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Comprehensive understanding of the roles of water molecules in aqueous Zn-ion batteries: from electrolytes to electrode materials

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Benefiting from loose assembly conditions, a high level of safety and environmentally friendly characteristics, rechargeable aqueous Zn-ion batteries (AZIBs) have attracted significant attention. The electrochemical kinetics and performance of the AZIBs are greatly affected by water in electrolytes or electrode materials. The corrosion and passivation of the Zn electrode caused by the inevitable solvation process of water molecules can lead to the growth of dendrites, thus resulting in a limited cycle life. Moreover, water in the electrode material, whether in the form of structural water or co-intercalated hydrated cations, can greatly affect the electrochemical behavior due to its small size, high polarity and hydrogen bonding. Unlike previous reports, this review focuses on the roles of water molecules during electrochemical processes in AZIBs. We comprehensively summarize the influencing mechanisms of water molecules during the energy storage process from the perspectives of the electrolyte, Zn anode, and cathode materials, and further include the basic theory, modification methods, and practical applications. The mystery concerning the water molecules and the electrochemical performance of AZIBs is revealed herein, and we also propose novel insights and actionable methods regarding the potential future directions in the design of high-performance AZIBs.

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Broader context

Rechargeable secondary batteries play an important role in modern life as a critical part of energy storage. Although lithium-ion batteries have achieved great success and are widely used in smartphones, electric vehicles and other electronic devices, due to the limitations of cost and the safety of organic electrolytes, it is still worth developing new energy storage devices as a supplement. The utilization of water-based electrolytes can significantly improve safety, reduce costs, and provide higher conductivity than most of the organic electrolytes. In this context, rechargeable aqueous zinc-ion batteries (AZIBs) based on Zn^{2+} ions as charge carriers have received unprecedented attention due to their high theoretical capacity and the low cost of the zinc bulk electrode. However, the unique aqueous environment can lead to a series of profound effects on the energy storage process and raise a number of positive or negative influences. In this review, we systematically discuss the effects of water molecules on the anode, cathode and electrolytes based on the latest research, the remaining challenges, and the reported relevant solutions. The future research directions and prospects for improving the performance of ZIBs are also presented.

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1. Introduction

With the sharp increase in fossil fuel (*e.g.*, coal, oil, natural gas) consumption in the past decades, social problems including environmental damage, smog, air pollution, and increased greenhouse gases (407.8 \pm 0.1 ppm, 74%) have become unprecedentedly serious.¹⁻⁴ As such, renewable clean energy technologies such as hydro energy, tidal energy, solar energy, and wind energy are attracting increasing attention.⁵ Developing efficient, affordable, and highly secure energy storage devices at the grid level is a crucial component in the better utilization of energy. With the increasing demands of smart equipment (*e.g.*, smartwatches, health bracelets, wearable devices), it is of



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great significance to find energy storage systems with high safety, rapid reaction kinetics, excellent cycle performance, and high energy density.⁶ Commercial lithium-ion batteries (LIBs), developed in the 1970s, have dominated the market in electric vehicles and portable electronics due to their excellent integrated electrochemical performance.^{7–10} However, the high cost caused by the shortage of lithium resources (\$34 kg⁻¹ and \$55 kg⁻¹ for Li(NiMnCo)O₂ and LiCoO₂, respectively) and the safety hazards caused by flammable electrode materials and organic electrolytes hinder their further grid-level applications.^{11,12} Some researchers have turned their attention to sodium-ion¹³ and potassium-ion¹⁴ batteries because of their adequate resources, similar working mechanisms, and lower raw materials prices as compared to LIBs. However, the highly toxic organic electrolytes and assembly costs are still unavoidable.15 The shortcomings of these organic-based systems have pushed scholars to explore alternative batteries with low cost, high safety, and long cycle life.

Aqueous rechargeable batteries as potential large-scale energy storage systems are attracting unparalleled attention.¹⁶ The aqueous electrolytes in energy storage systems mainly consist of water and acids (acid electrolyte)/17 alkaline hydroxides¹⁸ (alkaline electrolyte)/soluble salts¹⁹ (mild electrolyte). Compared with traditional organic electrolytes, aqueous electrolytes have better ionic conductivities (~1 S cm⁻¹ > > ~1-10 mS cm⁻¹), which can lead to better performances due to fast ion diffusion kinetics.²⁰ So far, the aqueous battery systems can be divided into the following categories according to the different charge carriers: Li⁺, Na⁺, K⁺, Ca²⁺, Mg²⁺, Zn²⁺, Al³⁺, non-metal charge carriers (NH4⁺, H⁺, Cl⁻, and OH⁻) and hybrid systems.²¹⁻²⁴ Multivalent ion batteries (Ca²⁺, Mg²⁺, Zn²⁺, Al³⁺) have recently attracted considerable interest as promising substitutes for future large-scale energy storage devices due to their natural abundance and multi-electron redox capability.²⁵ Although metal Ca/Mg/Al in multivalent battery systems have larger theoretical capacities (11 337, 2206, and 2980 mA h g^{-1} , respectively) than Zn (820 mA h g^{-1}), the passivated anode

surface and the inappropriate electrode potential (-2.84, -2.36)and -1.68 V vs. standard hydrogen electrode) in the aqueous electrolytes (the narrow voltage window of water splitting-1.23 V) severely limit their applications.²⁶ As a result, the abovementioned multivalent ion battery systems always use an embeddable host material as the anode instead of highcapacity Ca/Mg/Al metal, which inevitably reduces the electrochemical performance of the batteries and limits their largescale applications. Particularly, the higher volumetric capacity $(5851 \text{ mA h cm}^{-3})$ of Zn is approximately equal to the sum of Ca (2072 mA h cm⁻³) and Mg metal (3834 mA h cm⁻³).²⁷ As potential candidates, aqueous Zn-ion batteries (AZIBs) have attracted tremendous attention due to their low redox potential (-0.76 vs. standard hydrogen electrode), easy largescale fabrication production, superior safety, and low cost (\sim 2 USD per kg, metal Zn price; \sim 75 ppm, abundance).^{28–30} Compared with traditional LIBs (\$300 kW h⁻¹), the much lower projected capital cost of \$65 LIBs (\$300 kW h^{-1}), and the much lower projected capital cost of \$65 kW h⁻¹ can be achieved in AZIBs.³¹ It is worth noting that the AZIBs mentioned here refer to the insertion/extraction of the charge carrier Zn²⁺ on the cathode and the deposition/stripping of Zn²⁺ on the Zn anode within a mild electrolyte, which is different from Zn batteries based reversible conversion reactions in alkaline electrolytes with hydroxide ions.32

However, the large-scale applications of AZIBs still face enormous challenges. The first problem is the corrosion and parasitic reactions of the Zn anode in aqueous electrolyte.³³ Unlike the electrochemical process of the LIBs anode in a non-aqueous system, the higher polarity and smaller radius $(2-3 \text{ Å})^{34,35}$ of water molecules can participate in, and bring about the occurrence of corrosion in the Zn anode due to the solvation process.³⁶ The more serious issue is that it may induce the growth of Zn dendrites, and lead to the irreversible failure and short circuit of the battery. Therefore, how to control the excessive participation of water molecules in the Zn anode



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versity of California, Berkeley in 2017. His current research interests are focused on new nanomaterials for electrochemical energy storage and micro/nano energy devices. reaction is a core problem that needs to be resolved urgently. Considering the ultrahigh capacity of the Zn anode, the cathode materials, as an important part of the batteries, largely determine the electrochemical performance of AZIBs, especially the capacity and rate, according to Cannikin's law. Based on the current research, the bottlenecks restricting development can be divided into the following categories:^{1,27,37–41}

(a) The significant desolvation penalty and electrostatic interactions of Zn^{2+} ions in the solid-state diffusion interface between cathode materials and electrolytes.

(b) The unstable Zn electrode includes side reactions, corrosion, and dendrites.

(c) The repulsion of the host material to external charges of Zn^{2+} ions due to electrostatic interactions.

(d) The irreversible structural damage caused by the repeated interactions and extraction of Zn^{2+} ions in the host cathode material.

In the bottlenecks mentioned above, the presence of water notably affects the electrode reaction process and becomes the key to solving the problem. On the one hand, the interaction between water and metal cations in the electrolyte to form large-sized hydrated Zn^{2+} ions is the pivotal factor affecting the solid-state diffusion of Zn^{2+} ions at the interface. On the other hand, structural water is a widely used tool that can effectively solve the charge repulsion effect through electrostatic shielding. At the same time, the water molecules in materials can often lead to a change in the crystal structure, which generally causes the expansion of the interlayer spacing while acting as a pillar to stabilize the skeleton structure. In particular, the narrow voltage window is also a huge challenge to further improve the energy density of AZIBs owing to the splitting of water; therefore, water is a double-edged sword. Better understanding the impacts of water in AZIBs and maintaining the balance between the advantages of its strengths and weaknesses are particularly important for further developing practical AZIBs.

Although water plays an unparalleled role in the AZIBs, the systematic overviews about the impacts of the water molecules in AZIBs including the electrolyte, Zn anode, and cathode, have not yet been reviewed comprehensively. In this review, we focus on the water molecule and divide it into three types according to its position and function: solvated water and free water in the electrolytes, and structural water in cathode materials. The effects of water molecules on the performance of AZIBs and strategies to control them are discussed. The point-to-point discussion of existing problems and their internal mechanisms are presented. Since it is directly related to the stability of the Zn anode, strategies on how to reasonably control the corrosion and side reactions on the Zn surface by the solvation effect have also been further discussed. Apart from solvated water, the structural water in the host materials can also markedly affect



Fig. 1 Schematic diagram of the merits, drawbacks and influence of water in AZIB.

the crystal structure of the material and improve its electrochemical performance. The methods of introducing structural water and its influence on material structure and energy storage process are also discussed. In particular, the structural water in electrode material and the solvated water in the electrolyte could also interact with each other with/without an electric field. This process in detail and its influence on the energy storage process are summarized separately. Finally, based on the existing research foundation, we put forward outlooks for future development and direction for maximizing the strengths and avoiding the weaknesses of water to achieve high-performance aqueous AZIBs. As shown in Fig. 1, the anode and cathode reactions in which water molecules participate and their results are enumerated.

2. Water molecules in electrolytes

2.1. Hydrated zinc ion— $[Zn(H_2O)_6]^{2+}$

Water, as the fundamental part of the aqueous electrolyte, provides an environment for the charge transport of the Zn²⁺ ion and dramatically affects the final performance of the battery. However, Zn²⁺ ions do not exist alone in water but form a highly oriented and ordered structure due to the polar nature of an aqueous electrolyte.^{42,43} Taking the most common ZnSO₄ electrolyte as an example, the free water molecules can combine with Zn²⁺ ions and solvate to form a hydrated zinc ion of $[Zn(H_2O)_6]^{2+,44,45}$ The hydration effect has been widely observed in thermophysics experiments, X-ray absorption spectroscopy (XAS) or neutron scattering, electrochemical experiments, infrared photodissociation spectroscopy, Raman spectroscopy, luminescence, nuclear magnetic resonance, and so forth in combination with molecular dynamics simulation.⁴⁶⁻⁴⁸ The structure of the hydrated Zn^{2+} ion is shown in Fig. 2a. Its structure conforms to the spherical approximation model and can be divided into two layers.⁴² The inner layer is coordinated by cations and six water molecules connected by hydration coordination bonds. The outer layer of the hydrated sphere is formed by loosely combining free water molecules far from the hydrated inner shell through hydrogen bonds.

Considering only the ion-dipole interaction, the standard Gibbs solvation energy of the cation within the mean spherical

approximation (MSA) is as follows:

$$G_{\rm s}^0 = -\frac{N_0 Z_{\rm i}^2 e_0^2}{8\pi\varepsilon_0} \left(1 - \frac{1}{\varepsilon_{\rm s}}\right) \left(\frac{1}{r_{\rm i} + \frac{r_{\rm s}}{\lambda}}\right)$$

where N_0 is the Avogadro constant, Z_i is the ionic charge, ε_0 is the fundamental electronic charge, ε_0 is the permittivity of free space, ε_s is the relative permittivity of the pure solvent, r_i is the ionic radius of the cation. The value can be obtained directly from the Gibbs solvation energy data of metal cations and halide ions.⁴² In different solvents, this value is entirely different, reflecting the discrepancy in the ion solvation mechanism and related distance.

For cations, replacing " $\frac{P_s}{\lambda}$ " with the polar alkalinity parameter B_p , the equation could be rewritten as

$$G_{\rm s}^0(\mathbf{C}_+) = -\frac{N_0 Z_{\rm i}^2 e_0^2}{8\pi\varepsilon_0} \left(1 - \frac{1}{\varepsilon_{\rm s}}\right) \left(\frac{B_{\rm p}}{1 + r_{\rm i}\cdot B_{\rm p}}\right)$$

This relationship demonstrates that the Gibbs solvation energy of a cation is linear in the basicity.⁴⁹ According to previous research reports, the B_p alkalinity value of water is 12.1.⁴² Due to the existence of lone pairs of electrons, the alkalinity can be used to measure the ability of water to donate electrons. The radius of the hydrated ion is related to the radius of the cation. As shown in Fig. 2b and c, when the charge is the same, the smaller the metal cation radius, the greater the energy barrier brought by Gibbs free energy and the larger hydrated radius, which is the same as the enthalpy change of hydration. In contrast, although the radii of non-metallic ions are larger, it results in a smaller radius of hydrated ions and enthalpy of hydration (Table 1). Considering that the radius of the Zn²⁺ ion is small, the radius of hydrated Zn²⁺ ions is larger as compared to the other most common metal or non-metal ion charge carriers (Li⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺, and NH₄⁺), which leads to its slow diffusion kinetics in the aqueous electrolyte. This is also the main reason limiting the kinetic process of insertion and extraction of Zn²⁺ ions in the anode and cathode.

2.2. Oxygen solubility

In general, both CO_2 and O_2 are part of the air and can be dissolved in water to a certain extent. Theoretically, the presence of CO_2 in electrolytes could lead to the formation of



Fig. 2 (a) Schematic diagram of the hydrated Zn²⁺ ion. Comparison of the ionic radius, hydrated radius, hydration enthalpy of (b) metal cation charge carriers, (c) non-metal charge carriers.

 Table 1
 The ionic radius, hydrated radius and hydration enthalpy of different ions. Data derived from ref. 50

Ion	Ionic radius (Å)	Hydrated radius (Å)	Hydration enthalpy (kJ mol ⁻¹)
Zn ²⁺	0.74	4.3	-1969
Mg ²⁺	0.72	4.28	-1922
Ca ²⁺	0.99	4.12	-1592
Li^+	0.6	3.82	-515
Na^+	0.95	3.58	-405
K^+	1.33	3.31	-321
\mathbf{F}^{-}	1.36	3.52	-465
Cl^{-}	1.81	3.32	-340
${\rm NH_4}^+$	1.48	3.31	-285
OH	1.76	3	-430
H_3O^+	1.15	2.82	-1063

carbonic acid (CO₂ + H₂O \rightarrow H₂CO₃), which affects the pH of the electrolyte, and may lead to the formation of precipitation.⁵³ The solubility of CO_2 increases with temperature, but it is much less soluble than O₂ (Fig. 3a and b). The main components of the atmosphere are nitrogen and oxygen, and the CO₂ content in the atmosphere is only 0.03%. Hence, there is no research on the impact of CO₂ on AZIBs, which may be related to the lower content and weak solubility in the atmosphere (Fig. 3c). Compared to CO_2 , the redox ability of O_2 can affect electrode materials and interfere with the electrochemical stability of dissociated salt species. Although the hazards of O₂ are widely known in organic battery systems, studies on its effects on AZIBs performance when dissolved in aqueous electrolyte are rare to date. Due to the active characteristics of Zn metal, its surface can easily be oxidized to form ZnO in the air. According to Fig. 3b, the solubility of oxygen in pure water at 25 °C was about 6 mL L⁻¹ under a standard atmospheric pressure, which is as high as the oxygen content in the air. Therefore, the dissolved oxygen in the electrolyte may oxidize the Zn anode and affect the battery cycle performance.

Very recently, Yang *et al.*,⁵⁴ for the first time, explored the influence of dissolved oxygen in the water-based electrolyte on the battery. Compared with Zn in the presence of O_2 , the corrosion potential increased from 1.004 V to 0.973 V in the absence of O_2 . The Zn//Zn symmetric battery showed a more than 20-fold improvement in cycle performance as compared to the presence of O_2 (Fig. 4a). The visible bulges can be observed

due to water splitting and side reactions (Fig. 4b). By artificially controlling the O_2 content in the electrolyte, they found that as the oxygen content increased, the emerging characteristic peaks of ZnO, Zn(OH)₂, and Zn₄(OH)₆SO₄ on the Zn anode were substantially intensified (Fig. 4c). This means that the presence of dissolved oxygen would accelerate the corrosion process on the surface of Zn and form a metal oxide/hydroxide layer, resulting in electronic insulation on the surface of the Zn.

In addition to the impact on the Zn anode, the presence of dissolved O_2 could also affect the cathode materials. For the MnO_2 cathode materials, it showed the dramatically smaller overpotential (58 mV) in the absence of O_2 as compared with the presence of O_2 at 5 mA cm⁻², which indicated that the decomposition of water is more likely to occur in the presence of O_2 (Fig. 4d). Galvanostatic charge–discharge (GCD) curves of the Zn–MnO₂ battery with O_2 showed a higher specific capacity and a more obvious third discharge platform at 1.2 V (Fig. 4e). Therefore, the presence of O_2 conduced to the capacity contribution of MnO₂ cathode. The overall reactions for the Zn–MnO₂ battery in ZnSO₄ electrolyte with the presence of O_2 can be summarized during the electrochemical process as follows:

$$\begin{split} \mathrm{MnO}_{2} + \frac{1}{4}\mathrm{O}_{2} + \mathrm{Zn} + \frac{15 + 4x}{12}\mathrm{H}_{2}\mathrm{O} + \frac{1}{3}\mathrm{ZnSO}_{4} \\ \leftrightarrow \mathrm{4MnOOH} + \frac{1}{3}\mathrm{ZnSO}_{4}\big[\mathrm{Zn}(\mathrm{OH})_{2}\big]_{3} \cdot x\mathrm{H}_{2}\mathrm{O}. \end{split}$$

However, this kind of improvement was extremely limited and only worked in the first few cycles, and then it decayed quickly. The full battery exhibited worse cycling performance due to O_2 (Fig. 4f). Yang *et al.*⁵⁴ further proved the same results by using other cathode materials: VO₂, V₂O₅, Na_{0.55}Mn₂O₄·1.5H₂O, and K₂Zn₃[Fe(CN)₆]₂·(H₂O)₉.

In summary, the O_2 can dissolve in aqueous electrolyte and generate an obvious effect on the entire battery system. In an oxygen-rich environment, the corrosion of Zn will increase, and the charge/discharge process of the positive electrode would also be affected, resulting in limited electrochemical performance, regardless of cycles or capacity. Therefore, we believe that it is beneficial to remove the dissolved oxygen in the electrolyte in advance by nitrogen purging or adding an oxygen scavenger.⁵⁵



Fig. 3 The solubility of (a) CO_2 and (b) O_2 at 1 atm (standard atmospheric pressure) in pure water with different temperatures. Data derived from ref. 51 and 52. (c) Percentage diagram of atmospheric composition.



