Chinese Chemical Letters 35 (2024) 108337

Contents lists available at ScienceDirect

Chinese Chemical Letters

journal homepage: www.elsevier.com/locate/cclet

Insight into the development of electrolytes for aqueous zinc metal batteries from alkaline to neutral

An Duan, Sha Luo*, Wei Sun*

School of Materials and Energy, University of Electronic Science and Technology of China, Chengdu 611731, China

ARTICLE INFO

Article history:
Received 13 February 2023
Revised 22 February 2023
Accepted 13 March 2023
Available online 15 March 2023

Keywords:
Aqueous electrolytes
Zinc metal batteries
pH-dependent chemistry
Electrolyte regulation
Additives engineering

ABSTRACT

Aqueous zinc metal batteries are considered as promising candidates for next-generation electrochemical energy storage devices, especially for large-scale energy storage, due to the advantages of high-safety, high energy density and low cost. As the bridge connecting cathode and anode, electrolyte provides a realistic operating environment. In alkaline and neutral aqueous zinc metal batteries, issues associated with electrolyte and anode are still intractable. In this review, we reveal the development and evolution of electrolytes for aqueous zinc metal batteries from alkaline to neutral *via* the description of fundamentals and challenges in terms of comparison and connection. We also elaborate the strategies in electrolytes regulation and highlight the basic roles and progresses in additives engineering.

1. Introduction

With the restructuring of traditional fossil energy system and the rise of renewable energy resources, the need of building the innovative electrochemical energy storage solutions has become critical in the past decades [1–3]. There is no doubt about the success of lithium-ion batteries (LIBs) as energy storage devices in portable electronic devices and new electric vehicles due to their high energy density and power density [4–6]. Despite the dominance of LIBs in the energy storage market, the exorbitant cost and disturbing safety issues limit their further application in many ways [7]. In order to avoid the safety concerns of flammable and toxic properties associated with organic electrolytes, aqueous batteries are regarded as promising next generation energy storage devices [8,9]. At present, the research efforts in aqueous batteries focus on naturally abundant and low-cost metal resources, including Na^+, K^+, Ca^{2+}, Zn^{2+}, Mg^{2+} and Al^{3+} [10–15].

Among them, zinc metal batteries (ZMBs) are particularly attractive owing to the advantages of zinc metal in high theoretical capacity (820 mAh/g and 5855 mAh/cm^3), low redox potential (−0.76 V *vs.* SHE), favorable stability and good compatibility with aqueous electrolytes [16–18]. Since the creation of the first primary battery, Voltaic pile, aqueous ZMBs had gone through 200 years of development, giving birth to a wealth of primary and secondary battery systems [19,20]. Among these are the zinc-manganese primary batteries, zinc-air primary batteries, zinc-silver primary/rechargeable batteries and zinc-nickel primary/rechargeable batteries, which have been already commercialized [21–24]. However, almost all of these commercial batteries are based on alkaline systems, while high performance rechargeable batteries are still lacking. It is because ZMBs based on alkaline electrolytes inevitably faced with the limitations of strong corrosion, unsatisfied cycling life and calendrer life and poor energy density [25,26]. With the goal of high energy density and long cycle life, the past decade has witnessed a surge in the development of rechargeable ZMBs based on neutral or weak acidity aqueous electrolytes using zinc inorganic or organic salts [27–29]. The ideal battery chemistry is similar to that of the rocking-chair lithium-ion batteries, which theoretically has an almost constant and settled electrolyte system [30,31].

As the bridge between the anode and cathode, the electrolyte enables ion conduction and plays a crucial role in electrochemical reactions, ensuring efficient charge transfer within the batteries [32,33]. Compared with organic electrolyte, the aqueous electrolyte provides faster ion conductivity and also attracts more attention due to its high safety, environmental friendliness and affordability [34,35]. Presently, research on ZMBs primarily concentrates on aqueous electrolytes, encompassing the fundamental concepts of electrolyte, the interface between the electrolyte and electrode, and practical considerations [36–39]. There have been excellent reviews presents electrolyte fundamentals, improvement strategies, additive modulation and recent advances of aqueous electrolytes for ZMBs, while most of them focused on the last decade of researches on neutral zinc salt electrolytes [34–39]. Few of them fo-

---

* Corresponding authors.
E-mail addresses: luosha@uestc.edu.cn (S. Luo), weisun@uestc.edu.cn (W. Sun).

https://doi.org/10.1016/j.cclet.2023.108337
1001-8417/

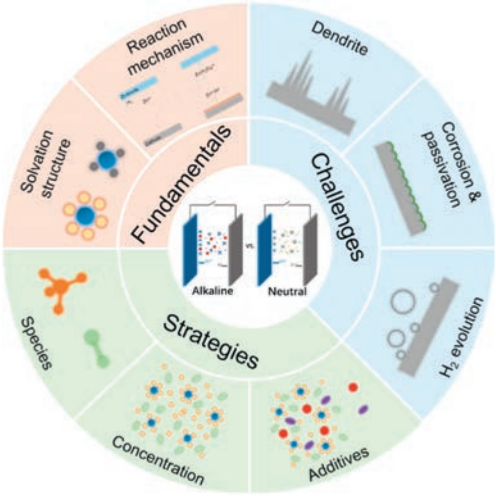


Fig. 1. Overview of fundamentals, challenges and strategies of alkaline and neutral electrolytes for aqueous ZMBs.

cus on the evolution of ZMB electrolytes from alkaline to neutral, with little coverage of the connections and similarities and differences.

Despite the growing interest in ZMBs, a comprehensive and up-to-date overview and discussion of the evolution of aqueous electrolytes from alkaline to neutral is currently lacking. In this review, we particularly present the chemistry and electrochemistry of zinc metal and zinc ion in different electrolytes, as well as an overview of the evolution and progress of aqueous electrolytes from alkaline to neutral (Fig. 1). This review highlights the fundamentals of alkaline and neutral electrolytes *via* the description of similarities and differences in electrolyte chemistry. The challenges and issues in alkaline and neutral electrolytes are revealed through the interpretation of Zn stripping/plating process under different chemical surroundings. Furthermore, we elaborate the strategies of electrolyte regulation from three perspectives of species, concentration and additive. By outlining the functional mechanism, we specify the basic roles and progresses of additive engineering in stabilizing Zn anode in alkaline and neutral electrolytes. This review summarizes the general laws governing the development of electrolytes for ZMBs and enables the development of alkaline and neutral electrolytes to be linked and mutually reinforced by an exposition of the fundamental principles.

2. The overview of aqueous electrolytes for ZMBs

2.1. History of aqueous electrolytes for ZMBs

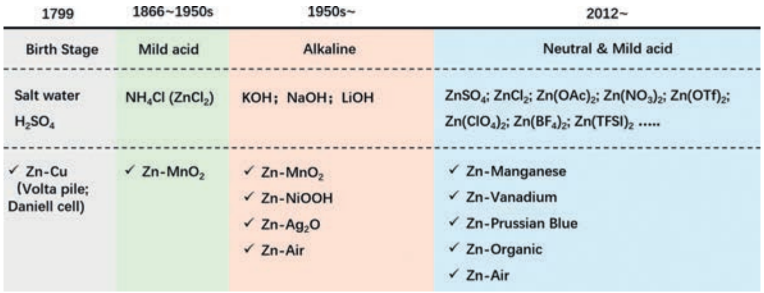
Zinc metal has the longest history as a battery electrode, dating back to the creation of the first primary battery made of zinc and copper in 1799 (Fig. 2) [40]. The electrolyte composition in that was salt water, which was later improved by Daniell to a dilute sulfuric acid solution [41]. Zinc metal and electrolyte played a crucial role in the early development of electrochemical batteries. Subsequently, early aqueous zinc-manganese oxide (Zn-MnO_2) batteries were invented in 1866 where mild acidic solution of NH_4Cl with/without $ZnCl_2$ was used as electrolyte, as well as in zinc-carbon battery [19,42].

Later in the 20th century, alkaline zinc-based batteries became the primary focus of research and widely used commercially ever since. Starting with the invention of Edison in 1901, rechargeable zinc-nickel (Zn-Ni) batteries were developed and recognized as the candidates for electric vehicles [43,44]. In the 1950s, alkaline electrolytes were first formally introduced to zinc-based batteries [19]. And the alkaline Zn-MnO_2 batteries began to come into view and dominated the primary battery market. In the early-mild 20th century, alkaline zinc-silver (Zn-Ag) and zinc-air batteries based on KOH and NaOH electrolytes were also developed [45,46].

