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Electrolyte engineering for optimizing anode/electrolyte interface towards superior aqueous zinc-ion batteries: A review

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Abstract: Aqueous zinc-ion batteries (AZIBs) are promising candidates for the large-scale energy storage systems due to their high intrinsic safety, cost-effectiveness and environmental friendliness. However, issues such as dendrite growth, hydrogen evolution reaction, and interfacial passivation occurring at the anode/electrolyte interface (AEI) have hindered their practical application. Constructing a stable AEI plays a key role in regulating zinc deposition and improving the cycle life of AZIBs. The fundamentals of AEI and the challenges faced by the Zn anode due to unstable interfaces are discussed. A comprehensive summary of electrolyte regulation strategies by electrolyte engineering to achieve a stable Zn anode is provided. The effectiveness evaluation techniques for stable AEI are also analyzed, including the interfacial chemistry and surface morphology evolution of the Zn anode. Finally, suggestions and perspectives for future research are offered about enabling a durable and stable AEI via electrolyte engineering, which may pave the way for developing high-performance AZIBs.

Key words: aqueous zinc-ion battery; anode/electrolyte interface; zinc anode; aqueous electrolyte; electrolyte engineering; electrolyte additives

1 Introduction

In the past two decades, lithium-ion batteries (LIBs) have been a hot topic of research in electrochemical energy storage systems in both academia and industry [1−3]. However, prominent safety issues during service, limited energy density, and extremely low elemental reserves are the main obstacles to the further development of LIBs [4−7]. Therefore, the design and application of new environmentally friendly electrochemical energy storage systems are urgently needed [8−10]. In recent years, metal batteries based on aqueous electrolytes, such as aqueous zinc-ion batteries (AZIBs), have attracted considerable interests due to their simple preparation, low cost, and high safety [11,12]. AZIBs can directly use zinc metal as the anode, and zinc metal has the advantages of abundant crust reserves, obvious cost-effectiveness, and high volumetric capacity (5851 mA·h/cm^3) and gravimetric capacity (820 mA·h/g) [13−15]. The manufacturing cost of AZIBs is approximately 65 US$/(kW·h), much lower than that of existing LIBs (181 US$/(kW·h)) and sodium-ion batteries [16−18]. Moreover, AZIBs can offer a higher volumetric energy density in comparison to the commercial lead-acid batteries. Therefore, compared to other energy storage battery systems, AZIBs have significant advantages in terms of the environmental friendliness, safety, and manufacturing cost, holding a grand promise for the field of portable and stationary energy storage applications.

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Since first establishment of the concept of AZIBs, research on AZIBs has progressed rapidly and achieved significant breakthroughs [19]. However, the practical application of AZIBs is largely limited by the interface issues between the zinc metal anode and the aqueous electrolyte. The anode/electrolyte interface (AEI) in aqueous rechargeable batteries is crucial in terms of electrode/electrolyte stability, charge dynamics, and overall battery performance [20]. During the charging and discharging process of the battery, electrons and charge carriers are transferred and transported through the AEI [12]. During the electrode operation, interfacial reactions triggered by different chemical potentials of the anode and the electrolyte lead to the formation of a depletion zone, which affects the redistribution of the charge carriers in the AEI and the generation of electrode polarization [21]. Moreover, Zn metal is thermodynamically unstable in an aqueous environment [22]. Therefore, the separation of zinc ions from the solvation structure and their migration and diffusion in the double electric layer play a decisive role in the nucleation and growth of zinc. The continuous cycling of zinc deposition/stripping inevitably leads to the dendrite growth, hydrogen evolution reaction (HER), and zinc corrosion or passivation at the interface [23]. Although difference of the rampant dendrites in organic batteries can puncture the separator and cause battery explosions with fire risks, the continuous consumption of the electrode/electrolyte and uncontrollable growth of dendrites in aqueous electrolytes can still cause battery swelling and a decline in reversible capacity [24]. Therefore, understanding the interfacial chemistry and physical characteristics of AZIBs is critically important.

Currently, to construct a stable Zn metal anode, numerous strategies have been developed, such as using protective coating layers, building three-dimensional anodes, or fabricating alloy anodes. However, the complex preparation conditions and unstable products make it difficult to achieve large-scale applications. In contrast, electrolyte optimization strategies are widely seen to be practically expedient due to their simplicity, low cost, and significant improvement in cycle stability. Impressively, many cost-effective and environmentally friendly electrolyte systems have been developed, which further expand the inherent advantages of AZIBs. This work provides a concise overview of the challenges faced by the AEI in AZIBs. Some strategies to address the challenges are proposed from the perspective of how the electrolyte regulation strategies can stabilize AEI. Additionally, some characterization measurements and computational simulations on the AEI are summarized. Finally, the remaining challenges and future perspectives on constructing a stable AEI are also provided.

2 Zn anode interface chemistry

Like other secondary batteries, AZIBs consist of four basic components: cathode, anode, electrolyte, and separator. Typically, the anode material in AZIBs is zinc metal, and the separator is a porous polymer film or glass fiber membrane which allows the passage of zinc ions while preventing electron exchange in the internal circuit. The electrolyte is an aqueous solution containing zinc salts, acting as a conductive medium that allows Zn^{2+} to shuttle between the electrodes, which is the most distinct difference between AZIBs and other metal batteries. Due to the continuous and irreversible consumption of zinc metal by alkaline electrolytes, most current research on AZIBs is focused on neutral or weakly acidic aqueous electrolytes. However, the electrochemical processes of anodes in aqueous electrolytes are much more complex than those in organic electrolytes [25]. Taking the commonly used zinc sulfate electrolyte as an example, zinc ions as Lewis acids always combine with free water molecules in the electrolyte to form octahedral units of hydrated zinc ions, $[Zn(H_2O)_6]^{2+}$ [26,27]. During the electrodeposition process, hydrated zinc ions release a large number of free water molecules at the anode surface, and the water molecules generated by desolvation are more likely to capture electrons and undergo decomposition, accompanied by additional energy consumption [28,29]. In the operation of AZIBs, complex chemical reactions continue to occur at the anode interface, including the desolvation of zinc ions, the decomposition of electrolyte salts or water solvents, and various parasitic side reactions, ultimately causing severe damage to the anode [30]. Therefore, a deeper understanding of the origins of adverse reactions on the AEI is crucial to find effective measures to address these issues.

2.1 Chemical reaction at anode/electrolyte interface

In neutral or weakly acidic aqueous electrolytes, Zn ions in the electrolyte tend to combine with water molecules to form hydrated zinc ions. The chemical reactions at the anode are as follows [31]:

$$Zn-2e\rightarrow Zn^{2+} \quad (1)$$

$$Zn^{2+}+6H_2O\rightarrow Zn(H_2O)_6^{2+} \quad (2)$$

The electrochemical reaction mechanism during the charging and discharging process of zinc anode can generally be simply represented by the following equations:

Discharging:

$$Zn\rightarrow Zn^{2+}+2e \quad (3)$$

Charging:

$$Zn^{2+}+2e\rightarrow Zn \quad (4)$$

Overall electrochemical reaction:

$$Zn^{2+}+2e\rightleftharpoons Zn,\ \varphi^0=-0.76\ V\ (vs\ SHE) \quad (5)$$

It is generally believed that the process of zinc electrodeposition typically involves the following steps. First, hydrated zinc ions move within the electrolyte under the influence of an external electric field. Upon reaching the inner Helmholtz plane, the zinc ions are released through a desolvation process which involves the removal of solvent molecules from the solvation shell [32,33]. Subsequently, the zinc ions receive electrons on the surface of the anode to form a zinc nucleus. Following this, additional zinc ions successively receive electrons at the nucleation sites to undergo reduction, ultimately achieving zinc electrodeposition.

2.2 Challenges at electrode/electrolyte interface

It is worth noting that every step in the electrodeposition process can affect the final electrodeposits morphology, which determines largely the electrochemical reversibility of the zinc metal anode. Under ideal conditions, the abundance of nucleation sites on the zinc anode, and the dense and smooth electrodeposition layer can achieve long-term reversible deposition/stripping [34,35]. However, in practical applications, influenced by factors such as the uneven initial electrode interface, electrode polarization, and uneven ion flux, the deposited zinc often forms non-uniform dendrites, which severely reduce the stability of the electrode [36]. Meanwhile, various interfacial side reactions also accompany the zinc electrodeposition process, further increasing the difficulty in developing high-performance Zn metal anodes.

2.2.1 Zn dendrite growth

Due to the surface roughness and mechanical processing marks on commercial zinc foils, many high-curvature protrusions or scratches are formed on the surface of the zinc anode. These sites can cause higher local current densities, thereby attracting and accumulating zinc ions [37,38]. As a result, a large number of zinc ions are deposited at these tip sites, gradually forming zinc dendrites, which is also known as the “tip effect”. The rapid consumption of zinc ions at the tip also causes lateral diffusion of zinc ions along the electrode plane (two-dimensional diffusion), further reducing the deposition rate of zinc at other sites. The continuously accumulating zinc dendrites may break off and loosely adhere to electrode surface. Once dendritic electrodeposits detach from the zinc anode surface, “dead zinc” will be formed, leading to rapid consumption of active Zn metal and a decrease in the coulombic efficiency [39−41]. Generally, Zn^{2+} ions are typically deposited as hexagonal platelets to reduce the thermodynamic free energy. The continuous accumulation of zinc dendrites can cause growth perpendicular to the electrode surface and eventually puncture into the separator, resulting in an internal short circuit and fail of the battery [42]. The formation of zinc dendrites is influenced by various parameters, including the concentration of zinc ions, current density, electrode structure, electronic conductivity, and temperature. Noticeably, the current theories on zinc dendrite formation, such as Sand’s time (τ_s), are essentially qualitative rather than quantitative.

2.2.2 Corrosion and passivation

Because the standard reduction potential of Zn/Zn^{2+} (−0.76 V vs SHE) is lower than that of H^+/H_2 (0 V vs SHE), zinc metal is thermodynamically unstable in aqueous solutions:

$$Zn^{2+}+2e\rightleftharpoons Zn\ (-0.76\ V) \quad (6)$$

$$2H^++2e\rightleftharpoons H_2\uparrow\ (0\ V) \quad (7)$$

Even worse, when the battery is at rest, active zinc metal can also react with the electrolyte. The basic HER occurring at the anode interface can be described as follows:

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

$$2H_2O+2e\rightarrow H_2\uparrow+2OH^{-} \quad (9)$$

$$Zn+2H_2O\rightarrow Zn(OH)_2+H_2\uparrow \quad (10)$$

In the actual operation of the battery, the HER in neutral and mild electrolytes is also influenced by kinetic factors such as electrochemical polarization, temperature, and current density. Moreover, the uneven anode surface and accumulated zinc dendrites can significantly promote HER by affecting the aforementioned factors [43]. HER adversely affects the battery in many ways: (1) The irreversible HER competes with the zinc ion deposition process for electrons, reducing the coulombic and current efficiency; (2) The produced hydrogen gas can adsorb on the electrode surface or form holes through corrosion side reactions, further exacerbating the uneven zinc deposition and increasing the nucleation overpotential; (3) The continuous HER leads to the consumption of active zinc metal and aqueous electrolyte, reducing the coulombic efficiency and lifespan of batteries; (4) The occurrence of HER raises the concentration of OH^{-} at the interface, which can form a local alkaline environment, promoting the corrosion of the zinc anode and the formation of a surface passivation layer; (5) The accumulation of hydrogen gas increases the internal pressure of sealed batteries, leading to battery expansion with electrolyte leakage and even explosion.

During the deposition/stripping process of zinc, in addition to the HER, the chemical and electrochemical corrosion of the zinc anode is another main reason which limits the electrochemical reversibility of the zinc anode [44]. When using $ZnSO_4$ aqueous solution as the electrolyte, zinc ions attract SO_4^{2-} or OH^{-} under the influence of electrostatic forces to form the passivation product precipitate $Zn_4SO_4(OH)_6{\cdot}xH_2O$ (ZHS), and the corresponding reactions are shown as follows:

$$Zn^{2+}+2OH^{-}\rightarrow ZnO+H_2O \quad (11)$$

$$3Zn^{2+}+6OH^{-}+ZnSO_4+xH_2O\rightarrow Zn_4SO_4(OH)_6{\cdot}xH_2O \quad (12)$$

These side reactions consume the electrolyte, and produce byproducts with low solubility and conductivity, which gradually cover the electrode surface and block the active area of the electrochemical reaction, known as “passivation”. The loose and porous passivation layer is difficult to prevent the continuation of side reactions [45]. In addition, due to the coexistence of different metals in the electrolyte, galvanic corrosion may also occur in addition to HER, thereby reducing the calendar life of the battery.

It is noteworthy that the growth of zinc dendrites and interfacial side reactions are intertwined in nature, as illustrated in Fig. 1. Specifically, the growth of zinc dendrites increases the electrode surface area, which promotes the occurrence of HER and corrosion. In turn, the byproducts accumulated on the electrode surface cause an uneven distribution of current density and zinc ion flux, further stimulating dendrite growth [46]. This is a vicious cycle process, which is difficult to fundamentally improve by solving a

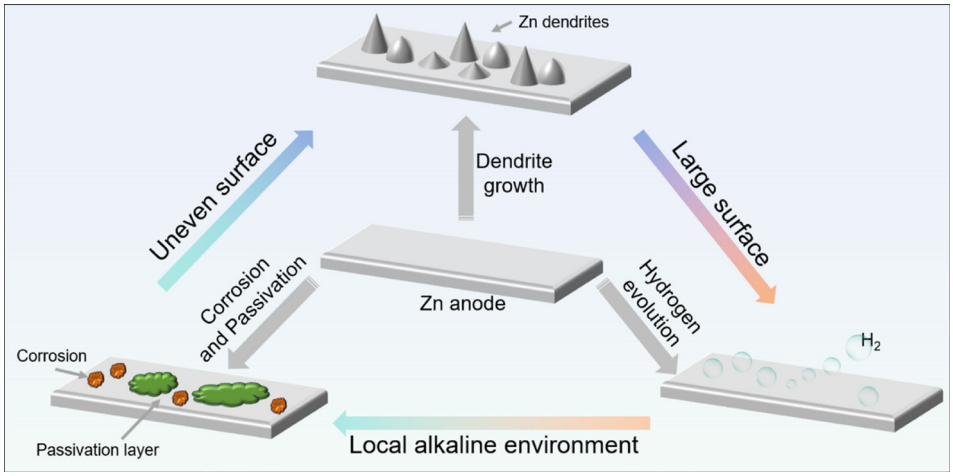

Fig. 1 Schematic illustration of relationship of Zn dendrite growth, corrosion and passivation

single problem. Fortunately, both of these issues occur at the AEI and are closely related to the electrolyte, so they can be simultaneously suppressed by electrolyte regulation strategies to pursue high-performance AZIBs.