Fig. 4 (a) A comparison of the effects of the presence and absence of O_2 on the cycle performance. (b) The optical photographs of Zn/Zn cells after the 120 h galvanostatic cycles in the presence/absence of O_2 . (c) XRD patterns of the Zn anode after 120 h cycles in the presence/absence of O_2 . (d) Linear sweep voltammetry (LSV), (e) initial charge/discharge curves, and (f) cycle performances in the presence/absence of O_2 . Reproduced with permission from ref. 54. Copyright 2020, Elsevier Inc.

2.3. Water splitting and the electrochemical window

Water splitting includes two half-reactions, namely the oxygen evolution reaction (OER) and the hydrogen evolution reduction (HER). The whole process requires four electrons or two electrons and the reaction kinetics are closely related to the electrolyte's pH. As shown in Fig. 5a, the OER in acidic or alkaline solution is

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \text{ or } 4OH^- \rightarrow O_2 + 2H_2O + 4e^-,$$

and HER in acidic or alkaline solution is

$$2H^+ + 2e^- \rightarrow H_2 \text{ or } 2H_2O + 2e^- \rightarrow H_2 + 2OH^-.$$

Therefore, water molecules could be decomposed to release O_2 or H_2 when the applied voltage is higher or lower than a certain value, theoretically. Under normal circumstances, the HER occurs at the negative electrode and releases H_2 , while the OER occurs at the positive electrode and releases O_2 . The gas produced by water decomposition will have a severe negative impact on the battery. On the one hand, the decomposition of

water will cause the consumption of electrolyte and change the pressure inside the battery, and the generated gas will cause the battery to bulge and cause safety problems. On the other hand, water decomposition will consume part of the electrons and decrease the coulombic efficiency (CE) of the battery. At the same time, the O_2 generated by the decomposition of the electrolyte may be partially dissolved in the electrolyte under the influence of internal pressure, increasing the concentration of dissolved O2. Based on the previous discussion, it will lead to the aggravated instability of the Zn anode and a serious decrease in cycle performance. Finally, the violent water decomposition on the surface of the electrode would destroy the microstructure of the material, and in a severe case might even cause the active materials to fall off the current collector. The electrochemical window of AZIBs commonly depends on electrode materials and electrolytes. To ensure the normal operation of the battery without water decomposition, the redox potential of the material itself should be within the voltage range of the water decomposition.



Fig. 5 (a) The Pourbaix diagram of water. (b) The balance relationship among the electrochemical window of the battery, the electric potential and the electrolyte. (c) Schematic diagram of the electrolyte separation strategy. (d) Triangular diagram of electrolyte, pH, and electrode materials.

As shown in Fig. 5b, the μ_a is the highest chemical potential at which redox reactions can occur in the cathode. When the potential further increases beyond μ_a , an OER reaction will occur on the cathode surface. On the contrary, the μ_c is the lowest chemical potential at which redox reactions can occur in the anode. When the potential further decreases beyond μ_c , the HER reaction will occur on the anode surface. Hence, the μ_a should be lower than the highest value of the OER, and μ_c should be higher than the minimum value of the HER. As a result, the difference of $\mu_a - \mu_c$ determines the electrochemical voltage window of the AZIBs. In addition to selecting suitable electrode materials, it is also a feasible strategy to control the electrolyte and widen the water splitting window of $\mu_a - \mu_c$. Compared with pure water, high-concentration salt solutions can significantly increase the decomposition window of water and broaden the value of $\mu_{\rm a} - \mu_{\rm c}$. It has been proven that when the electrolyte concentration increases to a certain degree (water in salt), the electrochemical window can be widened to more than 2.0 V.

In addition to the increase in electrolyte concentration, separating the electrolyte is also a strategy to increase the working window of the AZIBs. Specifically, the water splitting voltage is closely related to the pH of the electrolyte (Fig. 5a). In an alkaline environment, the maximum decomposition

voltage of the HER occurring at the anode can be extended to -0.82 V. In an acidic environment, the maximum decomposition voltage of the OER occurring at the cathode can be extended to 1.23 V. Therefore, in theory, a voltage window exceeding 2 V can be achieved by dividing the electrolyte. In AZIBs, the overpotential of hydrogen evolution on the Zn anode in a basic environment can be memorably decreased. In contrast, the overpotential of the oxygen evolution of the cathode under acidic conditions will increase significantly. Acid electrolytes and base electrolytes are separated by special ion-selective membranes (Fig. 5c).⁵⁶⁻⁵⁸ Thus, the assembled AZIBs could achieve a high voltage due to the expanded splitting voltage of water. In particular, due to the expansion of the electrolyte stability window, materials with high chemical potential and reaction processes can be introduced, thereby achieving a significant increase in the voltage platform.^{17,59} In summary, the overpotential window of water decomposition directly determines the final output voltage and working window of the AZIBs. It is closely related to the chemical potential of the material, the pH of the electrolyte, and the water content of the electrolyte (Fig. 5d). Coordinating the relationship between the three is an effective way to ultimately improve the electrochemical stability window and assemble high output voltage AZIBs.

2.4. Electrochemical effects of H₂O in electrolyte

Extensive studies have shown that the electrochemical performance of the same material in aqueous electrolyte dramatically differs from that in organic electrolyte. Considering the similar structural transformation during the Zn2+ ion intercalated process, the properties of structural energetics and solid diffusion of Zn²⁺ cannot be considered as significant determinants of the electrochemical performance of the two media. Nazar et al.60 proved that water-containing systems exhibited substantially lower charge transfer resistance and related activation energy for Zn²⁺ ion transport as compared to those in organic systems via electrochemical impedance studies (EIS). At the cathode materials, the organic electrolytes hold a higher desolvation penalty due to the consequence of ion-pair formation, whereas shielding of the Zn²⁺ charge by water molecules facilitates its facile interfacial diffusion in the water-containing system. Remarkably, the presence of water molecules enables a unique 'Janus interface⁶¹', which has been shown to accelerate the migration of lithium ions at the solid/liquid interface.62 Similarly, the transport of Zn²⁺ ions can be enhanced by forming the Janus interface between the different components.^{60,63}

In addition to affecting the charge transfer at the interface, Wang *et al.*⁶⁴ demonstrated that the free water in the electrolyte played a positive role in the electrochemical performance. The X-ray diffraction (XRD) results show that the H₂O in the electrolyte could be successfully inserted into the layered VOPO₄ (Fig. 6a); the basal spacing expanded from 7.4 to 11.98 Å. To explore the influence of moisture in the electrolyte on the electrolyte consisting of 0.1 M Zn(OTf)₂ and acetonitrile (AN) for comparison. The XRD results did not show any changes in AN with 0% water content.

However, with the addition of water, an obvious characteristic peak of hydrated VOPO4·2H2O appears, which demonstrates that the water molecules of the electrolyte can enter the crystal structure (Fig. 6b). The corresponding galvanostatic charge-discharge (GCD) curves show the sharply increased battery capacity accompanied by an increase in the water content of the electrolyte, which can be attributed to the hydrated VOPO4 2H2O (Fig. 6c). The schematic diagram of water transfer between VOPO4 and electrolyte is shown in Fig. 6d. Next, hydrated VOPO4·2H2O was used to explore the influence of structural water on materials. The GCD curves of VOPO₄·2H₂O in AN electrolyte containing 1% water exhibited the highest voltage and capacity (Fig. 6e). This is because the exchange of water molecules occurs in the material and electrolyte, and the structural water can expand the interlayer spacing and accelerate ion diffusion, thereby helping to achieve high capacity. Then, once the structural water molecules are lost to the electrolyte in the exchange, it will cause irreversible capacity loss. Therefore, it is essential to prevent the electrolyte from "grabbing" the structural water molecules in VOPO4. 2H₂O. The kind of interaction between this electrolytic material and the electrolyte is shown in Fig. 6f. This is why hydrated VOPO₄·2H₂O in a water-poor electrolyte will suffer rapid capacity decay (Fig. 6g). Therefore, a small amount of water in the electrolyte was used as an additive to guarantee a dynamic

water balance. Electrochemical impedance spectroscopy (EIS) results showed that when the hydrated VOPO₄·2H₂O is in 1% H_2O + AN electrolyte, the interface resistance between the electrode and electrolyte is the smallest (Fig. 6h), which is consistent with the previous analysis. Density functional theory (DFT) simulations revealed the phase diagram of zinc ionized VOPO₄·2H₂O (Zn_xVOPO₄·nH₂O) based on water activity (α_{H_2O}) and Zn chemical potential (μ_{Zn}) . According to different concentrations of water content, the phase change process could be divided into three regions. In region I with high α_{H_2O} , the reversible Zn (de)insertion occurs between the two hydrated phases through route a. In the region III with low α_{H_2O} , the zincification is irreversible. When in region II, the phase transition proceeds along route b and the situation is unstable. This suggests water molecules could also affect the phase transition process in addition to affecting the intercalation process of Zn²⁺ ions (Fig. 6i).

The presence of free water in the electrolytes can also change the coordination state and diffusion path of the intercalated Zn^{2+} ions in the structure of the host material. Choi *et al.*⁶⁵ discovered that water could be inserted into the crystal structure together with Zn^{2+} ions and affect the coordination of Zn with the V₆O₁₃ host material. When the electrolyte contains water, the water can enter the crystal structure of the host material through an electrochemical exchange, and finally achieve dynamic equilibrium.

 Zn^{2+} ions tend to be octahedrally coordinated in V₆O₁₃. Compared with the non-coordination method in the pristine V_6O_{13} , this kind of Zn^{2+} ion storage mechanism is more stable and causes minimal distortion of the host lattice (Fig. 6j). The predicted Zn²⁺ ion diffusion path is shown in Fig. 6k. In the presence of free water, Zn2+ ions tend to move from one octahedral position to an adjacent octahedral position along the *b*-axis along a *z*-shaped path, rearranging with water molecules to minimize the oxygen atoms from the lattice electrostatic repulsion. In the absence of free water in electrolytes, the diffusion path of Zn²⁺ ions is more direct, but there is a tendency toward one side at the end. When Zn2+ ions diffuse from one position to the same symmetrical position, the intercalation water has the effect of expanding the diffusion channel, allowing Zn²⁺ ions to pass through more freely. As such, the free water in the electrolyte will affect the charge transfer resistance, Zn2+ transport activation energy, layer spacing, the phase transition of host materials, coordination state, and diffusion path of Zn²⁺, which will be ultimately reflected in the electrochemical performance.

Active free water on Zn anode protection

3.1. Water-induced Zn corrosion and side reactions

As mentioned earlier, the unparalleled application potential of AZIBs comes from the metallic Zn anode. Unsatisfactorily, constrained by the lower standard electrode potential of Zn^{2+}/Zn , the Zn metal is thermodynamically unstable in water during the electrochemical processes.⁶⁶

HER: $H^+ + 2e^- \rightarrow H_2$ (0 V vs. SHE)





Fig. 6 (a) XRD results of pristine VOPO₄, VOPO₄·2H₂O before and after dehydration, and the corresponding structure diagram. (b) XRD results of dry VOPO₄ in electrolyte with different water contents. (c and e). Charging–discharging curves of dry VOPO₄ and VOPO₄·2H₂O in different electrolytes. (d and f) Schematic illustrations of how the water accelerates the Zn²⁺ diffusion at the electrolyte/electrode interface of VOPO₄ and VOPO₄·2H₂O. (g) EIS results and (h) cycle performance of VOPO₄ and VOPO₄·2H₂O in different electrolytes with/without water. (i) The phase diagram of Zn_xVOPO₄·nH₂O-based water activity (α_{H_2O}) and Zn chemical potential (μ_{Zn}). Reproduced with permission from ref. 64. Copyright 2018, Wiley-VCH (j) DFT calculation results for V₆O₁₃ with Zn intercalation with/without water. (k) Comparison of the kinetic behaviour of Zn with/without water. Reproduced with permission from ref. 65. Copyright 2019, Wiley-VCH.

Zn reduction: $\operatorname{Zn}^{2^+} + 2e^- \rightarrow \operatorname{Zn} \quad (-0.762 \text{ V} \nu s. \text{ SHE})$

The Zn passivation caused by side reactions and corrosion is closely related to the hydrated Zn²⁺ ions in the electrolyte.⁶⁷ Generally, the electroplating/stripping of the Zn anode during

the charge–discharge process is based on Zn^{2+} ions, and the whole process is depicted in Fig. 7a. However, Zn^{2+} ions in the electrolyte will be surrounded by six water molecules to form solvated Zn^{2+} ions instead of existing alone. Hence, solvated $[Zn(H_2O)_6]^{2+}$ located in the electric double layer has to overcome



Fig. 7 (a) Schematic illustration of the Zn electroplating/stripping process. (b) Pourbaix diagram of the Zn/H₂O system. Reproduced with permission from ref. 69. Copyright 2020, American Chemical Society. (c) Schematic diagram of the influencing factors on the decay performance of the Zn anode.

the energy barrier to de-solvate and release a large amount of electrochemically reactive free water molecules to form Zn^{2+} ions:

$$Zn(H_2O)_6^{2+} \leftrightarrow Zn^{2+} + 6H_2O$$
 (desolvation)

Compared with the bulk water molecules connected by water–water hydrogen bonds, the active water molecules have weakened H–O bonds, thus leading to the deprotonation of water and promotion of water hydrolysis. It led to the active water molecules near the Zn foil are more likely to decompose to produce hydrogen, especially with the high redox overpotential of Zn^{2+}/Zn , causing the increasing pH of the local microenvironment based on the following reaction:⁶⁸

$$2H_2O + 2e^- \leftrightarrow 2OH^- + H_2$$
 (HER)

There are still doubts about the formation mechanism of another side reaction product, ZnO. The alkaline state near the electrode can cause micro side reactions to cause the corrosion of Zn and the generation of ZnO is attributed to the elimination of protons (Fig. 7b), which will gradually accumulate as the charging process proceeds. The corresponding chemical reaction equation can be expressed as follows:⁶⁹

$$Zn^{2+} + 2OH^- \leftrightarrow Zn(OH)_2 \leftrightarrow ZnO + H_2O$$
 (corrosion)

The solvation effect will promote the charge transfer of solvated Zn^{2+} through the Zn-OH₂ bond, which significantly

weakens the O–H bond produced by electrons moving from the 3a1 bonded molecular orbital of the coordination water to the unoccupied Zn^{2+} orbital.^{70,71} The weak O–H bonds within the solvated $Zn(OH_2)_6^{2+}$ are easily attracted by strong O–H bonds with enough hydroxide ions available to form $Zn(OH_2)_2$ complexes. Hydrated zinc ions can also directly participate in side reactions, and the corresponding chemical reaction equation can be expressed as follows:⁷²

$$4[\operatorname{Zn}(\operatorname{H}_2\operatorname{O})_6]^{2^+} + 6\operatorname{OH}^- + \operatorname{SO}_4^{2^-} + (n - 24) \operatorname{H}_2\operatorname{O}$$

$$\leftrightarrow \operatorname{Zn}_4\operatorname{SO}_4(\operatorname{OH})_6 \cdot n\operatorname{H}_2\operatorname{O} \text{ (side reaction)}$$

According to the solubility product constant (K_{sp}) ,

$$K_{\rm sp}({\rm Zn}_4{\rm SO}_4({\rm OH})_6 \cdot n{\rm H}_2{\rm O}) = C([{\rm Zn}({\rm H}_2{\rm O})_6]^{2+})^4 \cdot C({\rm OH}^-)^6 \cdot C({\rm SO}_4^{2-})$$

When the critical solubility of $C(OH^-)$ is reached, side reaction products of $Zn_4SO_4(OH)_6 \cdot nH_2O$ will appear according to the equation:

$$C(\mathrm{OH}^{-}) = \sqrt[6]{\frac{K_{\mathrm{sp}}(\mathrm{Zn}_{4}\mathrm{SO}_{4}(\mathrm{OH})_{6} \cdot n\mathrm{H}_{2}\mathrm{O})}{C([\mathrm{Zn}(\mathrm{H}_{2}\mathrm{O})_{6}]^{2+})^{4} \cdot C(\mathrm{SO}_{4}^{2-})}}$$

For instance, if the electrolyte is a conventional electrolyte of the Zn–MnO₂ battery consisting of 2 M ZnSO₄ + 0.1 M ZnSO₄ (M = mol kg⁻¹), and the value of the critical concentration $C(OH^-)$ is calculated as 1.64×10^{-9} M, when OH^- reaches a specific concentration order of magnitude (about 10^{-9} – 10^{-8}),

it will react with Zn^{2+} , SO_4^{2-} , and H_2O to form $Zn_4SO_4(OH)_6$. nH_2O . These by-products of low conductivity are randomly formed on the surface of the Zn foil to roughen the electrode, thereby changing the original uniform distribution of current and triggering the growth of Zn dendrites. When the dendrite grows to a certain extent, it may pierce the separator to result in the battery failure or break and separate from the Zn electrode to form so-called "dead Zn".

The negative impacts of de-solvation are summarized in Fig. 7c. These side reactions and their products caused by the de-solvation of solvated water molecules can cause a series of problems that dramatically limit the further development of AZIBs. Firstly, it can seriously affect the CE and cycle stability of the battery. Secondly, the gas produced by the side reactions can change the internal environment of the battery and increase the pressure, causing the battery to bulge. Consequently, finding an effective strategy to avoid the negative influence of the active solvated water molecules on the anode is very important for the promotion of AZIBs.

Corrosion, water splitting, Zn dendrites, passivation, and other side reactions, are closely interconnected. We believe that controlling the formation of active free water near the surface of the Zn anode is one of the reliable methods. Besides, decreasing the content of solvated $[Zn(H_2O)_6]^{2+}$ through the electrolyte modification strategy can also reduce the amount of active free water produced by desolvation. It is also a feasible strategy to construct corrosion-resistant materials on the surface of the Zn anode. These strategies will be systematically elaborated on in the subsequent sections of Water regulation on the Zn surface and Water regulation in electrolyte.

3.2. Water regulation on the Zn Surface

Regulating the hydrated Zn²⁺ ions on the surface of the Zn anode is an effective strategy to inhibit surface corrosion and side reactions, thereby improving the stability of the Zn anode. It is a simple and efficient strategy to directly modify the surface of the Zn anode with acid/alkali-resistant, chemically stable anti-corrosion materials, which helps to control and isolate the active water molecules on the surface of the Zn anode. Based on the different material properties, we summarize them into two categories, namely, conductive materials protection and chemically inert materials protection.