In the 1970s and 1980s, a lot of research were reported on the understanding of electrochemical mechanism and strategies to improve the reversibility of Zn anode which prompted the first attempt on the neutral $ZnSO_4$ electrolyte to achieve a rechargeable Zn-MnO_2 battery [47–49]. However, this part of research did not receive much attention from the market due to the rise and commercialization of LIBs in 1990s [4–7]. In 2012, Kang *et al.* proposed the new concept of zinc ion battery using $ZnSO_4$ and $Zn(NO_3)_2$ as the electrolyte and analyzed the intercalation of Zn^{2+} into MnO_2 [50]. With the limitations of LIBs and the increased demands in energy storage, an explosion of research into ZIBs based on neutral electrolytes occurred [16–18]. In 2016, Chen *et al.* reported the application of the organic zinc salt $Zn(CF_3SO_3)_2$ with bulky $CF_3SO_3^-$ anions which can improve the electrolyte performance because of reduced solvation effect [51]. At the same time, the concept of water-in-salt electrolyte with ultra-high concentration was proposed [52–54]. Recently, novel electrolyte systems based on various zinc salts emerges and electrolyte regulation strategies based on additive engineering have also been widely reported [37–39].

2.2. Basic principles of aqueous electrolytes

An ideal electrolyte should possess the following characteristics: good electrical insulation and excellent ionic conductivity, a broad electrochemical window, thermally stablility, significant interfacial kinetics, low cost, non-toxicity and environmental friendliness [35,55]. Unfortunately, very few electrolytes can fulfill all of these requirements. The organic-based electrolytes, which have been widely used in commercial LIBs, possess the disadvantages of being flammable and toxic [56–58]. A typical aqueous electrolyte contains averagely more than 70 wt% water and is therefore hardly flammable [57]. Aqueous electrolytes are naturally non-hazardous and environmentally friendly and are also much cheaper



1799	1866~1950s	1950s~	2012~
Birth Stage	Mild acid	Alkaline	Neutral & Mild acid
Salt water H_2SO_4	NH_4Cl ($ZnCl_2$)	KOH; NaOH; LiOH	$ZnSO_4$; $ZnCl_2$; $Zn(OAc)_2$; $Zn(NO_3)_2$; $Zn(OTf)_2$; $Zn(ClO_4)_2$; $Zn(BF_4)_2$; $Zn(TFSI)_2$ .....
✓ Zn-Cu (Volta pile; Daniell cell)	✓ Zn-MnO_2	✓ Zn-MnO_2 ✓ Zn-NiOOH ✓ Zn-Ag_2O ✓ Zn-Air	✓ Zn-Manganese ✓ Zn-Vanadium ✓ Zn-Prussian Blue ✓ Zn-Organic ✓ Zn-Air

Fig. 2. Timeline of electrolyte development for ZMBs.

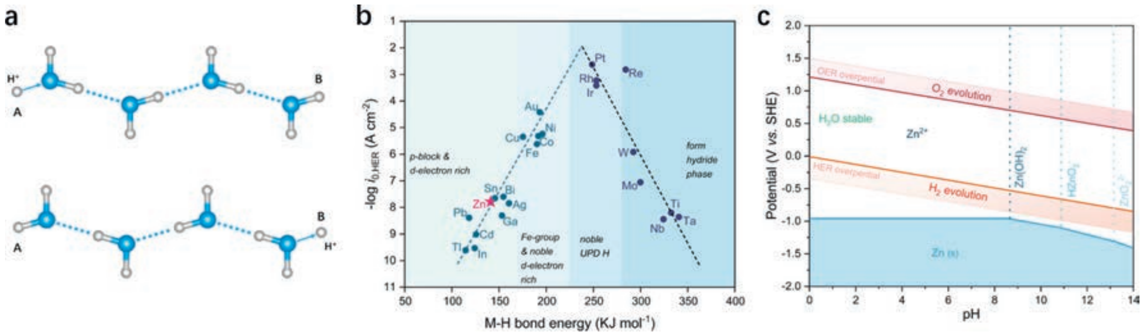


Fig. 3. Chemistry of electrolytes for aqueous ZMBs. (a) Schematic diagram of Grotthus mechanism of proton conduction. (b) Volcano plot of Trasatti for logi_0 values for HER as a function of M-H bond energy. Reproduced with permission [71]. Copyright 1972, Elsevier. (c) Pourbaix diagram of HER, OER and Zn in aqueous solutions with changed pH. Reproduced with permission [39]. Copyright 2022, Wiley-VCH.

to produce and recycle than organic electrolytes. In this section, we present the basic principles of aqueous electrolytes in several ways.

Water is an abundant substance in nature, so aqueous electrolytes are less costly in terms of raw material availability than the ether and carbonate electrolytes used in LIBs. Aqueous ZMBs use electrolytes, such as alkali and zinc salts, which are much less expensive than $LiPF_6$ used in LIBs. Organic electrolytes also require a water and oxygen free environment to be constructed during production and transport, whereas aqueous electrolytes do not do not have these requirements. Aqueous electrolytes are essentially harmless and environmentally friendly in compositions and do not require tedious conditions in battery recycling, with simple treatment to meet emission and reproduction requirements [59,60]. Aqueous electrolytes are considered to be more stable and safer due to their non-flammable and non-hazardous water base. Almost all of the electrolyte salts used in aqueous electrolytes are non-metamorphic to air conditions with less tendency to decompose or react and act only as ion transport conductors [61,62]. Unlike LIBs, aqueous ZMBs require little in the way of complex battery management systems, as they are much less likely to be subject to hazards such as explosion and burning due to faulty operation.

Aqueous electrolytes universally exhibit higher ionic conductivity than non-aqueous electrolytes under the same conditions, owing to high ionic dissociation and low viscosity [35,56]. In conventional aqueous electrolytes, there is also a unique hopping mechanism of ionic conduction, known as the Grotthuss mechanism of proton conduction [63,64]. An extensive network of hydrogen bonds exists between water molecules, as with the Newtonian pendulum, the transport of protons can be realized by a single vibration between hand-in-hand water molecules instead of a heavy movement from point A to B (Fig. 3a). One proton is attached to one end of the chain of water molecules, causing a vibration occurs in the H-O bonds between the water molecules. At the other end of the chain, another proton is released [65]. Thanks to such a unique ionic conduction mechanism, the ionic conductivity of aqueous electrolytes is several orders of magnitude higher than that of commercial LIBs electrolytes [66,67]. The high ionic conductivity and good interfacial wettability not only result in excellent charge/discharge rate performance, but also have the potential to achieve thicker electrode loading and thus higher overall energy density [68,69].

It is worth noting that advanced theoretical and simulation analyses have been applied to provide theoretical guidance and prediction for understanding the basic principles and electrochemistry in various aqueous ZMBs. MD simulations are widely used for the analyses of the solvation structure of Zn^{2+} cations in different electrolytes [34]. The resulting radial distribution functions (RDFs) can provide additional evidence of the coordination structure of Zn^{2+} closest to reality. DFT calculations are the most popular theoretical simulation technology employed to analyze the absorption energy and charge density distribution. DFT calculations play a crucial role in revealing and understanding electrochemical reactions on the interface of the electrode and electrolyte [35]. COMSOL Multiphysics is mainly used to calculate the local current density and electric field distribution. With the development of theoretical simulations and calculations, results obtained from experiments can be verified by the underlying theory, while results that are difficult to obtain experimentally can also be presented to some extent.

2.3. *pH-dependent chemistry of zinc anode in aqueous electrolytes*

Despite the unique performance and safety advantages of aqueous electrolytes, the relatively reactive nature of water poses certain limitations and challenges to their application. Due to the potential of hydrolysis reactions, the thermodynamic electro-chemical stability window (ESW) for aqueous electrolytes is only 1.23 V, much lower than that of non-aqueous electrolytes [56]. According to Sabatier principle, when considering metals as catalyst media for hydrogen evolution reactions (HER), the interaction between reactants and the catalyst must be optimal in strength [70,71]. If the interaction between H_2 and the metal is too strong, as determined by the M-H bond energy, the active sites will be blocked and further reactions will not take place. Conversely, if the M-H bond energy is relatively weak, such as with Zn metal, the HER reaction cannot get activated. Thus, Zn metal exhibits a high kinetic overpotential for HER, ensuring its compatibility with aqueous electrolytes (Fig. 3b).

Excluding the merit of Zn metal in triggering HER, zinc metal is generally thermodynamically unstable in aqueous electrolytes [39]. The Pourbaix diagram illustrates the two side reactions of water (HER and oxygen evolution reaction (OER)) and the pH-dependent behavior of zinc compounds (Fig. 3c). It is easy to see that HER is more likely to occur at low pH, while OER tends to occur at high pH. Therefore, theoretically, a moderate pH is a suitable choice for the application of aqueous electrolytes. Although zinc metal possesses a high kinetic overpotential for HER, the practice potential of HER is still more positive than the zinc deposition potential, resulting in the inevitable occurrence of HER in ZMBs [72,73].