3 Aqueous electrolyte regulation for anode/electrolyte interface

Electrolyte is an important component of the battery operation, serving as a conduit for the transfer of charge carriers between the anode and cathode. More importantly, the problems faced by the Zn metal anode can all be attributed to an unstable AEI, and the electrolyte plays a crucial role in determining the stability of AEI and the electrochemical behavior [47,48]. In an ideal state, the electrolyte can not only achieve fast zinc ion dynamics but also suppress the growth of zinc dendrites and the occurrence of parasitic side reactions by stabilizing the AEI, ultimately achieving the highly reversible electrochemical performance. Enhancing AEI through electrolyte regulation strategies can be mainly divided into three categories (Fig. 2): (1) by adjusting the type of salts, concentration, or composition of solvents in the electrolyte, changing the interactions between cations and anions, promoting the participation of anions in the solvation structure or regulating the activity of water molecules to facilitate the formation of inorganic solid electrolyte interphase (SEI) layers on the anode surface or inhibit the decomposition of water molecules; (2) constructing new water-poor functional electrolytes, such as eutectic electrolytes and hydrogel electrolytes, to regulate the competitive interactions among solvents, cations, and anions, optimize the solvation structure of electrolyte and reduce water content, thereby improving the stability and kinetics of electrochemical reactions; (3) using film-forming additives in the electrolyte to construct a stable SEI.

3.1 Types of electrolyte salts

Electrolytes are commonly prepared by mixing Zn salts into water solution. The choice of Zn salt is crucial because anions can significantly influence the Zn^{2+} ions and alter the electrolyte properties, which in turn affects the performance of zinc metal anodes.

$ZnSO_4$ is the most widely used zinc salt solute in AZIBs due to its stable structure, low cost, and high compatibility with cathode materials [31]. As

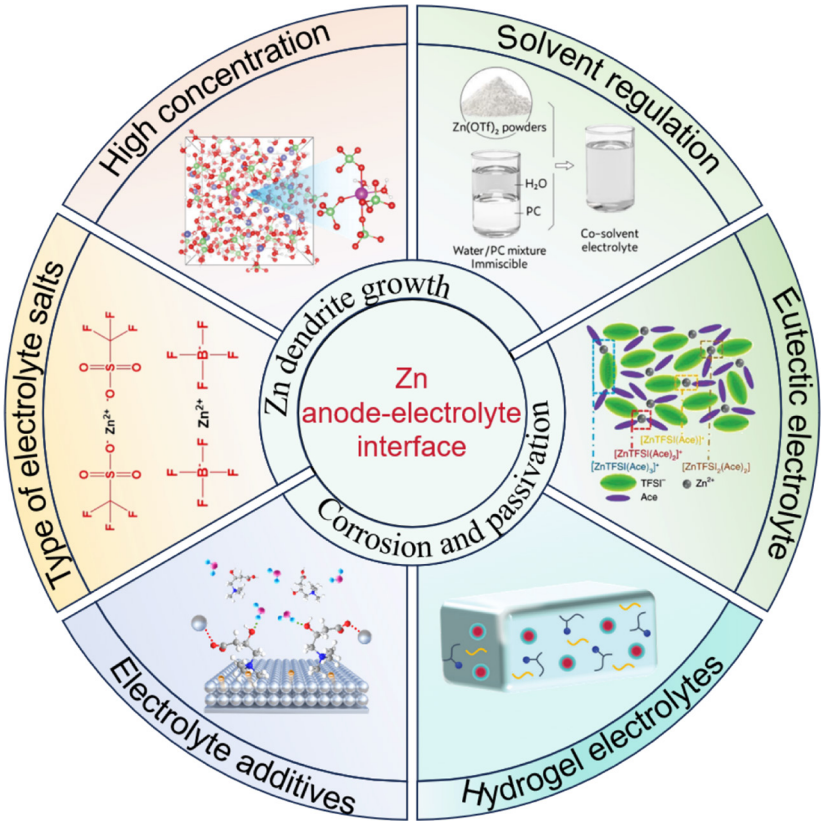

Fig. 2 Schematic illustration of electrolyte regulation for stable anode/electrolyte interface

shown in cyclic voltammetry results in Fig. 3(a), the electrochemical stability window (ESW) of the zinc sulfate electrolyte is between 0.2 and 2.0 V [49]. However, this voltage window is still difficult to meet the practical applications and requirements, as dendrite formation and side reactions often occur during anode operation. As also mentioned in the previous section, SO_4^{2-} can participate in the electrochemical corrosion process at the anode, generating insulating ZHS by-products and reducing electrode reversibility. Although $ZnCl_2$ has poor stability at high current densities and poor compatibility with cathode materials, it is widely used in the development of high salt concentration electrolytes attributed to its high solubility in water (~31 mol/L) and extremely low cost [50]. In addition, other electrolyte additives can be added to the zinc chloride electrolyte to further improve the cycle performance of AZIBs. Compared with zinc sulfate, $Zn(CH_3COO)_2$ can increase the pH value of the electrolyte, which is not only beneficial for suppressing the occurrence of HER but also compatible with some cathode materials that are sensitive to hydrogen ions. Moreover, a smaller potential separation is observed in the $Zn(CH_3COO)_2$ electrolyte, reflecting better reversibility than the $ZnSO_4$ electrolyte (Fig. 3(b)) [51]. However, the ionic conductivity of the $Zn(CH_3COO)_2$ electrolyte is considered to be inferior to that of $ZnSO_4$ electrolyte, which affects the migration and diffusion dynamics of zinc ions [52].

As for $Zn(NO_3)_2$, since the NO_3^- anion is an oxidizing anion, it is unstable and prone to produce hazardous gases such as NO and NO_2, which are detrimental to battery performance [49]. According to the cyclic voltammetry, no characteristic peak pairs corresponding to the dissolution/deposition of Zn can be found in 1 mol/L $Zn(NO_3)_2$ electrolyte. Moreover, as a strong oxidizer, the NO_3^- anion is prone to side reactions with zinc metal, forming an oxidative SEI at the interface during the initial cycles of the battery, affecting the transport and transfer of electrons and ions [53]. Although $Zn(NO_3)_2$ is not suitable for direct use as a zinc salt in the electrolyte, it can be added to the $Zn(CF_3SO_3)_2$ electrolyte as an effective additive, which can induce the in-situ formation of a robust inorganic−organic bilayer SEI. The inorganic inner layer promotes the diffusion of Zn ions, while the organic outer layer inhibits the permeation of water, significantly enhancing the cycle lifespan of batteries (Fig. 4(a)) [54]. Similarly, the $Zn(ClO_4)_2$ electrolyte can form a Cl^- containing layer on the anode surface through the controlled reduction of ClO_4^- on Zn, effectively limiting side reactions at the interface. As shown in Fig. 4(b), XRD test results of the surface of the zinc electrode after cycling indicate that no obvious by-products are produced on the electrode surface using the $Zn(ClO_4)_2$ electrolyte [55]. In addition to $Zn(NO_3)_2$ and $Zn(ClO_4)_2$, $Zn(H_2PO_4)_2$ salt can also be used as a component of the electrolyte in AZIBs (Fig. 4(c)). The addition of $Zn(H_2PO_4)_2$ can construct a dense, stable, and high Zn^{2+} conductive SEI layer on the surface of zinc metal (approximately 140 nm thick), achieving rapid Zn^{2+} transport kinetics while enabling uniform zinc deposition, and suppressing the occurrence of side reactions by separating the active zinc from the aqueous electrolyte through the SEI layer [56].

Currently, the zinc trifluoromethanesulfonate ($Zn(OTf)_2$) has become the most widely used organic zinc salt in AZIBs due to its wide operation

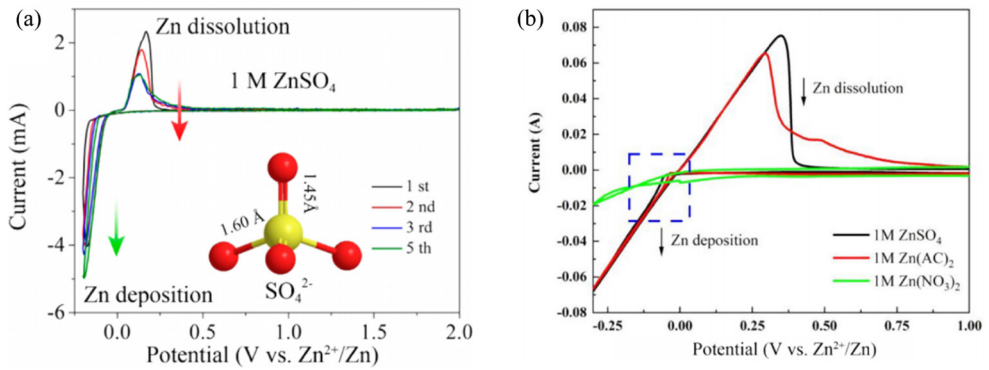

Fig. 3 Cyclic voltammograms of Zn electrode in $ZnSO_4$ electrolyte (a) (Reproduced with permission from Ref. [49]); Cyclic voltammetry curves of different electrolytes (b) (Reproduced with permission from Ref. [51])

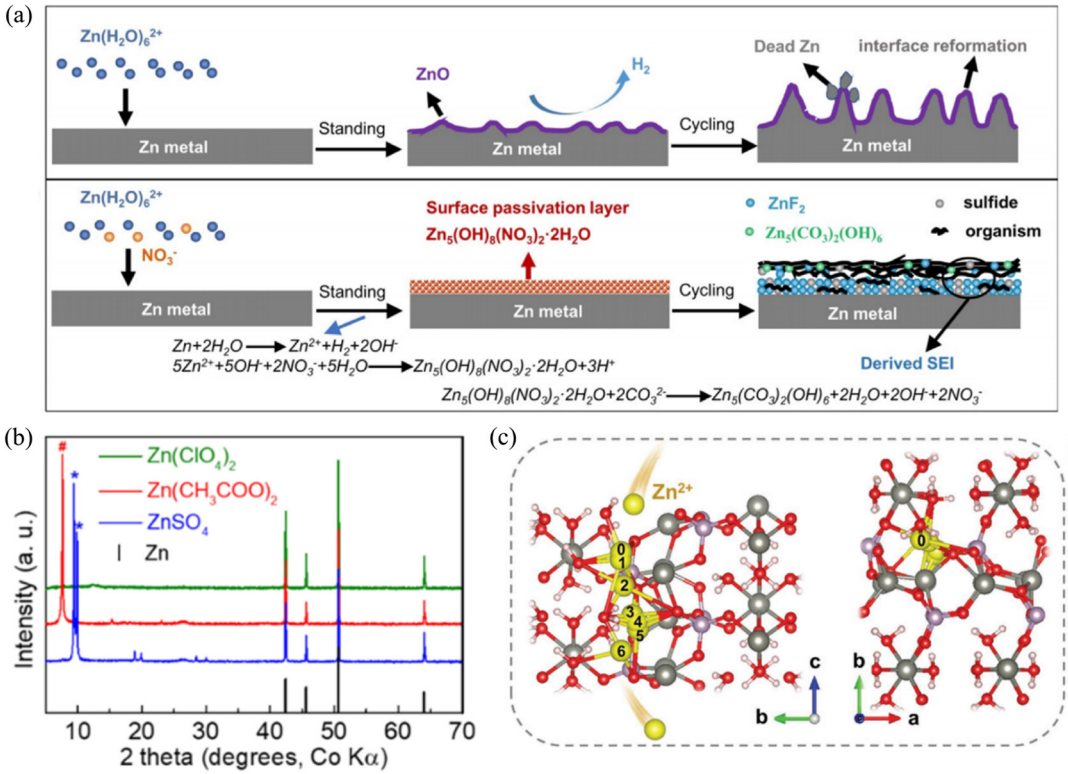

Fig. 4 Illustration of surface evolution mechanism of electrolytes with/without $Zn(NO_3)_2$ (a) (Reproduced with permission from Ref. [54]); XRD of Zn foils after 50 cycles in different electrolytes (b) (Reproduced with permission from Ref. [55]); DFT calculations of optimum Zn^{2+} diffusion pathway in SEI layer (c) (Reproduced with permission from Ref. [56])

potential. Compared to traditional inorganic zinc salts, the OTF^- anion can partially replace water in the solvation shell of Zn^{2+}, thus promoting the transport of Zn^{2+} and the transfer of charge, ultimately enhancing the reaction kinetics and interfacial reversibility [57]. In addition, $Zn(OTf)_2$ electrolyte can promote the formation of a ZnF_2-containing SEI during the electrochemical reaction process, acting as an electrochemically stable electronic barrier to prevent the reduction of water molecules and provide a fast zinc ion transport channel [58]. Another organic salt, $Zn(TFSI)_2$, has a similar function to the $Zn(OTf)_2$ [59]. The large $TFSI^-$ anion can form a strong bond with Zn^{2+} cations, thereby reducing the number of coordinated water molecules while forming an inorganic SEI protective layer on the anode (Fig. 5) [60]. However, it is worth noting that the high cost of $Zn(TFSI)_2$ has impeded its current large-scale application.

Recently, zinc gluconate obtained by choosing the appropriate anion has also been applied in AZIBs and has achieved a certain performance improvement (Fig. 6) [61]. The electrochemical

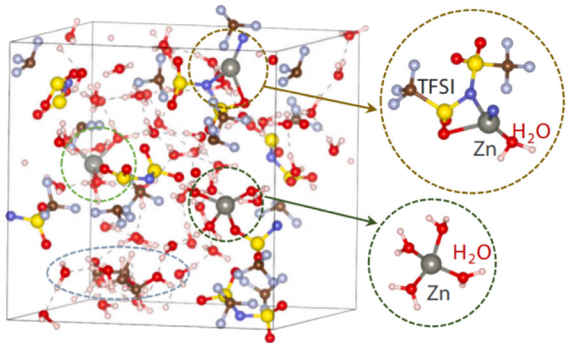

Fig. 5 Snapshots of MD simulation for H_2O–$Zn(TFSI)_2$–EO (Reproduced with permission from Ref. [60])

performance of different electrolytes are given in Table 1. Although more and more zinc salts are being selected and developed, all show sufficient application potential to replace $ZnSO_4$ in different aspects. However, considering the cost, toxicity, and compatibility with cathode materials of the salts, more in-depth research is still needed to evaluate their feasibility in the practical application process of AZIBs.

