the commercialization of AZIBs, it is necessary to find the solution that satisfies the requirements of both dendrite-free deposition and side-reaction inhibition.

This review can provide some new insights from the point of electrolyte modification for the researchers who aim to develop practical AZIBs. Further exploration is still needed for the commercialization of AZIBs and the key is to integrate existing technologies to simultaneously optimize the cathode, anode, and electrolyte. Given their high-security and low-cost advantages, it is believed that AZIBs have great potential in large-scale ESS.

CONFLICT OF INTEREST
The authors declare no conflict of interest.

ACKNOWLEDGEMENTS
This research was financially supported by the National Science Foundation of China (Nos. 21975289 and U19A2019), Hunan Provincial Research and Development Plan in Key Areas (No. 2019GK2033), and Hunan Provincial Science and Technology Plan Project of China (Nos. 2017TP1001, 2020JJ2042, and 2018RS3009).

ORCID
Haiyan Wang https://orcid.org/0000-0003-4206-0215

REFERENCES
1. Gür TM. Review of electrical energy storage technologies, materials and systems: challenges and prospects for large-scale grid storage. Energy Environ Sci. 2018;11:2696-2767.
2. Lee B, Paek E, Mitlin D, Lee SW. Sodium metal anodes: emerging solutions to dendrite growth. Chem Rev. 2019;119:5416-5460.
3. Li H, Ma L, Han C, et al. Advanced rechargeable zinc-based batteries: recent progress and future perspectives. Nano Energy. 2019;62:550-587.
4. Song M, Tan H, Chao D, Fan HJ. Recent advances in Zn-ion batteries. Adv Funct Mater. 2018;28:1802564.
5. Zhao Z, Fan X, Ding J, et al. Challenges in zinc electrodes for alkaline zinc-air batteries: obstacles to commercialization. ACS Energy Lett. 2019;4:2259-2270.
6. Xu C, Li B, Du H, Kang F. Energetic zinc ion chemistry: the rechargeable zinc ion battery. Angew Chem Int Ed. 2012;51:933-935.
7. Fang G, Zhu C, Chen M, et al. Suppressing manganese dissolution in potassium manganese with rich oxygen defects engaged high-energy-density and durable aqueous zinc-ion battery. Adv Funct Mater. 2019;29:1808375.
8. Wan F, Niu Z. Design strategies for vanadium-based aqueous zinc-ion batteries. Angew Chem Int Ed. 2019;58:16358-16367.
9. Zeng Y, Zhang X, Qin R, et al. Dendrite-free zinc deposition induced by multifunctional CNT frameworks for stable flexible Zn-ion batteries. Adv Mater. 2019;31:1903675.
10. Kim JY, Liu G, Shim GY, et al. Functionalized Zn@ZnO hexagonal pyramid array for dendrite-free and ultrastable zinc metal anodes. Adv Funct Mater. 2020;30:2004210.
11. Zhang Q, Luan J, Fu L, et al. The three-dimensional dendrite-free zinc anode on a copper mesh with a zinc-oriented polyacrylamide electrolyte additive. Angew Chem Int Ed. 2019;58:15841-15847.
12. Xu W, Zhao K, Huo W, et al. Diethyl ether as self-healing electrolyte additive enabling long-life rechargeable aqueous zinc ion batteries. Nano Energy. 2019;62:275-281.
13. Wu X, Xu Y, Zhang C, et al. Reverse dual-ion battery via a ZnCl2 water-in-salt electrolyte. J Am Chem Soc. 2019;141:6338-6344.
14. Zhao J, Zhang J, Yang W, et al. Water-in-deep eutectic solvent electrolytes enable zinc metal anodes for rechargeable aqueous batteries. Nano Energy. 2019;57:625-634.
15. Huang S, Zhu J, Tian J, Niu Z. Recent progress in the electrolytes of aqueous zinc-ion batteries. Chem Eur J. 2019;25:14480-14494.
16. Fang G, Zhou J, Pan A, Liang S. Recent advances in aqueous zinc-ion batteries. ACS Energy Lett. 2018;3:2480-2501.
17. Yang W, Du X, Zhao J, et al. Hydrated eutectic electrolytes with ligand-oriented solvation shells for long-cycling zinc-organic batteries. Joule. 2020;4:1557-1574.
18. Chao D, Zhou W, Ye C, et al. An electrolytic Zn-MnO2 battery for high-voltage and scalable energy storage. Angew Chem Int Ed. 2019;58:7823-7828.