Simultaneously, zinc metal in aqueous electrolytes is always exposed to corrosion and dissolution, which leads to the depletion of zinc anode [74]. Corrosion of zinc is divided into hydrogen evolution corrosion and oxygen absorption corrosion [75]. In neutral and mild acid electrolytes, Zn metal prefers to react with active protons, while in alkaline electrolytes, oxygen absorption corrosion is more likely to occur. Since the byproduct of corrosion, zinc hydroxide, is poorly soluble and only dissolves in strongly alkaline electrolytes, the neutral electrolyte is accompanied by the formation of alkaline hydrate zinc salts, such as $Zn_4(OH)_6SO_4{\cdot}xH_2O$, which can cause degradation of battery performance [76]. And in alkaline electrolytes, zinc hydroxide and its derivatives also decompose to produce zinc oxide (ZnO) passivation layers under conditions of localized concentration changes [77].

As can be seen from the Pourbaix diagram, although in low pH range the stable form of zinc compounds is zinc ion, local pH changes due to water instability can also irreversibly generate the byproduct of alkaline hydrate zinc salts. The activity of water molecules is a significant factor in the electrode potential, and most side reactions can hardly occur with a substantially reduced activity coefficient [39,56]. Overall, the thermodynamic instabilities of zinc anode and aqueous electrolytes pose a number of challenges and issues in the development of aqueous ZMBs.

3. Differences, similarities and challenges of aqueous electrolytes for ZMBs

3.1. Differences and similarities of alkaline and neutral electrolytes

In battery systems, storage and release of energy are always accompanied by the transfer of electrons and transport of ions at the electrode-electrolyte interface (EEI) [34]. The characteristics of EEI, are greatly connected with the electrolyte, play a critical role in the electrochemical performance of rechargeable batteries. In the Zn anode side, energy storage and release are achieved by Zn deposition/dissolution both in alkaline and neutral electrolytes. What differs is the specific state of Zn metal and Zn ions and the reaction course, which are accompanied by different mechanistic interpretations.

Outside the electrochemical processes, the Zn anode itself has an unstable thermodynamic chemistry in aqueous electrolytes, which occurs in both alkaline and neutral systems. Zn metal is a relatively reactive metal and is often used as an anti-corrosion protectant for iron-based materials in marine vessels [78]. In general, the side reactions of Zn metal in aqueous media can be expressed as follows [39,77,79],

In neutral and mild acid electrolytes:

$$2Zn + 4H_2O \rightarrow 2Zn(OH)_2 + H_2\uparrow \tag{1}$$

Involved the dissolved oxygen:

$$2Zn + O_2 + 2H_2O \rightarrow 2Zn(OH)_2 \tag{2}$$

In acid electrolytes:

$$Zn + 2H^+ \rightarrow Zn^{2+} + H_2\uparrow \tag{3}$$

In alkaline electrolytes:

$$Zn(OH)_2 + 2OH^- \rightarrow Zn(OH)_4^{2-} \tag{4}$$

In neutral electrolytes, the reacting Zn metal forms a precipitate as $Zn(OH)_2$, while in alkaline systems, $Zn(OH)_2$ can dissolve with high pH and OH^- concentration [77]. The spontaneous Zn-H_2O reaction consumes the Zn anode and changes the composition of the electrolyte, and the escaping gasses can destroy the battery devices. It is therefore inevitable that the inherent instability of Zn-H_2O has to be taken into account in the battery principle and design process, which has an impact on both battery efficiency and cycle life (Table 1).

Due to the different composition and ionic concentration of the electrolyte in the neutral and alkaline systems, the free Zn ions have a diverse solvation structure. Although this structure is currently difficult to verify by substantial characterization, it is generally accepted that the solvation structures of the Zn ions in neutral and alkaline electrolytes are $[Zn(H_2O)_6]^{2+}$ and $[Zn(OH)_4]^{2-}$, respectively (Figs. 4a and b) [20,37]. For the neutral system, electrolyte based on $ZnSO_4$ is generally used as an example, and some of the organic Zn salts may have a different result [80]. The bivalent nature of Zn^{2+} cation induces strong interaction with surrounding electron donors [39]. In neutral electrolyte, oxygen atom in the water molecule carries two lone-pair electrons and has a strong electron-donating effect, thus Zn^{2+} cations are solvated by dipolar water molecules [81]. While in alkaline electrolyte, with a high concentration of OH^- anions and electrostatic interaction, free Zn^{2+} cations tend to form a more stable solvation structure binding with OH^- anions [19]. Solvated Zn^{2+} cations participate in ion transport and are involved in charge transfer and electrochemical reactions, which is an important research target.

The initial subject involved in the deposition reaction of the Zn anode is the solvated Zn^{2+} cation, and the specific process follows the classical electrical double layer theory as generally understood. First, the migration of charged solvated Zn^{2+} cations from bulk towards the electrode surface occurs under the drive of electrical field. Second, the Zn^{2+} cations enter the electrical double layer and gradually de-solvated through the inner Helmholtz layer (IHL). Third, the Zn^{2+} cations adsorb on the electrode surface, undergo electron transfer and then are reduced and deposited [39]. In alkaline and neutral electrolytes, Zn^{2+} cations with different solvated structures have different de-solvating ability and deposition processes. Apparently, Zn^{2+} cations in alkaline electrolytes have strong interactions with OH^- by the presence of electrostatic attraction. Thus, the deposition in alkaline electrolytes is a complex mechanism on which several assumptions have been done in literature [77]. The main points of contention in these assumptions are the presence of intermediates with solvation structures involving water molecules and the presence of multi-step reactions, as well as the behavioral changes brought about in relation to pH. While in neutral electrolytes, the deposition mechanism lacks extensive and substantial research, and even the solvation structure of Zn^{2+} cation is controversial due to the unpredictable anion effect. It is generally accepted that the water molecule solvent sheath is difficult to completely decompose and migrates to the electrode surface with the Zn^{2+} cations [34].

During zinc deposition/dissolution, alkaline and neutral electrolytes are accompanied by different ion migration and reaction histories, and therefore different side reactions and issues (Figs. 4c and d) [19]. In alkaline electrolytes, where there are no Zn^{2+} cations in the bulk, dissolution of the Zn anode produces a limited amount of free Zn^{2+} cations, which the combine with abundant OH^- anions. Driven by the ionic concentration, chemical reactions associated with H^+ and OH^- generally occur at cathode and it is generally assumed that Zn^{2+} cations are not involved in the cathode reactions [29]. If the limited amount of free Zn^{2+} cations diffuse under the concentration gradient, the efficiency of the anode deposition reaction is greatly affected, bringing about severe anode losses. Therefore, saturated ZnO is generally added to the alkaline electrolyte to reduce the effect of low Zn^{2+} cation concentrations on the reversibility of the electrode reaction [77]. In contrast, there is an abundance of Zn^{2+} cations in the neutral electrolytes, which is theoretically more favorable to anodic reactions [20]. As with the rocking-chair process in LIBs, the composition of neutral electrolyte is guaranteed to be constant as long as a stable Zn embedding reaction can take place in the cathode, an important difference compared to alkaline electrolytes [31]. In practice, the electrode reactions in neutral electrolytes are more complex, involving Zn^{2+} cations and protons, and there are still major challenges in terms of reversibility of the reactions and suppression of side reactions [13].

3.2. Challenges and issues of alkaline and neutral electrolytes

On the Zn anode, the side reactions and challenges involved are largely the interconnected, regardless of the electrolyte system, and

Table 1
Comparison between alkaline and neutral electrolytes for ZMBs.

Parameter	Alkaline electrolyte	Neutral and mild acid electrolyte
Species	KOH, NaOH, LiOH	$ZnSO_4$, $ZnCl_2$, $Zn(OAc)_2$, $Zn(NO_3)_2$, $Zn(OTf)_2$, $Zn(ClO_4)_2$, $Zn(BF_4)_2$, $Zn(TFSI)_2$, *etc.*
Anode chemistry	$Zn(s) \leftrightarrow Zn^{2+} + 2e^-$ $Zn^{2+} + 4OH^- \leftrightarrow Zn(OH)_4{}^{2-}$ $Zn(OH)_4{}^{2-} \rightarrow ZnO(s) + H_2O + 2OH^-$	$Zn(s) \leftrightarrow Zn^{2+} + 2e^-$
Device parameters	Anode: slurry with Zn metal and ZnO Separator: polypropylene (PP) Cathode: $Ni(OH)_2$, Ag_2O, Air, *etc.*	Anode: Zn metal Separator: glass fiber (GF) Cathode: MnO_2, V_2O_5, *etc.*
Battery performance	Specific capacity: 506 mAh/g at 0.1 C Cycling stability: 62% after 100 cycles Testing voltage: 0.5–1.8 V Composition: β-MnO_2 with Bi_2O_3 in 1 mol/L KOH + 3 mol/L LiOH	Specific capacity: 570 mAh/g at 2 mA/cm^2 Cycling stability: 92% after 1800 cycles Testing voltage: 0.8–2.2 V Composition: MnO_2 in 1 mol/L $ZnSO_4$ + 1 mol/L $MnSO_4$ + 0.1 mol/L H_2SO_4
Future directions	Additive engineering Practical consideration Novel electrolyte system	Specie excavation Additive engineering Advanced characterization