3.2.1. Conductive materials protection. Constructing a conductive front surface on the surface of the Zn anode is an effective strategy to separate the active water molecules generated by the desolvation from the Zn as a protective barrier. The currently reported conductive materials mainly focus on carbon-based materials (including graphene,⁷³ graphdiyne,⁷⁴ carbon nanotubes,⁷⁵ organic-derived carbon,⁷⁶ acetylene black/ carbon black⁷⁷), metal (gold,⁷⁸ indium,⁷⁹ and copper⁸⁰), and conductive polymers.⁸¹ Recently, Mai *et al.*⁸² reported a novel strategy that directly coated the uniformly dispersed CNTs ink on the surface of the Zn anode to form a uniform conductive coating layer. As shown in Fig. 8a, scanning electron microscope (SEM) images demonstrated that uniform nano-zinc flakes instead of dendrites appeared on the electrode, and no

other by-products were observed after over 400 h cycles. On the contrary, Zn₄SO₄(OH)₆·4H₂O appeared on the CNT protective layer. By DFT calculations, the protective layer of CNTs with rich N and O elements exhibited the strong ability to adsorb S and O. Similarly, the utilization of graphene oxide (Zn@GO),⁷³ and carbon⁸³ also showed significant improvement in the cycle performance of the Zn anode (Fig. 8b and c). In particular, Wang's group⁷⁵ fabricated free-standing CNT/paper as scaffolds that were placed between the separator and the Zn electrode instead of direct coating as mentioned above (Fig. 8d). Due to the thicker CNTs protective layer, this strategy can extend the cycle time up to 1800 h without increasing voltage hysteresis, which exceeds most previous reports. However, it can be expected that this strategy will ineluctably lead to another problem, namely the reduction of the mass/volume energy density of the overall battery. Benefiting from the special sodalite topology and porosity, metal-organic framework (MOFs)-derived carbon is a promising candidate for Zn protection.⁸⁴ As a member of the MOF family, ZIF-8 (zeolitelike metal-organic frameworks) has a three-dimensional network structure formed by the four-coordination of Zn²⁺ ions with nitrogen in imidazole organic ligands. After hightemperature annealing, the Zn²⁺ ions are converted into Zn⁰ quantum dots, and uniformly loaded in the carbon framework formed by organic ligands; meanwhile, the original porous structure of the material is maintained.^{85,86} It was also proved that the trace amount of Zn in the frame structure contributes to the high overpotential of hydrogen evolution and alleviates the undesired decomposition of H2O, evidenced by the recent research (Fig. 8e).76,87

In addition to carbon-based materials, highly conductive, and corrosion-resistant metal deposition on the Zn surface is also a viable strategy for Zn protection. Kang et al.⁷⁸ introduced a sputtering-deposited method to fabricate the nano-Au particles@Zn anode, which increased the stability of Zn to more than 2000 h. However, the initial overpotential (342 mV) was much higher than that of Zn (137 mV) during the Zn plating/ stripping process with the nano-Au layer coverage, which accelerated the formation of Zn₄SO₄(OH)₆·nH₂O due to the splitting of active water molecules (Fig. 8f). Meanwhile, the high cost of Au and equipment further limited its widespread practical application. More unsatisfactorily, the Zn electroplating process will inevitably proceed on the surface of the conductive materials and cause unbalanced Zn quantity transfer from the Zn protective layer. Therefore, avoiding side reactions and uneven Zn deposition on the surface of the conductive layer are still huge challenges. Sun et al.⁸⁰ introduced corrosion-resistant metallic copper into the Zn anode through a simple displacement reaction in ethanol. Then, during the long cycle processes, the Zn electroplated on the copper surface was transformed into a dense Cu-Zn alloy during the long cycle tests (Fig. 8g). The linear polarization curve shows that alloy-modified Cu-Zn/Zn had a higher corrosion potential of -0.964 V and a smaller corrosion current of 6.03 μ A cm⁻² as compared to those of bare Zn (-0.976 V and 37.15 μ A cm⁻²), which indicates the better corrosion resistance



Fig. 8 (a) Schematic illustrations of the morphology evolution/anticorrosion mechanism for CNTs-coated Zn foils during the cycling process and the corresponding SEM images during the cycling process. Reproduced with permission from ref. 82. Copyright 2019, Wiley-VCH. (b) Schematic of the morphological changes of the bare Zn and Zn@GO electrode during the electrochemical electroplating/stripping process. Reproduced with permission from ref. 73. Copyright 2019, Elsevier Inc. (c) Schematic of the ion-sieving carbon nanoshell for Zn anode protection. Reproduced with permission from ref. 83. Copyright 2019, Wiley-VCH. (d) Schematic diagram of the CNTs between the Zn anode and the separator for the inhibition of corrosion. Reproduced with permission from ref. 75. Copyright 2020, Elsevier Inc. (e) Schematic diagram of ZIF-derived carbon for the enhanced stability of Zn foil. Reproduced with permission from ref. 87. Copyright 2019, Elsevier Inc. (left). Reproduced with permission from ref. 76. Copyright 2020, Wiley-VCH (right). (f) Schematic diagram of surface nano-Au particles coating-induced deposition to reduce side reactions. Reproduced with permission from ref. 78. Copyright 2019, American Chemical Society. (g) Schematic illustration of the fabrication process of the anti-corrosion Cu/Zn electrode and the corresponding inhibition mechanism. Reproduced with permission from ref. 80. Copyright 2020, American Chemical Society.

of Cu–Zn/Zn. Therefore, the corrosion reactions in the entire electrochemical process are markedly inhibited, and the electrochemical performance of the electrode is greatly optimized.

As for conductive polymers, the current reports are still in their infancy. Qian *et al.*⁸¹ used the polypyrrole (PPy) coating layer to modify the Zn surface to improve the stability. Its working mechanism is similar to carbon coating. On the one hand, it can isolate water from the Zn surface and reduce the corrosion of the Zn anode. More importantly, the PPy protective layer can guide Zn^{2+} ion deposition through the –NH polar groups to accelerate the nucleation/growth of Zn nanocrystals. However, the high conductivity and zincophilicity can also cause the deposition of Zn at the PPy/electrolyte interface rather than the surface of the Zn anode. This is probably the reason for the large number of reports currently focusing on inert polymers.

In summary, through physically isolating active free water molecules from the Zn anode, the tactics of conductive materials protection can effectively inhibit the growth of dendrites, corrosion, and side reactions on the surface of the Zn anode. The synthesis methods that directly coat the conductive material on the Zn are feasible and straightforward, and thus have broad prospects in practical applications. However, two obvious disadvantages remain unsolved.

(1) The side reaction products on the surface of the protective layer due to the high conductivity and zincophilicity.⁸⁸ When the cycle number is further increased, the passivation layer composed of low conductivity by-products will ineluctably appear on the surface of the integrated anode (Zn@protective layer) surface, resulting in a similar negative effect to simply using Zn foil.



Fig. 9 (a) Schematic illustrations of the morphology evolution/anticorrosion mechanism of the nano-CaCO_x-coated Zn and bare Zn electrodes. Reproduced with permission from ref. 90. Copyright 2018. Wiley-VCH. (b) Schematic diagram of anti-corrosion ZrO₂-coated Zn foil. Reproduced with permission from ref. 91. Copyright 2020, Wiley-VCH. (c) Schematic diagram of the anti-corrosion mechanism of Zn foil under the protection of kaolin coating. Reproduced with permission from ref. 92. Copyright 2020, Wiley-VCH. (d) Schematic illustration of ALD-TiO₂ coating in stabilizing the Zn anode. Reproduced with permission from ref. 93. Copyright 2020, Wiley-VCH. (e) Comparisons of ALD-Al₂O₃@ Zn and bare Zn surface topography changes. Reproduced with permission from ref. 94. Copyright 2020, The Royal Society of Chemistry. (f) Schematic diagram of the reaction process on the surface of the Sc₂O₃-coated Zn anode. Reproduced with permission from ref. 95. Copyright 2021, Elsevier Inc. (g) Schematic diagram of the anti-corrosion mechanism of Zn foil under the protection of 3D ZnO coating and its corresponding energy barrier as compared with bare Zn. Reproduced with permission from ref. 96. Copyright 2020, The Royal Society of Chemistry. (h) Schematic diagram of the MOF structure, mechanism of the MOF coating layer to reject H_2O , and the desolvation process of $Zn^{2+}-H_2O$ ions. Reproduced with permission from ref. 97. Copyright 2020, Wiley-VCH. (i) The atomic force microscopy (AFM)-3D morphology of the Zn@ZIF sample and schematic diagram of its morphology evolution during the cycles. Reproduced with permission from ref. 98. Copyright 2020, Wiley-VCH. (j) Schematic diagram of the MOF-confined Zn(TFSI)₂-TFEP in isolating water molecules, forming the SEI film, and inhibiting side reactions. Reproduced with permission from ref. 99. Copyright 2020, Wiley-VCH. (k) Schematic diagram for Zn deposition on PA coated Zn, suggesting the role of the PA layer in restricting active water molecules. Reproduced with permission from ref. 38. Copyright 2019, The Royal Society of Chemistry. (I) Coordination environment of Zn²⁺ in Nafion and the corresponding protection effect and ion transport mechanisms of Zn@Nafion-Zn-X. Reproduced with permission from ref. 102. Copyright 2020, Wiley-VCH. (m) Schematic diagram showing the protection effect of AEC-Zn as compared with PVDF-Zn and bare Zn. Reproduced with permission from ref. 103. Copyright 2020, Wiley-VCH.

(2) Zn electroplating will partially occur on the surface of the conductive protective layer, resulting in Zn mass transfer.

3.2.2. Chemically inert materials protection. Constructing corrosion-resistant and inert inorganics, organic, or organic-inorganic composite materials to repel water molecules from the Zn surface is another feasible method as compared with the protection of the conductive materials; *e.g.*, carbonate, metallic oxides, metal sulfides, and porous organic materials.⁸⁹ Kang *et al.*⁹⁰ reported for the first time in 2018 that a non-conductive nano-CaCO₃ protective layer induced the orderly nucleation of Zn while reducing Zn^{2+}/Zn overpotential to alleviate the corrosion (Fig. 9a). Symmetrical Zn cells assembled with a nano-CaCO₃ coating Zn worked well during the 836 h test period with an initial polarization of only 80 mV. In contrast, the bare Zn

symmetrical battery was initially polarized up to 230 mV and showed a significant increase in polarization after 55 hours of electroplating/stripping. Furthermore, other materials, such as nano-SiO₂, have been proved to play a similar role to nano-CaCO₃. Based on this kind of strategy, Xia *et al.*⁹¹ utilized the ceramic insulating ZrO₂ as a protective layer (Fig. 9b), showing a significant improvement in stability due to its high dielectric constant ($\varepsilon \approx 25$) and low conductivity. It is worth noting that ZrO₂ had much better chemical stability and corrosion resistance than CaCO₃ in the water-based electrolyte.

Recently, Zhou *et al.*⁹² used electrically insulating and ionconductive kaolin with layer channels and abundant adsorption sites to control the migration of Zn^{2+} ions on the Zn surface, which suppressed side reactions as well as the formation of Zn

dendrites (Fig. 9c). In particular, the thickness of the kaolin layer on the electrode is a key factor. When the kaolin coating exceeds a certain thickness, it could hinder the reduction from Zn²⁺ to Zn⁰ due to the low electronic conductivity and interface resistance. The more severe side reactions could be observed. To control the thickness of the protective layer more accurately, a simple squeegee or immersion method is not enough. Zhao et al.⁹³ precisely controlled the coating layer of TiO₂ at the nanometer level through atomic layer deposition (ALD) technology (Fig. 9d). Similarly, Liu et al.94 successfully controlled the deposited Al₂O₃ layer at the atomic level in this way (Fig. 9e). In addition to physically shielding water molecules, Liang et al.95 scraped insulated Sc₂O₃ directly on the Zn foil as a protective layer material. Experimental results and DFT calculations showed that the Sc₂O₃-coated layer not only prevented direct contact between Zn and the electrolyte, but also relieved the desolvated barrier of $[Zn(H_2O)_6]^{2+}$ and captured the active water molecules. Thus, it achieved a significant increase in stability and reduction of side reaction products. The innovation of this strategy is that Sc₂O₃ can proactively immobilize active water molecules by forming hydrogen bonds with H2O molecules (Fig. 9f). Similarly, Zhou et al.96 reported a stable Zn anode modified by a three-dimensional (3D) nanoporous ZnO architectural coating Zn sheet (called Zn@ZnO-3D). Experimental results proved that ZnO could also reduce the activation energy required for the desolvation of water, and simultaneously enhance the attraction of Zn2+ ions instead of hydrated Zn2+ ions (Fig. 9g).

The porous non-conductive MOF materials mentioned in the previous part can be directly used as a protective layer without carbonized processes. Yang et al.97 built a supersaturated electrolyte on the surface of the Zn anode using the small pore size of ZIF-7 (2.94 Å) (Fig. 9h). The large hydrated ions can only be allowed to pass through the MOF tunnel by removing the solvent to form highly coordinated H₂O-Zn²⁺ ions, which is different from the dissolved structure in the bulk electrolyte. Hence, the cycle life of the MOF-modified Zn electrode is superior, and without obvious overpotential fluctuation after 3000 h (125 days). A similar tactic was also reported in the study by Lu et al.98 based on ZIF-8 (Fig. 9i). To better release the inherent advantages of the porous MOF, Wang et al.⁹⁹ coated a thin layer of MOF on the surface of Zn, and sealed the hydrophobic Zn(TFSI)₂-tris(2,2,2-trifluoroethyl)-phosphate (TFEP) organic molecule in the pores of the organophilic Cu₃(BTC)₂ (HKUST-1) MOF. Compared with the bare MOF protective layer, this strategy masterly exploits the MOF channels. During the Zn electroplating process, the part of Zn(TFSI)2-TFEP near the Zn foil can be converted into $ZnF_2-Zn_3(PO_4)_2$ with high Zn^{2+} ion conductivity due to the low overpotential, which is in a manner analogous to the solid electrolyte interphase (SEI) in LIBs (Fig. 9j).¹⁰⁰ Since the MOF@Zn(TFSI)2-TFEP organic electrolyte and waterbased electrolyte are immiscible, the active water molecules in the solvated $[Zn(OH_2)_6]^{2+}$ can be replaced with Zn^{2+} through the Zn(TFSI)₂-TFEP organic electrolyte. Even though there are trace amounts of residual solvated H2O in the Zn(TFSI)2-TFEP organic electrolyte, the ZnF2-Zn3(PO4)2 SEI layer can completely remove it.

The solid polymer coating is also an attractive and rational candidate for Zn protection. When a solid polymer is used as a coating material, it can act as an artificial SEI film for the Zn anode. Very recently, Guo's group¹⁰¹ reported that poly(vinyl butyral) (PVB) exhibited excellent protective performance as a coating material. Cui et al.³⁸ built a polyamide-6 (PA-6) protective layer on the surface of the Zn foil, which effectively inhibited the hydrogen evolution and side reactions caused by the decomposition of active free water. The unique PA layer isolates water molecules while exhibiting excellent ordered Zn deposition due to the presence of an abundant network of -NH polar groups and hydrogen bonds. It can also play a role in restraining the movement of active water molecules and limiting the number of water molecules participating in side reactions, thereby reducing side reactions and their products (Fig. 9k). The exploitation of inorganic or organic materials alone is sometimes insufficient. For example, although improving electrode hydrophilicity is quite significant for aqueous battery systems, it is a double-edged sword for the Zn anode. On the one hand, increasing the hydrophilicity helps accelerate the diffusion kinetics of Zn²⁺ ions and thus avoids dendrite formation. However, the high hydrophilicity usually leads to a more adequate contact between Zn and water, aggravating side reactions. A single-material coating will inevitably lead to changes in hydrophilicity (rising or falling), and will therefore be in a dilemma. In this case, through the combination of inorganic and organic materials, more ideal results can be achieved. Pan et al.¹⁰² ingeniously designed an inorganicorganic composite material by combining the advantages of the two materials. It purposely changed the local hydrophilicity without affecting the transmission of Zn²⁺ ions. They selected the Nafion membrane with selective cation transport properties as protective materials, which consists of a hydrophilic zone and a hydrophobic zone. Since the hydrophilic pore channel size in the non-hydrophilic area is only 4 µm, it can shield most water molecules. To prevent a small number of active water molecules from still entering through the pores, Zn-X zeolite as inorganic filler is introduced into the pore channels of the Nafion membrane. The Zn in Zn-X zeolite can dynamically cross-link with $-SO_3^-$ of Nafion via Zn^{2+} to form well-bridged compact organic-inorganic interfaces that restrains SO_4^{2-} and H_2O transport without affecting the passability of Zn^{2+} (Fig. 9l). Qie et al.¹⁰³ also reported the organic-inorganic composite material polyvinylidene fluoride (PVDF) matrix combined with TiO₂ for Zn protection, realizing better results than bare PVDF or TiO_2^{93} (Fig. 9m).

These materials present a porous and multichannel structure with the properties of low conductivity or even insulation. Hence, they can substantially hinder the transfer of electrons between hydrated ions and metal Zn foil without affecting the passage of Zn^{2+} ions. As a result, the active hydrated ions cannot be easily decomposed on the Zn surface, and this fundamentally solves the problems of corrosion and side reactions. In particular, the poor electrical conductivity can reduce the overpotential on the Zn surface, decrease the cracking of active water molecules, and thereby reduce side reaction products. In general, many factors determine the ultimate protection effect for insulation materials, including the size of the pores, electronic/ionic conductivity, solubility, hydrophilic, zincophilicity, strength, preparative technique, coating thickness, and resistance to H_2O/O_2 . Particularly, if the coating material can interact with the Zn or be rich in certain chemical bonds to inhibit the movement of water molecules, or lower the desolvation barrier, it can often achieve a better protective effect. Therefore, the selection of suitable coating materials and the optimization of coating preparation technology are the keys to improving the protection performance. Finally, the combination of different materials is also an effective strategy that could achieve more satisfactory results as compared to a single one.

3.3. Water regulation in electrolytes

Due to the inescapable solvation and de-solvation, a large number of active free water molecules can cause passivation and corrosion of the Zn anode, resulting in instability and low CE of the Zn anode. In addition to the aforementioned coating protection strategy on the Zn anode surface, reducing the active water molecules through electrolyte optimization is an intriguing approach. As early as 2016, Chen et al.¹⁰⁴ studied ZnSO₄, ZnCl₂, ZnNO₃, and Zn(CF₃SO₃)₂ electrolytes, and found that $Zn(CF_3SO_3)_2$ electrolyte could achieve the best electrochemical performance including high CE and a wide electrochemical window. Compared with the traditional ZnSO₄ electrolyte, the large bulk $CF_3SO_3^-$ monovalent ion (versus multivalent SO_4^{2-}) reduced the number of water molecules around the Zn²⁺ ion and alleviated the solvation to a certain extent like bis-(trifluoromethane sulfonyl)imide (TFSI⁻).¹⁰⁵ Hence, faster Zn²⁺ transportation kinetics, smaller overpotential of Zn²⁺/Zn and higher CE were attained as compared to ZnSO₄. Sun et al.¹⁰⁶ developed a new electrolyte of $Zn(ClO_4)_2$ in which ClO₄⁻ was reduced during the cycles, thus forming an insoluble thin protective layer containing Cl⁻ on the surface of Zn. Electrolyte engineering is a feasible strategy for relieving the negative effects of active water molecules. Besides the choice of zinc salt, to date, three main types of electrolyte control methods have been applied to inhibit side reactions and stabilize the Zn anode.

(1) Configuring a "water-in-salt" electrolyte with a super high concentration of salt.