19. Hou Z, Zhang X, Li X, et al. Surfactant widens the electrochemical window of an aqueous electrolyte for better rechargeable aqueous sodium/zinc battery. J Mater Chem A. 2017;5:730-738.
20. Naveed A, Yang H, Yang J, et al. Highly reversible and rechargeable safe Zn batteries based on a triethyl phosphate electrolyte. Angew Chem Int Ed. 2019;58:2760-2764.
21. Naveed A, Yang H, Shao Y, et al. A highly reversible zn anode with intrinsically safe organic electrolyte for long-cycle-life batteries. Adv Mater. 2019;31:e1900668.
22. Kundu D, Hosseini Vajargah S, Wan L. Aqueous vs. nonaqueous Zn-ion batteries: consequences of the desolvation penalty at the interface. Energy Environ Sci. 2018;11:881-892.
23. Cheng X-B, Liu H, Yuan H, et al. A perspective on sustainable energy materials for lithium batteries. SusMat. 2021;1:38-50.
24. Han C, Li W, Liu HK, et al. Principals and strategies for constructing a highly reversible zinc metal anode in aqueous batteries. Nano Energy. 2020;74:104880.
25. Kasiri G, Trócoli R, Bani Hashemi A, La Mantia F. An electrochemical investigation of the aging of copper hexacyanoferrate during the operation in zinc-ion batteries. Electrochim Acta. 2016;222:74-83.
26. Kim S, Lee J, Kim S, et al. Electrochemical lithium recovery with a LiMn2O4-zinc battery system using zinc as a negative electrode. Energy Technol. 2018;6:340-344.
27. Li G, Yang Z, Jiang Y, et al. Towards polyvalent ion batteries: a zinc-ion battery based on NASICON structured Na3V2(PO4)3. Nano Energy. 2016;25:211-217.
28. Chae MS, Heo JW, Kwak HH, et al. Organic electrolyte-based rechargeable zinc-ion batteries using potassium nickel hexacyanoferrate as a cathode material. J Power Sources. 2017;337:204-211.
29. Li M, Wang C, Chen Z, et al. New concepts in electrolytes. Chem Rev. 2020;120:6783-6819.
30. Zhang N, Cheng F, Liu Y, et al. Cation-deficient spinel ZnMn2O4 cathode in Zn(CF3SO3)2 electrolyte for rechargeable aqueous Zn-ion battery. J Am Chem Soc. 2016;138:12894-12901.
31. Kim D, Lee C, Jeong S. A concentrated electrolyte for zinc hexacyanoferrate electrodes in aqueous rechargeable zinc-ion batteries. IOP Conf Ser: Mater Sci Eng. 2018;284:012001.
32. Glatz H, Tervoort E, Kundu D. Unveiling critical insight into the zn metal anode cyclability in mildly acidic aqueous electrolytes: implications for aqueous zinc batteries. ACS Appl Mater Interfaces. 2020;12:3522-3530.
33. Pan F, Zhang Y, Zhang L, et al. Reversible oxygen redox chemistry in aqueous zinc-ion batteries. Angew Chem Int Ed. 2019;58:7062-7067.
34. Wang Z, Ruan Z, Liu Z, et al. A flexible rechargeable zinc-ion wire-shaped battery with shape memory function. J Mater Chem A. 2018;6:8549-8557.
35. Zhang C, Holoubek J, Wu X, et al. A ZnCl2 water-in-salt electrolyte for a reversible Zn metal anode. Chem Commun. 2018;54:14097-14099.
36. Pan H, Shao Y, Yan P, et al. Reversible aqueous zinc/manganese oxide energy storage from conversion reactions. Nat Energy. 2016;1:16039.
37. Soundharrajan V, Sambandam B, Kim S, et al. Aqueous magnesium zinc hybrid battery: an advanced high-voltage and high-energy MgMn2O4 cathode. ACS Energy Lett. 2018;3:1998-2004.
38. Tang B, Shan L, Liang S, Zhou J. Issues and opportunities facing aqueous zinc-ion batteries. Energy Environ Sci. 2019;12:3288-3304.
39. Ma L, Chen S, Li N, et al. Hydrogen-free and dendrite-free all-solid-state Zn-ion batteries. Adv Mater. 2020;32:1908121.
40. Kühnel R-S, Reber D, Battaglia C. A high-voltage aqueous electrolyte for sodium-ion batteries. ACS Energy Lett. 2017;2:2005-2006.
41. Sheng W, Zhuang Z, Gao M, et al. Correlating hydrogen oxidation and evolution activity on platinum at different pH with measured hydrogen binding energy. Nat Commun. 2015;6:5848.