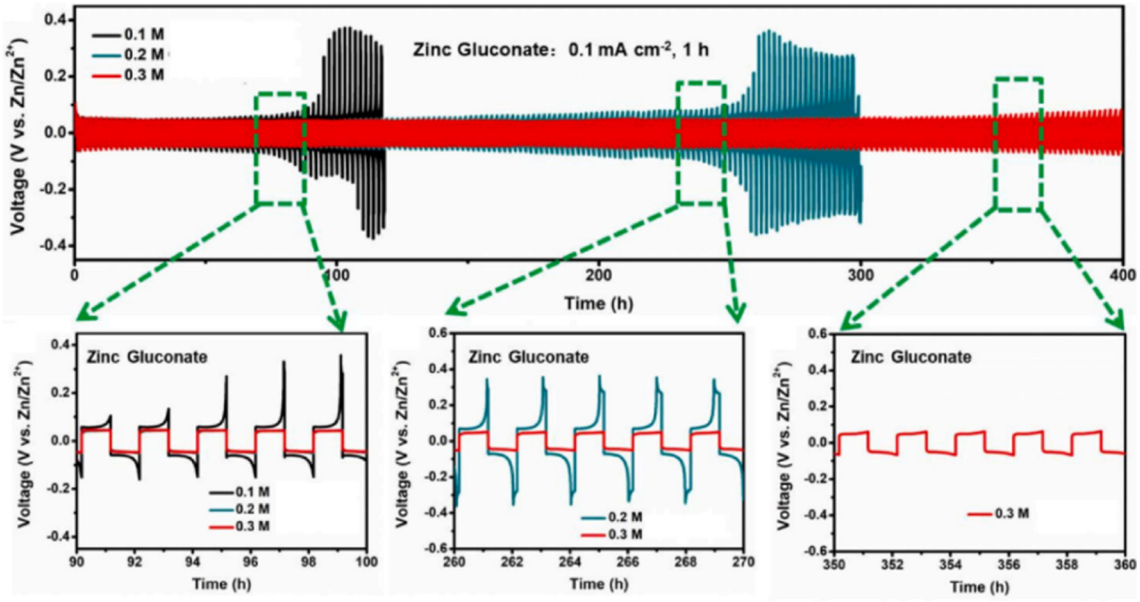

Fig. 6 Cycling performances of Zn plating/stripping in electrolytes with various concentrations of zinc gluconate (Reproduced with permission from Ref. [61])

Table 1 Comparison of electrochemical performance of electrolytes with different Zn salts

Electrolyte	Concentration/(mol·L^{-1})	Current density/(mA·cm^{-2})	Area capacity/(mA·h·cm^{-2})	Life/h	Ref.
$ZnCl_2$	2	0.5	0.5	70	[62]
$ZnSO_4$	1	1	1	340	[55]
$Zn(ClO_4)_2$	1	1	1	3000	[55]
$Zn(CF_3SO_3)_2$	3	2	2	90	[63]
$Zn(CH_3COO)_2$	1	1	1	225	[55]
$Zn(TFSI)_2$	0.3	0.1	0.1	120	[64]
$C_{12}H_{22}O_{14}Zn$	0.3	0.25	0.25	125	[61]

3.2 Solvent regulation

Solvents are crucial components of electrolytes, not only providing a medium for the dissolution of zinc salts and the transport of ions, but also influencing the charge transport mechanism, as well as the electrochemical and thermal stability of the battery. AZIBs utilize aqueous electrolytes with inherent safety and rapid ion transport kinetics. However, specific interactions and configurations among cations, anions, and solvent molecules can lead to structural instability of the active materials of the anode and cathode, as well as a narrow electrochemical window during the battery operation [65]. Moreover, the strong solvation of Zn^{2+} ions results in a high energy barrier for desolvation and deposition, which leads to high overpotentials for zinc plating/stripping [66]. Therefore, adjusting the solvent composition in the AZIBs electrolyte to reduce the solvation effect between Zn^{2+} and water is essential for improving the performance of the zinc anode and achieving uniform deposition. To date, the "co-solvent" or "anti-solvent" strategies have been adopted, which introduce nonaqueous solvents into traditional aqueous electrolytes to reduce the amount of water molecules in the solvation structure, thereby significantly alleviating the aforementioned issues [67,68]. The main nonaqueous solvents currently used through solvent regulation strategies are polar organic solvents and polymers with polar functional groups [69]. These polar organic solvents include sulfoxides, ethers, sulfones, alcohols, esters, amides, and other polar solvents.

LIU et al [70] employed lg P as a metric to select suitable cosolvents for the aqueous $Zn(CF_3SO_3)_2$ electrolyte system, where P is the

octanol−water partition coefficient. As displayed in Fig. 7(a), the lg *P* values among the carboxylic esters studied range from 0.18 to 2.82, including methyl heptanoate (MHEP), methyl hexanoate (MHEX), methyl valerate (MV), ethyl propionate (EP), propyl acetate (PA), methyl butyrate (MB), methyl propionate (MP), ethyl acetate (EA), and methyl acetate (MA). MA shows the closest lg *P* value (0.18) to $CF_3SO_3^-$ with the lowest binding energy, which can lead to a reconstruction of the electrolyte solvation structure (Fig. 7(b)). MA molecules enter into the solvation shell and create a core−shell solvation structure containing both MA and $CF_3SO_3^-$. ZHANG et al [71] found trimethyl phosphate (TMP), as a non-protonic polar small molecule, can be added into traditional $ZnSO_4$ electrolyte as a co-solvent. TMP molecules have the ability to interact with Zn^{2+} ions to alter the solvation structure. Additionally, TMP molecules tend to be preferentially adsorbed onto the anode surface, which helps in reshaping the electric double layer (EDL), reducing the water activity and content at the interface (Fig. 7(c)).

Ethers, with their strong polarity, chemical stability, and low freezing points, are often used as cosolvents to stabilize AEI while also achieving enhanced low-temperature performance for the batteries. HAN' group [72] designed a novel electrolyte comprising 2 mol/L $Zn(OTF)_2$ in a hybrid solvent consisting of 12 mol.% tetraglyme (TG) and 88 mol.% H_2O co-solvent. This electrolyte demonstrates an adaptive solvation behavior, which fosters the formation of an inorganic-rich SEI at lower temperatures, and a SEI containing organic alkyl ethers and alkyl carbonates at higher temperatures, as displayed in Fig. 8.

The Zn//Zn symmetrical cells, based on such electrolyte, showcases reversible plating/stripping exceeding 400 h at −35 or 70 °C. Analogously, KANG et al [73] introduced low-polarity diglyme into $Zn(ClO_4)_2$ aqueous solution to develop a low-temperature electrolyte for low-temperature AZIBs. The diglyme molecules effectively disrupt the hydrogen bonding network of water, thereby significantly reducing the freezing point to as low as −105 °C. With this design, the electrolyte achieves an impressive ionic conductivity up to 16.18 mS/cm at −45 °C (Fig. 9(a)). Furthermore, the diglyme plays a crucial role in mitigating the formation of dendrites, suppressing HER, and minimizing the generation of by-products at the zinc anode, thereby enhancing the cycle stability of the battery (Fig. 9(b)).

In addition to small organic molecules, polymers with polar functional groups also can significantly influence the reshaping of solvation

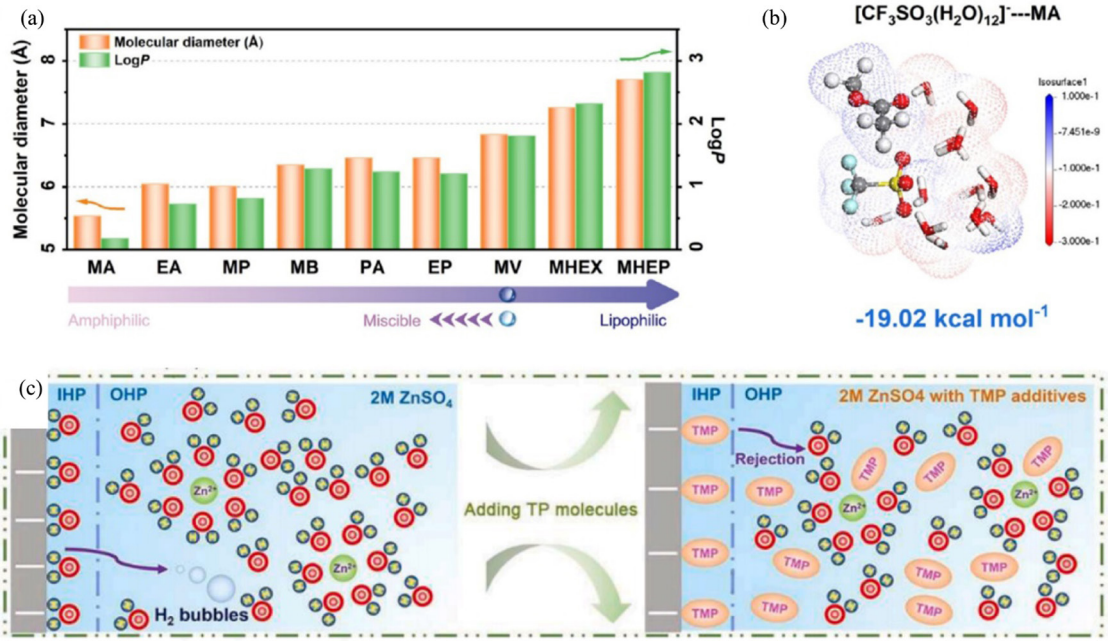

Fig. 7 Molecular diameter and lg *P* values of different carboxylic esters (a) and binding energy of $[CF_3SO_3(H_2O)_{12}]^-$ and MA (b) (Reproduced with permission from Ref. [70]); Illustration of EDL structure with/without TMP additives (c) (Reproduced with permission from Ref. [71])

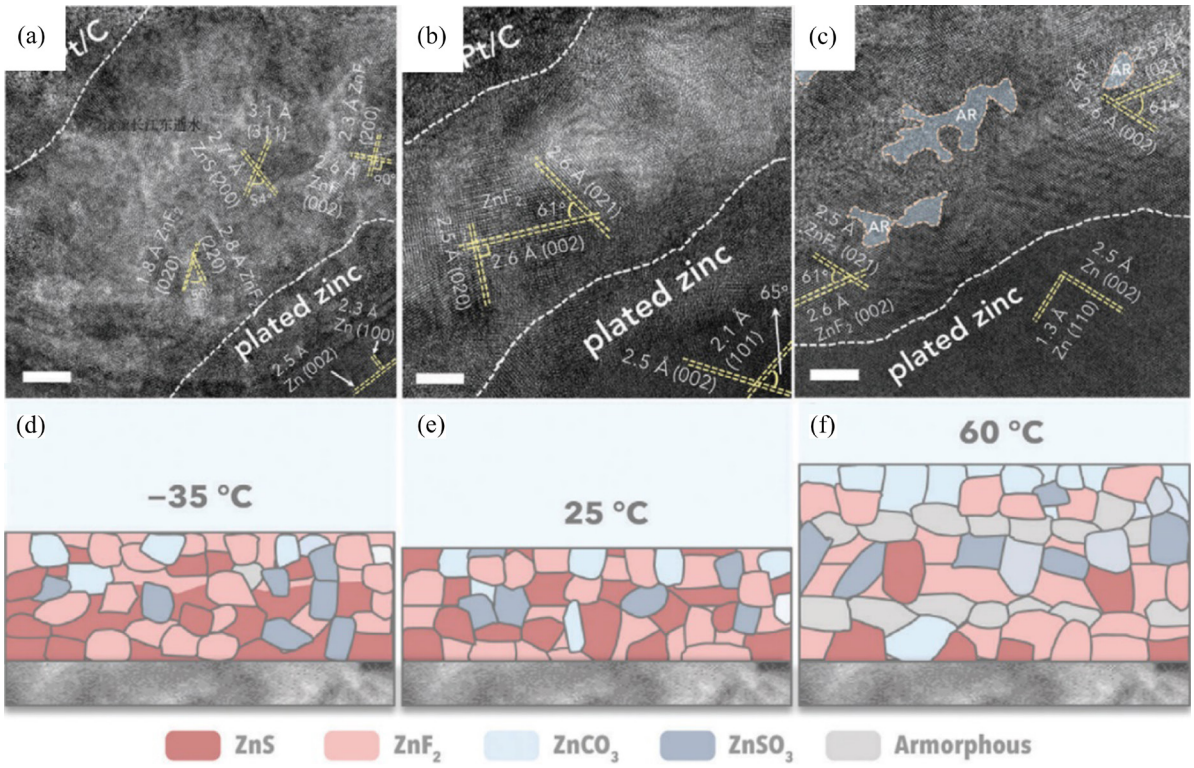

Fig. 8 FIB-TEM images of SEIs (a−c) and schematics of SEI structure (d−f) at different temperatures (Reproduced with permission from Ref. [72]): (a, d) −35 °C; (b, e) 25 °C; (c, f) 60 °C

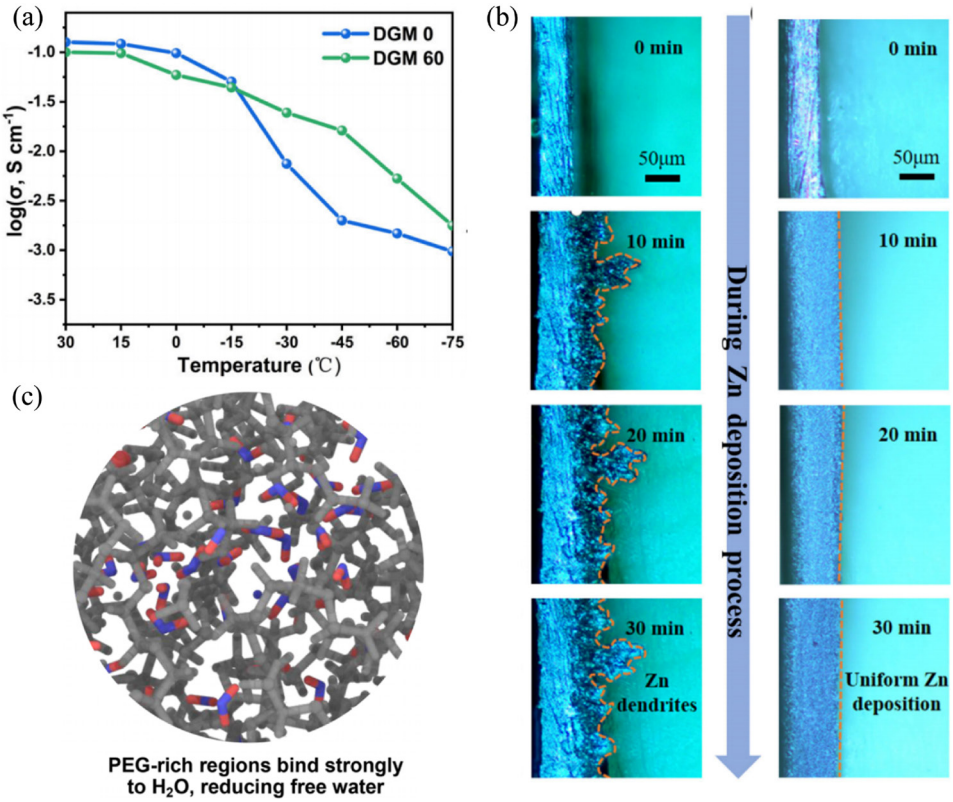

Fig. 9 Ionic conductivity of DGM 0 and DGM 60 electrolytes (a) and optical microscope images of Zn deposition using DGM 0 and DGM 60 electrolytes (b) (Reproduced with permission from Ref. [73]); Water molecules absorbed into PEG-rich region (c) (Reproduced with permission from Ref. [74])

chemistry. Polyethylene glycol (PEG), as a quintessential polar polymer, has been investigated. LI et al [74] discovered that with the incremental addition of PEG, both PEG and anions were integrated into the solvation structures surrounding Zn^{2+} ions. Moreover, the fraction of free water is only 16% in 70PEG, compared to 47% in 4 mol/L $Zn(OTf)_2$, presumably resulting in reduced content and activity of water molecules in the solvation structures (Fig. 9(c)).