(2) Configuring a hybrid electrolyte by adding a soluble substance (solid) or other solvents (liquid).

(3) Configuring a quasi-solid electrolyte with a small amount of water.

It is worth noting that other types of electrolytes, including ionic liquids,¹⁰⁷ molten hydrate electrolytes,¹⁰⁸ eutectic electrolytes (a hydrated salt dissolved in another salt with similar chemical properties),¹⁰⁹ solid electrolytes,^{110,111} and organic electrolytes¹¹² can also restrain side effects and Zn corrosion problems by greatly reducing the water content and even completely removing water molecules. However, this review focuses on traditional AZIBs, so these electrolytes are not in the scope of discussion.

3.3.1. Highly concentrated electrolytes (water-in-salt). Highly concentrated electrolytes (HCE) were firstly applied in AZIBs to

broaden the voltage window via inhibiting water decomposition in 2016.¹¹³ It was termed as a water-in-salt electrolyte because the weight and volume of the salt far exceeded those of water. Wang et al.44 reported a HCE electrolyte composed of 20 M lithium bis(trifluoromethane sulfonyl)imide (LiTFSI) + 1 M Zn(TFSI)2. The Zn symmetric battery based on such an electrolyte showed outstanding electrochemical stability with almost 100% CE, and no ZnO byproduct was detected after more than 500 cycles. The mechanism was revealed by the structural and spectroscopic studies combined with molecular-scale modelling (MD). In the highly concentrated aqueous electrolyte, the large number of anions enter the vicinity of Zn²⁺ to form a tight ion pair (Zn-TFSI)⁺, which significantly inhibits the existence of $[Zn(H_2O)_6]^{2+}$ (Fig. 10a). At the same time, water molecules tend to coordinate with lithium ions to form Li⁺ solvation structures due to the smaller enthalpy of hydrated Li⁺ ions as previously mentioned (Fig. 10b);¹¹⁴ this situation is further promoted under a high concentration of lithium ions. Therefore, the activity of the water molecules is greatly suppressed under the dual function of high concentrations of Li⁺ and TFSI⁻ ions, which effectively inhibit side reactions and water decomposition (Fig. 10c).

As an inorganic metal salt, ZnCl₂ is a strong candidate for high-concentration electrolytes due to its super water solubility. Considering the high price $(\geq 40\% \text{ g}^{-1})^{115}$ and toxicity concerns¹¹⁶ of fluorinated lithium salts, Ji et al.¹¹⁷ developed a water-in-salt ZnCl₂ electrolyte with a high concentration of 30 M. The Raman spectroscopy measurements for different concentrations showed the stronger intensities of [Zn(OH₂)₂Cl₄]²⁻ and $[\text{ZnCl}_4]^{2-}$ at 290 and 245 cm⁻¹ with increasing concentration, respectively (Fig. 10d). As a comparison, the intensity of $[Zn(OH_2)_6]^{2+}$ showed that the hydration effect was observably weakened. In addition, the widened electrochemical window indicated that a high concentration of electrolytes could effectively inhibit the decomposition of active water molecules (Fig. 10e). Consequently, the side reactions on the Zn anode were inhibited, and the byproducts almost vanished in the HCE (Fig. 10f). In particular, researchers have recently discovered that chloride ions can enter the hydration structure in a highconcentration environment.^{118–120} The newly formed $[ZnCl(H_2O)_5]^+$ clusters are more likely to lose water molecules due to the low stepwise desolvation energies. In general, in a super-concentrated electrolyte with a very high level of salt concentration, the amount of water that can be used to form a hydration structure is seriously insufficient.¹²¹ The outer hydration layer is therefore replaced by anions. This structure can preferentially reduce anions instead of water and form a stable interface, which avoids the corrosion of Zn due to the decomposition of active free water molecules.

3.3.2. Hybrid electrolytes. Although HCE can substantially inhibit side reactions, their high cost limits their further application. The development of new hybrid electrolytes has received increasing attention by introducing other solutes or solvents. It has been proven that monovalent ions (such as Na⁺/Li⁺) can reduce the Zn²⁺ solvation and the redox overpotential of Zn²⁺/Zn through the electrostatic shielding mechanism; thereby, the suppression of hydrogen evolution and side reactions



Fig. 10 (a) MD simulation cell for HCE (1 M Zn(TFSI)₂ + 20 M LiTFSI), Zn^{2+} -solvation structures in the different concentrations of electrolytes. (b) The coordination numbers of Zn^{2+} -O(TFSI) and Zn^{2+} -O(water) in the different electrolyte concentration. (c) SEM images and (inset) XRD patterns of pristine Zn and Zn plate after 500 stripping/plating cycles in HCE. Reproduced with permission from ref. 44. Copyright 2018, Springer Nature. (d) Raman spectra and (e) electrochemical voltage window of ZnCl₂ solutions in different concentrations. (f) XRD results after stripping/plating cycles. Reproduced with permission from ref. 117. Copyright 2018, The Royal Society of Chemistry.

caused by active water molecules could finally be achieved.¹²² In addition to inorganic salts, surfactants are another kind of useful additive. Guo et al.¹²³ developed a cheap sodium dodecyl benzene sulfonate (SDBS) as an electrolyte additive, demonstrating an obvious inhibitory effect on side reactions. Research results indicated that the strong blocking effect of SDBS was beneficial. Surfactant additive molecules were absorbed by the electrode and formed a surface protective film, which is similar to the artificial SEI layer optimization mechanism mentioned in the previous section. In addition to constructing an *in situ* protective layer, electrolyte additives can also suppress water decomposition by reducing water activity, thereby alleviating side reactions. As early as 2016, Qian *et al.*¹²⁴ reported that the application of additive sodium dodecyl sulfate (SDS) surfactant could achieve a significant improvement in electrochemical performance. A model of DFT calculations showed a much higher energy barrier when free water molecules passed through the SDS adsorption interlayer. This could be attributed to the adsorption of SDS on the surface of the electrode with its hydrophilic group facing the electrode and hydrophobic groups

facing the medium, which prevented water molecules from entering the surface of the Zn foil (Fig. 11a). Therefore, the electrochemical window could also be dramatically widened due to the restricted hydrogen and oxygen evolution (Fig. 11b). The CE was also significantly enhanced (Fig. 11c). Similarly, the mechanism of function of polyethylene oxide (PEO),¹²⁵ anhydrous acetonitrile (ACN)¹²⁶ (Fig. 11d), polyacrylamide¹²⁷(PAM) (Fig. 11e), and other additives such as silica-based materials^{128,129} are the same as that of SDS or SDBS, which forms a protective layer by adsorbing on the surface of the Zn electrode. However, there is still controversy regarding the change in wettability caused by the introduction of additives, and the effect of increased or decreased hydrophilicity on electrode optimization seems to be contradictory. Therefore, other factors than the infiltration effect should also be considered to explain the mechanism behind it.

Apart from soluble solid substances, there is another feasible strategy to change the structure of zinc hydrate by adding other solvents. For organic solvent-based additives in aqueous electrolytes, safety, environmental protection, and low price are



Fig. 11 (a) A model of DFT calculations where a water molecule passes through the SDS adsorption interlayer at different positions, and optical photographs of contact angles without (top)/with additive (bottom). (b) The measured values of the electrochemical stability window in different electrolytes. (c) Comparison of the cycle stability and CE in electrolytes with and without additives. Reproduced with permission from ref. 124. Copyright 2017, The Royal Society of Chemistry. (d) Schematic diagram of Zn foil absorbing ACN additive as a protective layer. Reproduced with permission from ref. 126. Copyright 2020, Elsevier Inc. (e) Schematic diagram of Zn foil absorbing PAM additive as a protective layer. Reproduced with permission from ref. 127. Copyright 2019, Wiley-VCH. (f) Schematic diagrams of different solvation structures in electrolytes with and without additives and the corresponding de-solvation process. Reproduced with permission from ref. 132. Copyright 2020, Wiley-VCH. (h) Schematic diagram of the anti-corrosion mechanism in the "water-in-deep eutectic solvent" electrolyte. Reproduced with permission from ref. 135. Copyright 2019, Elsevier Inc.

the most important requirements. Very recently, dimethyl sulfoxide (DMSO) was reported and added to electrolytes to reduce the water activity due to the strong interaction of stable hydrogen bonds with water. More importantly, DMSO could preferentially solvate with Zn²⁺ ions and expel water from the solvated sheath of Zn²⁺ owing to the high dielectric constant and Gutmann donor number (29.8).¹³⁰ Zhang et al.¹³¹ used the organic solvent AN as an additive to change the coordination mode of water molecules and Zn2+ ions, successfully. DFT calculations indicated stronger dissociation energies of $Zn(H_2O)_x(AN)_{6-x}^{2+}$ complexes than $Zn(H_2O)_6^{2+}$ in the electrolyte containing AN, which suggested that the AN molecule has a stronger affinity for Zn^{2+} as compared to H_2O . When the ratio of hybrid AN in water/An mixtures is 10 (HWA-0), the $[Zn(H_2O)_3(AN)_3]^{2+}$ was stable based on *ab initio* molecular dynamics (AIMD) simulations, which is different from $[Zn(H_2O)_6]^{2+}$ in HWA-0. The Zn/Cu cells in HWA-0 exhibited a lower and more unstable CE than in HWA-0 due to the dendrite and side reactions (Fig. 11f). Considering that the molecular

structure of ethylene glycol (EG) has a flexible C-C single bond and can form two EG-water and four water-EG H-bonds, EG is a potential additive for inhibiting active water molecules and reducing the effect of solvation. On the one hand, it can restrict the movement of free water molecules to trap them as a "water blocker" through hydrogen bonds. On the other hand, EG will absorb and coordinate with de-solvated active water molecules on the electrode surface during the electroplating process (Fig. 11g);¹³² therefore, the side reactions and corresponding products were suppressed effectively. In particular, the content of EG in water will also apparently affect the solvation structure. Recent studies have further confirmed that as the concentration of EG increases, it will gradually replace water molecules from $[Zn(H_2O)_6]^{2+}$ to form $[Zn(H_2O)_m(EG)_n]^{2+}$, until $[Zn(EG)_3]^{2+}$ is completely formed.¹³³ At this time, the electrolyte should be more inclined to have the properties of an organic electrolyte rather than an aqueous electrolyte. Generally, the above solvent additives have a higher Gutmann donor number than bare H₂O, enabling it to substitute H₂O in the Zn²⁺ solventized

sheath without seriously affecting the transfer kinetics of the Zn^{2+} ions. The decreased number of active waters can suppress the corrosion and passivation of Zn.

Deep eutectic solvents (DES) were first proposed by Abbott et al. in 2003, and have similar properties to ionic liquids.¹³⁴ They are usually obtained by simply mixing a Lewis acid and base in a eutectic molar ratio, which is becoming an attractive alternative to ionic liquids. In view of their internal coordination and hydrogen bonding substances (ions or molecules), DES causes them to have strong water miscibility and high hygroscopicity.¹⁰⁹ Cui's group¹³⁵ reported a new type of hybrid electrolyte by combining water molecules with a urea-based DES matrix (water-in-DES). Water molecules help to reduce the viscosity of the DES and increase the ionic conductivity. At the same time, the strong interaction (H-bonding and coordinating) network within DES also greatly inhibits the activity of water. The spectroscopic analysis and DFT-modelling simulations showed that no free water molecules were detected in water-in-DES, which avoids corrosion and side reactions (Fig. 11h).

In summary, the mechanisms for inhibiting side reactions through hybrid electrolyte regulation include the following:

(1) Reducing the water content in the electrolyte limits the transfer of water molecules.

(2) The adsorption of additives on the Zn surface forms a protective layer similar to SEI.

3.3.3. Quasi-solid electrolytes. Different from all-solid-state electrolytes without water molecules, quasi-solid electrolytes (QSEs) are a type of gel with high ionic conductivity formed by a polymer matrix containing Zn²⁺ and a small amount of highly constrained water molecules. They usually utilize chemical crosslinking to polymerize monomers and have excellent mechanical strength. Due to the proximity to the solid-state characteristics. OSEs usually simultaneously act as a separator in batteries. Pan and his colleagues¹³⁶ developed a zinc perfluorinated sulfonic acid membrane (ZPSAM) as an electrolyte (Fig. 12a). In addition to building fast Zn²⁺ ion channels due to the presence of negatively charged branched chains, the absence of SO₄²⁻ and active water molecules (restricted solvation process) markedly inhibited side reactions (Fig. 12b). Compared with the ZnSO₄ electrolyte, no obvious XRD peaks of by-products on the Zn surface were observed when using the ZPSAM electrolyte (Fig. 12c). Zhou *et al.*¹³⁷ prepared a new type of QSEs via a direct ion crosslinking method where Zn²⁺ crosslinked carboxylate groups of alginate; the sodium alginate (Alg-Na) solution became the alginate zinc gel (Fig. 12d). Although the author did not explain the reason in detail, according to our knowledge, the chemical cross-linked framework effectively limits the Zn²⁺ ions, thus reducing the solvation effect with water molecules. The SEM and XRD results further confirmed a significant side reaction inhibitory effect (Fig. 12e and f).



Fig. 12 (a) Optical photographs of the ZPSAM electrolyte. (b) Schematic diagram of the corrosion resistance of the ZPSAM electrolyte. (c) XRD results of Zn foil in the ZPSAM electrolyte before and after cycles. Reproduced with permission from ref. 136. Copyright 2020, Elsevier Inc. (d) Structure diagram and optical photograph of the Alg–Na electrolyte. (e) SEM images and (f) XRD results of the Zn anode before and after the cycles in an ordinary liquid electrolyte and Alg–Na electrolyte. Reproduced with permission from ref. 137. Copyright 2020, Elsevier Inc. (g) Optical photograph of PZHE, and an anti-corrosion diagram of Zn in PZHE and liquid electrolyte. (h) *In situ* optical microscope images exhibiting cross-sections of the Zn surface during the electroplating process in PZHE. Reproduced with permission from ref. 138. Copyright 2020, Wiley-VCH.

Luo et al.¹³⁸ demonstrated a class of polyzwitterionic hydrogel electrolytes (PZHE) composed of poly[2-(methacryloyloxy)ethyl]dimethyl-(3-sulfopropyl) (PSBMA) for Zn protection (Fig. 12g). Compared with liquid electrolytes, zwitterionic polymers have a strong capacity to "capture water" due to the strong interaction between water molecules and charged groups, and hydrophilic groups based on hydrogen bonds. On observing the change in the Zn anode through an *in situ* optical microscope at a current density of 5 mA cm⁻², obvious H₂ bubbles appeared on the Zn electrode due to the decomposition of active water molecules in the liquid water-electrolyte (Fig. 12h). In sharp contrast, there were no bubbles and dendrites in PZHE even after 40 minutes of electroplating. The anti-icing test showed that HZPE did not freeze, even at -20 °C, and its excellent frost resistance further proved that PZHE had a strong restriction on water molecules. The reported gelatin-based hydrogel electrolyte (GHE), poly-(vinyl alcohol) (PVA), polyacrylamide (PAM), xanthan gum, carboxymethyl cellulose sodium (CMC), poly(vinylidene fluoride) (PVDF), polyacrylic acid (PAA), sodium polyacrylate (PANa), polyethylene oxide (PEO), kappa-carrageenan, etc., 139-141 are based on a similar mechanism. The restriction of water molecules by hydrogen bonding or electrostatic interactions and selecting a suitable polymer as the gel matrix to achieve excellent ionic conductivity while effectively controlling water molecules is the current challenge.

To sum up, water regulation in electrolytes is an efficient and feasible strategy for inhibiting side reactions and Zn corrosion. All three of these approaches work by limiting the number and movement of active water molecules. Among these three approaches, considering the price factor, the highconcentration electrolyte can only perform on the laboratory stage, rather than large-scale energy storage, with a high probability. As for the QSEs, their advantage mainly lies in stretchability and mechanical strength, and their relatively low electronic conductivity is an inherent disadvantage that could not be solved as compared with liquid electrolyte, so it is more used in special scenarios such as wearable devices. From the perspective of commercial viability and large-scale production, we considered that the most promising strategy for optimizing water-based electrolytes may be developing new hybrid electrolytes among the above three types of strategies.

4. Water molecules on the cathode

Water molecules play an important role in AZIBs, not only as an important part of the electrolyte, but they also determine the transfer kinetics of Zn^{2+} ions from the electrolyte to electrolytic materials. Water molecules affect the whole battery system. In addition to the huge impact on the Zn anode mentioned in the previous section, H₂O also memorably affects many factors including the crystal structure of the cathode material, the type of chemical bond formation, the electrochemical reaction kinetics, the conductivity, the internal interaction, and other properties. In particular, the water molecules mentioned here refer to the structural water in the framework of the host material, rather than adsorption water. This section will classify and summarize these influences of water molecules on electrode materials, and further explain their influence on the reaction processes and final electrochemical performance.

4.1. Free water-induced side reaction on the electrode

In addition to the side reaction of the Zn anode caused by the active free water molecules, the cathode has a similar side reaction process, and even the by-products are similar. It was first reported because researchers discovered that a flakey substance covered the surface of the electrolyte/electrode when AZIBs was in the discharge state.^{142,143} With the deepening of the research, similar results have been reported for vanadium-based materials, manganese-based materials, and even organic materials.¹⁴⁴ Although its functionality during the electrochemical reaction process is still controversial, its formation process can be attributed to proton intercalation.

Depending on the type of electrolyte, the side reaction products will also change. As shown in Fig. 13a, Zn₄(OH)₆(SO₄). xH₂O nanosheets appeared on the surface of the cathode in the ZnSO₄ electrolyte during the discharge process.¹⁴⁵ In the $Zn(CF_3SO_3)_2$ electrolyte, the side reaction product was $Zn_m(OH)_{2m-n}$ - $(CF_3SO_3)_n \cdot xH_2O$ nanosheets (Fig. 13b).¹⁴⁶ It is worth noting that the amount of product is also closely related to the amount of free water in the electrolyte. Taking ZnCl₂ electrolyte as an example, although the side reaction products are all Zn₅(OH)₈Cl₂·nH₂O nanosheets, the side reaction products at low concentration (1 M) are more than those at high concentration (30 M), according to the ex situ XRD results (Fig. 13c).¹¹⁹ In addition to the above-mentioned common electrolytes, other Zn-based $(Zn(CH_3COO)_2 \text{ and } Zn(C_6H_5O_4S)_2)$ electrolytes have also reported by-products of zinc hydroxide salts and approximate XRD results, but the chemical composition has not been further revealed (Fig. 13d).¹⁴⁷ We have reason to infer that the products may be $Zn_m(OH)_{2m-n}(CH_3COO)_n \cdot xH_2O$ and $Zn_m(OH)_{2m-n}(C_6H_5O_4S)_n \cdot xH_2O$ xH₂O nanosheets, respectively. Therefore, based on the current reports, we conclude that the by-products are mainly composed of Zn²⁺ ions, OH⁻, anions and water molecules from the electrolyte $(Zn(OH)_{\nu}(anion)_{z}^{+1/+2} \cdot xH_{2}O)$. It is worth mentioning that regardless of the kind of electrolyte, the appearance and disappearance of by-products are highly reversible in the process of discharging and charging.