42. Zou H, Chen J, Fang Y, et al. Dual-electrolyte based air-breathing regenerative microfluidic fuel cell with 1.76 V open-circuit-voltage and 0.74 V water-splitting voltage. Nano Energy. 2016;27:619-626.
43. Fic K, Lota G, Mellier M, Frackowiak E. Novel insight into neutral medium as electrolyte for high-voltage supercapacitors. Energy Environ Sci. 2012;5:5842-5850.
44. Yu F, Pang L, Wang X, et al. Aqueous alkaline–acid hybrid electrolyte for zinc-bromine battery with 3V voltage window. Energy Storage Mater. 2019;19:56-61.
45. Zhang X, Shen C, Sanghadasa M, Lin L. High-voltage supercapacitors based on aqueous electrolytes. ChemElectroChem. 2019;6:976-988.
46. Borodin O, Self J, Persson KA, et al. Uncharted waters: superconcentrated electrolytes. Joule. 2020;4:69-100.
47. Zheng J, Tan G, Shan P, et al. Understanding thermodynamic and kinetic contributions in expanding the stability window of aqueous electrolytes. Chem. 2018;4:2872-2882.
48. Li W, Wang K, Zhou M, et al. Advanced low-cost, high-voltage, long-life aqueous hybrid sodium/zinc batteries enabled by a dendrite-free zinc anode and concentrated electrolyte. ACS Appl Mater Interfaces. 2018;10:22059-22066.
49. Cui J, Liu X, Xie Y, et al. Improved electrochemical reversibility of Zn plating/stripping: a promising approach to suppress water-induced issues through the formation of H-bonding. Mater Today Energy. 2020;18:100563.
50. Liu Z, Huang Y, Huang Y, et al. Voltage issue of aqueous rechargeable metal-ion batteries. Chem Soc Rev. 2020;49:180-232.
51. Wu X, Xiang Y, Peng Q, et al. Green-low-cost rechargeable aqueous zinc-ion batteries using hollow porous spinel ZnMn2O4 as the cathode material. J Mater Chem A. 2017;5:17990-17997.
52. Chamoun M, Brant WR, Tai C-W, et al. Rechargeability of aqueous sulfate Zn/MnO2 batteries enhanced by accessible Mn2+ ions. Energy Storage Mater. 2018;15:351-360.
53. Wan F, Zhang L, Dai X, et al. Aqueous rechargeable zinc/sodium vanadate batteries with enhanced performance from simultaneous insertion of dual carriers. Nat Commun. 2018;9:1656.
54. Shi H-Y, Song Y, Qin Z, et al. Inhibiting VOPO4-xH2O Decomposition and dissolution in rechargeable aqueous zinc batteries to promote voltage and capacity stabilities. Angew Chem Int Ed. 2019;58:16057-16061.
55. Lu Y, Zhu T, van den Bergh W, Stefik M, Huang K. A high performing Zn-ion battery cathode enabled by in situ transformation of V2O5 atomic layers. Angew Chem Int Ed. 2020;59:17004-17011.
56. Hou Z, Dong M, Xiong Y, et al. A high-energy and long-life aqueous Zn/birnessite battery via reversible water and Zn2+ coinversion. Small. 2020;16:2001228.
57. Shin J, Choi DS, Lee HJ, Jung Y, Choi JW. Hydrated intercalation for high-performance aqueous zinc ion batteries. Adv Energy Mater. 2019;9:1900083.
58. Dubouis N, Lemaire P, Mirvaux B, et al. The role of the hydrogen evolution reaction in the solid–electrolyte interphase formation mechanism for “water-in-salt” electrolytes. Energy Environ Sci. 2018;11:3491-3499.
59. Shin J, Lee J, Park Y, Choi JW. Aqueous zinc ion batteries: focus on zinc metal anodes. Chem Sci. 2020;11:2028-2044.
60. Konarov A, Voronina N, Jo JH, et al. Present and future perspective on electrode materials for rechargeable zinc-ion batteries. ACS Energy Lett. 2018;3:2620-2640.
61. Cai Z, Ou Y, Wang J, et al. Chemically resistant Cu–Zn/Zn composite anode for long cycling aqueous batteries. Energy Storage Mater. 2020;27:205-211.
62. Su L, Liu L, Liu B, et al. Revealing the impact of oxygen dissolved in electrolytes on aqueous zinc-ion batteries. iScience. 2020;23:100995.
63. Huang J, Wang Z, Hou M, et al. Polyaniline-intercalated manganese dioxide nanolayers as a high-performance cathode material for an aqueous zinc-ion battery. *Nat Commun*. 2018;9:2906.