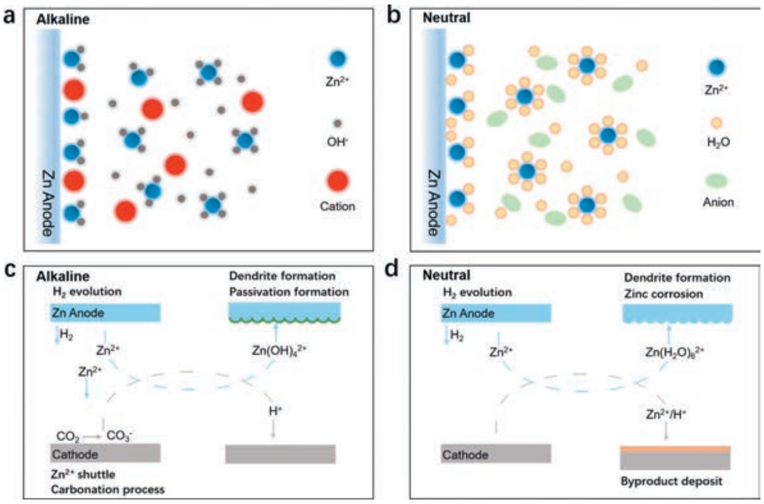


Fig. 4. Different parameters of alkaline and neutral electrolytes. Solvation structures and deposition of Zn^{2+} in (a) alkaline and (b) neutralelectrolytes. Reaction mechanisms, schematic diagrams of the battery structure and some challenges based on (c) alkaline and (d) neutral electrolytes. Reproduced with permission [19]. Copyright 2021, Elsevier.

include mainly hydrogen evolution side reactions, zinc corrosion (passivation) and zinc dendrite generation (Fig. 5) [18]. These issues greatly affect the efficiency of Zn deposition-dissolution, as well as the overall energy output and cycle life of batteries. Firstly, HER is a common problem in aqueous batteries and occurs mainly during the deposition of Zn, where protons inevitably gain electrons to produce hydrogen, given the dominance of the electrode potential (Fig. 5a) [39]. Theoretically, HER can only be alleviated indefinitely and cannot be eliminated as long as water is present. HER reduces the Coulombic efficiency in Zn deposition change the composition of the electrolyte. The high volume of gas output also can cause bulging of the batteries and electrolyte leakage, and the flammable nature of the electrolyte poses a safety hazard. The probability of HER is greater in neutral and mild acidic electrolytes than in alkaline ones.

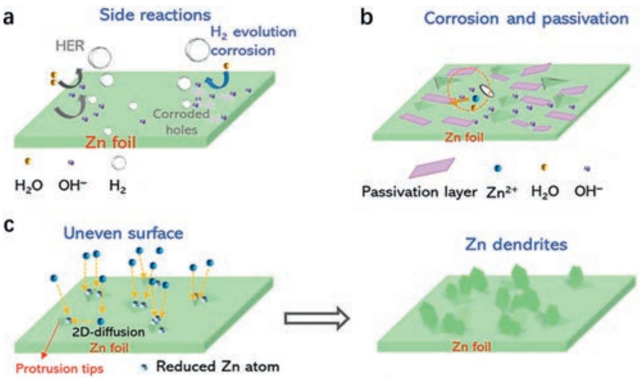


Fig. 5. Challenges and issues associated with aqueous electrolytes and Zn metal anode. (a) Side reactions of HER on Zn anode in aqueous electrolytes. (b) Corrosion and passivation of Zn anode in aqueous electrolytes. (c) The formation and growth of Zn dendrites during on uneven surface of Zn anode. Reproduced with permission [39]. Copyright 2021, Wiley-VCH.

Zinc corrosion and passivation is a superimposition of chemical and electrochemical reactions, with zinc being consumed with water (Fig. 5b). In neutral electrolytes, the side reactions of hydrolysis that proceed in the local high-energy area result in an elevation of the concentration of OH^- anions. Thus, harmful reactions between Zn^{2+} cations and OH^- anions would produce zinc hydroxides and zincates, which passivate fresh zinc [38]. In alkaline electrolytes, when the local concentration of zinc hydroxides or salts exceeds the solubility limit, precipitation occurs, leading to the formation of a dense passivation film layer [20]. The passivation layer in neutral electrolytes is mainly alkaline hydrates, whereas in alkaline electrolytes zinc oxide is predominant and passivation issue is more problematic in alkaline. The passivation in alkaline electrolytes has been associated to two layers: an external porous layer

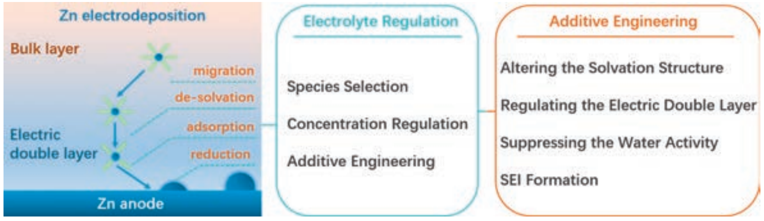


Fig. 6. Schematic of Zn electrodeposition and corresponding strategies in the electrolyte regulation and principles of additive engineering.

of saturated zincate in the closer region and an inside dense layer of ZnO [77]. With a lower pH nearby electrode surface, internal ZnO passivation layer gradually forms and acts at a barrier of OH^- transport, promoting the creation of a new passivation layer [82]. All passivation layers are virtually non-conductive, which affects the energy efficiency by consuming the Zn anodes. They also having hindrance on the transport of Zn^{2+} cations, increasing the overall internal resistance of the battery [19,83]. In addition, in open alkaline systems, such as zinc-air batteries, there is also the problem of dissolved carbon dioxide, which irreversibly generates insoluble carbonates that adhere to the electrode to create a passivation layer [77].

Dendrites formation, on the other hand, is a common problem in metal-based batteries and is generally acknowledged to be related to inhomogeneous ion stripping/plating [35]. In different electrolyte systems, zinc nucleation always carries on in local regions with a relatively high Zn^{2+} concentration initially (Fig. 5c) [18]. Then, due to a lower surface energy, Zn^{2+} cations subsequently prefer to deposit in areas of crystals already present. After that, zinc nucleation keeps growing and generate harsh dendrite growth [84]. The tip ends of dendrites continue to act as charge centers and trigger the cusp effect, bringing about a continuous charge accumulation that further promotes dendrite growth [85], leading to capacity fading and eventually short circuiting. The growth of zinc dendrites is mainly related to the inhomogeneous charge density and ion concentration [38,77]. Further considerations are also connected to the surface state of Zn anode and the composition of electrolyte, so an important strategy in solutions is the regulation of electrolyte.

Another important factor that is easily overlooked in alkaline and neutral electrolytes is pH and oxygen cycle. In alkaline electrolytes and acidic electrolytes such as conventional lead-acid batteries, high OH^- and H^+ concentrations can have the ability of mitigating changes in pH [86], whereas changes in neutral electrolytes without buffering would cause many issues. In fact, aqueous batteries are designed with electrode reactions close to the hydrolysis potentials at the outset and overcharging will inevitably lead to oxygen evolution [56]. The oxygen cycle involves the oxidation of water on the cathode to produce oxygen, the diffusion of dissolved oxygen through electrolyte to the anode side, and the reduction back to electrolyte system on the anode. This process does not result in the loss of water components, but it does lower and raise the local pH of the anode and cathode, affecting the reversibility of electrode reactions and bringing about side reactions [87]. Electrode reactions are especially concerning for ZMBs with neutral electrolytes, which lack the inherent pH-buffering capability in comparison with alkaline ones [56]. Once irreversible side reactions occur at the cathode or anode, the oxygen cycle can be disrupted, thus affecting battery performance. For example, the passivation of the zinc anode and the dissolution of cathode materials are closely related to the disruption of the oxygen cycle. Therefore, a stabilized pH operating range is required for the electrode material and a certain pH-buffering capability is required for the electrolyte regulation.

4. Strategies towards advanced alkaline and neutral electrolytes

The regulation of electrolyte composition has always been a critical subject in the development of high-performance aqueous batteries. In terms of strategies to improve the electrolyte intrinsic properties, three aspects are generally inseparable: species selection, concentration regulation and additive engineering. In this chapter, we present the strategies and research progress in the regulation of electrolytes for alkaline and neutral aqueous ZMBs, and outline the parallel design ideas and core perspectives (Fig. 6).