The same phenomenon occurs with manganese-based materials and conforms to our above summary. In the ZnSO₄ electrolyte, the product is also $Zn_4(OH)_6(SO_4)\cdot xH_2O$ nanosheets. Wang *et al.*¹⁴⁸ reported that the side reaction on the polyaniline (PANI)-intercalated MnO₂ cathode followed these results during the discharging process. *Ex situ* XRD patterns and SEM images confirmed that the formation and disappearance of side reactions was a highly reversible process along with the (de)intercalation of Zn^{2+} ions and protons during the discharging/charging process (Fig. 13e). In the highconcentration electrolyte, due to the large reduction of water molecules, a similar result occurs; that is, the by-products are significantly suppressed (Fig. 13f).¹⁴³



Fig. 13 (a–d) Schematic of the side reaction process on V-based cathode materials in different kinds of electrolyte and corresponding by-products. (e and f) Schematic of the side reaction process on Mn-based cathode materials. (g and h) Schematic of the side reaction process on organic compounds-based cathode materials. (i and j) Schematic illustration of the $Zn_m(OH)_{2m-n}(CF_3SO_3)_n \cdot XH_2O/Zn_4(OH)_6(SO_4) \cdot XH_2O$ precipitate formation and *in situ/ex situ* pH evolution process. (k) Schematic diagram of the inhibition effect of by-products on material dissolution. (a) Reproduced with permission from ref. 145. Copyright 2019, Wiley-VCH. (b) Reproduced with permission from ref. 146. Copyright 2020, American Chemical Society. (c) Reproduced with permission from ref. 147. Copyright 2019, Elsevier Inc. (e) Reproduced with permission from ref. 148. Copyright 2018, Springer Nature. (f) Reproduced with permission from ref. 143. Copyright 2020, Wiley-VCH. (g) Reproduced with permission from ref. 149. Copyright 2020, American Chemical Society. (h) Reproduced with permission from ref. 150. Copyright 2020, Wiley-VCH. (i) Reproduced with permission from ref. 146. Copyright 2020, American Chemical Society. (j) Reproduced with permission from ref. 150. Copyright 2020, Wiley-VCH. (i) Reproduced with permission from ref. 146. Copyright 2020, American Chemical Society. (j) Reproduced with permission from ref. 151. Copyright 2020, American Chemical Society. (k) Reproduced with permission from ref. 152. Copyright 2020, Elsevier Inc.

In addition to the common vanadium- and manganese-based cathode materials, organic materials have also reported a similar side reaction. The same $Zn_4(OH)_6(SO_4)\cdot nH_2O$ nanosheets

appeared on the 1,4,5,8-naphthalene diimide (NDI)¹⁴⁹ and [2,3-a:2',3'-c]phenazine (HATN)¹⁵⁰ surface of the cathode during the discharge process in ZnSO₄ electrolyte (Fig. 13g and h).

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The electrochemical reaction process is further divided into two types. One is the continuous insertion of protons. In a nutshell, the intercalation of Zn²⁺ ions is sometimes not carried out alone and will be accompanied by the intercalation of protons, leading to the insertion/extraction of dual carriers $(H^{+} and Zn^{2+})$. The inserted protons in the cathode material were produced by the decomposition of active water molecules $(H_2O \leftrightarrow H^+ + OH^-)$. Hence, in the traditional ZnSO₄ electrolyte, the cathode will undergo a side reaction and form layered double hydroxide (LDH)-Zn4(OH)6(SO4)·nH2O (or written as $ZnSO_4[Zn(OH)_2]_3 \cdot nH_2O)$ due to the existing $[Zn(H_2O)_6]^{2+}$, Zn^{2+} , SO4²⁻, and OH⁻ species on the surface of the electrolyte/ electrode.¹⁴⁸ The whole process is the continuous insertion and accumulation of protons until the end of the discharge. The second type of process is that protons and Zn²⁺ ions are co-inserted in stages, rather than in full synchronization. At the beginning of the discharge, the intercalation of protons is dominant, and then as the discharge progresses, the local pH increases and the intercalation of protons is inhibited. The intercalation of Zn²⁺ ions then becomes dominant, and side reaction products of $Zn_4(OH)_6(SO_4) \cdot 5H_2O$ appear near the electrode surface. Although reports are still controversial about the process of proton insertion, by studying the evolution process of electrolyte pH in different stages (Fig. 13i), researchers have found that the pH will temporarily increase during discharge, and then decrease during subsequent discharges, which confirms the process of proton insertion and extraction from another perspective.^{146,151} In particular, for organic cathode materials, protons participate in the reaction in the form of a redox reaction instead of being intercalated in the material layers or the frame.

In all current reports, not all materials will have side reaction products and the internal driving factors of side reactions are unclear. Kundu et al.151 investigated the electrochemical processes of two oxide materials (tunnel-type MnO₂ and layered V₃O₇·H₂O) and non-oxide materials (layered VS₂ and tunneltype $Zn_3[Fe(CN)_6]_2$) using a combination of electrochemistry, XRD, electron microscopy and energy-dispersive X-ray spectroscopy (EDX). The results showed that oxides and non-oxides follow two different charge storage mechanisms. The oxide electrodes showed obvious side reactions and non-oxides did not, suggesting that the protons can be inserted in the oxide. In contrast, the non-oxides undergo an intercalation process with only Zn²⁺ ions. They put forward a view that stable proton insertion is more likely to occur on hydroxyl-terminated oxides, which was further confirmed by molecular dynamics simulations (Fig. 13j).

In summary, the occurrence of side reactions is closely related to proton intercalation and depends heavily on free water molecules. The merits of side reaction products on electrochemical properties can be divided into three aspects (Fig. 13k).¹⁵² First, the intercalation of protons can provide an additional capacity contribution without significant damage to the structure due to the small ionic size. Secondly, protons can help to achieve more pseudo-capacitance contributions and a higher rate performance due to their fast diffusion kinetics. Third, the by-product coating layer on the surface can suppress the dissolution of the material to a certain extent in some

reports. According to our understanding, this can be attributed to two reasons. On the one hand, the by-product coating layer on the electrode surface can reduce the effective contact area between the active material and the electrolyte, thereby inhibiting dissolution. On the other hand, many dissolution situations are closely related to pH changes during electrochemical processes. The formation and dissolution of by-products play the role of absorbing and releasing a certain amount of OH⁻ ions to a certain extent, which helps to buffer the changes in pH, especially for the positive electrode materials that are not resistant to acid and alkali environments.

However, it is worth noting that a large number of lowconductivity by-products covering the surface of the electrode may increase the transmission barrier of Zn²⁺ ions and hinder the diffusion process. Although the effect on battery dynamics may not be fatal, considering the reversible precipitation/dissolution of by-products. However, it is still significant to regulate side reaction products on the electrode surface without affecting the proton intercalation process.

4.2. Pre-intercalated structural water molecules

In recent years, pre-intercalation strategies have received widespread attention in the research of various battery systems.¹⁵³ The pre-intercalated technology provides the basic and problemoriented optimization of battery electrode materials, breaks the limitations of the inherent crystal structure in cathode materials, and plays an important role in developing AZIBs. By adjusting the synthesis method, structural water can be successfully introduced into the host material. So far, the reported hosts for preintercalated water molecules in AZIBs mainly involve vanadiumand manganese-based materials. According to different reaction mechanisms, it can be divided into the following categories: Chemical Pre-intercalation and Electrochemical Pre-intercalation.

4.2.1. Chemical pre-intercalation

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(I) Quenching method. The melt-quenching method is a relatively old colloidal preparation technology that was used as early as at the beginning of this century. This preparation process is very simple, as long as the vanadium pentoxide is heated to 700-800 °C to form a melt, and then quickly poured into water to form a V2O5 sol. The reaction process is summarized as follows: vanadium pentoxide is amorphous at high temperature (crystal V₂O₅ is difficult to dissolve in water), and after quenching in water, the neutral group $VO(OH)_3$ is obtained. VO(OH)3 will further react with water to form $VO(OH)_3(OH_2)_2$ and finally, through the action of olation and oxolation, vanadium oxide with structural water is formed.¹⁵⁴

$$\begin{split} 2V_2O_5 + 3H_2O &\rightarrow 2VO(OH)_3\\ VO(OH)_3 + 2H_2O &\rightarrow VO(OH)_3(OH_2)_2\\ H_2O-V-OH + H_2O-V-OH &\rightarrow H_2O-V-OH-V-OH + H_2O \end{split}$$

(II) Ionic exchange method. The ion exchange method is divided into two steps. First, the metavanadate needs to be

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acidified, and then it is passed through a proton exchange resin to produce a pale-yellow clear solution of decavanadic acid. In particular, the acidified metavanadate solution is the key to the formation of $[H_2V_{10}O_{28}]_4^{-.155}$

$$[VO_4]_3^- \rightarrow [V_{10}O_{28}]_6^- \rightarrow [H_2V_{10}O_{28}]_4^- \text{ (decavanadic acid)}$$

Finally, after a period of free polymerization (similar to the quenching method), the color of the solution deepens and gradually turns into a red gel to realize the intercalation of water molecules.

$$[H_2V_{10}O_{28}]_4^- + 4H^+ + 12H_2O \rightarrow H_6V_{10}O_{28} \rightarrow 10VO(OH)_3$$
$$VO(OH)_3 + 2H_2O \rightarrow VO(OH)_3(OH_2)_2$$

$$\mathrm{H_2O}\text{-}\mathrm{V}\text{-}\mathrm{OH} + \mathrm{H_2O}\text{-}\mathrm{V}\text{-}\mathrm{OH} \ \rightarrow \ \mathrm{H_2O}\text{-}\mathrm{V}\text{-}\mathrm{OH}\text{-}\mathrm{V}\text{-}\mathrm{OH} + \mathrm{H_2O}$$

(III) Hydrolysis of vanadium alkoxides¹⁵⁶. $V_2O_5 \cdot nH_2O$ gels can also be synthesized *via* the hydrolysis and condensation of vanadium oxoalkoxides VO(OR)₃ (R = Et) as follows:

$$NH_4VO_3 + 3ROH^- \rightarrow [VO(OR)_3] + 2H_2O + NH_3$$
$$2VO(OR)_3 + (3 + n)H_2O \rightarrow V_2O_5 \cdot nH_2O + 6ROH$$

(IV) Liquid phase method. The liquid phase method refers to using the reaction of V_2O_5 and H_2O_2 or acid to form $V_2O_5 \cdot nH_2O$ gels. In summary, V_2O_5 dissolves in water to form an orange-yellow solution containing a monoperoxo species $[VO(O_2)]^+$, which is formed from the decomposition of the unstable diperoxide $[VO(O_2)_2]^-$. It further reacts to form vanadate and decavanadate entities, and finally forms vanadium oxide with structural water through a similar polymerization reaction as before. The specific reaction process is as follows:¹⁵⁷

$$V_2O_5 + 2H^+ + 2H_2O_2 + 3H_2O \rightarrow 2VO(O_2)(OH_2)_3^+$$
$$VO(O_2)(OH_2)_3^+ + H_2O_2 \leftrightarrow VO(O_2)_2(OH_2)^- + 2H^+ + 2H_2O$$
$$2VO(O_2)_2(OH_2)^- + 4H^+ + 4H_2O \rightarrow 2VO(O_2)(OH_2)_3^+ + O_2$$

In the above four synthesis methods, the quenching method needs to be carried out under high-temperature conditions, the hydrolysis of vanadium alkoxide is often expensive, and the ion exchange method may cause additional water and other cations are not exchanged. Considering the low cost of mass production, easy-to-operate methods have more advantages. Therefore, most of the studies currently use the liquid phase method.¹⁵⁸

4.2.2. Electrochemical pre-intercalation. Recently, some researchers successfully introduced water molecules into vanadium-based and manganese-based materials through electrochemical methods. Zhang *et al.*¹⁵⁹ used a stainless steel mesh as a substrate and VOSO₄ as an electrolyte and formed a vanadium oxide containing structural water in an electrolytic bath by electrochemical oxidation and deposition at a constant potential of 1.7 V. The electrodeposition reaction was

 5VO^{2^+} + $13\text{H}_2\text{O} \rightarrow \text{V}_5\text{O}_{12}\cdot6\text{H}_2\text{O}$ + 4e^- + 14H^+ . In addition to the constant potential oxidation method, the LSV method was conducted to pre-intercalate water molecules in the material. Choi *et al.*¹⁶⁰ prepared the layered MnO₂ that contains a high content of crystal water (10 wt%) by LSV in the potential range of 0.2 to 0.9 V (*vs.* Ag/AgCl). The same method has also successfully achieved the intercalation of water molecules between MoO₃.¹⁶¹ By controlling different cut-off voltages, the different intercalated amounts could be obtained. In general, electrochemical pre-intercalation as a new method is gradually attracting the attention of researchers. Its fast and controllable insertion process is also superior to ordinary chemical methods.

4.3. Effects of structural water molecules

The solid-state diffusion kinetics of Zn^{2+} ions within the cathode materials, the insertion barrier of Zn^{2+} across the electrode/electrolyte interfaces, and the stability of the crystal structure determine the overall electrochemical performance. In this section, the influence of these factors on AZIBs will be discussed based on pre-intercalated water molecules.

4.3.1. Crystal structure change. How exactly do water molecules affect the crystal structure? First, considering the size and the location of the pre-intercalated water molecules, the most obvious change for the host material is the layer spacing. Taking V_2O_5 as an example, pristine V_2O_5 showed a layer spacing of only 4.4 Å.^{162,163} In contrast, the radius of hydrated Zn^{2+} ions is approximately equal to 4.3 Å, which results in poor rate performance and cycle performance as electrode materials. Too small interlayer spacing is not conducive to the intercalation of Zn²⁺ ions and can also cause excessive volume expansion. Yan et al.¹⁶⁴ conducted a detailed study on the role of structural water in bilayer V₂O₅ nH₂O/graphene(VOG) cathode materials in aqueous AZIBs. The XRD results indicated that the interlayer spacing expands to 12.6 Å after water molecules are intercalated. The presence of water molecules also affects the change of the interlayer spacing during charge and discharge. As shown in Fig. 14a, when charged to 1.3 V as compared with initial VOG, the hydrogen bond formed between H₂O with Zn^{2+} , $CF_3SO_3^-$, and lattice oxygen tightens the layer spacing, resulting in a decrease from 12.6 to 10.4 Å. As a reversible process, when discharged to 0.2 V, the interlayer distance will increase to 13.5 Å due to the intercalation of water and electrolyte ions. Benefiting from the modulating effect of water molecules on the layer spacing, the VOG showed an excellent rate performance and stable cycle performance (Fig. 14b). The significant improvement in electrochemical performance, especially for rate properties, is mainly due to the following reasons. On the one hand, the shielding effect of the interlayer water reduces the effective charge of Zn²⁺ ions to some extent, resulting in faster Zn²⁺ diffusion dynamics. On the other hand, the reduced electrostatic bond strength also reduces the diffusion barrier. According to the formula

$$\propto \frac{1}{\epsilon r^2}$$



Fig. 14 (a) Schematic diagram of the structure of $V_2O_5 \cdot nH_2O$ in different electrochemical states. (b) Rate cycle performance of $V_2O_5 \cdot nH_2O$ /graphene and V_2O_5 /graphene. Reproduced with permission from ref. 164. Copyright 2018, Wiley-VCH. (c) The simulated structures of α -MoO₃ and waterintercalation MoO₃. (d) Radial distribution functions of α -MoO₃ and water-intercalation MoO₃ obtained from the $k_{\chi}^2(k)$ by Fourier transform, and the various simulated O atoms of α -MoO₃. Reproduced with permission from ref. 161. Copyright 2020, Wiley-VCH. (e) Schematic diagram of the adjustment of hydrophilicity and interlayer spacing by water intercalation. Reproduced with permission from ref. 165. Copyright 2019, American Chemical Society. (f) Schematic diagram of water-induced crystal structure changes of spinel Mn₃O₄. Reproduced with permission from ref. 168. Copyright 2018, The Royal Society of Chemistry. (g) Crystal structure of α -MnO₂ and water-intercalation MnO₂. Reproduced with permission from ref. 160. Copyright 2019, The Royal Society of Chemistry.

 ε is the permittivity of water and *r* is the distance between Zn²⁺ and the closest ions. ε will increase due to the existence of water molecules, and *r* will also increase due to the expanded layer spacing and eventually reduce the electrostatic force between the layers.

In addition to V-based materials, the intercalation of water molecules also affects the crystal structure of Mo-based materials. Lu *et al.*¹⁶¹ proved that the significant layer expansion from 6.7 to 7.6 Å could also be observed in the α -MoO₃ (typical layered structure with distorted [MoO₆] octahedra bilayers) due to the intercalation of water molecules. As shown in Fig. 14c, the intercalated water molecules can form hydrogen bonds through H^w (H atom from H₂O)···O^{Mo} (O atom from MoO₃). *R* space curves after $k^2_{\chi}(k)$ -weighted Fourier transform of the extended X-ray absorption fine structure (EXAFS) and quantitatively fitting spectra showed the minor length difference between α -MoO₃ (1.72 & 1.96 Å) and water-intercalation MoO₃ (1.73 & 1.97 Å) due to the slight distortion of the octahedral [MoO₆] layer. Due to the formation of hydrogen bonds, three types of oxygen exist inside the material structure (O₁, O₂, and O₃). Therefore, the two types of bonds can be obtained as Mo=O and Mo-O, respectively (Fig. 14d). Water molecules can also improve the hydrophilicity of the material. Taking MoS₂ as an example, the original Mo-S layer spacing is only 3.1 Å. Considering the large size of $[Zn(H_2O)_6]^{2+}$ (4.3 Å), the Zn²⁺ storage capacity is extremely limited. In addition, due to the weak interaction between Zn-H₂O and S, layered MoS₂ has hydrophobic properties, which are not conducive to the intercalation process. The existence of water molecules not only increases the interlayer spacing of MoS₂ from 6.2 to 9.5 Å, but also significantly improves its hydrophilicity due to a small amount of oxygen incorporation (Fig. 14e).¹⁶⁵

Structural water also affects the crystal structure of Mnbased materials, and ultimately reflects on the electrochemical performances. For example, in the case of MnO₂, the basic building block is the [MnO₆] octahedron. Through different connections, various crystal structures such as chains/tunnels/ layers can be obtained. Apart from the chain structure, the Mn-based materials reported so far focus on tunnel-type α -MnO₂ (hollandite-type MnO₂), β -MnO₂ (pyrolusite-type), and γ -MnO₂ (spinel-type) polymorphs, as well as layered δ -MnO₂ (birnessite-type) in AZIBs. This is because the tunnels/layerstype structures can provide sites for Zn²⁺ ions storage. Current reports on water molecules intercalated in crystal structure to achieve enhanced electrochemical performance of AZIBs are mainly focused on the layer-type MnO₂ instead of the tunnel type. This is because the tunnel structure is more stable than the laminated structure and therefore less affected by water molecules. Zhu et al.¹⁶⁶ successfully intercalated water molecules and Na⁺ into layer-type γ -MnO₂ (Na_{0.1}MnO₂·0.5H₂O) by a simple hydrothermal method. The intercalation of water molecules helped to achieve a large layer spacing of 7.2 Å. When using Na_{0.1}MnO₂·0.5H₂O as the cathode material, outstanding rate performance (100 mA h g⁻¹ at 20 C) and cycling performance (almost 100% after 5000 cycles at 10C) were achieved. Apart from MnO₂, water molecules can also affect other manganese oxides. Typically, spinel Mn₃O₄ can undergo a structural transformation process driven by partial Mn dissolution/oxidation and water intercalation, culminating in the formation of layer-type δ -MnO₂ with water molecules (Fig. 14f).^{160,167,168} Likewise, hydrogen bonds can form between water and the MnO₂ framework. Choi et al.¹⁶⁰ demonstrated that water-containing layered δ -MnO₂ provides more Zn²⁺-intercalated sites than tunnel-type α -MnO₂ due to expanding the layer spacing to achieve a significant increase in the specific capacity from 210 to 350 mA h g^{-1} (Fig. 14g). Further, the presence of water molecules also stabilized the crystal structure, preventing the structural degradation of the layered $\delta\text{-MnO}_2$ to the spinel phase ($\gamma\text{-MnO}_2$) after long-term cycling. The results further indicate that the synergistic effect of the layered structure and crystalline water can effectively reduce the interfacial resistance between the material/electrolyte, thus facilitating the diffusion of Zn^{2+} ions.