64. Zhao S, Han B, Zhang D, et al. Unravelling the reaction chemistry and degradation mechanism in aqueous Zn/MnO₂ rechargeable batteries. *J Mater Chem A*. 2018;6:5733-5739.

65. Hao J, Li X, Zhang S, et al. Designing dendrite-free zinc anodes for advanced aqueous zinc batteries. *Adv Funct Mater*. 2020;30:2001263.

66. Chen M, Chen J, Zhou W, et al. Realizing an all-round hydrogel electrolyte toward environmentally adaptive dendrite-free aqueous Zn–MnO₂ batteries. *Adv Mater*. 2021;33:2007559.

67. Stankiewicz A, Jagoda Z, Zielińska K, Szczygiel I. Gelatin microgels as a potential corrosion inhibitor carriers for self-healing coatings: preparation and co-deposition. *Mater Corros*. 2015;66:1391-1396.

68. Liu Y, Shi Q, Wu Y, et al. Highly efficient dendrite suppressor and corrosion inhibitor based on gelatin/Mn²⁺ co-additives for rechargeable zinc-manganese dioxide battery. *Chem Eng J*. 2021;407:127189.

69. Wang L, Zhang Y, Hu H, et al. A Zn(ClO₄)₂ electrolyte enabling long-life zinc metal electrodes for rechargeable aqueous zinc batteries. *ACS Appl Mater Interfaces*. 2019;11:42000-42005.

70. Huang J, Chi X, Han Q, et al. Thickening and homogenizing aqueous electrolyte towards highly efficient and stable Zn metal batteries. *J Electrochem Soc*. 2019;166:A1211-A1216.

71. Zhang Q, Luan J, Tang Y, et al. Interfacial design of dendrite-free zinc anodes for aqueous zinc-ion batteries. *Angew Chem Int Ed*. 2020;59:13180-13191.

72. Yin Y, Wang S, Zhang Q, et al. Dendrite-free zinc deposition induced by tin-modified multifunctional 3D host for stable zinc-based flow battery. *Adv Mater*. 2020;32:1906803.