4.1. Species selection

The variety of electrolyte species is predictable for alkaline system due to limited soluble bases, which is still in the process of being developed and enriched in neutral systems because of the abundance of diverse anions. The most commonly used alkaline electrolytes for aqueous ZMBs are those containing KOH, NaOH and LiOH. These inorganic electrolytes have the advantages of low overpotential, high solubility and high ionic conductivity (even at low temperatures) [37]. Alkaline electrolytes are generally considered to have higher ionic conductivity than neutral electrolytes because of the enhanced proton conductivity associated with high pH [66,67]. NaOH and KOH with a concentration of 20–40 wt% are generally used as common alkaline electrolytes and are capable of providing a pH close to around 14 [44]. Among them, electrolytes based on KOH can provide enhanced ionic conductivity and lower freezing points that NaOH at certain concentrations. The conductivity of KOH is more than 40% higher than NaOH over most concentration ranges, mainly due to the lower heat of dissociation of K^+ cation, which is related to factors such as ionic radius and electronic structure [34,77]. Electrolytes containing LiOH are used to solve the undesirable intercalation of Zn^{2+} [88]. However, pure LiOH electrolytes can cause short circuits in a short time due to Zn passivation and LiOH is generally mixed with other electrolytes in practice use [20]. Additionally, saturated LiOH is used as an electrolyte which can form a layer of insoluble solid electrolyte interface (SEI) and inhibit the formation of by-products [89]. KOH-based electrolyte is used in the current commercial aqueous ZMBs, including zinc-manganese dry batteries, zinc-air batteries and zinc-nickel batteries.

Neutral electrolytes, whose solute is a metallic zinc salt, have a theoretically more stable electrolyte composition compared to alkaline electrolytes, which can reduce the formation of by-products and therefore take the dominance in current research into ZMBs [34]. To date, numerous zinc salts have been reported, including $ZnSO_4$, $ZnCl_2$, $Zn(OAc)_2$, $Zn(NO_3)_2$, $Zn(OTf)_2$, $Zn(ClO_4)_2$, $Zn(BF_4)_2$, ZnF_2 and $Zn(TFSI)_2$, where OAc^- refers to CH_3COO^-, OTf^- refers to $CF_3SO_3^-$ and $TFSI^-$ refers to $[N(SO_2CF_3)_2]^-$ [34,37-39]. During the past history of research, $ZnSO_4$ has been the most widely used electrolyte salt, due to the considerable ionic conductivity, the stable anion structure and the good compatibility with the Zn anode [90,91]. However, $ZnSO_4$ electrolyte still faces the issues of zinc corrosion, hydrogen evolution and the formation of byproducts. In the local region with an increased alkalinity, $ZnSO_4$ would combine with OH^- to form an insulating and harmful alkaline hydrate zinc sulfate, $Zn_4(OH)_6SO_4 \cdot xH_2O$ [76]. The formation of alkaline hydrate affects the efficiency and kinetics of Zn stripping/plating, while the uneven byproduct layer exacerbates electrode polarization, passivation and dendrite growth [92]. The unfavorable issues in $ZnSO_4$ electrolyte are generally considered to be related to the high activity of water, while the bulky size of OTf^- anion is thought to have the effect of reducing the number of water molecules around Zn^{2+} cations, thereby reducing the motivation of water in reactions [38]. Compared to $ZnSO_4$, $Zn(OTf)_2$ has a higher ionic conductivity, which enhances the migration and charge transfer of Zn^{2+} cations, thereby reducing the polarization of Zn dissolution/deposition [51,93]. The trifluoromethyl group in the OTf^- molecule is also thought to be hydrophobic, inhibiting the side reactions of hydrolysis and therefore widening the electrochemical stability window and improving the Coulombic efficiency of electrode reactions. Analogically, the structurally similar $TFSI^-$ anion is thought to serve the same purpose, but whether or not they alter the solvation structure of Zn^{2+} cations are currently validated by theoretical model construction instead of solid evidence. While both salts offer excellent performance, the high cost seems to be an obstacle to their practical application and development [37]. $Zn(NO_3)_2$ and $Zn(ClO_4)_2$ are relatively inexpensive zinc salts, but are not perfectly compatible with aqueous ZMBs due to the strong oxidative nature of the anions. The unstable NO_3^- and ClO_4^- can oxidize and decompose, causing severe corrosion of the Zn and the formation of a dense passivation layer [94,95]. $ZnCl_2$ and ZnF_2 are the representatives of zinc salts with halogenated anions, but Cl^- has a low electrochemical stability window and is prone to decomposition, while ZnF_2 has poor solubility and both of them have limitations in practical applications [51,96]. $Zn(OAc)_2$ is a relatively rare salt with a pair of weak acid and mild base possessing pH-buffering capacity that is effective in increasing the pH of the electrolyte [97]. Unfortunately, the same as $ZnSO_4$, alkaline hydrate byproducts are formed in $Zn(OAc)_2$. However, recent studies have shown that the alkaline hydrate based on $Zn(OAc)_2$ is capable of reversible redox reactions in certain conditions [98]. The anion in $Zn(BF_4)_2$ contains strongly electron-accepting fluorine, which theoretical calculations can offer an altered Zn^{2+} solvation structure and is therefore capable of a more reversible and stable Zn stripping/plating [80]. The good solubility of $Zn(BF_4)_2$ also gives it the capacity for low temperature energy storage applications [99]. The problem with this electrolyte is that it is stronger acidic, prone to self-corrosion and difficult to make compatible with other battery components [80]. In addition, new zinc salts, including zinc gluconate and zinc alginate, also show some potential for development [100,101]. An extra point worth noting here is that there are almost no reported zinc salts with divalent anions other than $ZnSO_4$, meaning that the number of anions in aqueous electrolytes is twice that of Zn^{2+} cations, whether this has an influence on battery performance has not been discussed in the past research.

4.2. Concentration regulation

The electrolyte concentration can alter the ionic conductivity, viscosity and ion mobility of the electrolyte, which directly affects the efficiency of the electrode reaction and thus the overall electrochemical performance of batteries. The electrolyte has a complex anion and cation chemistry and either too high or too low a concentration is detrimental to the development of battery performance. Also, electrolyte concentration affects the ratio of electrolyte ions to water molecules, which can have a variation on the solvation effect [37,38].

In alkaline electrolytes, it is worth noting that the mechanism of Zn dissolution/deposition is dependent on the concentration of the base [77]. $Zn(OH)_2$, ZnO and other byproducts are produced in electrolytes with low concentrations of base, therefore ensuring a certain alkalinity is fundamental for an alkaline ZMB to operate. An increase in concentration results in a boost in the solubility of ZnO and a decrease in electrode potential, thus improving the electrochemical performance. However, as the concentration increases, the conductivity and limiting current declines after a certain level [37,77]. Studies and results show that a KOH concentration of around 30% achieves the maximum ionic conductivity [102]. At this concentration, zinc corrosion and other device damage are also prevented, which has gained most research and commercial acceptance.

In neutral electrolytes, the pivotal parameter is that the solvation structure varies as the concentration changes. In contrast to alkaline electrolytes, the manifold anions in neutral electrolytes can produce large varieties, and the research on concentration regulation are plentiful which can be divided into moderate concentration electrolytes and ultra-high concentration electrolytes. An increase in zinc salt concentration can improve ionic conductivity, beneficial to an efficient Zn stripping/plating [51,103]. However, in some electrolytes with specific compositions, the increased concentration can ruin the stability of other battery components and reduce the electrochemical response, thereby disrupting battery performance [51,94]. With high Zn^{2+} content, the activity of the electrode depends on the chemistry of the anion and it is also predictable that increasing the concentration to improve electrochemical performance is limited [37]. An exception is the ultra-high concentration electrolyte, known as the water-in-salt electrolyte [52]. It is generally accepted that in neutral electrolytes Zn^{2+} cations are surrounded by strongly polar water molecules, but as the concentration increases to maximum, the situation that water molecules are surrounded by anions and cations occurs. Typical examples among them are electrolytes of 30 mol/L $ZnCl_2$ and 20 mol/L LiTFSI/1 mol/L $Zn(TFSI)_2$ in which Zn^{2+} solvated sheath is mainly occupied by anions from molecular dynamic [53,104]. In the ultra-high concentration electrolyte, the limitation of ion migration by the solvated sheath of water molecules is overcome, greatly improving ion transport efficiency. At the same time, the altered solvation structure of Zn^{2+} vastly lessens the side reactions generated by the active water, achieving high zinc stripping/plating efficiency and also primely widening the ESW of batteries [105,106]. This strategy is limited by the physical nature of solubility and a handful of systems have been developed, while the high cost is a challenge for further extension.

4.3. Additive engineering

Additive engineering is the most underlying and widespread electrolyte regulation strategy and there have been numerous articles presenting the applications of various additives. We focus in this section on a summary of the fundamental principles of additive action. Universal rules can be concluded in both alkaline and neutral electrolytes and that the history of additives in alkaline electrolytes can be drawn upon to drive the current research and development of neutral systems. We have summarized the roles of electrolyte additives according to the principle of action in four areas: altering the solvation structure, regulating the electric double layer, suppressing the water activity and SEI formation.