It is worth mentioning that although a large number of reports have proved that water molecules change the crystal structure of the material and ultimately reduce the diffusion and migration barriers of Zn^{2+} ions, they are mainly concentrated in the above-mentioned types of materials. There are almost no reports on Prussian blue analogues and organics. We think this may be due to the following reasons:

(1) Most of the Prussian blue analogues are stable and open frame structures. Although the water molecules can be intercalated, they cannot expand as much as the layered structure; on the contrary, the presence of water molecules will occupy the storage space of Zn^{2+} ions.

(2) For organic materials, the storage mechanism of Zn^{2+} is different from other types of cathode materials, mainly relying on its own redox-active centers based on C=O, =NH⁺-, and C=N groups, *etc.* Therefore, there is no influence of structural water in it.

In particular, the content of intercalated water molecules also directly affects the structure of the cathode material. Huang *et al.*¹⁶⁹ investigated the influence of water molecules on the structure by DFT calculations. V_2O_5 consists of layers perpendicular to the [001]-crystallographic direction and are stacked along the *c*-axis, held together by weak van der Waals interactions. As shown in Fig. 15a–c, two obvious structural changes could be observed. The expanded distance between the two V_2O_5 sheets from 2.23 to 5.04 Å with the increasing water content indicated a high correlation between the water and bilayer distance. At the same time, the structure was also slightly twisted, causing the *a*-axis and *c*-axis to deviate from the vertical direction.

In conclusion, water molecules have an apparent positive effect on the structure of materials. First, they can expand the



Fig. 15 Optimized $(1 \times 2 \times 1)$ supercell of bilayer (a) V_2O_5 , (b) V_2O_5 ·H₂O and (c) V_2O_5 ·1.75H₂O. Reproduced with permission from ref. 169. Copyright 2019, The Royal Society of Chemistry.

layer spacing to facilitate the intercalation of Zn²⁺ ions and the solid-state diffusion process. The size of the layer spacing is closely related to the amount of water between layers. Secondly, the formation of hydrogen bonds and the distortion of structural building units may also occur. Third, a small number of oxygen atoms will enter the material structure to improve the hydrophilicity of the material. Fourth, water molecules can also transform the type of crystal structure from the spinel type to the layer type.

4.3.2. Bonding type change. In addition to the influence of the crystal structure, the effect of bonding type changes caused by water intercalation in AZIBs is not to be ignored. With the intercalation of water molecules, H^w can interact with O (from the framework) to form hydrogen bonds. Compared to isolated water molecules, hydrogen-bonded water molecules provide a certain amount of electron transfer to the connected O–M structural unit (where M is a transition metal atom), thus leading to a slight reduction of M. In addition to the formation of hydrogen bonds, the intercalation of Zn²⁺ ions can also lead to changes in the types of bonds. Typically, AZIBs are used as a

cationic rocker cell configuration where metal ion carriers form pure ionic bonds with structural counter ions within the electrode framework. As shown in Fig. 16a-d, the intercalated Zn²⁺ ion forms a Zn–O–M bond with negatively charged structural atoms (O²⁻ from transition metal oxides) in commonly used transition metal oxides. Here, M stands for the transition metal ion such as V, Mn, Fe, Ni, Co, and Cu (involving V-based materials, Mn-based materials, and Prussian blue analogues).41,170-175 This kind of pure ionic bonding, where there is almost no charge transfer between the Zn²⁺ ions and the electrode material, leads to a local charge distribution (Fig. 16e). The subsequent intercalation of Zn²⁺ ions would be hindered by the restriction of electron localization, which may be explained by the electrostatic repulsion between the layers.¹⁷⁶ The presence of structural water molecules within the material framework can effectively optimize this situation. When Zn²⁺ ions are intercalated in the material, they interact simultaneously with the oxygen atoms between the layers and the oxygen in some of the water molecules to form two types of bonds. In addition to the traditional ionic bonds, new covalent-ionic bonds are formed (Fig. 16f).¹⁷⁷ Covalent ionic



Fig. 16 Schematic diagrams of (a) Prussian blue analogues, (b) tunnel-type Mn-based materials, (c) layer-type Mn-based, and (d) layer-type V-based cathode materials after Zn^{2+} ions intercalation in the presence or absence of structured water. (e) Schematic diagram of charge distribution and bonding type after Zn^{2+} ion intercalation without structured water. (f) The effect of water molecules on bond formation and charge distribution between the Zn^{2+} and negatively charged structural atoms.

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bonding allows electrons to leave the domain by transferring them from the central electrode framework to the inserted water molecule. According to the donor-acceptor principle, the Zn^{2+} ion acts as the Lewis acceptor and the O^{2-} of structural H_2O acts as the Lewis donor in newly formed ion-covalent bonds. The inserted electrophilic carrier binds to the electron-donating atom in the electrode. Therefore, the presence of water molecules can also affect the insertion position of Zn^{2+} ions and contribute to decreasing the electron charge accumulation and avoiding the repulsion triggered by charge concentration.

4.3.3. Boosting the proton migration process. The intercalation process of Zn²⁺ ions in most cathode materials follows the faradaic reaction process, which has the advantage of allowing higher capacity and voltage plateaus to be output and ultimately high energy densities to be achieved. The rate performance of Faraday electrodes depend in part on the migration of ion carriers within the electrode, which in turn depends on the type of ion carriers. Compared to Zn^{2+} ions, the proton is derived from a water molecule and has a smaller ionic radius (0.88 fm),¹⁷⁸ thus allowing for faster diffusion kinetics. As a result, the intercalation process of Zn²⁺ ions is often accompanied by the intercalation of protons, i.e., the side reactions on the cathode described previously. The protonintercalation process contributes to providing additional specific capacity without causing severe damage to the structure of cathode materials,¹⁷⁹ the hydrogen ions—a single proton—can achieve a rapid transport process in water, which was first discovered by von Grotthuss in 1806.180 In this process of the Grotthuss interaction, water molecules are connected by hydrogen bonds. The linked hydrogen atoms are transferred from one water molecule to another along the direction of the hydrogen bond, after receiving a new proton. Here, the proton transmission process is completed not by combining structural atoms, but by continuously constructing and breaking hydrogen bonds with continuous lattice H₂O, which penetrates the electrode frame. It has been proved that the Grotthuss transport can not only occur in water, but also in electrode materials.^{161,179,181-184} Fan et al.¹⁸⁵ indicated the correlation between the hydrogen bond of the ion electrode and the more apparent pseudocapacitive behavior in the ion intercalation

process, and pointed out that the NH_4^+ ion is based on a jumping mechanism like a "monkey swinging", thereby realizing rapid ion transmission in the energy storage process. Ji et al.¹⁷⁹ reported an electrode material-a Prussian blue analogue (PBA) with hydrogen-bonded structural water, which helps achieve a fast Grotthuss proton transport process and ultimately achieve an ultra-high rate electrochemical performance. As a proof-of-concept model, Grotthuss transport had been proved by researchers that the intercalation of water molecules can indeed facilitate the intercalation of protons in MoO₃ cathode materials for AZIBs.¹⁸³ Considering that this process is based on water molecule chains and hydrogen bonds, the structural water between layers is an important guarantee to ensure its smooth progress. The general approach is shown in Fig. 17a. In simple terms, when a proton is intercalated in the cathode material, it combines with the oxygen atoms in the water molecules between the crystal layers to form hydrogen bonds $(H^+ \cdots H_2O)$ and becomes part of the water chain. The hydrogen bond then becomes an H-O covalent bond, which breaks the original O-H bond in the H₂O molecule and creates a hydrogen bond, forming H₂O···H+. Grotthuss proton transfer mechanism effectively accelerates the proton intercalation process and lowers the charge transfer potential barrier through hydrogen bonding. As shown in Fig. 17b, the process is similar to dominoes and therefore has the capacitance-mimetic properties of ultrafast dynamics. In conclusion, proton intercalation as an extraordinary side reaction is a typical but usually restricted electrochemical process. The presence of water in the interlayer structure helps accelerate the proton intercalation. Maximizing the exploitation of this process can prominently improve the electrochemical performance of the AZIBs due to their excellent pseudocapacitance-like properties. In particular, the water molecule intercalated strategy is widely reported in the cathode materials of AZIB. Thus, we consider that the improvement in rate performance may be primarily due to this mechanism. Therefore, although the research on Grotthuss proton transport is still in its infancy, this strategy has great potential to improve the electrochemical performance of AZIBs by making up for the deficiency of slow Zn²⁺ ion intercalation kinetics. Based on this, we believe that the



Fig. 17 (a) Schematic representation of proton transport based on the Grotthuss mechanism along a water chain. (b) A schematic of dominoes for the Grotthuss mechanism for the cooperative diffusion of a proton array.

development of other molecules or ions that can form hydrogen bonds in layered or tunnel-structure cathode materials is also significant, instead of being limited to water molecules.

4.3.4. \mathbf{Zn}^{2+} ion migration process change. In addition to affecting the structure of the cathode material, the intercalation of water molecules can also affect the migration process of \mathbf{Zn}^{2+} ions. When water molecules intercalate the interlayers, the oxygen atoms of water may interact with the cations of the host material and affect the electronic structure, resulting in changes in the migration path of \mathbf{Zn}^{2+} ions.

By calculating the electronic structure, it was determined that the valence and conduction bands are mainly contributed by O and V ions in the V_2O_5 layer (Fig. 18a).¹⁶⁹ For V_2O_5 containing structural water, it can be contributed by the O atoms of H₂O. This indicates that water can share part of the charge brought by the intercalated Zn^{2+} ion and plays a role in shielding the charge as we discussed before. The change of the electron structure of a host material caused by water molecules can further affect the charge transfer during the Zn^{2+} ion migration process. The deformation charge density is used to describe the charge migration of Zn^{2+} . For V_2O_5 , charge transfer only occurs in V and O from Zn.

Similarly, this charge transfer between H_2O and the Mnbased material framework can be seen from the projected density of states (PDOS) of the O^w-2p and Mn-3d states of the spinel and layered manganese oxide (Fig. 18b).¹⁶⁸ The highest occupied molecular orbital (HOMO) of an individual water molecule is 1b₁ (shown in the blue area). The 1b₁ orbital loses most of the spin electrons, resulting in a large number of unoccupied states above the Fermi level when water is inserted into the spinel Mn₂O₄. When crystal water is inserted, the antibonding orbital moves below the Fermi level (the red shaded line), indicating that manganese is reduced due to the insertion of crystal water. Thus, the evidence from PDOS clearly points to the charge transfer conclusion.

The intercalation of water molecules can affect the transfer of electric charges and change the electronic structure, which can lead to changes in the electric potential, charge distribution density, and diffusion barrier of Zn^{2+} , which ultimately affect the migration path of Zn^{2+} ions.

For the changes in electric potential, the cross-sectional views of the electrostatic potential for V2O5·H2O showed the observably smaller changes in the electrostatic potential (Fig. 18c), which proved the "charge shielding" and "O in H_2O interaction with Zn²⁺," effect on Zn²⁺ ion migration.¹⁶⁹ To date, other vanadium oxides such as V₃O₇·H₂O,¹⁸⁶ V₆O₁₃·nH₂O,¹⁸⁷ V₅O₁₂·H₂O,¹⁵⁹ and V₁₀O₂₄·12H₂O,¹⁸⁸ etc. have identical results after water intercalation. In addition to V-based materials, the migration of Zn²⁺ ions in Mn-based materials containing structural water shows similar results. Taking MnO₂ as an example, the potential energy surface illustrates the minimum potential difference of 0.25 eV along the direction of the water molecules (marked by dashed lines), which is much lower than other paths (the maximum value of 0.6 eV).¹⁶⁰ This indicates that Zn²⁺ ions preferentially move in the direction in which water molecules exist due to the lower potential difference. For the changes in charge

density, the charge distribution is also affected by charge transfer and affects the migration path of the Zn^{2+} ions. As shown in Fig. 18d, the yellow area and blue area correspond to the enrichment and depletion of electron density, respectively.¹⁶⁹ In the original V₂O₅, the intercalation of Zn^{2+} ions brings about obvious charge accumulation in V and O. In contrast, the deformation charge density shows significant charge distribution around water molecules, proving that the existence of H₂O can bear part of the transfer charge from Zn^{2+} , thus resulting in a reduced charge density of V and O. For the changes in diffusion barriers, regardless of V-based materials or Mn-based materials, DFT calculations show that along the direction of water molecules, the migration barrier of Zn^{2+} ions is significantly reduced, so the existence of water molecules determines the migration path of Zn^{2+} ions to a certain extent (Fig. 18e).^{160,169}

Interestingly, it has also been reported that the intercalation of water molecules can accelerate the intercalation of protons and at the same time hinder the intercalation of Zn^{2+} ions. Lu et al.¹⁶¹ found that the intercalation of water molecules between α -MoO₃ layers limits the transmission of Zn²⁺ ions (Fig. 18f). DFT calculations showed ion insertion energies of -1.49 and -1.61 eV for Zn^{2+} and hydrated protons (H₃O⁺) in α-MoO₃, respectively. As a comparison, the values of waterintercalated α -MoO₃ are -0.11 and -3.93 eV (Fig. 18f). This apparent change implies a significant increase in the resistance to intercalation of Zn²⁺ ions after the intercalation of water molecules. The reasons for this unique ion-selective embedding could be twofold. On the one hand, the presence of interlayer water molecules is more favorable for the intercalation of H_3O^+ , leading to the occupation of the active site of the Zn^{2+} ion. On the other hand, the remaining H₂O and H₃O⁺ in the space between the $[MoO_6]$ layers can bind to the terminal O atoms, further blocking the diffusion channel of Zn²⁺ in waterintercalated α -MoO₃ and restricting the charge transfer through interaction with the $[MoO_6]$ bilayer. Although this particular selective intercalation process initiated by water molecules is well documented in α-MoO₃, whether this is a universal conclusion for other materials still needs to be further explored.

In summary, structural water molecules can change the internal electronic structure of the material after water intercalation, thereby affecting the diffusion barrier of external charged Zn^{2+} ions through electrostatic interaction, charge density distribution, changes in electric potential, and finally changing the transfer path of Zn^{2+} ions.

4.3.5. Assisting other ion intercalation. Another function of structural water intercalation is to help other large-sized metal and non-metal ions, or organic molecules to be inserted between the host material layers. Water molecules play two roles in this process. The first is that the insertion of water molecules can increase the layer spacing and thus reduce the embedding barrier of these ions. Secondly, the electrostatic repulsion of foreign charged ions by the host frameworks can be reduced due to the shielding effect of water molecules on the charge. So far, water molecules have been reported to be co-intercalated in V-based materials together with non-metal cations (NH_4^+) ,¹⁸⁹ alkali metal cations (Li^+, Na^+, K^+) ,^{190,191}



Changing the electronic structure

Selective intercalation of Zn²⁺ ion

Fig. 18 The density of states for (a) V_2O_5 and $V_2O_5 + Zn$, $V_2O_5 \cdot H_2O$ and $V_2O_5 \cdot H_2O + Zn$. The red dashed lines represent the location of the Fermi level. (b) The PDOS of empty spinel Mn_2O_4 , spinel $Mn_2O_4 \cdot (H_2O)_{0.25}$ and layered $Mn_2O_4 \cdot (H_2O)_{0.25}$. (c) The cross-sectional views of the electrostatic potential for V-based materials and Mn-based materials. (d) Deformation charge density for V-based materials and Mn-based materials after water intercalation; blue represents the charge accumulation state; yellow represents the charge consumption state. (e) Zn^{2+} migration pathways of V-based materials and Mn-based materials after water intercalation. (a) Reproduced with permission from ref. 169. Copyright 2019, The Royal Society of Chemistry. (b) Reproduced with permission from ref. 168. Copyright 2019, The Royal Society of Chemistry. (c) Reproduced with permission from ref. 168. Copyright 2019, The Royal Society of Chemistry (top). Reproduced with permission from ref. 160. Copyright 2019, The Royal Society of Chemistry (bottom). (d) Reproduced with permission from ref. 169. Copyright 2019, The Royal Society of Chemistry (bottom). (d) Reproduced with permission from ref. 169. Copyright 2019, The Royal Society of Chemistry (bottom). (d) Reproduced with permission from ref. 169. Copyright 2019, The Royal Society of Chemistry (bottom). (f) Schematic diagram of the selective intercalation of water-inserted MoO₃ by Zn^{2+} and H_3O^+ ions. Reproduced with permission from ref. 161. Copyright 2020, Wiley-VCH.

alkali-earth metal ions $(Ca^{2+}, Mg^{2+}, Ba^{2+})$,^{192–194} and transition metal cations $(Fe^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+}, Zn^{2+})$, and Cu^{2+}).^{40,175,192,195} In addition to cation intercalation, organic molecules such as polyaniline (PANI),¹⁹⁶ pyridine,¹⁹⁷ and

poly(3,4-ethylenedioxythiophene),¹⁹⁸ are also candidates to be co-intercalated in cathode materials with H_2O . Compared with pre-inserted water molecules alone, the interlayer spacing after co-intercalation is generally larger. In general, intercalated

water molecules are attached to the host material by weak hydrogen bonds. They may deintercalate from the structure into the electrolyte together with Zn^{2+} ions in the subsequent cycles. Therefore, its stability for the structure is not enough. In contrast, co-intercalated ions can settle into the middle layer of the cathode structure and bond with oxygen atoms to form stronger ionic bonds. Therefore, the co-embedded ions can act as more stable "pillars" to keep the structure stable in subsequent cycles.

5. Water molecule exchange

Based on the previous introductions, there are three forms of water molecules: solvated water molecules and free water molecules in the electrolytes, and structural water in the electrode materials. The two kinds of water molecules in the electrolytes can be transformed into each other by the solvation process. Water molecules can also transfer between electrolytes and electrode materials. It has been confirmed that water molecules in the electrolytes can enter a part of cathode materials to further change the crystal structure, and the valence of the host material under an external electric field or spontaneously. Notably, in this section, we define the following three types of water molecule exchanges and describe their effects (layer spacing, phase transition, and valence) for electrode materials in this sequence:

(1) Free water molecules intercalated into the crystal structure of the host material from the electrolyte.