Remarkably, PEG can also be mixed with other polar organic solvents to obtain a stable aqueous electrolyte. ZOU and co-workers [75] introduced N,N-dimethylformamide (DMF) and PEG400 as co-solvents into $Zn(OTF)_2$ electrolyte to achieve a wide electrochemical window of 4.27 V, as shown in Fig. 10. PEG exhibits a strong affinity for water molecules, adeptly reconfiguring the hydrogen bond network. Furthermore, DMF can coordinate with Zn^{2+}, facilitating rapid desolvation and contributing to a stable plating/stripping process.

It should be noted that when evaluating and selecting suitable solvents, it is also crucial to consider various parameters, such as the solubility of zinc salts, the pH value of the solvent, hydrophilicity, chemical stability, electrochemical stability, thermal stability, ion conductivity of electrolytes, viscosity, cost, and other related factors, which will affect the practical application of electrolytes and the performance improvement of batteries [76]. In addition, the addition of a cosolvent significantly reduces the water content and reactivity in the electrolyte, while also increases the viscosity of the electrolyte and decreases its dynamics. Moreover, most organic compounds and polymers possess flammability and toxicity, posing challenges to the inherent safety and environmental friendliness of aqueous electrolytes. Therefore, when designing new electrolytes with cosolvents to enhance electrochemical performance, it is essential to opt for safer cosolvents with lower concentrations.

3.3 Highly concentrated electrolytes

The concentration of the electrolyte has a significant impact on the interfacial chemical properties of the battery. It directly determines the physicochemical properties such as the ionic conductivity, viscosity, stability, and pH value of the electrolyte, thereby affecting the electrochemical processes at the Zn electrode. The conventional electrolytes typically contain zinc salts at concentrations of 1−3 mol/L. In these electrolytes, water molecules are the majority. The zinc ions in the electrolyte coordinate with water molecules to form hydrated zinc ions under strong hydration. However, the hydrated zinc ions require a high energy barrier for desolvation at the anode surface, leading to sluggish electrochemical reaction kinetics. The thermodynamically unstable AEI necessitates the reduction of both coordinated water and free water content in the electrolyte. In this context, the most promising solution is to increase the salt concentration by using a high-concentration electrolyte. The increase in salt concentration enhances the overall interaction between cations and anions while reducing the overall interaction between cations and water, thereby decreasing the number of hydration water molecules around zinc ions and facilitating the de-solvation and electrodeposition kinetics of zinc ions. Additionally, the reduction in the number of coordinated and free water molecules can suppress side reactions of interfacial corrosion caused by the decomposition of water molecules at the interface. A lower water

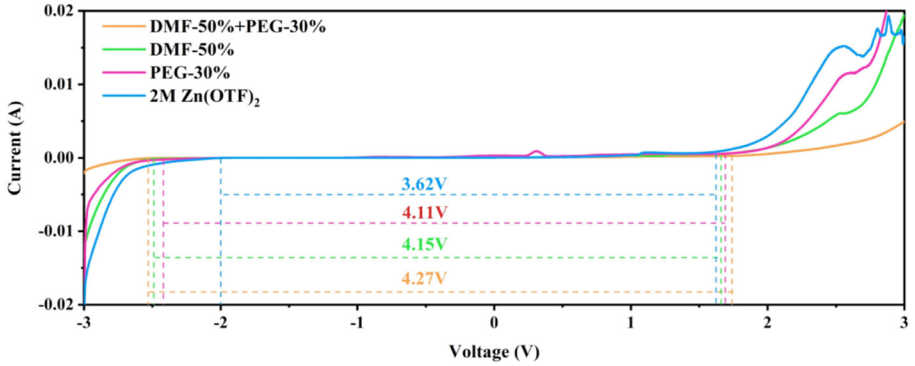

Fig. 10 Electrochemical stability window for various electrolytes (Reproduced with permission from Ref. [75])

content also significantly broadens electrochemical working window, which is confirmed in many aqueous battery systems [77].

Upon elevating the concentration of the $ZnCl_2$ electrolyte from 5 to 15 mol/L, there is a notable shift in the anodic limit potential of the electrolyte, which increases from 2.2 to 2.4 V, and the cathodic limit potential descends from 0.3 V to about 0 V, as shown in Fig. 11(a) [78]. ZHANG et al [79] found the strong interaction between Zn^{2+} and the water molecules in $ZnCl_2$ electrolyte by Fourier transform infrared (FTIR). As the concentration of $ZnCl_2$ rises from 5 to 30 mol/L, H—O—H bending vibration experiences a red-shift, shifting from 1623 to 1612 cm^{-1}. Concurrently, within O—H stretching region, there is a noticeable decrease in the symmetric stretch at 3200 cm^{-1} and an increase in the asymmetric stretch at 3400 cm^{-1} (Fig. 11(b)). These spectral changes suggest a disturbance in O—H hydrogen bonding network, attributed to the strong interaction between water molecules and Zn ions. Besides, these spectral results elucidate the absence and the pronounced formation of the undesired side reaction by-products, when utilizing 30 and 5 mol/L $ZnCl_2$ electrolytes, respectively (Fig. 11(c)). There is also research indicating that 31 mol/L $ZnCl_2$ electrolyte can elevate the onset potential for oxygen evolution reaction, enhancing the structural stability of cathode material while stabilizing AEI [80].

High-concentration electrolytes not only reduce the water content and reactivity in the electrolyte but also facilitate the formation of a stable interphase on anode surface by employing zinc salts such as $Zn(ClO_4)_2$ or $Zn(OTF)_2$, further constructing a stable interface. ZHU et al [81]

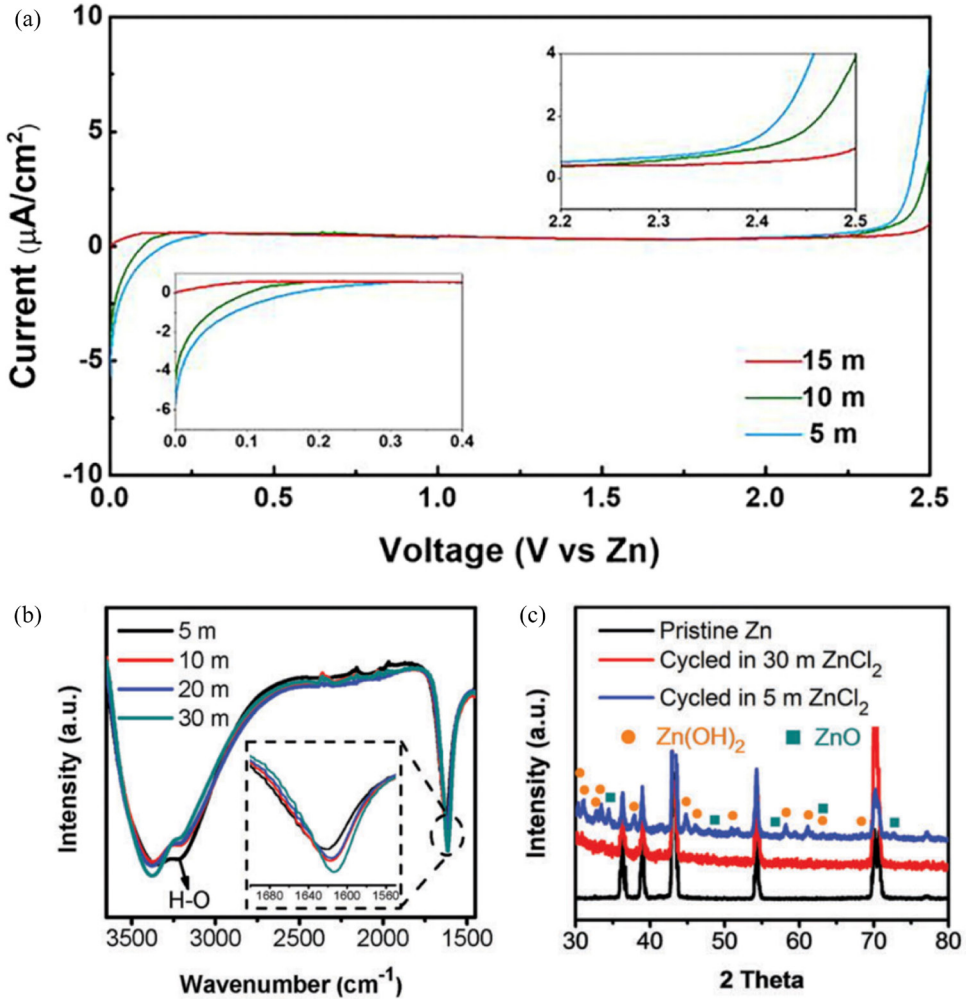

Fig. 11 ESW of electrolytes with different concentrations of $ZnCl_2$ (a) (Reproduced with permission from Ref. [78]); FTIR spectra of electrolytes with different concentrations of $ZnCl_2$ (b) and XRD patterns of Zn anodes cycled in different electrolytes (c) (Reproduced with permission from Ref. [79])

prepared an environmentally and low-cost highly concentrated electrolyte; for example, 0.5 mol/L $Zn(ClO_4)_2$ with 18 mol/L $NaClO_4$. Theoretical calculation results indicate that the highly concentrated solute diminishes the quantity of free water molecules and modulates the electronic state of the electrolyte. Additionally, the formation of a distinctive interphase on the Zn anode ensures reversible and uniform deposition of zinc (Fig. 12).

OLBASA et al [82] discovered the anion-derived passivation layer generated through the use of CHAE (4 mol/L $Zn(OTF)_2$ + 2 mol/L $LiClO_4$), promotes a homogeneous distribution of current, and more effectively isolates newly deposited zinc from being directly exposed to the electrolyte, compared to the solvent-derived layers that emerged from a dilute hybrid aqueous electrolyte [82]. As displayed in Figs. 13(a, b), highly stable Zn plating/stripping cycling for more than 580 h without a short-circuit and an average CE of ~99.43% can be obtained for >300 cycles by using the CHAE.

More recently, LU's group [83] introduced a hydrophilic agent into the zinc acetate electrolyte, transforming the acetate anionic ligands into hydrophilic coordination structures, achieving an unprecedented solubility (up to 23 mol/L). Molecular dynamics (MD) results display that two H_2O molecules exist in each Zn^{2+} primary solvation sheath in the 1.6 mol/L zinc acetate electrolyte, while 4.8 acetate anions and only 0.1 H_2O surround the zinc ion in HSE-10 m (10 mol/L $Zn(CH_3COO)_2$ with 15 mol/L CH_3COOK) (Figs. 14(a, b)).

Despite the fact that using highly concentrated electrolytes can significantly enhance the stability of the AEI and extend the cycle life of batteries, the high concentration of zinc salts inevitably increases the cost of electrolyte, undermining the advantage of low cost for aqueous batteries. Additionally, high salt concentrations typically compromise the ionic conductivity and inevitably increase its viscosity of the electrolyte, severely reducing the electrochemical

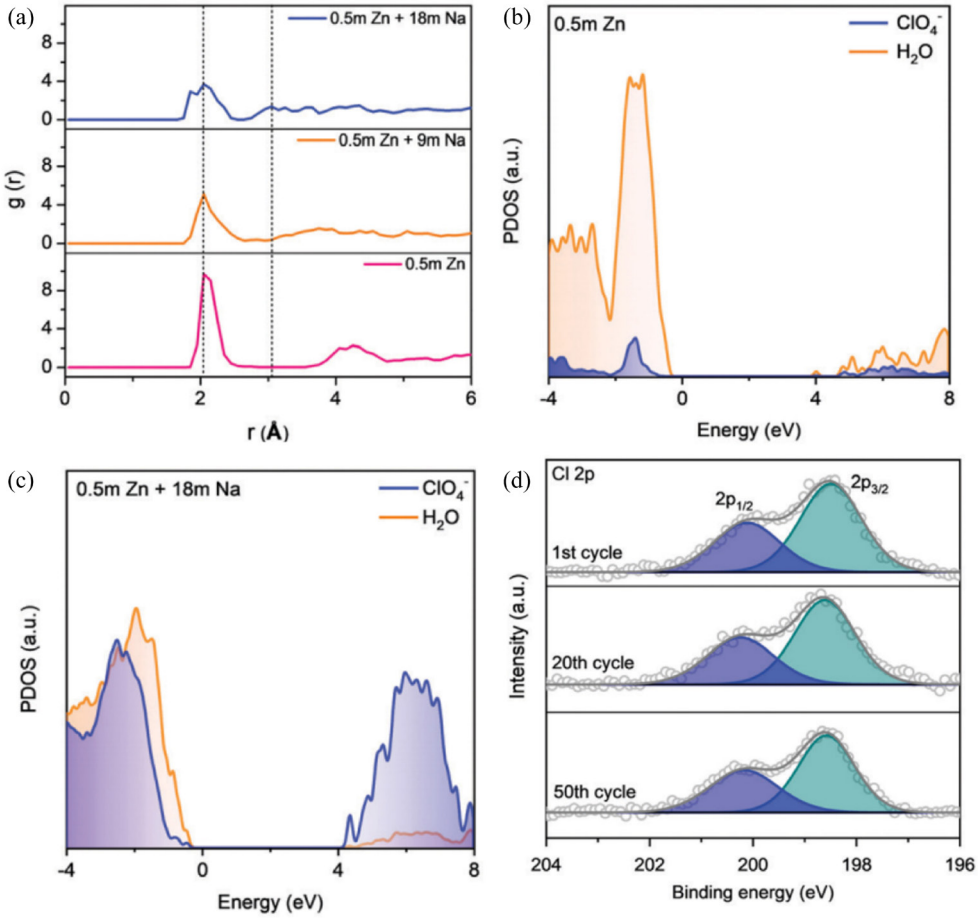

Fig. 12 RDF plots of three electrolytes (a); Projected density of states plots of 0.5 mol/L $Zn(ClO_4)_2$ (b) and 0.5 mol/L $Zn(ClO_4)_2$ (c) with 18 mol/L $NaClO_4$; Cl 2p spectra of Zn foil after different cycles with using HCZE (d) (Reproduced with permission from Ref. [81])

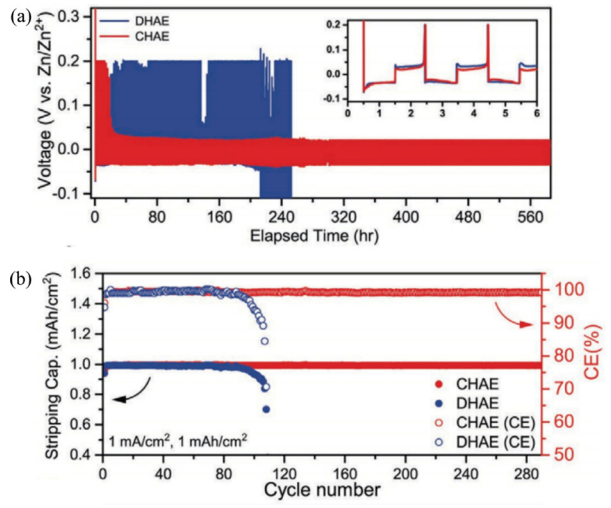

Fig. 13 Performance of galvanostatic Zn plating/stripping (a); CE profile of CHAE (b) (Reproduced with permission from Ref. [82])

reaction kinetics and the power density of the batteries. Therefore, more research and exploration are still needed in the future to unleash the potential of this strategy.