With the introduction of additives possessing higher electron-donating ability, the solvation structure of Zn^{2+} cation can be tuned through decreasing the H_2O or OH^- content and incorporating other ligands. Examples include ethylene diamine tetraacetic acid (EDTA) [107,108], tartaric acid [109,110], polyethylene glycol (PEG) [111,112], and methanol (Fig. 7a) [113,114], all of which have stronger coordinated functional groups and have been used in alkaline and neutral electrolytes to replace some of H_2O or OH^-

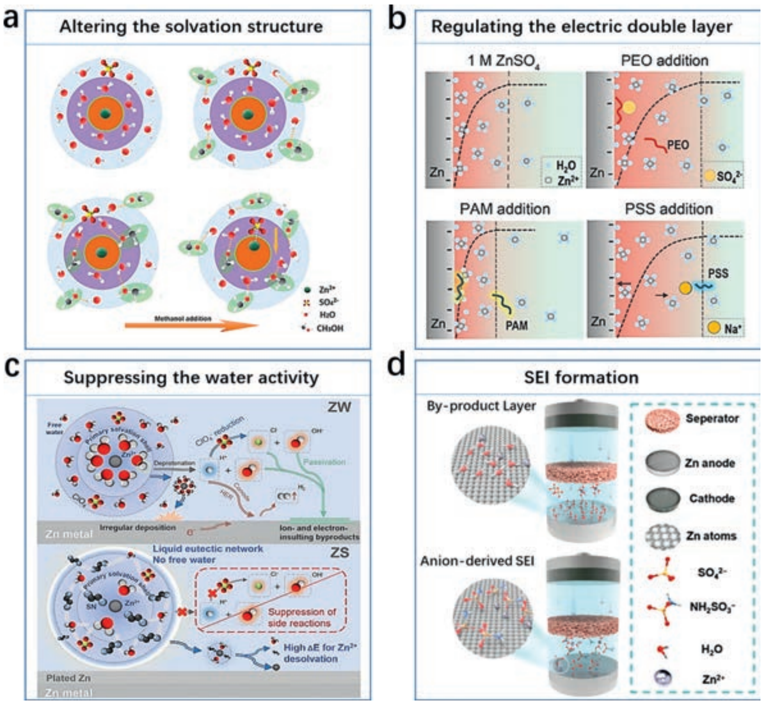


Fig. 7. Cases of additive engineering for stabilized Zn stripping/plating. (a) Schematic of the evolution in the Zn^{2+} solvent sheath with methanol addition. Reproduced with permission [114]. Copyright 2021, Wiley-VCH. (b) The evolutions of the electric double layer at the Zn anode interface in 1 mol/L $ZnSO_4$ with PEO, PAM and PSS additives. Reproduced with permission [120]. Copyright 2021, American Chemical Society. (c) Schematic of Zn^{2+} solvent structure with suppressed water. Reproduced with permission [116]. Copyright 2020, Elsevier. (d) Schematic of byproduct layer and anion-derived SEI layer to stabilize Zn anode. Reproduced with permission [133]. Copyright 2022, American Chemical Society.

around Zn^{2+} cations. With the weaker Zn-H_2O (or Zn-OH^-) bonds and stronger Zn-organic segments, the H_2O (or OH^-) would preferentially de-solvate during Zn deposition [115]. Hence the H_2O (or OH^-) molecules can hardly get close to the electrode surface with the migration of Zn^{2+} cations, which is in favor of the decrease of side reactions and facilitates homogeneous and smooth Zn deposition. Altering the solvation structure fairly boosts fast transportation of Zn^{2+} cations and diminishes the deformation of Zn anode and growth of dendrite. Of note, a certain number of H_2O (or OH^-) molecules should be kept in the solvation sheath to maintain the aqueous-like behavior as the Zn-organic bonds generate stronger de-solvation hindrance resulting in the sacrifice of kinetic parameters [116,117]. Therefore, in considering the regulation of solvation structure, the forces between Zn^{2+} cations and additives have to keep in a compromise, with a mild effect to have a positive result.

Regulating the electric double layer can effectively boost both thermodynamics and kinetics of Zn deposition/dissolution and inhibit the generation of Zn dendrites while improving the electrode reaction efficiency [39]. In general, Zn^{2+} cations along Zn anode surface suffer an uneven distribution due to the inferior interfacial contact between Zn metal and aqueous electrolyte. The current focus is on promoting the uniform distribution of Zn^{2+} cations through the polarity of the functional groups of some organic molecules, thus promoting homogeneous and orderly Zn deposition [118]. Such organic additives, including polyethylene oxide (PEO) [119,120] and polyacrylamide (PAM) (Fig. 7b) [120,121], have been reported in alkaline and neutral electrolytes. Inorganic additives, such as Na^+ [45,122] and $NH_4{}^+$ [48,123], are also regarded as effective parameters to modify the structure of the electric double layer. Zn deposition inevitably generates tips and these cations prefer to accumulate at the tips, thus creating an electrostatic shield and inhibiting the inhomogeneous deposition at the tips [124]. This effectively promotes homogeneous zinc deposition and reduces the formation of zinc dendrites. These non-reactive cations also act as electrostatic tuners in other parts of the battery, thereby improving the overall electrochemical performance.

Suppressing water activity at the interface is a pivotal direction in solving the instability of aqueous electrolytes, which is achieved through the use of additives, mainly through the reconfiguration of hydrogen bonding networks and the hydrophilic effect (Fig. 7c) [39]. Partly additives with adsorption effect such as surfactants [125,126] and phosphate analogues [109,127] are added to alkaline and neutral electrolytes. These additives prefer to adsorb onto the zinc metal surface and isolate the electrode surface from water molecules at a physical level through the hydrophobic effect, thus suppressing the water activity on the electrode surface. Dimethoxyethane (DME) [128] and dimethyl sulfoxide (DMSO) [129,130] have polar groups that also reconstruct the hydrogen bonding network with water molecules and the free water content is greatly reduced, which facilitates the transport of Zn^{2+} cations. As a result, the direct interaction between Zn anode and free water is avoided and side reactions such as chemical corrosion are prohibited. However, these non-ionizable additives also act as insulators on the electrolyte and electrode surfaces, increasing the impedance of the battery to some extent, hence the effect of the additive amount on the performance should be taken into consideration [39].

While the construction of SEI layers for LIBs has been a prominent success, the formation of SEI layers in ZMBs is currently controversial [131]. The main reported SEI layers are composed of zinc fluoride and zinc phosphate salts and are generally produced by autolytic decomposition of some fluoride containing additives and phosphate additives [99,117]. Research on zinc SEI layers is still in its infancy, with more research being carried out on artificial SEI films [132]. Artificial SEI is not self-repairable and will gradually lose the capacity of protection over time, whereas *in-situ* SEI constructed by electrolyte additives decomposition with self-healing ability is more desirable [39]. The SEI layer acts as a Zn^{2+} cation conductor and electron shield, theoretically enabling a high cycling performance of Zn deposition/dissolution reaction and separating water molecules to reduce side reactions. The presence of the SEI layer also smooths the morphology of the Zn deposit, inhibits the formation of Zn dendrites and insulates the electrolyte components from the corrosion of newborn Zn metal (Fig. 7d) [133]. Besides this, the SEI layer would increase partial impedance, while limiting the entry of hydrating ions reduces the rate performance [39]. For the present, there are still characterization and theoretical analysis difficulties in the study of zinc SEI layers.

Other strategies such as adding sorbitol and silicates [77] to alkaline electrolytes to increase the solubility of the by-product ZnO are reported, while few additives are currently available to promote the dissolution of alkaline hydrate zinc sulfate (ZHS). There are also strategies such as building a pH-buffer environment and ion trapping means to promote effective migration in neutral electrolytes [134,135]. Recently, screening of multifunctional additives has emerged as a crucial path to approach to efficiently alleviate the issues faced by aqueous ZMBs. Additives such as glycine, nitrogen-doped sulfonated carbon dots, and silk fibroin have been reported to have multiple functions in solvation restructuring and interfacial modification, effectively mitigating side reactions and improving the uniformity of zinc deposition. As far as additives to regulate the Zn anode are concerned, the mechanisms and types of additive action in alkaline and neutral electrolytes are essentially the same, to the extent that specific cases can be applied to each other. Consequently, the achievements of the research on additives for alkaline electrolytes can, for the most part, provide positive guidance for the development of neutral electrolyte systems [136,137]. Notably, we need to reduce the amount of repetitive and predictable research and explore the differences based on similarities, thus better enabling previous research to serve current and future research projects.

Furthermore, we need to note that many claims of outstanding electrochemical performance associated with electrolyte regulation are mostly based on cyclin performance results from coin cells [27]. For the further practical application of ZMBs, some basic parameters such as current density, electrolyte dosage, areal capacity and N/P ratio should be mentioned to measure the actual electrode utilization. Some related work have been reported to highlight the significance of practical considerations and attempt to call for a uniform evaluation criteria of aqueous ZMBs for practical applications [138–140]. Supplementary experiments are also encouraged to investigate the effect of electrolyte modification on battery performance in soft pack and cylindrical cell systems.