(2) Free water molecules deintercalated from the crystal structure and entering the electrolyte.

(3) Free water molecules in the electrolytes interacting with the materials to change the valence.

According to the reversibility of deintercalation, water molecule exchange can be divided into two types: reversible and irreversible. Furthermore, given the conditions required for water exchange, there are two reaction environments, namely the spontaneous process without external force, and relying on applied electric fields.

5.1. Water exchange

Reversible water exchange means that after water molecules intercalate the material framework, they can deintercalate from host materials in the subsequent charge/discharge process without structural transformation and phase separation. According to the current research, both spontaneous and electric field intercalation can be a reversible exchange process.

5.1.1. Spontaneous exchange. Here, we define the meaning of spontaneous intercalation; that is, just immersing the original electrode material in the electrolyte can complete the phenomenon that water enters the crystal structure from the electrolyte without external action. This process is completely reversible and cannot cause damage to the material structure. At present, there are relatively few reports on spontaneous intercalation and they are all concentrated on layered vanadium oxides. This may be because layered structures have

higher tunability than other structures and it is easier for water molecules to complete the spontaneous intercalation process.

The spontaneous intercalation can cause the layer spacing to expand. It is worth mentioning that the properties of water molecules intercalated in the layer structure seem to be between those of structural water and adsorption water. On the one hand, in terms of its position, it is similar to structural water, which does not simply adsorb on the surface or cracks of the material, but penetrates deep into the structure. On the other hand, the spontaneously inserted interlayer water molecules could be removed as the material dries at a lower temperature (usually below 100 °C), similar to adsorption water. Taking vanadium oxide as an example, water molecules in the electrolyte could spontaneously intercalate into the original sample and cause revisable water exchange. In 2016, Nazar et al.41 reported that when vanadium bronze (Zn_{0.25}V₂O₅·nH₂O) was immersed in water or electrolytic solution, there were structural changes that were reflected in the XRD results before and after comparison (Fig. 19a). The layer spacing increased from 10.8 to 12.9 Å due to the expansion of water molecules between the layers. Homologous results were also reported in V₃O₇·H₂O (Fig. 19b)¹⁹⁹ and other V-based materials.^{189,200} According to existing reports, the spontaneously inserted water molecules can deintercalate by heating the dried form, and the reversible (de)intercalation during the subsequent discharge/charge processes does not injure the layer structure.

5.1.2 Electrochemical exchange. In addition to spontaneous exchange, water molecules can undergo (ir)reversible exchange between the electrolyte and the electrode material under the action of an applied electric field. For $Zn_{0.25}V_2O_5 \cdot nH_2O_5$ during the discharge process, Zn²⁺ ions and water molecules in the electrolyte could co-intercalate, leading to the increase in the layer spacing to 12.3 Å. During the charging process, Zn²⁺ ions can deintercalate together with water; the resulting interlayer distance sharply decreased from 12.3 to 11.0 Å, which is the same as the 10.8 Å interlayer distance in the pristine sample (without immersion electrolyte). The reversible water molecule (de)intercalation process is usually associated with Zn²⁺ ions (Fig. 19c). The insertion of water molecules under the action of an electric field is not always completely reversible; in some cases, the water molecules will stably exist as crystal water after being embedded in the first discharge process and will not escape during the subsequent charging process (Fig. 19d).²⁰¹ Another special case is that water molecules enter the β -MnO₂ under an electric field and cause a complete structural transformation. The newly formed structure will remain unchanged during the subsequent charge and discharge process, which indicates that this transformation is irreversible (Fig. 19e).202

The spontaneous and electrochemical water exchange can also coexist in one material and appear at different electrochemical stages. When the batteries are assembled in a static state, rapid, spontaneous water intercalation could occur. The subsequent charge and discharge process (equivalent to an external electric field) present a reversible water exchange accompanied by Zn^{2+} ions (Fig. 19f).¹⁹⁴ Some researchers also reported that the reversible water exchange occurs only in the



Fig. 19 (a) Schematic diagram and XRD results of the spontaneous intercalation of water molecules in the non-battery state. (b) Schematic diagram of the spontaneous exchange of water molecules in the battery state. Schematic diagram of (c) reversible and (d) irreversible water exchange in V-based materials under the effect of an electric field. (e) Schematic diagram of irreversible water exchange in Mn-based materials under the effect of an electric field. (f) Schematic diagram of the coexistence of spontaneous/electrochemical exchange. (g) Schematic diagram of irreversible water exchange, and corresponding changes in specific capacity and morphological changes during the cycles due to water exchange. (a and c) Reproduced with permission from ref. 41. Copyright 2016, Springer Nature. (b) Reproduced with permission from ref. 199. Copyright 2018, American Chemical Society. (d) Reproduced with permission from ref. 201. Copyright 2018, American Chemical Society. (e) Reproduced with permission from ref. 202. Copyright 2017, Springer Nature. (f) Reproduced with permission from ref. 194. Copyright 2019, American Chemical Society. (g) Reproduced with permission from ref. 203. Copyright 2018, American Chemical Society. (g) Reproduced with permission from ref. 203. Copyright 2018, American Chemical Society. (g) Reproduced with permission from ref. 203. Copyright 2018, American Chemical Society. (g) Reproduced with permission from ref. 203. Copyright 2018, American Chemical Society.

subsequent cycles without going through a self-intercalation process in the static stage.

The electrochemical water exchange process sometimes continues for the first dozens of cycles and remains stable afterward, which results in increased capacity and changes in the original morphology. Researchers reported that the pristine V_2O_5 was transformed into $Zn_xV_2O_5 \cdot nH_2O$ in the initial multiple cycles.²⁰³ More cycles were required as the current density increased, implying that the transition process was highly dependent on the depth of charge/discharge processes. Under the electric field induction, the initial V_2O_5 bulk form gradually developed into complete thin and smooth nanosheets with porous structure due to the water intercalation (Fig. 19g). We strongly consider that the initial "electrochemical activation" process of electrode materials mentioned in literature is likely to be based on this kind of irreversible water exchange.

In summary, there are many types of water exchange, and sometimes the same kind of material has different reports on the exchange mechanism; in particular, the reversible exchange mechanism of water molecules is still controversial, and further in-depth study is always required. However, no matter how the water molecules enter the interlayer, from our point of view, the intercalated water molecules have a certain positive effect on improving the electrochemical performance in AZIBs. In general, when the Zn²⁺ ions are inserted in the cathode material, the strong electrostatic interaction between the bivalent Zn²⁺ ions and the host framework could cause a high diffusion barrier and slow solid-solid diffusion kinetics. Hence, the intercalated water molecule is equivalent to a "lubricant" and can play a role in electrostatic shielding, which accelerates the insertion and diffusion of Zn²⁺ ions in the host structure at the same time. The insertion of H₂O molecules between the interlayers of the host material also effectively supports the overall structural stability as a "pillar" and expands the diffusion channels throughout the discharge/charge process, thus ensuring high discharge capacity and excellent long-term cyclic stability. This has a similar effect to the previously mentioned preintercalated water molecules.

5.2. Phase transition and separation

The water molecule exchange mentioned above has one common ground, it only affects the layer spacing and structure type. However, in the other case, the exchange of water molecules is irreversible and under the action of electrochemistry, combined with Zn^{2+} ions they interact with the host material to cause phase transition. Here, we divide phase transition and separation into three types, namely complete phase transition, hybrid phase transition, and partial phase transition.

For the complete phase transition, current reports have focused on V-based materials. The newly formed phase is hydrated zinc pyrovanadate (Zn₃V₂O₇(OH)₂·2H₂O). Both OH⁻ and H₂O come from the electrolyte. The formation mechanism can be attributed to the co-intercalation of Zn²⁺ ions and water molecules. Chen et al.²⁰⁴ reported a rapid electrochemically induced structural evolution of porous orthorhombic V₂O₅ nanofibers due to the co-intercalated water/Zn²⁺. It achieved a transformation of VO₅ square pyramids to ZnO₆ octahedral layers separated by double VO₄ tetrahedral interlayer pillars with expanded layer spacing. The newly formed Zn_{3+x}(OH)₂V₂O₇·2H₂O with open-structured hosts during subsequent cycling is conducive to the insertion/extraction of Zn^{2+} ions (Fig. 20a). Taking into account the atomic composition of the material, the separation of metal elements sometimes occurs due to the formation of new phases (Fig. 20a). The new metallic phase is conducive to improving the conductivity of the material and has a significant positive effect on the electrochemical performance. $^{\rm 205}$

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The hybrid phase transition refers to the coexistence of complete phase transition and partial phase transition during a complete charge and discharge process. As shown in Fig. 20b, in polyaniline-intercalated vanadium oxide (PVO) cathode material, $Zn_3V_2O_7(OH)_2 \cdot 2H_2O$ appeared first and was then completely converted to $Zn_x(PVO)_y$ at the end of the discharge.²⁰⁶ Phase separation occurs during charging and remains until the end. The underlying mechanism of this process is still unclear and similar reports are rare. Researchers have considered that it may be related to the change in the internal stress and bonding mode of the structure caused by the insertion/ deintercalation of Zn^{2+} ions.

For the partial phase transition, it means that the material will not completely transform into a new phase, but will form a multi-phase coexistence with the original material; this has been widely reported in V-based and Mn-based materials. As shown in Fig. 20c, for V₆O₁₃·*n*H₂O, in addition to forming layered Zn₃V₂O₇(OH)₂·2H₂O based on an identical process as before, Zn_aV₆O₁₃·*m*H₂O (m > n) also appears due to the Zn²⁺ ions intercalated in the untransformed part simultaneously.¹⁸⁷ In the following cycles, two separated phases simultaneously



Fig. 20 (a) Schematic diagram of the complete phase transition. Reproduced with permission from ref. 204. Copyright 2019, Elsevier Inc (top). Reproduced with permission from ref. 205. Copyright 2020, Elsevier Inc (bottom). (b) Schematic diagram of the complete/partial phase transition. Reproduced with permission from ref. 206. Copyright 2019, The Royal Society of Chemistry. Reproduced with permission from ref. 204. Copyright 2019, Elsevier Inc. Schematic diagram of the partial phase transition in (c) V-based materials and (d) Mn-based materials. (c) Reproduced with permission from ref. 187. Copyright 2019, American Chemical Society (top). Reproduced with permission from ref. 189. Copyright 2019, The Royal Society of Chemistry (bottom). (d) Reproduced with permission from ref. 207. Copyright 2019, Springer (top). Reproduced with permission from ref. 208. Copyright 2020, American Chemical Society (bottom).

undergo reversible (de)intercalation of Zn^{2+} ions without further structural transformation. In particular, the new phase produced by phase transition can be reversible or irreversible, according to current reports. In the case of irreversibility, the new emerging phase can always exist and the Zn^{2+} ion (de)intercalation process can simultaneously occur in two phases smoothly. However, sometimes the new phase can disappear during charging due to the deintercalation of Zn^{2+} ions. For example, for $NH_4V_4O_{10}$ a similar incomplete conversion was also reported. However, the difference is that the new phase of $Zn_3V_2O_7(OH)_2.2H_2O$ reversible disappearance/appearance is accompanied by the extraction/intercalation of Zn^{2+} ions in the subsequent cycle (Fig. 20c).¹⁸⁹

In addition to V-based materials, Mn-based materials also undergo partial phase transitions. As shown in Fig. 20d, first, as Zn^{2+} ions intercalate into MnO₂, a ZnMn₂O₄ phase is formed. At the same time, a part of MnO₂ transforms into the Mn₂O₃ phase.²⁰⁷ Due to the intercalation of protons, the MnOOH phase is formed. Therefore, the three phases coexist when the discharge ends. Due to the high reversibility of the phase transition process, it will revert to MnO₂ during charging. Other manganese oxides such as MnO have also reported the appearance of the MnOOH phase.²⁰⁸

In summary, the phase transition must be under the action of an applied electric field and concentrate on V-based materials and Mn-based materials. Other common cathode materials such as Prussian blue analogues have not yet been reported, which may be able to accommodate Zn²⁺ ions and water molecules at the same time with their stable framework structure without being changed. Organic materials are not in the scope of discussion because of their unique Zn²⁺ storage mechanism. The phase transition can be reversible or irreversible, complete or partial, according to the different results. Regardless of the type of transformation, it is worth mentioning that all the new emerging phases reported so far can be divided into two types. One is Zn₃V₂O₇(OH)₂·2H₂O that appears in V-based materials due to the intercalation of active H₂O molecules, and the other is MnOOH that appears in Mn-based materials due to the intercalation of protons. Notably, the appearance of these two new phases is closely related to water molecules. However, the complex and diverse results are still confusing during the phase separation process. In particular, the factors affecting different results of phase separation in the same type of materials are still unclear. Therefore, it is still a huge challenge to figure out the internal mechanism.

5.3. Material oxidation

There is also a special case of water exchange that is different from the above process. As an oxidant, water molecules in electrolytes participate in the reaction to change the valence state, morphology, and other properties of electrode materials. Analogous to the phase transition mentioned in the previous section, this process must also take place under the action of an electric field. However, this process is achieved by direct *in situ* water exchange in the battery during charge and discharge, which is different from the previous synthesis technology of electric field-induced water intercalation. According to the conditions required for the oxidation process, we divide it into two types. One is one step *in situ* oxidation and the other is multi-step *in situ* oxidation.

As shown in Fig. 21a, V(+4)O₂ can be oxidized to $V_3(+4/+5)O_7$. H₂O at the first full charge to 1.7 V. The whole process is accompanied by obvious changes in the morphology (from the copper coin shape to the nanowire shape).²⁰⁹ Similarly, the crystalline $V_2(+3)O_3$ can be oxidized to amorphous $V_2(+5)O_5 \cdot H_2O_5$ at the first full charge to 1.9 V (Fig. 21b). The whole process is accompanied by obvious changes from the crystalline to amorphous state. Significantly higher valence can be obtained due to a higher charging voltage.²¹⁰ Wang et al.²¹¹ exploited this process to convert V_2O_3 into V_2O_{5-x} successfully. Considering the low saturation of dissolved oxygen in water (298 K, 8.25 mg L^{-1}), it is far from enough to rely on oxygen to oxidize materials. Therefore, it is reasonable to believe that water participates in the oxidation process as a reactant, and the mechanism can be formulated as follows $V_2O_3 + H_2O \rightarrow V_2O_{5-x} \cdot nH_2O + O_2 + H^+$. As shown in the schematic diagram, a fast valence transition from V_2O_3 to V_2O_{5-r} nH_2O can be completed during the first charge to 1.6 V in the water-based electrolyte (Fig. 21c). In contrast, this process cannot be achieved in organic electrolytes due to the absence of water (Fig. 21d). Benefiting from rising valence, the highest theoretical capacity could be enhanced to a value of 715 mA h g^{-1} through the +5/+3 (V⁵⁺ to V^{3+}) redox with a two-electron reaction (vs. V_2O_5). The obtained V_2O_{5-x} nH₂O material after oxidation could achieve an ultrahigh initial specific capacity of 655 mA h g^{-1} at 0.1 A g^{-1} . Similarly, Niu et al.²¹² converted V₂O₃@C to V₂O₅@C, achieving an excellent performance of 616.2 mA h g^{-1} at 0.3 A g^{-1} by the oxidation strategy. In addition to vanadium oxides, other vanadium compounds such as vanadium nitride (VN), vanadium sulfide (VS_2), and V₂C MXene (V₂CTx) could also be oxidized.²¹³ Du et al.²¹⁴ successfully converted VS_2 to VO_x through the same oxidation process. For a one-step oxidation process, the change in its morphology is usually rapid and obvious. As the voltage increases, the size of the material will decrease significantly, even to the nanoscale. As shown in Fig. 21e, Han et al.²¹⁵ transformed VN into the high-valence VO_x and achieved a record-breaking specific capacity of 705 mA h g^{-1} at 0.2 A g^{-1} . The original electrolytic material was lumpy and was oxidized into nanowires with smaller dimensions. This nanoization phenomenon accompanied by an increase in valence is also one of the reasons for the significant improvement in electrochemical performance.

For the multi-step oxidation process, related reports mainly focus on Mn-based materials. Among the cathode materials, manganese oxide has various structures, including various tunnels and layered structures. It has been widely investigated in recent years due to a series of advantages such as high abundance, excellent capacity, low cost, and non-toxicity. Similar to vanadium oxide, low-valence Mn is not suitable for the intercalation of Zn^{2+} ions. The current reports on manganese oxide are mostly concentrated on MnO_2 with different structures. The intercalation of Zn^{2+} ions will inevitably cause



One step in-situ oxidation

Fig. 21 (a) Schematic illustration of the one-step *in situ* oxidation from VO₂ to V_3O_7 ·H₂O during the first full charge to 1.7 V. Reproduced with permission from ref. 209. Copyright 2019, The Royal Society of Chemistry. (b) Schematic illustration of the one-step *in situ* oxidation from MOF-derived crystalline V_2O_3 to amorphous V_2O_5 during the first full charge to 1.9 V. Reproduced with permission from ref. 210. Copyright 2020, Wiley-VCH. (c) Schematic illustration of the one-step *in situ* oxidation from V_2O_3 to $V_2O_5_{-x'}$ ·nH₂O during the first full charge to 1.6 V. (d) Comparison of the effects of organic electrolyte and water-based electrolyte on the anodic oxidation process. Reproduced with permission from ref. 211. Copyright 2020, American Chemical Society. (e) Schematic diagram of the morphology change during one-step oxidation. Reproduced with permission from ref. 215. Copyright 2021, Elsevier Inc. (f) Schematic illustration of the multi-step *in situ* oxidation from Mn₃O₄ to layered MnO₂. (g) The electrochemical performance of the assembled Zn/2 M ZnSO₄/Mn₃O₄ battery. Reproduced with permission from ref. 216. Copyright 2019, American Association for the Advancement of Science.

the valence of Mn to decrease; therefore, Mn^{4+} has a higher theoretical capacity than low-valence Mn such as Mn^{3+} or Mn^{2+} . The theoretical specific capacity can reach 308 mA h g⁻¹ through a +4/+3 (Mn^{4+} to Mn^{3+}) redox with a one-electron reaction. Kang *et al.*¹⁶⁷ converted $Mn_3(Mn^{2+}/Mn^{3+})O_4$ into

water-intercalated Mn(Mn⁴⁺)O₂·*x*H₂O using an anodizing process based on the water exchange process. The whole process occurs when first charged to 1.9 V and can be divided into two stages (Fig. 21f). Mn₃O₄ was first oxidized to Mn₅(Mn²⁺ and Mn⁴⁺)O₈ during the charging process with the dissolution of

 $\rm Mn^{2+}$ ions and the valence transformation from $\rm Mn^{3+}$ to $\rm Mn^{4+}$. Due to the dissolution of $\rm Mn^{2+}$ ions and the intercalation of water molecules, $\rm Mn_5O_8$ was transformed into birnessite. Among them, $\rm Mn_5O_8$ and birnessite coexist during the first charge due to incomplete electrochemical oxidation. $\rm Zn^{2+}$ ions were intercalated into the interlayers of birnessite during the subsequent discharge process, resulting in the formation of Zn-birnessite. This process gradually continues until it stabilizes in the first ten cycles, resulting in a gradual increase in capacity (Fig. 21g). The reaction processes can be described by the following chemical equation:

$$2Mn_3O_4 \rightarrow Mn_5O_8 + Mn^{2+} + 2e^-$$

 $Mn_5O_8 + xH_2O \rightarrow 4MnO_2 \cdot xH_2O + Mn^{2+} + 2e^-$

Morphological changes also occur, from initial nanoparticles to layered particles. Vanadium oxide has also been reported to undergo a multi-step oxidation process. By using this process, Zheng *et al.*²¹⁶ transformed V(+3)OOH hollow nanospheres into hierarchical $Zn_{0.3}V(+4/+5)_2O_5 \cdot 1.5H_2O$ nanoflowers, resulting in increasing specific capacity and more stable cycle performance (Fig. 21h).