3.4 Deep eutectic electrolytes

Eutectic mixtures are composed with two or more components which integrate cohesively when the intermolecular interactions, including hydrogen bonding, Lewis acid-base reactions, and van der Waals forces, exceed the strength of the individual components' internal reactions. Eutectic electrolyte, as a novel type of electrolyte, has been widely reported and explored due to the high feasibility and tunability of the preparation methods [84,85]. Compared to organic electrolytes and ionic liquid electrolytes, eutectic electrolytes offer greater environmental friendliness and cost-effectiveness. Besides, benefiting from the high ionic conductivity and low water content provided by eutectic electrolytes, especially hydrated eutectics, the ESW can be significantly expanded, the electrode interface can be stabilized, and the cycling stability can be enhanced. Unlike the solvent regulation strategies, hydrophilic eutectic electrolytes are focused on mixing metal salts with water or other hydrogen bond donors (such as polyols and carboxylic acids) to form a low eutectic mixture at certain proportions to optimize the performance of the electrolyte.

Deep eutectic electrolytes (DEEs) were first studied by ABBOTT et al in 2001, utilizing a selection of the quaternary ammonium salts in conjunction with $ZnCl_2$, where the mixture is heated to achieve resulting liquids with low melting points (23−25 °C) [85]. $ZnCl_2$-based DEEs, such as

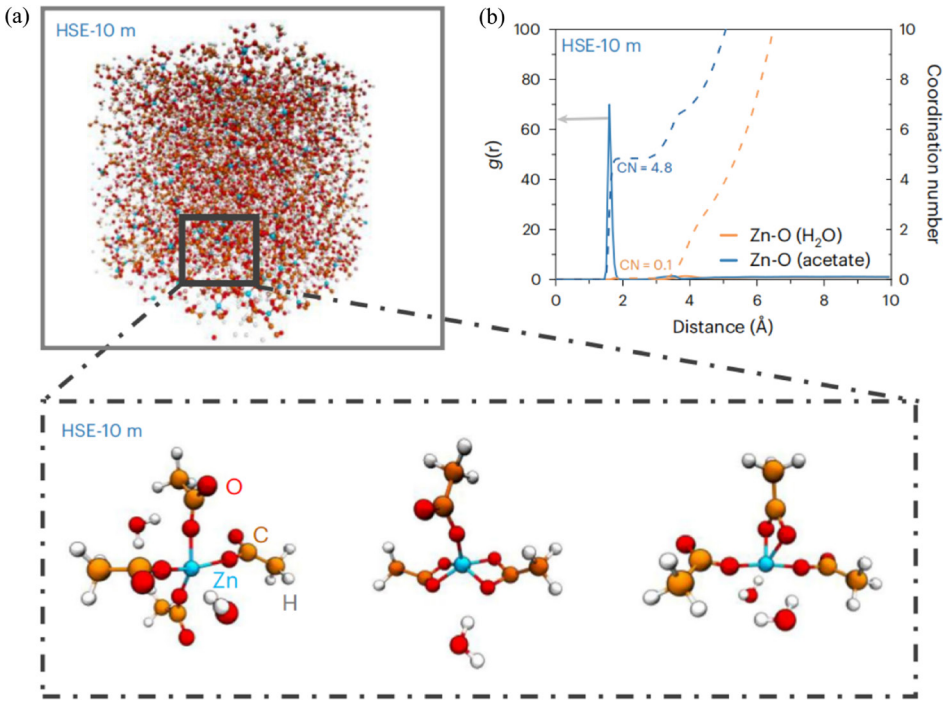

Fig. 14 Snapshot of MD simulated for HSE-10 m electrolyte (a); RDF plots and CN distribution functions of HSE-10 m electrolyte (b) (Reproduced with permission from Ref. [83])

$ZnCl_2$/ChCl/urea and $ZnCl_2$/acetamide (Ace), have been reported extensively in early works during the past decades [86,87]. A substantial amount of research has demonstrated that Zn metal can be reversibly deposited and stripped in these DEEs.

In 2022, HAN et al [88] developed a eutectic electrolyte consisting tetramethylurea (TMU), $ZnCl_2$ and H_2O with the optimal molar ratio of 1:3:1. In this system, water molecules are doubly bound through coordination with the Zn^{2+} and hydrogen bonding with TMU, which significantly suppresses the reactivity of water. Furthermore, during the desolvation process of the complex $ZnCl_2(TMU)(H_2O)$, both water and TMU molecules are sequentially removed, preceding the deposition of $[ZnCl_2]$ at the zinc anode interface. Consequently, the tendency of HER, dendrite formation, and by-products of the corrosion resulting from the decomposition of water molecules at the AEI are minimized (Fig. 15).

Given the oxidative sensitivity of chloride ions that limits their performance and applications, there have been numerous recent studies using non-toxic and stable $ZnSO_4$ to prepare DEEs. HAO et al [89] presented a series of $ZnSO_4$-based eutectic electrolytes by using polyhydric alcohols, including glycerol, propylene glycol (PG) and ethylene glycol (EG). As shown in Figs. 16(a, b), MD simulation and DFT calculations have unveiled the distinctive formation of Zn^{2+} solvation with polyhydric alcohols. Unlike the solvation shell of $Zn(H_2O)_6^{2+}$ in a 2.0 mol/L aqueous $ZnSO_4$ electrolyte, a unique solvation complex, $Zn(H_2O)_4PG_2^{2+}$ is established in the hydrated eutectic electrolyte (HEE). Moreover, the hydrogen bonding interactions between water molecules and PG in HEE substantially diminish activity of water, thereby effectively suppressing the HER and corrosion of zinc metal.

To obtain a more stable AEI, zinc salts that can form a SEI in situ on the anode surface can be selected to create DEEs. WANG et al [90] pointed out that BF_4^- anions and succinonitrile molecules have the capability to lock water molecules through hydrogen bonding, thereby inhibiting the decomposition of water and the subsequent corrosion of Zn (Figs. 17(a−d)). Additionally, BF_4^- anions are also capable of forming an in-situ ZnF_2 layer, serving as an efficient SEI, which contributes to enhancing interface stability (Fig. 17(e)). The water-locking DEEs disrupt the hydrogen bond network among the original water molecules, significantly lowering the freezing point to nearly −100 °C and expanding electrochemical window to exceed 3.2 V.

MENG et al [91] discovered that a variety of species with distinct thermodynamic stabilities engage in interfacial chemical reactions, leading to the formation of a gradient organic/inorganic hybrid SEI layer in situ on the zinc metal anode. This is achieved by employing a specific DEE composed of BF_4^- and dimethoxyethane (DME). The gradient hybrid SEI (GHS) layer with a gradient structure and composition mitigates the corrosion and passivation issues on the Zn anode and suppresses the HER. More importantly, it can optimize the diffusion behavior of Zn^{2+} ions at the interface and facilitate the epitaxial deposition of Zn^{2+} along the (002) plane, which helps to eliminate dendrite growth (Fig. 18).

Electrolyte additives can also be incorporated into DEEs to further enhance their performance. For example, $InCl_3$ is added as an additive in a

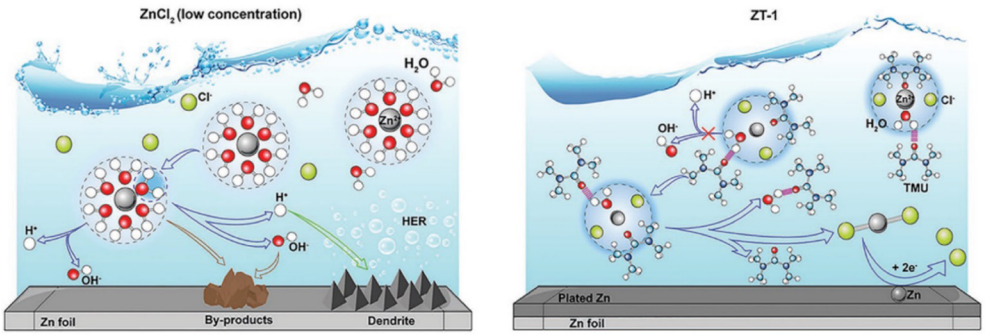

Fig. 15 Schematic illustration of zinc ions solvation structures and AEI reactions in different electrolytes (Reproduced with permission from Ref. [88])

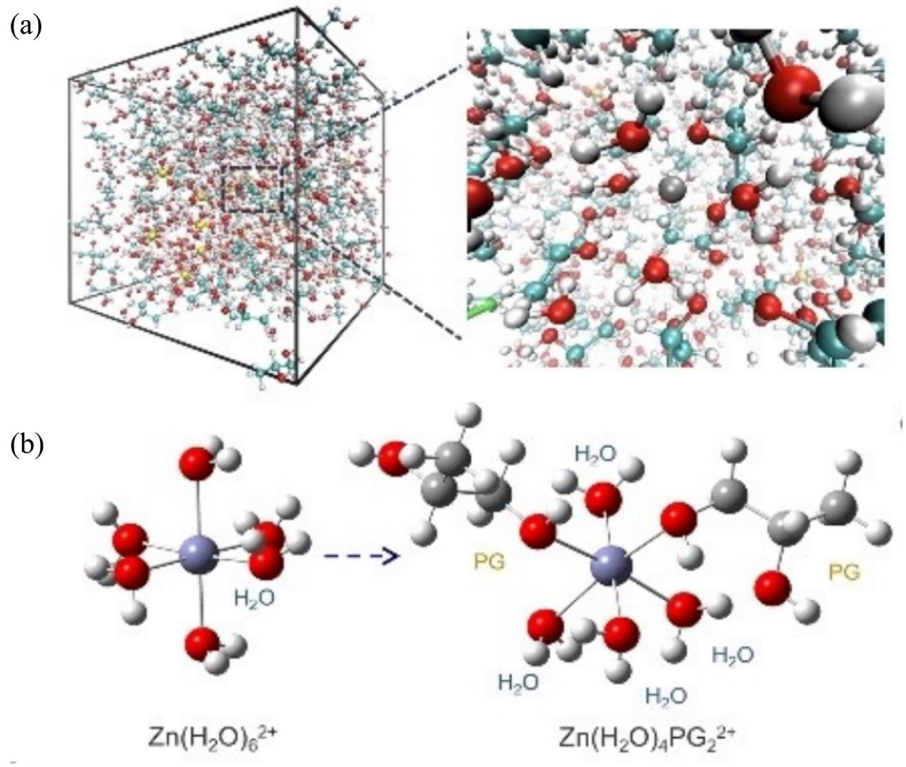

Fig. 16 MD simulation of 2 mol/L HEE (a); RDF and CN of Zn^{2+} and O in water and PG molecular (b) (Reproduced with permission from Ref. [89])

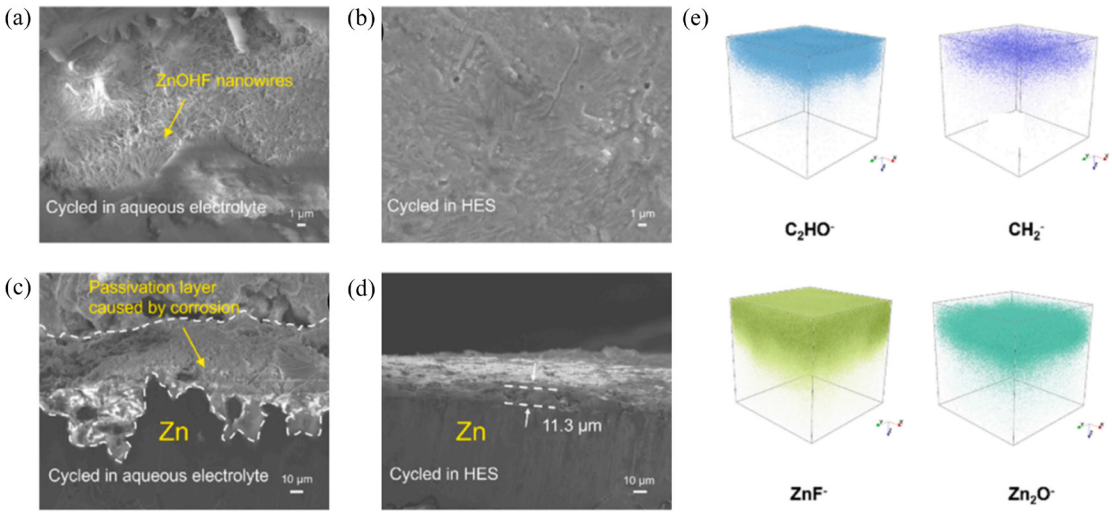

Fig. 17 Surface SEM images of Zn foil after cycling in aqueous electrolyte (a) and HES (b); Cross-section SEM images after cycling in aqueous electrolyte (c) and HES (d); 3D view of different ions distributions of Zn anode after cycling with HES in TOF-SIMS sputtered volumes (e) (Reproduced with permission from Ref. [90])

hydrated eutectic electrolyte system composed of $Zn(ClO_4)_2{\cdot}6H_2O$ and EG [92]. The decomposition of these complex molecules within the HEE leads to the creation of a bilayer interphase on the surface of the Zn anode during battery operation, consisting of the zincophobic and zincophilic layer. The zincophilic layer decreases the energy barrier for Zn nucleation, encouraging uniform deposition of zinc. Concurrently, the zincophobic layer serves as protective barrier that prevents water from permeating the anode surface, thereby curbing unwanted side reactions.

Compared to traditional organic electrolyte systems, DEEs offer several advantages, such as

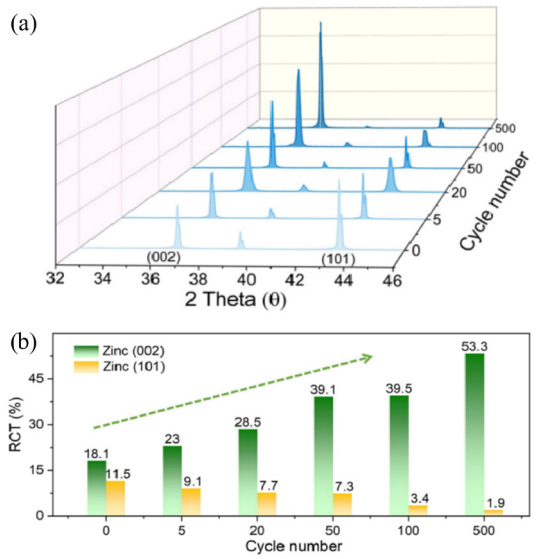

Fig. 18 XRD patterns of Zn anode after cycling in DEE (a); Calculated RTC values of different crystal planes (b) (Reproduced with permission from Ref. [91])

non-flammability, thermal stability, non-toxicity, high ionic conductivity, and low cost. These features indicate that DEEs are a promising class of green electrolytes which can be applied to AZIBs. However, the ionic conductivity and viscosity of DEEs still require attention compared to dilute aqueous electrolytes. DEEs derived from the interaction between organic zinc salts and Lewis acid-base often contain larger-sized ions and relatively free volume, which can result in poor conductivity and unfavorable viscosity at room temperature. Additionally, the high concentration of zinc salts in the eutectic electrolyte system may alter the activity and reversibility of redox reactions within the battery system. The compatibility of the electrolyte with the cathode materials also needs to be considered. Overall, the rational design of advanced DEEs should give full consideration to the solvation structure, ion transfer mechanisms, electrochemical reaction pathways, advanced experimental techniques, and multi-scale simulation methods.