5. Conclusion and perspectives

Aqueous ZMBs have been considered as one of the most promising battery technologies for the large-scale energy storage. Research on the electrolyte regulation is a pivotal step in the development and commercialization of aqueous ZMBs. In this review evolution and progresses from alkaline to neutral electrolytes were reviewed and fundamental principles, challenges and regulation strategies of alkaline and neutral electrolytes were covered and compared to each other. It is worth noting that the history and achievements of alkaline electrolytes provide a wealth of guidance for the research on neutral or mild acid electrolytes. Currently, the comprehensive understanding of the solvation and dissolution/deposition chemistry of zinc ions is still lacking. We believe that more work needs to be focused on the uncovering mechanisms, insightful characterization and multifunctional regulation strategies to advance the electrolytes development.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The authors acknowledge the Natural Science Foundation of Sichuan Province (No. 2023NSFSC0116) and the University of Electronic Science and Technology of China for startup funding (No. A1098531023601355).

References

[1] M. Li, J. Lu, Z. Chen, K. Amine, Adv. Mater. 14 (2018) 1800561.
[2] D. Larcher, J.M. Tarascon, Nat. Chem. 7 (2015) 19–29.
[3] B. Scrosati, J. Hassoun, Y.K. Sun, Energy Environ. Sci. 4 (2011) 3287–3295.
[4] Q. Yu, K. Jiang, C. Yu, et al., Chin. Chem. Lett. 32 (2021) 2659–2678.
[5] G. Jeong, Y.U. Kim, H. Kim, Y.J. Kim, H.J. Sohn, Energy Environ. Sci. 4 (2011) 1986–2002.
[6] Y.M. Chiang, Science 330 (2010) 1485–1486.
[7] J.M. Tarascon, M. Armand, Nature 414 (2001) 359–367.
[8] D. Chao, W. Zhou, F. Xie, et al., Sci. Adv. 6 (2020) eaba4098.
[9] A. Eftekhari, Adv. Energy Mater. 8 (2018) 1801156.
[10] X. Deng, Jiang Z, Y. Chen, et al., Chin. Chem. Lett. 34 (2023) 107389.
[11] J. Yu, C.X. Zhao, J.N. Liu, et al., Green Chem. Eng. 1 (2020) 117–123.
[12] S. Gheytani, Y. Liang, F. Wu, et al., Adv. Sci. 4 (2017) 1700465.
[13] X. Jia, C. Liu, Z.G. Neale, J. Yang, G. Cao, Chem. Rev. 120 (2020) 7795–7866.
[14] M. Tang, H. Li, E. Wang, C. Wang, Chin. Chem. Lett. 29 (2018) 232–244.
[15] B.E. Jia, A.Q. Thang, C. Yan, et al., Small 18 (2022) 2107773.
[16] L. Su, L. Liu, Y. Wang, Y. Lu, X. Yan, Chin. Chem. Lett. 31 (2020) 2358–2364.
[17] J. Shin, J. Lee, Y. Park, J.W. Choi, Chem. Sci. 11 (2020) 2028–2044.
[18] B. Tang, L. Shan, S. Liang, J. Zhou, Energy Environ. Sci. 12 (2019) 3288–3304.
[19] J. Song, K. Xu, N. Liu, D. Reed, X. Li, Mater. Today 45 (2021) 191–212.
[20] N. Wang, H. Wan, J. Duan, et al., Mater. Today Adv. 11 (2021) 100149.
[21] W. Shang, W. Yu, Y. Liu, et al., Energy Storage Mater. 31 (2020) 44–57.
[22] L. Li, Y.C.A. Tsang, D. Xiao, et al., Nat. Commun. 13 (2022) 2870.
[23] Z. Xu, N. Zhang, X. Wang, Nano Energy 102 (2022) 107724.
[24] L. Yin, J. Scharf, J. Ma, et al., Joule 5 (2021) 228–248.
[25] Z. Zhao, X. Fan, J. Ding, et al., ACS Energy Lett. 4 (2019) 2259–2270.
[26] S. Jin, P.Y. Chen, Y. Qiu, et al., J. Am. Chem. Soc. 144 (2022) 19344–19352.
[27] C. Li, S. Jin, L.A. Archer, L.F. Nazar, Joule 6 (2022) 1727–1742.
[28] M. Song, H. Tan, D. Chao, H.J. Fan, Adv. Funt. Mater. 28 (2018) 1802564.
[29] G. Fang, J. Zhou, A. Pan, S. Liang, ACS Energy Lett. 3 (2018) 2480–2501.
[30] D. Zhao, S. Chen, Y. Lai, et al., Nano Energy 100 (2022) 107520.
[31] Y. Tian, Y. An, C. Wei, et al., Adv. Energy Mater. 11 (2021) 2002529.
[32] S. Huang, J. Zhu, J. Tian, Z. Niu, Chem. Eur. J. 25 (2019) 14480–14494.
[33] J. Yin, X. Feng, Z. Gan, et al., Energy Storage Mater. 54 (2023) 623–640.
[34] T. Zhang, Y. Tang, S. Guo, et al., Energy Environ. Sci. 13 (2020) 4625–4665.
[35] S. Chen, M. Zhang, P. Zou, B. Sun, S. Tao, Energy Environ. Sci. 15 (2022) 1805–1839.
[36] H. Li, S. Guo, H. Zhou, Energy Storage Mater. 56 (2023) 227–257.
[37] H. Yan, X. Zhang, Z. Yang, et al., Coord. Chem. Rev. 452 (2022) 214297.
[38] C. Liu, X. Xie, B. Lu, J. Zhou, S. Liang, ACS Energy Lett. 6 (2021) 1015–1033.
[39] D. Wang, Q. Li, Y. Zhao, et al., Adv. Energy Mater. 12 (2022) 2102707.
[40] D. Aurbach, Electrochim. Acta 47 (2002) 3561.
[41] C.A. Vincent, Modern Batteries, 2nd ed., Elsevier, Amsterdam, 1997.
[42] K.V. Kordesch, C. Fabjan, J.D. Ivad, J. Oliveira, J. Power Sources 65 (1997) 77–80.
[43] B. Sundén, Hydrogen, Batteries and Fuel Cells, Elsevier, Amsterdam, 2019.
[44] D. Linden, T.B. Reddy, Linden's Handbook of Batteries, 4th ed., McGraw-Hill, New York, 2011.
[45] F.R. McLarnon, E.J. Cairns, J. Electrochem. Soc. 138 (1991) 645–664.
[46] P. Pei, K. Wang, Z. Ma, Appl. Energy 128 (2014) 315–324.
[47] L. Binder, W. Odar, K. Kordesch, J. Power Sources 6 (1981) 271–289.
[48] R. Shivkumar, G.P. Kalaignan, T. Vasudevan, J. Power Sources 55 (1995) 53–62.
[49] T. Shoji, M. Hishinuma, T. Yamamoto, J. Appl. Electrochem. 18 (1987) 521–526.
[50] C. Xu, B. Li, H. Du, F. Kang, Angew. Chem. Int. Ed. 51 (2012) 933–935.
[51] N. Zhang, F. Cheng, Y. Liu, et al., J. Am. Chem. Soc. 138 (2016) 12894–12901.
[52] L. Suo, O. Borodin, T. Gao, et al., Science 350 (2015) 938–943.
[53] C. Zhang, J. Holoubek, X. Wu, et al., Chem. Commun. 54 (2018) 14097–14099.
[54] A.G. Bosca, D. Bélanger, J. Power Sources 326 (2016) 595–603.
[55] J. Janek, W.G. Zeier, Nat. Energy 1 (2016) 16141.
[56] Y. Liang, Y. Yao, Nat. Rev. Mater. 8 (2023) 109–122.
[57] M. Zhang, W. Wang, X. Liang, et al., Chin. Chem. Lett. 32 (2021) 2217–2221.
[58] L. Zhang, D. Wu, G. Wang, et al., Chin. Chem. Lett. 32 (2021) 926–931.
[59] H. Zhang, X. Liu, H. Li, I. Hasa, S. Passerini, Angew. Chem. Int. Ed. 60 (2020) 598–616.
[60] J. Huang, Z. Guo, Y. Ma, et al., Small Methods 3 (2018) 1800272.
[61] F. Beck, P. Rüetschi, Electrochim. Acta 45 (2000) 15–16.
[62] Y.H. Zhu, Y.F. Cui, Z.L. Xie, et al., Nat. Rev. Chem. 6 (2022) 505–517.