In summary, considering that the low-valence transition metal oxides limit the amount of Zn²⁺ ions inserted, this kind of unique water exchange process can increase the valence of materials and significantly improve the performance of the battery. In particular, it is usually accompanied by water intercalation and morphology changes in the materials. In many reports, the so-called "electrochemical activation" is also likely to be caused by this process.²¹⁷⁻²²² The apparent increasing electrode capacity could be achieved after an in situ anodic oxidation strategy in the electrolyte; however, the in situ oxidation process may have the following problems. On the one hand, other side effects may be triggered by water decomposition during the oxidation process, and they can be dramatically inhibited by electrolyte optimization. On the other hand, this activation process can also lead to an issue in specific capacity calculations. Since the calculation of the specific capacity is based on the mass of the active materials, the oxidation process involving water will often lead to changes in the actual mass of the materials, thereby affecting the final calculation of the specific capacity of the material. This also explains why some materials can achieve super-theoretical capacity results. Therefore, we recommend that after the oxidation process is over, the mass of the active substance should be revised, and the specific capacity calculation should be based on this.

6. Conclusions and outlooks

In recent years, energy storage systems have been undergoing a rapid development stage. Due to a series of metallic Zn merits, AZIBs have unparalleled advantages as compared to other energy storage systems. The presence of water not only improves battery safety but also reduces production costs. The water can also profoundly affect the entire electrochemical energy storage process of AZIBs. In this review, we have analysed the influences of water molecules on these effects and the existing problems from the perspectives of the electrolyte, anode, and cathode.

6.1. Regulation of electrolyte

From the electrolytes' perspective, there are two kinds of free and solvated water due to the inescapable solvation process. Among them, the solvated water molecules coordinated with the Zn²⁺ ions can be separated from the Zn²⁺ ions in the electrochemical process, resulting in the formation of highly active free water molecules on the surface of the electrodes. This desolvated process is also widely reported in organic systems. However, the low stable voltage of only 1.23 V in the water system differs from the organic systems, which leads to the splitting of active free water molecules. Although waterbased electrolytes have many advantages, how to inhibit the splitting of active water molecules is indeed an inevitable problem. The electrochemical instability of water causes the narrow voltage window of the AZIBs and severely limits the device's energy density. In addition, the HER reaction on the Zn anode has a massive impact on the performance of the battery. Reasonable electrolyte regulation is an effective strategy to alleviate this issue. Based on our analysis, three types of strategies for inhibiting active free water molecules can be summarized as follows:

(1) Configure high-concentration electrolytes

(a) Fabricating a high molality of 20-30 M aqueous solution with low cost and highly soluble zinc salt (ZnCl₂, Zn(OAc)₂, and ZnBr₂).

(b) Preparing the eutectic/ H_2O or ion liquids/ H_2O hybrid system by introducing an appropriate amount of water or using soluble zinc salts-rich crystalline water. The introduction of a small number of water molecules can improve ion conductivity and ion mobility without affecting electrochemical stability windows.

(c) Synthesizing super-high concentration electrolytes (>40 M) by exploiting the synergistic effect of different component zinc salts.

(2) Introduce additives

(a) Adding organic solvents such as AN (acetonitrile), DMSO (dimethyl sulfoxide), and EG (ethylene glycol), *etc.* into conventional aqueous electrolytes.

(b) Adding surfactants such as SDBS, SDS, SCC (sodium carboxymethylcellulose), DTAB (dodecyltrimethylammonium bromide), *etc.*, into conventional aqueous electrolytes.

(c) Adding inorganic insoluble materials such as silica nanoparticles, fumed silica into conventional aqueous electrolytes

(d) Adding different types of substances to form mixed systems of three or more phases.

(3) Prepare quasi-solid polymer electrolytes

(a) Synthesizing gel polymer electrolytes with a small amount of water based on the polymer chains and salt mediums.

(b) Synthesizing polymer electrolytes based on two or more types of polymers through crosslinking, self-assembling, or copolymerization. In general, all the above methods improve the electrolyte's stability by limiting the number, electrochemical activity, and transport of free water molecules. Among them, high-concentration electrolytes and quasi-solid electrolytes directly reduce the water content in the electrolyte. Nevertheless, the increase of production cost and the transfer impedance of the charge in the electrolyte weaken the inherent advantages of the aqueous battery system to a certain extent. By comparing different parameters, we believe that the hybrid electrolyte has greater potential for mainstream research in the future (Fig. 22a–c); hence, the reasonable selection of additives will be critical. Based on the previous analysis, suitable electrolyte additives should meet the following criteria:

(1) The additives should have the characteristics of environmental friendliness, low toxicity, or non-toxicity.

(2) The additives should preferentially form solvated ions with water or Zn^{2+} to inhibit the hydration number, thereby reducing the production of a large number of active free water molecules during the desolvation of Zn^{2+} ions (Fig. 22d).

(3) The additives should repress the H_2O activity *via* forming hydrogen bonds with H_2O .

(4) The additives should hardly change the inherent characteristics of water-based electrolytes such as fluidity, viscosity, electronic/ion conductivity, and the kinetics transmission of Zn^{2+} ions.

It is worth mentioning that considering the small dose of the electrolyte additives, the cost is no longer the critical limiting factor. The actual effect of soluble solids (mostly various salts) is generally not as good as organic solvent additives at suppressing the active water. Considering the solubility of salt, organic solvents that are miscible with water are a better field of choice. In summary, by optimizing the electrolyte, the solvation process of Zn^{2+} ions can be suppressed, thereby reducing the solvent removal barrier. It can also broaden the electrochemical voltage window to achieve higher energy density. The dissolved oxygen in the electrolyte is also worthy of attention. The presence of oxygen dissolved in the electrolyte can aggravate the side reaction of the Zn anode and promote the OER reaction (Fig. 22e).

6.2. Construction of the electrolyte/electrode interface

From the perspective of the electrolyte/anode interface, the Zn corrosion and passivation layer induced by active free water near the interface are two major obstacles to developing the Zn anode. In particular, the unexpected Zn corrosion always results in Zn dendrites and the early failure of AZIBs. The protection of the Zn anode can effectively improve the stability of AZIBs. In addition to the electrolyte control, the most effective method currently is to build an electrochemically and chemically stable interface between the electrolyte and Zn surface. Based on our analysis, three types of strategies to construct electrolyte/electrode interface can be summarized as follows:

(1) Construct an artificial SEI

(a) In situ electrochemical deposition or adsorption of electrolyte additives (such as PEO, ACN, PAM, SDBS, SDS, $Zn(H_2PO_4)_2$, *etc.*) to form a unique SEI between the Zn anode and electrolyte.

(b) Coat inorganic/organic/organic-inorganic composite materials on the surface of the Zn anode through scraping, immersion, CVD (chemical vapor deposition), ALD (atomic layer deposition), replacement reaction, electroplating, spraying, and other methods.



Fig. 22 (a-c) A summary of the general performance metrics for different electrolyte control strategies. (d) Schematic diagram of the inhibition of Zn^{2+} ion solvation. (e) Schematic classification of the strategies to optimize electrolyte.

(2) Construct a zincophilic interface

(a) Introduce polar functional groups (*e.g.*, C==O or -NH), zincophilic active sites (pyridine N), heteroatoms, and defect-doping, *etc.*

- (b) Coat the zincophilic metal such as Cu, Sn, Au, and Ag.
- (3) Other strategies
- (a) Introduce a Janus interface by plasma treatment.
- (b) Modification and selection of a separator.²²³

Based on comprehensive considerations including operational complexity and cost, we believe that the construction of an artificial SEI is still the most promising method. Therefore, the most critical point is to select a suitable coating material to protect the surface of the Zn anode from active water molecules (Fig. 23). For conductive materials, mainly carbon materials, metal coating, or conductive polymer are used. By comparing the coating of different materials, we believe that the biggest problem is the regulation of the desolvation process of $[Zn(H_2O)_6]^{2+}$ ions, which causes side reaction products to accumulate on the surface of the protective layer to prevent further Zn^{2+} ion stripping and plating. It is, therefore, worth considering how to avoid Zn deposition on the surface of conductive materials such as the carbon protective layer. First, the existence of a large number of mesopores and micropores can allow Zn^{2+} ions to pass through the protective layer to complete the deposition on the Zn anode surface. Secondly, since the radii of water molecules and hydrated Zn^{2+} are about 2–3 Å and 4.3 Å, respectively, the small pore size (<5 Å) facilitates the regulation of desolvation and isolates the water molecules from the protective layer.

For the chemically inert materials, they are mainly divided into organic and inorganic molecules. Compared with conductive materials, they have a series of intrinsic advantages. First, the excellent ion conductivity and electron transport inertia avoid the deposition of Zn on the surface of the protective layer. Second, its optional materials are diverse and are not restricted by temperature and other conditions. Third, its optional materials are diverse and are not restricted by temperature and other conditions. Fourth, the adjustable pore size and structure are conducive to the control of the desolvation process. Based on the previous discussion, we believe that the following materials have great research potential and have not yet been well developed.



Mesoporous/Microporous Zeolite

Fig. 23 A summary of the general performance metrics for water regulation on the Zn surface by different protective materials, and a series of candidates with great potential predicted to be used in the next stage of Zn anode protection research.

For inorganic materials, we believe that zeolite molecular sieves have great advantages in the protection of Zn anodes. At present, zeolite molecular sieves are mainly focused on the adsorption and separation of gases or molecules in the environmental field. Zeolite molecular sieves are a hydrate of crystal-line aluminosilicate metal salt, and its general chemical formula is $M_{x/m}[(AlO_2)_x(SiO_2)_y]\cdot zH_2O$; M stands for cation, which means its valence number, and *z* stands for the hydration number. M can be a monovalent Li⁺/Na⁺/K⁺ ion or a multivalent Ca²⁺/Mg²⁺/Zn²⁺ ion. In zeolite molecular sieves, each atom can form a cage structure with a pore size of 3–10 Å.^{224,225} There are many holes of a certain size in the crystal structure, and the holes are connected by pores of the same diameter. Therefore, zeolite molecular sieves have the following advantages when applied to Zn anode protection:

(1) They have strong adsorption and separation properties for ions or molecules. Large solvated molecules can be excluded while attracting Zn^{2+} ions with a smaller radius.

(2) The hydrophilicity of the molecular sieve framework can be adjusted by adjusting the ratio of silicon to aluminum.

(3) They are composed of silicon and aluminum with strong water stability and corrosion resistance.

For organic materials, MOF materials with rich mesoporous/ microporous structures are also potential candidates and some types have been confirmed for the protection of the Zn anode. MOFs are easily synthesized in laboratory-scale approaches in numerous combinations of metal clusters and organic ligands, and more than 70 000 different MOFs have been reported experimentally among about 500 000 hypothetical MOF frameworks.²²⁶ There are only a few types of Zn anodes, and there are only a few types that are used in Zn anode protection. Therefore, the development of MOFs that can be used in Zn anodes is very much anticipated, however, the following points need to be noted:

(1) In the water environment, the organic ligands of MOF materials are easily replaced by water molecules, which will eventually lead to the collapse of the framework. Therefore, it is very important to choose stable MOFs in the water such as SIFSIX, NbOFFIVE, AlFFIVE, *etc.*

(2) To better realize the selective passage of Zn^{2+} ions, hydrated Zn^{2+} ions and active water molecules, suitable pore size is very important. We recommend that MOF materials with a pore size smaller than 5 Å should be selected.

In addition to MOF materials, porous COFs (covalent organic frameworks) formed by the strong covalent bonding of organic building units are also a class of optional materials, that have not yet been reported in Zn protection.²²⁷ Compared to most MOFs with poor water stability, most COFs are stable in water and rich in polar functional groups such as –NH and hydrogen bonds, which have been proven to effectively restrict the movement of active water molecules on the surface of the Zn anode.²²⁸

In summary, based on the above analysis, we consider that in the selection of coating materials, one should pay attention to the following points:

(1) The coating materials should have abundant micropores and channel structures, which limit the large-sized hydrated Zn^{2+} ions while not affecting the transport of bare Zn^{2+} ions. (2) The coating materials should have corrosion resistance and chemical stability in water-based electrolytes.

(3) The coating materials are supposed to have high ionic conductivity and low electronic conductivity.

It is worth noting that the thickness of the protective layer is also pivotal. Therefore, the development of efficient and controllable coating technology is also very meaningful.

6.3. Optimization of the cathode

Based on the influence of water molecules, the optimization strategies can be divided into the following four categories in this review (Fig. 24a):

- (1) Change the crystal structure.
- (2) Change the type of compound bond.
- (3) Change the electronic structure.
- (4) Change the valence.

In addition to these effects, here we consider that the existence of water molecules also has a special effect that facilitates the insertion of protons based on the hydrogen bond. Based on the previous discussion, the utilization of fast proton transport can achieve a noticeable effect in improving the electrochemical performance of the AZIBs. More critically, the intercalation of protons can compensate for the slow Zn²⁺ ion transfer kinetics and the disruption of the material structure by (de)intercalation, thus playing an essential role in improving rate performance and maintaining stable cycling performance. Hence, accelerating the protons' intercalation by constructing the hydrogen-bonding network within the material is also a viable strategy. All currently reported cathode materials are mainly concentrated in the frame or layered structure. For frame structures, the effect of structural water is very limited for accelerating protons due to structural limitations. The frame structure can be opened by manufacturing defects to accelerate the embedding of protons based on the Grotthuss mechanism (Fig. 24b). For the layered structure, we propose to effectively utilize the interlayer space to construct a hydrogen bond network that can accelerate the insertion of protons. As shown in Fig. 24c, the feasible methods are summarized as follows:

(1) Introduce ammonium ions rich in hydrogen bonds (an ammonium ion can carry four hydrogen bonds) to build a hydrogen bond network between layers.

(2) Adjusting the number of water molecules between layers is also very important for hydrogen bond formation and structural influence.

(3) Introduce small organic molecules with C—N, C—O, –NH– groups, *etc.*, between layers. These organic molecules can undergo a reversible redox reaction with protons to achieve proton storage and release.

From the perspective of the cathode, there are two notable issues:

(1) The slow transport of $\mathbb{Z}n^{2+}$ ions at the material/electrolyte interface and inner structure.

(2) The degradation of the material structure during the insertion and extraction of Zn^{2+} ions.



Fig. 24 (a) Schematic classification of the strategies to optimize cathode materials. (b) Accelerate proton intercalation by constructing defects. (c) Facilitate proton intercalation through interlayer engineering. (d) The Tai Chi diagram represents the relationship between the various components of the AZIBs based on the water molecules, and illustrates the effects of water molecules on the aqueous AZIBs.

Based on other perspectives (except for water molecules), we also summarize three types of methods to optimize materials as follows:

(1) Enlarge the interlayer spacing and stable crystal structure through ion/molecule preintercalation.

(2) Introduce other types of electrochemical reactions in the cathode.

(3) Other structural engineering: high-conductivity material coating, heteroatom doping, introduce vacancies, nanostructure design, new materials development, *etc.*

For the first methods, the intercalation of water molecules can effectively expand the interlayer spacing and accelerate the diffusion kinetics of Zn^{2+} ions. However, the mere insertion of water molecules can no longer meet the requirements of high-performance AZIBs due to the thermodynamic and electrochemical chemical instability. The current research on AZIBs mainly focuses on the co-intercalation of metal cations and water molecules. Despite the fact that investigations on the intercalated small molecules of the organic polymer are in their infancy, they are still potential candidates for electrode material optimization due to their rich π -conjugated structure.²²⁹

For the second method, the introduction of new reaction mechanisms is very attractive for increasing the overall energy density of the battery. For example, by introducing a twoelectron reaction for Mn²⁺/Mn⁴⁺ based on the deposition and dissolution of MnO₂ on the cathode, the output voltage and energy density of the Zn-Mn battery can be prominently improved. Niu et al.⁵⁹ used the introduction of anionic redox reactions $(O^{2-} \leftrightarrow O^{-})$ to substantially increase the energy density of the AZIBs. It has been proved that the co-insertion of Zn^{2+}/NH_4^+ dual ions can make full use of the active sites of the cathode material and exert a synergistic effect to achieve the improvement of the electrochemical performance.²³⁰ The third method is also a hot topic of interest for current researchers. Defects (e.g., vanadium vacancies, oxygen vacancies, manganese vacancies, heteroatom doping, etc.), conductive material coating, and nanostructure design are available to facilitate the transport of Zn²⁺ ions.

There are still some controversies in the current research on the mechanism of cathode materials. For the variety of cathode materials and the complex reaction processes, the influences of water molecules are also different. On the one hand, the formation of the intercalated water molecules in materials is still controversial. Some scholars have reported that it is a hydrated Zn^{2+} ion, while others believe it is an active free water molecule. On the other hand, the selective appearance of cathode side reactions in some materials is unsolved. These problems rely on developing advanced *in situ* characterization techniques such as *in situ* hydrogen nuclear magnetic resonance, *in situ* extended X-ray absorption spectroscopy, *in situ* Fourier transform infrared spectroscopy, *in situ* neutron scattering.

In summary, the water molecules could affect the electrode, active material, electrolyte, and the overall battery performance of AZIBs from different aspects. Therefore, the influence of water does not exist alone, and the water in the electrolyte will affect the anode and cathode materials at the same time. This is like "Tai Chi" in ancient Chinese culture, where yin and yang correspond to the anode and cathode of the battery (Fig. 24d). The two parts are connected through the electrolyte, and the free water molecules in the electrolyte move back and forth between the two and affect the cathode and anode. When moving to the cathode, it will cause the intercalation of water molecules, the change of the material structure, and the occurrence of reversible side reactions. When moving to the anode, corrosion, and passivation of the Zn electrode will occur. These interactions between the cathode, anode, and electrolyte are very interesting. In general, everything has two sides. As the ancient Chinese saying goes, "water can carry a boat and it can overturn it". The presence of water in the electrolyte is like a coin with two sides. The future goal is to curb the bad and take advantage of water molecules. Although there are unresolved problems, it is foreseeable that the future development of AZIBs must be magnificent.

Conflicts of 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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