3.5 Hydrogel electrolytes

The inherent issues present in dilute aqueous electrolytes have spurred the development of hydrogel electrolytes. Hydrogel electrolytes are typically prepared by incorporating a metal salt solution into a polymer matrix, which are synthesized through in situ or ex situ ionic/covalent crosslinking [93]. Hydrogels, with their polymer chains containing hydrophilic groups such as —OH, —COOH, and —NH_2, can fully absorb solvents and expand significantly [94,95]. Therefore, hydrogels are soft materials which possess both solid and liquid characteristics. Because of the aforementioned features, hydrogels can serve dual roles as electrolytes and separator in AZIBs [96]. The abundant hydrophilic groups in hydrogels can adsorb solvents through non-covalent interactions, significantly reducing the reactivity of water in the electrolyte. The numerous functional groups within hydrogels can interact with zinc ions to regulate Zn^{2+} transport and flux, thereby stabilizing the AEI and suppressing the growth of zinc dendrites. Moreover, hydrogels possess the unique mechanical properties of solid electrolytes, such as flexibility, foldability, and stretchability [97,98]. A certain level of mechanical strength can also physically inhibit the growth of zinc dendrites [99]. Multifunctional characteristics of hydrogels have also garnered widespread attention in smart functionalities such as self-healing, temperature adaptability, and thermal conductivity.

Hydrogels are capable of retaining water molecules and offering high ionic conductivity, but the presence of numerous free water molecules can lead to unwanted side reactions at the zinc anode. To counter this, ZHI's group [100] has chosen a polymeric zwitterion (PZI) as the polymer skeleton. This PZI features sulfonate terminals which merge hydrophilic and zincophilic attributes, with a zinc salt serving as the coordination unit. The sulfonate anions act as hydrogen bond acceptors, which are hydrated by water molecules, facilitating the dissociation of zinc ions and bolstering the electrochemical stability of water (Figs. 19(a, b)). The designed lean-water hydrogel electrolyte shows an expanded voltage window and an ionic conductivity of 2.6×10^{-3} S/cm with a reduced water content of 20 wt.% (Fig. 19(c)).

Some gel electrolytes can also further reduce mass transfer overpotential and decrease water-related side reactions, leading to uniform zinc deposition by in-situ formation of a hybrid SEI. HE et al [101] employed a betaine-type zwitterionic monomer 3-((2-(methacryloyloxy)ethyl) dimethylammonio) propane-1-sulfonate (DMAPS) to copolymerize with acrylamide (AM) to further enhance the electrochemical performance of the

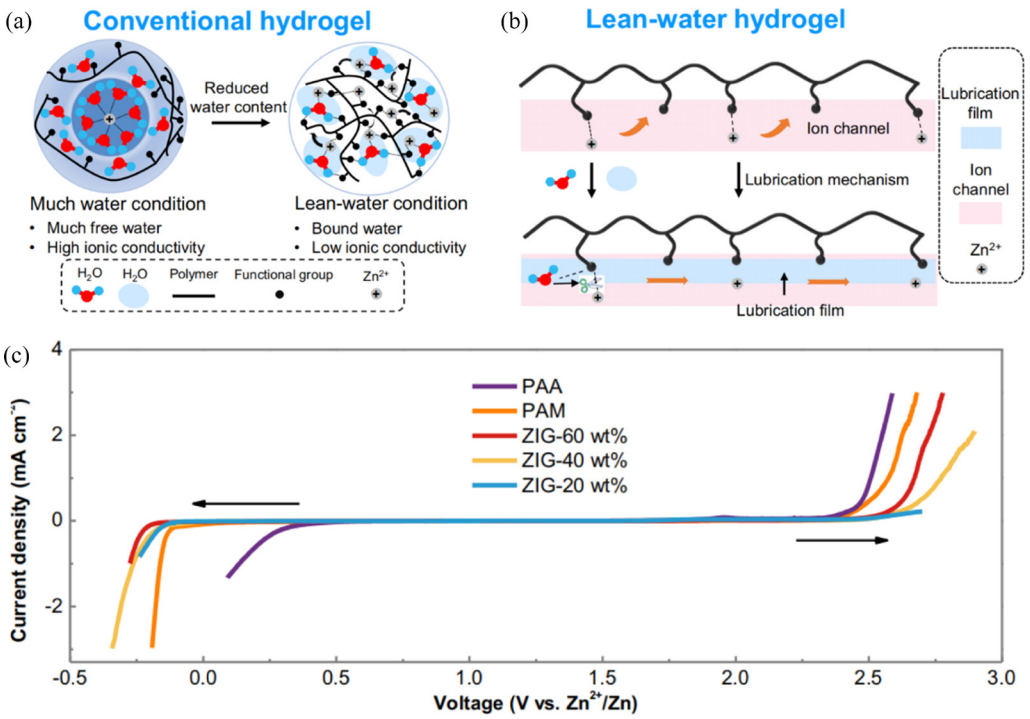

Fig. 19 Schematic illustration of hydrogel electrolytes under much and water−poor conditions (a); Expected ionic transportation mechanism for hydrogel electrolyte under water-poor condition (b); Linear sweep voltammetry of ZIG with different water contents (c) (Reproduced with permission from Ref. [100])

hydrogel electrolyte. Owing to the zwitterionic characteristic and the heightened hydration ability of the charged groups in the hydrogel electrolyte, ions can be readily separated from the counterions, leading to the accelerated ion migration and enhanced rate performance (Fig. 20(a)). Furthermore, substituting the conventional $ZnSO_4$ with $Zn(ClO_4)_2$ salt fosters the in-situ formation of a Cl^--containing insulating layer on Zn anode, which is beneficial for ZIBs to have minimal voltage polarization and an exceptionally extended cycle life (Fig. 20(b)) .

Developing a hydrogel electrolyte that harmonizes the mechanical properties, ionic conductivity, and interfacial stability presents a formidable challenge [102]. HE et al [103] have prepared a unique fabric-like hydrogel derived from precursor solutions with high concentration of monomers and a low content of crosslinkers, resulting in long polymer chains that are predominantly entangled rather than cross-linked. As depicted in Figs. 21(a, b), this polymer endowed with long energy-absorbing chains, dense entanglement, and reversible conformational change, exhibits exceptional mechanical properties, including high strength (with tensile strength of 446 kPa), high toughness (with an elongation of 350%), and low hysteresis. High ion diffusivity and interfacial connectivity of the polar electrolyte synergistically achieve outstanding ionic conductivity (3.93 mS/cm) and the tradeoff between mechanical strength and ionic conductivity. The stiffness of hydrogel electrolytes, often fall short of ideal standards, a limitation primarily attributed to their high content of water. This limitation can significantly impede the effectiveness of dendrite suppression, particularly when dealing with substantial mass loading of active materials. Drawing inspiration from structural attributes of wood, CHEN et al [104] developed an anisotropic carboxymethyl cellulose hydrogel electrolyte, through a process which includes directional freezing, a salting-out effect, and compression reinforcement, with the goal of significantly enhancing the modulus in the direction perpendicular to the electrode surface. The increased stiffness not only aids in contributing to the suppression of dendrite growth but also curbs the vertical deposition of intermediate products

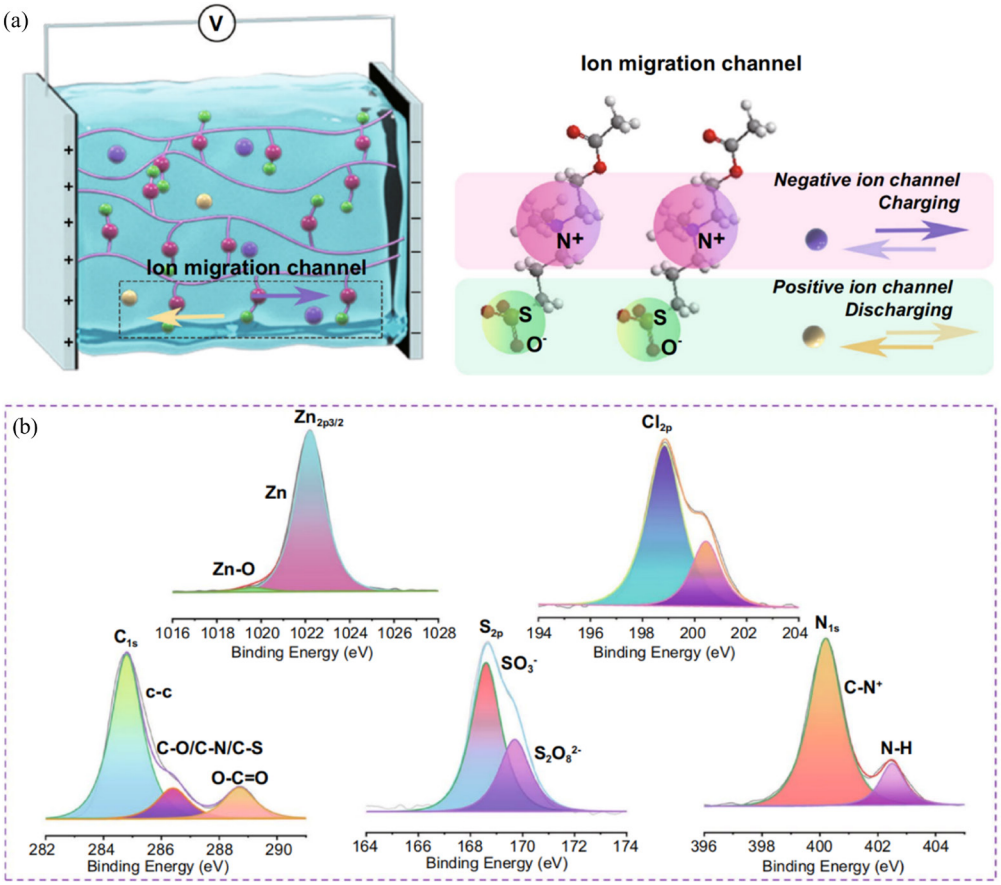

Fig. 20 Schematic illustration of construction of ion migration channel (a); XPS spectra of surface of cycled zinc electrode (b) (Reproduced with permission from Ref. [101])

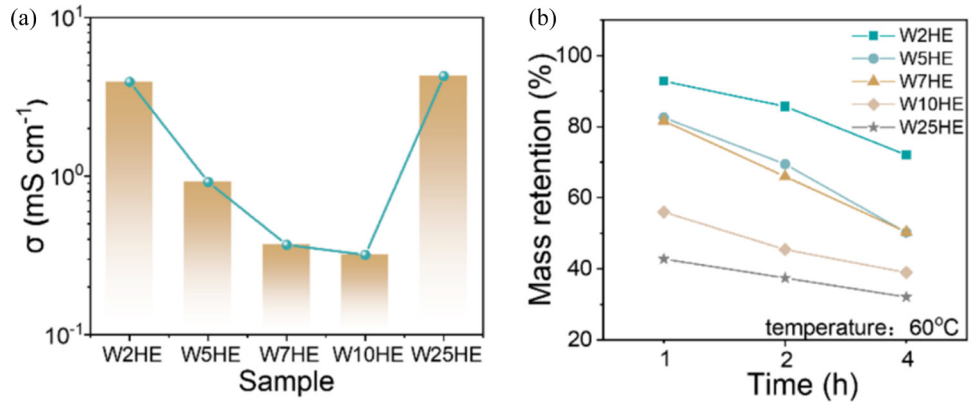

Fig. 21 Tensile stress−strain curves of single-network polymer electrolytes with different W values (a); Tensile strength and elastic modulus of different hydrogels (b) (Reproduced with permission from Ref. [103])

at the cathode. This hydrogel electrolyte achieves a substantial volumetric energy density of 132.2 mW·h/cm^3 along with excellent cycling stability.

Typical gel electrolytes are usually prepared as thin films outside the battery and then sandwiched between the electrodes. This can lead to poor solid−liquid interfacial contact, resulting in increased interfacial impedance. More seriously, it may gradually deteriorate due to side reactions and dendrite growth during repeated cycling. Fortunately, the in-situ polymerization of gel electrolyte network on the surface of the zinc anode can demonstrate a well-bonded interface, because liquid monomer molecules can fully penetrate the solid electrodes beforehand (Fig. 22). QIN

et al [105] harness the inherent reducibility of metallic Zn anodes to prepare a gel electrolyte in situ. The redox reaction effectively peels the Zn surface, smoothing out the surface heterogeneity which arises during industrial-scale production of commercial Zn foils. This process encourages uniform nucleation and growth of the initial Zn layers. The in-situ formed gel polymer electrolytes establish a robustly bonded interface with well-connected ion channels and diminished side reactions, which contributes to the improved reversibility of Zn and reduced interfacial impedance. Furthermore, the in-situ gel electrolyte fosters a preferential planar-oriented (002) deposition, leading to symmetric cells exhibiting an exceptionally long cycle life of 5100 h with a low voltage hysteresis of 90 mV at a current density of 1 mA/cm^2 and a capacity of 1 mA·h/cm^2.

The robust flexibility of hydrogel electrolytes enables the fabrication of AZIBs in various shapes and sizes [106−108]. Their unique polymer structure and low water content can meet the needs of multiple environmental conditions. Therefore, they hold great promise in wearable devices and special load working environments. However, we still need to further improve the ionic conductivity of the gel electrolyte, balance its mechanical properties, focus on optimizing the AEI and improve interfacial contact to enhance the performance of AZIBs.

3.6 Electrolyte additives

The solvation structure, desolvation energy barrier, charge transfer kinetics, and difficulty of nucleation determine the fundamental technology challenges in electrolytes [109−111]. Introducing additives into the electrolyte has been proven to be the most economical, viable and effective approach to enhance the performance of AZIBs. The electrolyte additive strategy relies on the unique advantages of different additives, such as their special polarity, functional groups, hydrophilicity/hydrophobicity, and redox reactivity, to influence the electrodeposition process of zinc ions and achieve stable AEI [112−114]. Some zincophilic additive molecules containing electron donors can replace water molecules in the solvation sheath of zinc ions, constructing a new solvation structure through coordination with zinc ions [115,116]. Besides, a large number of polar functional groups can disrupt the hydrogen bond network of water molecules or construct a water-poor double electric layer, thereby reducing the quantity and activity of water molecules in the electrolyte. Furthermore, some additives, due to the unique valence bonds in their structure, can adsorb on the surface of the zinc anode or form a SEI in situ on the surface, effectively regulating the deposition/stripping of zinc, and suppressing the growth of zinc dendrites and the occurrence of side reactions at the interface. Noticeably, some additives can form a protective layer on the electrode surface, which not only eliminates turbulent parasitic reactions at the Zn/electrolyte interface but also significantly improves the utilization efficiency of cathode active materials [117].