[63] B. Lafitte, P. Jannasch, Advances in Fuel Cells, Elsevier, Amsterdam, 2007.
[64] Y. Tian, J. Hong, D. Cao, et al., Science 377 (2022) 315–319.
[65] N. Agmon, Chem. Phys. Lett. 244 (1995) 456–462.
[66] F. Allebrod, C. Chatzichristodoulou, P.L. Mollerup, M.B. Mogensen, Int. J. Hydrog. Energy 37 (2015) 16505–16514.
[67] A. Carton, F. Sobron, S. Bolado, J.I. Gerboles, J. Chem. Eng. Data 40 (1995) 987–991.
[68] M. Singh, J. Kaiser, H. Hahn, J. Electrochem. Soc. 162 (2015) A1196–A1201.
[69] W. Wu, S. Shabhag, J. Chang, A. Rutt, J.F. Whitacre, J. Electrochem. Soc. 162 (2015) A803–A808.
[70] I. Roger, M.A. Shipman, M.D. Symes, Nat. Rev. Chem. 1 (2017) 0003.
[71] S. Trasatti, J. Electroanal. Chem. 39 (1972) 163–184.
[72] D. Chao, S.Z. Qiao, Joule 4 (2020) 1846–1851.
[73] Z. Liu, Y. Huang, Y. Huang, et al., Chem. Soc. Rev. 49 (2020) 180–232.
[74] D. Han, S. Wu, S. Zhang, et al., Small 16 (2020) 2001736.
[75] Q. Li, Q. Luo, X. Liu, J. Yi, Batteries Supercaps 5 (2022) e202100417.
[76] L. Hong, X. Wu, L.Y. Wang, et al., ACS Nano 16 (2022) 6906–6915.
[77] A.R. Mainar, O. Leonet, M. Bengoechea, et al., Int. J. Energy Res. 40 (2016) 1032–1049.
[78] P.P. Wu, G.L. Song, Y.X. Zhu, D.J. Zheng, Corro. Sci. 194 (2022) 109943.
[79] J. Hao, L. Yuan, Y. Zhu, M. Jaroniec, S.Z. Qiao, Adv. Mater. 34 (2022) 2206963.
[80] T. Sun, X. Yuan, K. Wang, et al., J. Mater. Chem. A 9 (2021) 7042–7047.
[81] X. Tang, D. Zhou, B. Zhang, et al., Nat. Commun. 12 (2021) 2857.
[82] M. Cai, S.M. Park, J. Electrochem. Soc. 143 (1996) 2125–2131.
[83] X. Zhou, Y. Lu, Q. Zhang, et al., ACS Appl. Mater. Interfaces 12 (2020) 55476–55482.
[84] Z. Zhao, J. Zhao, Z. Hu, et al., Energy Environ. Sci. 12 (2019) 1938–1949.
[85] W. Lu, C. Xie, H. Zhang, X. Li, ChemSusChem 11 (2018) 3996–4006.
[86] R. Nelson, JOM 53 (2001) 28–33.
[87] Y. Liang, Y. Jing, S. Gheytani, et al., Nat. Mater. 16 (2017) 841–848.
[88] M. Minakshi, P. Singh, M. Carter, K. Prince, Electrochem. Solid-State Lett. 11 (2008) A145–A149.
[89] M. Manickam, P. Singh, T.B. Issa, S. Thurgate, R.D. Macro, J. Power Sources 130 (2004) 254–259.
[90] B. Wu, Y. Mu, Z. Li, et al., Chin. Chem. Lett. 34 (2023) 107629.
[91] H. Zhang, Q. Liu, Y. Fang, et al., Adv. Mater. 31 (2019) 1904948.
[92] B. Lee, H.R. Seo, H.R. Lee, et al., ChemSusChem 9 (2016) 2948–2956.
[93] N. Zhang, F. Cheng, J. Liu, et al., Nat. Commun. 8 (2017) 405.
[94] G. Kasiri, R. Trócoli, A.B. Hashemi, F.L. Mantia, Electrochim. Acta 222 (2016) 74–83.
[95] N.S.V. Narayanan, B.V. Ashokraj, S. Sampath, J. Colloid Interface Sci. 342 (2010) 505–512.
[96] L. Wang, Y. Zhang, H. Hu, et al., ACS Appl. Mater. Interfaces 11 (2019) 42000–42005.
[97] G.L. Li, Z. Yang, Y. Jiang, et al., Nano Energy 25 (2016) 211–217.
[98] W. Sun, V. Küpers, F. Wang, P. Bieker, M. Winter, Angew. Chem. Int. Ed. 61 (2022) e202207353.
[99] D. Han, C. Cui, K. Zhang, et al., Nat. Sustain. 5 (2022) 205–213.
[100] X. Xu, M. Song, M. Li, et al., Chem. Eng. J. 454 (2023) 140364.
[101] Q. Liu, Y. Wang, X. Hong, et al., Adv. Energy Mater. 12 (2022) 2200318.
[102] K. Kordesh, M. Weissenbacher, J. Power Sources 51 (1994) 61–78.
[103] J. Zhou, L. Shan, Z. Wu, et al., Chem. Commun. 54 (2018) 4457–4460.
[104] F. Wang, O. Borodin, T. Gao, et al., Nat. Mater. 17 (2018) 543–549.
[105] T. Liang, R. Hou, Q. Dou, H. Zhang, X. Yan, Adv. Funct. Mater. 31 (2021) 2006749.
[106] P. Kulkarni, D. Ghosh, R.G. Balakrishna, Sustain. Energ. Fuels 5 (2021) 1619–1654.
[107] M.R.H. Almeida, E.P. Barbano, M.F. Carvalho, et al., Surf. Coat. Technol. 206 (2011) 95–102.
[108] J. Cao, D. Zhang, R. Chanajaree, et al., Adv. Powder Mater. 1 (2022) 100007.
[109] C.W. Lee, K. Sathiyanarayanan, S.W. Eom, H.S. Kim, M.S. Yun, J. Power Sources 159 (2007) 1474–1477.
[110] J. Wan, R. Wang, Z. Liu, et al., ACS Nano 17 (2023) 1610–1621.
[111] L. Lyu, Y. Gao, Y. Wang, et al., Chem. Phys. Lett. 723 (2019) 102–110.
[112] Y. Wu, Z. Zhu, D. Shen, et al., Energy Storage Mater. 45 (2021) 1084–1091.
[113] G. Koscher, K. Kordesch, J. Power Sources 136 (2004) 215–219.
[114] J. Hao, L. Yuan, C. Ye, et al., Angew. Chem. Int. Ed. 60 (2021) 7366–7375.
[115] N. Chang, T. Li, R. Li, et al., Energy Environ. Sci. 13 (2020) 3527–3535.
[116] W. Yang, X. Du, J. Zhao, et al., Joule 4 (2020) 1557–1574.
[117] A. Naveed, H. Yang, J. Yang, Y. Nuli, J. Wang, Angew. Chem. Int. Ed. 58 (2019) 2760–2764.
[118] L. Cao, D. Li, T. Pollard, et al., Nat. Nanotechnol. 16 (2021) 902–910.
[119] Z. Zhang, Y. Shen, Z. Zhao, et al., J. Power Sources 542 (2022) 231815.
[120] M. Yan, N. Dong, X. Zhao, Y. Sun, H. Pan, ACS Energy Lett. 6 (2021) 3236–3243.
[121] Y. Zhang, H. Qin, M. Alfred, et al., Energy Storage Mater. 42 (2021) 88–96.
[122] F. Wan, L. Zhang, X. Dai, et al., Nat. Commun. 9 (2018) 1–11.
[123] S. Qian, J. Zhou, M. Peng, et al., Mater. Chem. Front. 7 (2022) 901–907.
[124] Y. Geng, L. Pan, Z. Peng, et al., Energy Storage Mater. 51 (2022) 733–755.
[125] K. Liu, P. He, H. Bai, et al., Mater. Chem. Phys. 199 (2017) 73–78.
[126] J. Hao, J. Long, B. Li, et al., Adv. Funct. Mater. 29 (2019) 1903605.
[127] L. Cao, D. Li, T. Deng, Q. Li, C. Wang, Angew. Chem. Int. Ed. 59 (2020) 19292–19296.
[128] J. Cui, X. Liu, Y. Xie, et al., Mater. Today Energy 18 (2020) 100563.
[129] S. Chen, C. Peng, D. Xue, L. Ma, C. Zhi, Angew. Chem. Int. Ed. 61 (2022) e202212767.
[130] L. Cao, D. Li, E. Hu, et al., J. Am. Chem. Soc. 142 (2020) 21404–21409.
[131] Y. Liu, Z. Yu, J. Chen, et al., Chin. Chem. Lett. 33 (2022) 1817–1830.
[132] A. Chen, C. Zhao, J. Gao, et al., Energy Environ. Sci. 16 (2023) 275–284.
[133] X. Xu, H. Su, J. Zhang, et al., ACS Energy Lett. 7 (2022) 4459–4468.
[134] W. Zhang, Y. Dai, R. Chen, et al., Angew. Chem. Int. Ed. 62 (2023) e202212695.
[135] M. Qiu, P. Sun, Y. Wang, et al., Angew. Chem. Int. Ed. 61 (2022) e202210979.
[136] J.N. Liu, C.X. Zhao, D. Ren, et al., Adv. Mater. 34 (2022) 2109407.
[137] X.M. Liu, X. Cui, K. Dastafkan, et al., J. Energy Chem. 53 (2021) 290–302.
[138] W. Cai, Y.X. Yao, G.L. Zhu, et al., Chem. Soc. Rev. 49 (2020) 3806–3833.
[139] J.F. Parker, J.S. Ko, D.R. Rolison, J.W. Long, Joule 2 (2018) 2519–2527.
[140] G. Zampardi, F.L. Mantia, Nat. Commun. 13 (2022) 687.