73. Naveed A, Yang H, Shao Y, et al. A highly reversible zn anode with intrinsically safe organic electrolyte for long-cycle-life batteries. *Adv Mater*. 2019;31:1906688.

74. Xie X, Liang S, Gao J, et al. Manipulating the ion-transfer kinetics and interface stability for high-performance zinc metal anodes. *Energy Environ Sci*. 2020;13:503-510.

75. Zhao Z, Zhao J, Hu Z, et al. Long-life and deeply rechargeable aqueous Zn anodes enabled by a multifunctional brightener-inspired interphase. *Energy Environ Sci*. 2019;12:1938-1949.

76. Mitha A, Yazdi AZ, Ahmed M, Chen P. Surface adsorption of polyethylene glycol to suppress dendrite formation on zinc anodes in rechargeable aqueous batteries. *ChemElectroChem*. 2018;5:2409-2418.

77. Bayaguud A, Luo X, Fu Y, Zhu C. Cationic surfactant-type electrolyte additive enables three-dimensional dendrite-free zinc anode for stable zinc-ion batteries. *ACS Energy Lett*. 2020;5:3012-3020.

78. Hao J, Long J, Li B, et al. Toward high-performance hybrid Zn-based batteries via deeply understanding their mechanism and using electrolyte additive. *Adv Funct Mater*. 2019;29:1903605.

79. Jin Y, Han KS, Shao Y, et al. Stabilizing zinc anode reactions by polyethylene oxide polymer in mild aqueous electrolytes. *Adv Funct Mater*. 2020;30:2003932.

80. Wang F, Borodin O, Gao T, et al. Highly reversible zinc metal anode for aqueous batteries. *Nat Mater*. 2018;17:543-549.

81. Mo F, Liang G, Meng Q, et al. A flexible rechargeable aqueous zinc manganese-dioxide battery working at −20°C. *Energ Environ Sci*. 2019;12:706-715.

82. Ueno K, Yoshida K, Tsuchiya M, et al. Glyme–lithium salt equimolar molten mixtures: concentrated solutions or solvate ionic liquids?. *J Phys Chem B*. 2012;116:11323-11331.

83. Otani T, Fukunaka Y, Homma T. Effect of lead and tin additives on surface morphology evolution of electrodeposited zinc. *Electrochim Acta*. 2017;242:364-372.

84. Liang Y, Dong H, Aurbach D, Yao Y. Current status and future directions of multivalent metal-ion batteries. *Nat Energy*. 2020;5:646-656.

85. Yufig V, Tariq F, Eastwood DS, et al. Operando visualization and multi-scale tomography studies of dendrite formation and dissolution in zinc batteries. *Joule*. 2019;3:485-502.

86. Li H, Han C, Huang Y, et al. An extremely safe and wearable solid-state zinc ion battery based on a hierarchical structured polymer electrolyte. *Energ Environ Sci*. 2018;11:941-951.

87. Fu J, Zhang J, Song X, et al. A flexible solid-state electrolyte for wide-scale integration of rechargeable zinc–air batteries. *Energ Environ Sci*. 2016;9:663-670.

88. Chao D, Zhu C, Song M, et al. A high-rate and stable quasi-solid-state zinc-ion battery with novel 2D layered zinc orthovanadate array. *Adv Mater*. 2018;30:1803181.

89. Huang S, Wan F, Bi S, et al. A self-healing integrated all-in-one zinc-ion battery. *Angew Chem Int Ed*. 2019;58:4313-4317.

90. Yang H, Chang Z, Qiao Y, et al. Constructing a super-saturated electrolyte front surface for stable rechargeable aqueous zinc batteries. *Angew Chem Int Ed*. 2020;59:9377-9381.

---

**How to cite this article:** Zhang Q, Yang Z, Ji H, et al. Issues and rational design of aqueous electrolyte for Zn-ion batteries. *SusMat*. 2021;1:432–447. [https://doi.org/10.1002/sus2.20](https://doi.org/10.1002/sus2.20)