In the early stages of additive research, salts containing different metal cations were commonly used as additives, relying on their own reduction potential to achieve surface metal displacement or electrostatic shielding to suppress zinc dendrites and side reactions. Representative of these additives are Bi^{3+} [118], Na^{+} [119], La^{3+} [120], In^{3+} [63], and Ce^{3+} [121]. In recent years, inorganic carbon-based

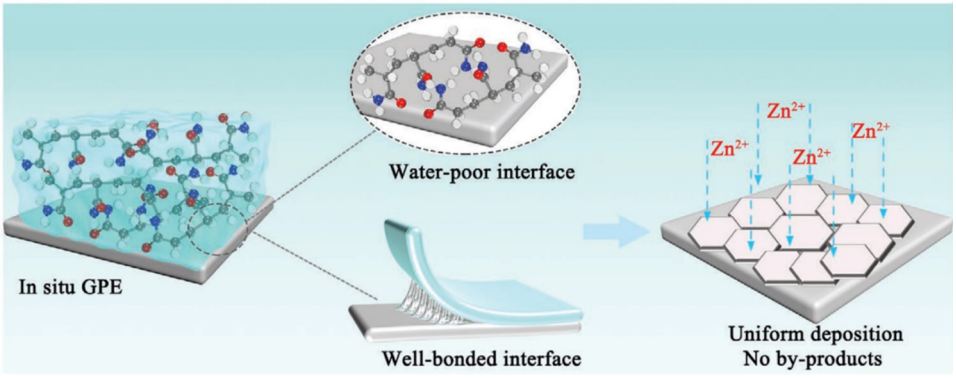

Fig. 22 Schematic of in-situ gel polymer electrolyte at AEI (Reproduced with permission from Ref. [105])

materials have attracted increasing attention in the field of AZIBs additives due to their unique physicochemical properties. ZHANG et al [122] added atomic-scale inorganic carbon nanomaterials (ICN) as multifunctional electrolyte additives to a common $ZnSO_4$ electrolyte, achieving a stable and reversible zinc anode with high utilization rate to improve the electrochemical performance of ZIBs. The rich polar groups, high negative charge, and low lattice mismatch with Zn(002) exhibit a synergistic effect in determining the behavior of zinc deposition. Atomic ICN with abundant surface polar groups (—OH, —COOH) have strong adsorption energy for Zn^{2+}, which can regulate the solvation structure of zinc ions and suppress water-induced side reactions. In addition, the negatively charged INC preferentially adsorbs on the Zn anode surface, forming a passivation protective interface to inhibit Zn corrosion and dendrite growth. As shown in Fig. 23, inorganic carbon nanoparticles have a low mismatch with Zn(002) nanosheets, fundamentally solving the problem of Zn orientation disorder and further growth of Zn dendrites, and thus guiding a closely packed Zn deposition morphology.

Organic molecules as electrolyte additives have been widely studied for their diversity. Due to the strong interaction between zinc and the polar groups in organic molecules, they can adsorb on the surface of zinc, enhancing the interfacial compatibility between the zinc anode and the electrolyte. LI et al [123] introduced 2-hydroxy-4′-(2-hydroxyethoxy)-2-methylpropiophenone (Irgacure 2959) as an effective additive. The Irgacure 2959 molecule preferentially interacts with zinc by the high electron-density carbonyl group, known by DFT calculation as presented in Fig. 24(a). The stable Zn−2959 interface spontaneously forms an EDL structure which is deficient in H_2O and SO_4^{2-}, significantly minimizing side reactions. Moreover, it facilitates a uniform distribution of interfacial Zn^{2+} ions and constrained two-dimensional diffusion. These factors contribute to preferential growth of Zn(002) plane stacking in the horizontal direction, which in turn suppresses the formation of dendrites (Fig. 24(b)). Such superiority is primarily attributed to the presence of functional groups which enhance intermolecular hydrogen bonding (hydroxyl groups), strengthen interfacial adsorption (ether and hydroxyl groups), and exert strong electrostatic effect (uncoordinated carbonyl groups).

Additionally, organic additives can reconfigure the Zn^{2+} solvation sheath, restrict free water molecules, suppress water-induced side reactions, and extend the decomposition voltage of the electrolyte. CHEN and co-workers [124] proposed a multifunctional cellulose nanocrystals (CNCs) as the electrolyte additive which regulates the coordination environment and enhances the interfacial chemistry of zinc, enabling ultra-long lifespan of zinc anodes for AZIBs. As depicted in

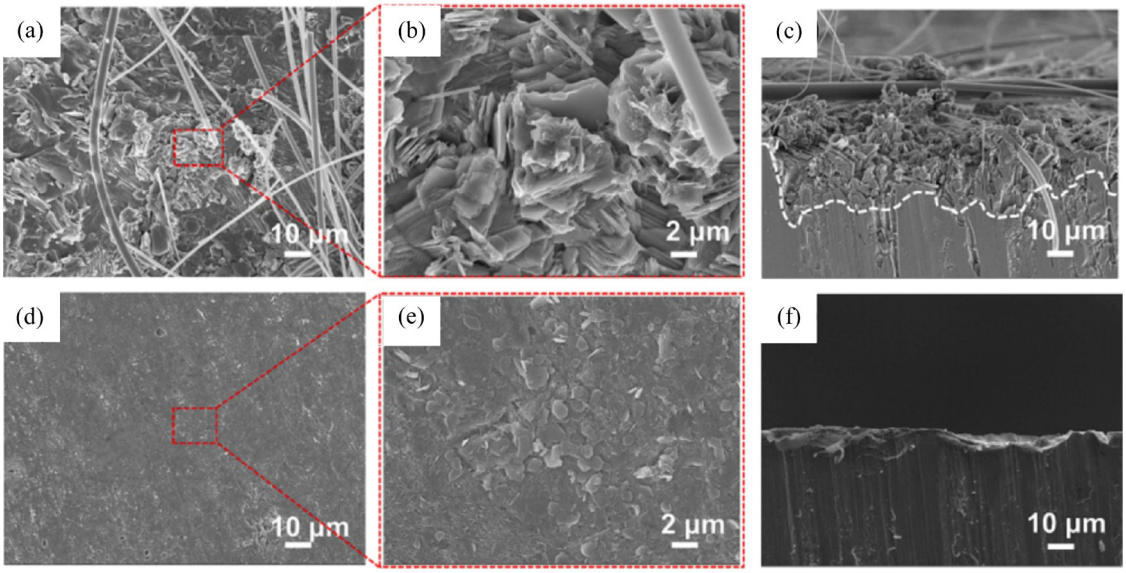

Fig. 23 Top-view and cross-sectional SEM images of zinc foils after cycling in electrolytes without (a−c) and with (d−f) ICN additive (Reproduced with permission from Ref. [122])

Fig. 25, the average number of H_2O molecules in the solvation sheath is reduced to approximately 2.9, while that of CNCs increases to around 2.6. This increase is due to the collective action of hydroxyl and carboxyl groups in CNCs enveloping Zn^{2+}, thereby enhancing the electrostatic coordination of Zn^{2+}—O. These results manifest that CNCs can reduce the number of H_2O molecules in proximity to Zn^{2+}, altering the solvation sheath of Zn^{2+} and subsequently influencing the electrochemical performance. Additionally, the zinc deposition in the CNCs−$ZnSO_4$ electrolyte was found to be uniformly distributed and compact, marked by the presence of small crystal particles. This observation further corroborates the exceptional function of CNCs in curbing dendrite growth. Some multi-functional additives can not only adjust the solvation structure of zinc ions through a large number of polar groups but also dynamically adsorb on the surface of the zinc anode. YU et al [125] choose a zwitterionic additive (*L*-carnitine) in a trace amount to stabilize the electrodes. Systematic experiments and theoretical calculations prove that *L*-carnitine (*L*-CN) can enter the inner solvation

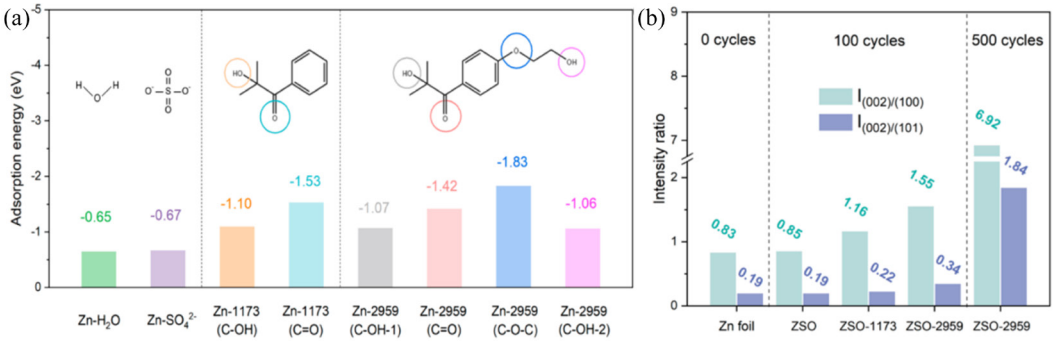

Fig. 24 Adsorption energies of different adsorbates on plane of Zn(002) (a); Peak intensity ratio of zinc anodes after cycles (b) (Reproduced with permission from Ref. [123])

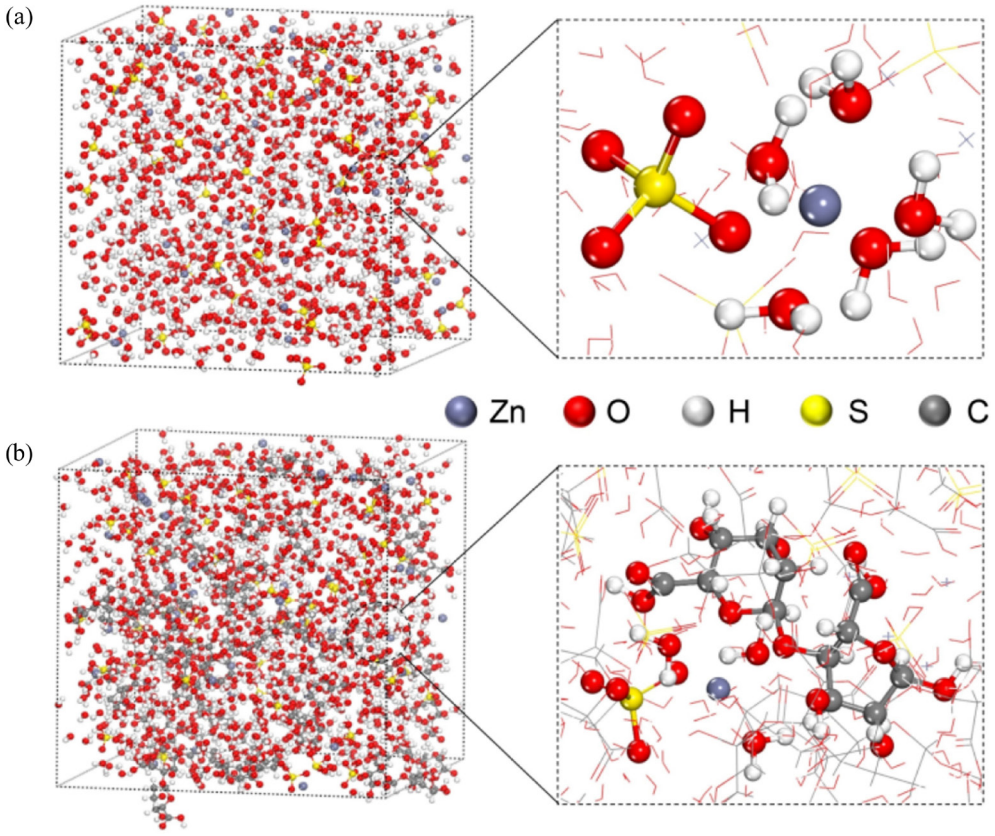

Fig. 25 3D snapshots of electrolyte without (a) and with (b) CNCs (Reproduced with permission from Ref. [124])

sheath of Zn^{2+} to diminish the amount of active water surrounding Zn^{2+} near the anodes. The *L*-CN molecule, equipped with a quaternary ammonium cation, a COO^- anion, and a hydroxyl group, exhibits a preferential adsorption capability, a robust interaction with Zn^{2+}, and a unique ability to capture active water. This leads to reversible adsorption on the anode surface, driven by the electric field, eventually resulting in even and stable electrochemical behaviors of Zn^{2+}. The assembled symmetrical cell reveals an ultra-long lifespan up to 6083 h at 1 mA/cm^2 and 1 mA·h/cm^2.

Some additives can also form a SEI-like protective interface phase in situ, such as Trifluoro ((4-methylmorpholino-4-ium) methyl) borate [126], *L*-cysteine [127], sucralose [128], potassium sorbate [129] and thiourea [130]. CHEN's group [131] proposed the use of hexamethylenetetramine (HMTA) as an additive to construct a stable anode−molecular interface layer in situ, thereby stabilizing zinc anodes. The presence of numerous nitrogen atoms with lone pairs of electrons in HMTA molecules fosters a strong interaction with Zn atoms, leading to a preferential adsorption of HMTA on the zinc metal surface with forming an anode−molecular interfacial layer in situ (Fig. 26). This distinctive interfacial layer effectively excludes active water molecules from the surface and facilitates fast ion transport dynamics.

It is worth noting that the introduction of additives may also lead to the emergence of other issues: (1) Some additives have a strong coordination ability with zinc ions, so they can replace the water molecules in the original zinc ion solvation sheath, forming a new solvation structure. However, a stronger binding energy and a larger solvation structure radius may imply a higher desolvation energy barrier; (2) If the formed zinc ion solvation structure is too large, it may lead to a decrease in the transport and migration kinetics of zinc ions; (3) Additives adsorbed on the surface of the zinc anode may fail to function due to the insufficient adsorption strength. The SEI constructed in situ on the surface of the zinc anode may not perform ideally due to low electrical conductivity or strength.

4 Characterization on interface of Zn anode/electrolyte

As described in the previous sections, to construct a stable AEI through electrolyte regulation, the following issues need to be considered: how to simultaneously achieve the suppression of zinc dendrites, HER, and interfacial passivation. A deep understanding of the relationship between the interfacial chemical properties of the zinc metal anode, deposition behavior, and the challenges faced is of great significance for guiding the rational design of a stable AEI. Therefore, precise characterization and analysis of the zinc metal anode and electrolyte are crucial. To qualitatively or quantitatively evaluate the effectiveness of various modification strategies, a variety of electrochemical methods, in-situ/ex-situ characterization, and theoretical analysis methods have been developed to study the characteristics of AEI (Fig. 27).

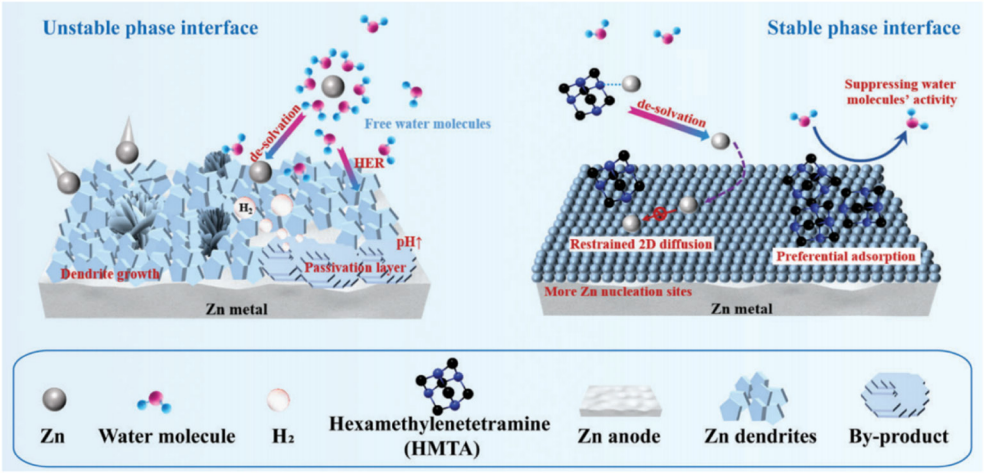

Fig. 26 Schematic illustration of regulation behavior of HMTA additive on AEI (Reproduced with permission from Ref. [131])

Although the deposition of zinc on the Zn metal anode is uneven, even dendritic, it is difficult to describe because the deposited material is mostly the same as the electrode. Therefore, in-situ optical microscopy is often used to observe the morphological evolution of the zinc anode during the plating/stripping process. However, due to its lower resolution, more refined and clear observation of the zinc deposition morphology is still needed. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are generally considered to be the most widely used and effective tools for studying the morphology of electrodeposited Zn metal at high resolution. In recent years, to exclude the effects of disassembling batteries and ambient air on the anodes, in-situ SEM and TEM have also been developed to visualize the zinc deposition process. The hydrogen evolution during the zinc deposition process also requires additional characterization for quantitative assessment [132,133]. Thus, the concentration of hydrogen can be quantitatively recorded by in-situ/ex-situ gas chromatography and in-situ differential electrochemical mass spectrometry (DEMS) to monitor the water-induced hydrogen evolution before and after cycling. It is worth noting that the in-situ electrochemical quartz crystal microbalance (EQCM) technology can be used to understand the contribution of unreacted Zn^0 metal to the total amount of inactive Zn [134].

Additionally, X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and Raman spectroscopy can effectively identify the components and chemical bonds of SEI film [135]. To assess the degree of corrosion of the zinc anode, the content and distribution of by-products can also be studied using SEM and XRD techniques. Other advanced characterizations, such as neutron scattering and synchrotron X-ray (SXR) also have related applications. However, the characterization of SEI and passivation layers can be affected by the operation and environment. In recent years, a large number of studies have used in-situ FTIR, in-situ Raman, in-situ XPS with depth etching or focused ion beam (FIB) cutting technology to determine the depth of the SEI or the passivation layer [136−138].

Although there are increasing number of advanced technologies to study the interface chemistry of zinc anodes, the understanding of the electrochemical behavior at the interface is still insufficient due to the complex composition of AEI and the dynamic process of zinc ion. Many computational simulations are widely used to understand the effectiveness of the electrolyte regulation strategies from a microscopic scale, especially under actual operating conditions and dynamic process simulations. Among them, the adsorption energy, charge density, and zinc ion diffusion paths calculated by density functional theory (DFT) are the most commonly used theoretical analysis methods for studying the interface evolution of the anode, which helps to further clarify the electrochemical reactions at the

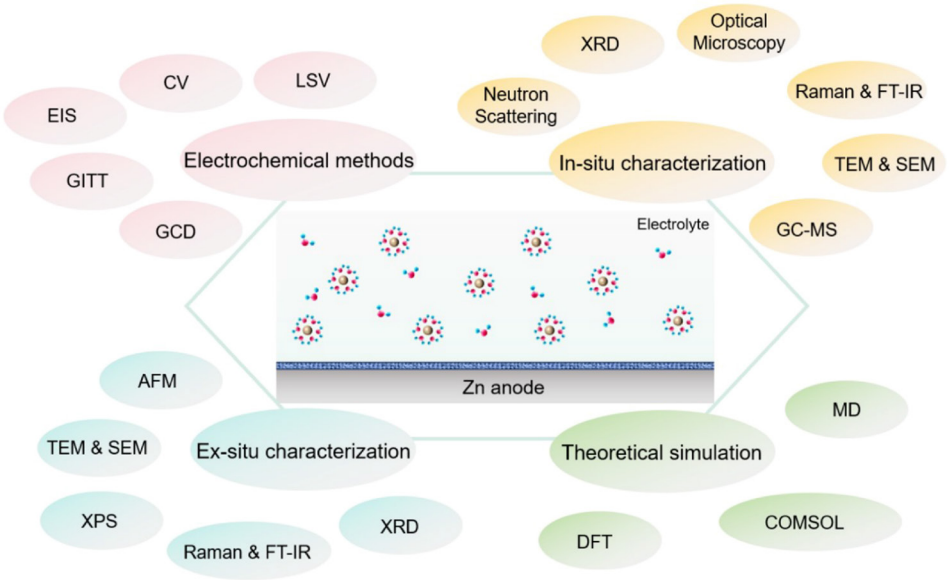

Fig. 27 Characterization techniques and analysis methods to evaluate effectiveness of interphase regulation strategies

interface. Molecular dynamics (MD) simulations are often used to simulate electrolyte systems containing a large number of molecules, which is conducive to reasonably deducing the interaction between the electrolyte and the electrode. Using COMSOL multiphysics method can simulate the local current density and electric field on the surface of the zinc anode, and even predict the formation of the initial nucleation sites and the growth process of zinc dendrites on a macroscopic scale [42,139].

In addition, using DFT calculations and MD simulations to predict the performance and mechanism of aqueous zinc ion batteries is a cutting-edge theoretical research method. DFT calculations can provide changes in the local geometry and charge distribution of materials after inserting ions, which is crucial for understanding the interaction between ions and materials. DFT calculations are also able to analyze the diffusion energy barriers and pathways of ions in materials, which helps to reveal ion diffusion mechanisms and predict battery charge and discharge performance. As for MD simulation, it can demonstrate the solvation structure of ions in the electrolyte and their dynamic changes under the action of an electric field, and can calculate and predict the evolution of hydrogen bonds, the formation of double layers, HER, and the plating/stripping process of zinc ions. This is of great significance for optimizing electrolyte design and improving AZIBs performance. In addition, simulation can be used to study the activity of water molecules in electrolytes of different concentrations, which can guide the design of stable electrolytes that meet complex operating conditions, reduce side reactions, and improve the electrochemical window. Through these calculation and simulation methods, researchers can predict and optimize the electrochemical performance of aqueous zinc ion batteries, providing theoretical guidance for experimental design and material selection.

5 Summary and perspective

Although AZIBs are considered a promising environmentally friendly and economical energy storage technology, the severe parasitic side effects caused by the thermodynamic instability of AEI limit the large-scale application. The interface between the zinc metal anode and the electrolyte is the fundamental pathway for the transfer and migration of zinc ions in the battery. The chemical properties of the interface are related to the properties of the electrolyte, the current density on the anode surface, and the compounds on the anode surface. Regulating AEI through electrolyte optimization strategies is expected to improve the migration and the interface distribution of zinc ions, thereby achieving dendrite-free zinc deposition and suppressed parasitic side reactions. At present, the AEI of AZIBS has been extensively studied, and a variety of advanced characterization techniques and computer simulations have been developed, which help researchers deeply understand the interface of the Zn metal anode. Although researchers have achieved good research results, establishing an efficient and stable AEI still requires overcoming many difficulties. This work provides a comprehensive analysis from the mechanism of interface chemistry and the key challenges caused by unstable AEI. From the perspective of optimizing AEI through electrolyte regulation strategies, the latest research progress is discussed, including the types of zinc salts, concentrations, solvent selection, eutectic electrolytes, hydrogel electrolytes, and electrolyte additives. Meanwhile, various testing methods and computer simulation techniques to provide guidance for accurately assessing these optimization strategies are also summarized, aiming to promote the development from the laboratory to the industry.

Although significant progress has been made in stabilizing AEI, there are still many challenges to be addressed. Some perspectives on the AEI are also proposed as follows (Fig. 28).

(1) There is an urgent need to further understand the interfacial reaction mechanism between the zinc metal anode and the aqueous electrolyte. To date, there has been a significant amount of research on AEI, and corresponding mechanisms have been proposed based on interface chemistry. However, due to the presence of the aqueous electrolyte, the interface chemistry at the anode is very complex, and parasitic reactions on the zinc surface are greatly affected by different zinc salt electrolytes. Research on the corrosion reactions of the zinc anode in other zinc salt electrolytes, such as $ZnCl_2$, $Zn(TFSI)_2$, and $Zn(OTF)_2$, is relatively scarce. In addition, during

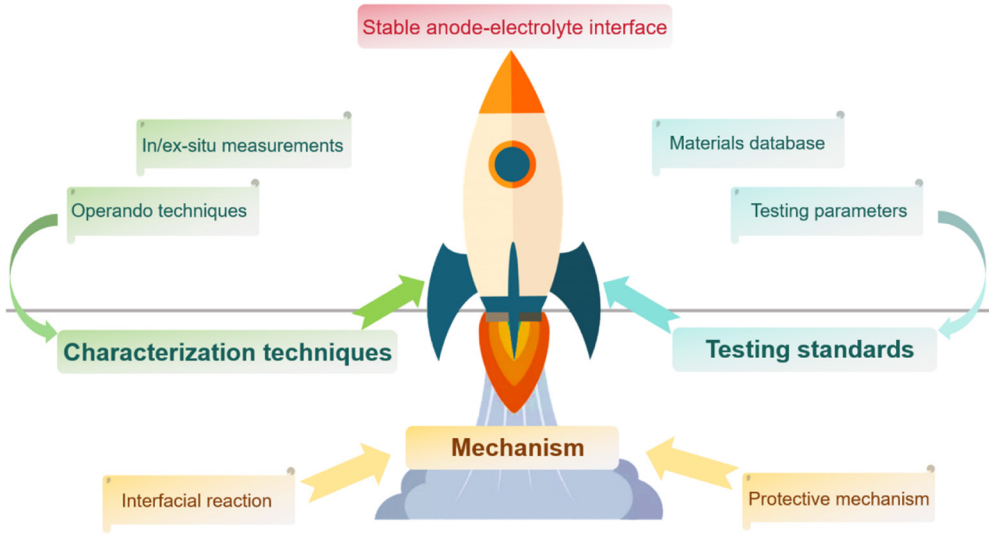

Fig. 28 Schematic illustration of perspectives for Zn anode/electrolyte interface

the process of optimizing AEI using electrolyte regulation strategies, there are still some puzzling results in different research reports. For example, the naturally formed almost insulating ZHS will reduce the electrode conductivity and accelerate the failure of the zinc anode, but the similar passivation layer formed by electrolyte regulation can act as a physical protective barrier to suppress the growth of dendrites. Moreover, attention should be paid to the adverse reactions caused by chemical corrosion when the anode surface is activated and the battery is at rest.

(2) New technologies and characterization to monitor the interfacial reaction process are also important. Unknown interfacial phenomena require an integrated understanding of the AEI through advanced characterization techniques. Currently, the characterization of AEI is still focused on traditional common technologies, such as XRD, XPS, SEM, and electrochemical techniques. However, due to the influence of temperature, humidity, and charge state on the zinc metal surface, ex-situ technologies often cannot accurately monitor the interface chemistry process. Therefore, the development of new characterization technologies, especially in-situ techniques, will help to deeply understand the interfacial reaction mechanism. In-situ characterization technology is of high significance and in urgent demand for real-time interface evolution. It is well-known that the failure of the zinc metal anode is attributed to zinc dendrites and parasitic side reactions, but most experiments are still at the qualitative stage. Therefore, it is crucial to clarify the amount of dead zinc on the electrode surface and how much hydrogen is produced during the battery cycle. In the future, more technologies such as synchrotron X-ray tomography and DEMS can be used to quantitatively describe these failure modes.

(3) There is still a lack of rigorous and standardized testing conditions and evaluation standards. In recent years, the number of researches on AZIBs shows an explosive growth trend. However, the large-scale commercial application of AZIBs is progressing slowly. This may mainly be due to the following two reasons. On the one hand, there is currently a lack of a universal testing standard. There are various types of electrolyte optimization strategies, and the testing conditions used by researchers are also very different. Different electrode sizes, current densities, capacities, matching separators, sources of zinc foil used, and even the pressure of battery packaging all have a significant impact on the performance of the battery. On the other hand, the lack of universal testing conditions makes it difficult to compare test data among different studies, severely hindering the exploration of commercialization. For example, although the use of organic zinc salts or high-concentration electrolytes in the electrolyte has a huge performance improvement, the significantly increased manufacturing difficulty and cost are unacceptable for commercialization. In addition, the data obtained by current research are mostly based on coin cells. To meet the needs of commercial applications, more attention should be

paid to the construction of large-capacity-size pouch cells or battery packs and the establishment of a unified evaluation standard.

CRediT authorship contribution statement

Hua-ming YU: Conceptualization, Experimental investigation, Writing − Original draft; **Dong-ping CHEN:** Methodology, Experimental investigation, Writing − Original draft; **Li-jin ZHANG:** Validation, Writing − Original draft; **Shao-zhen HUANG:** Visualization; **Liang-jun ZHOU:** Conceptualization, Supervision; **Gui-chao KUANG:** Investigation, Visualization; **Wei-feng WEI:** Supervision; **Li-bao CHEN:** Funding acquisition, Writing − Review & editing; **Yue-jiao CHEN:** Funding acquisition, Writing − Review & editing.

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.

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电解质工程策略优化水系锌离子电池负极/电解质界面的研究进展

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摘　要：水系锌离子电池因其固有的高安全性、经济效益和环境友好性，被认为是大规模储能系统的候选者。然而，负极/电解液界面上发生的枝晶生长、析氢反应和界面钝化等问题使其实际应用受到严重的阻碍。因此，构建稳定的负极/电解液界面在调节锌沉积和提高水系锌离子电池循环寿命等方面发挥着关键作用。基于对负极/电解液界面基础理论的研究，讨论了锌金属负极受制于不稳定界面而面临的诸多挑战，并系统总结了利用电解质工程稳定负极/电解液界面的调控策略。此外，介绍了包括分析锌金属负极的界面化学和表面形貌演变在内的有效性测试技术。最后，对未来研究提出建议和展望。这对构建高性能水系锌离子电池具有一定的借鉴意义。

关键词：水系锌离子电池；负极/电解质界面；锌负极；水系电解质；电解质工程；电解质添加剂

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