Author/s:
Chen, C;Long, Z;Du, X;Li, L;Liang, Q;Chao, D;Li, D

Title:
Interfacial ionic effects in aqueous zinc metal batteries

Date:
2024-08

Citation:
Chen, C., Long, Z., Du, X., Li, L., Liang, Q., Chao, D. & Li, D. (2024). Interfacial ionic effects in aqueous zinc metal batteries. Energy Storage Materials, 71, https://doi.org/10.1016/j.ensm.2024.103571.

Interfacial Ionic Effects in Aqueous Zinc Metal Batteries

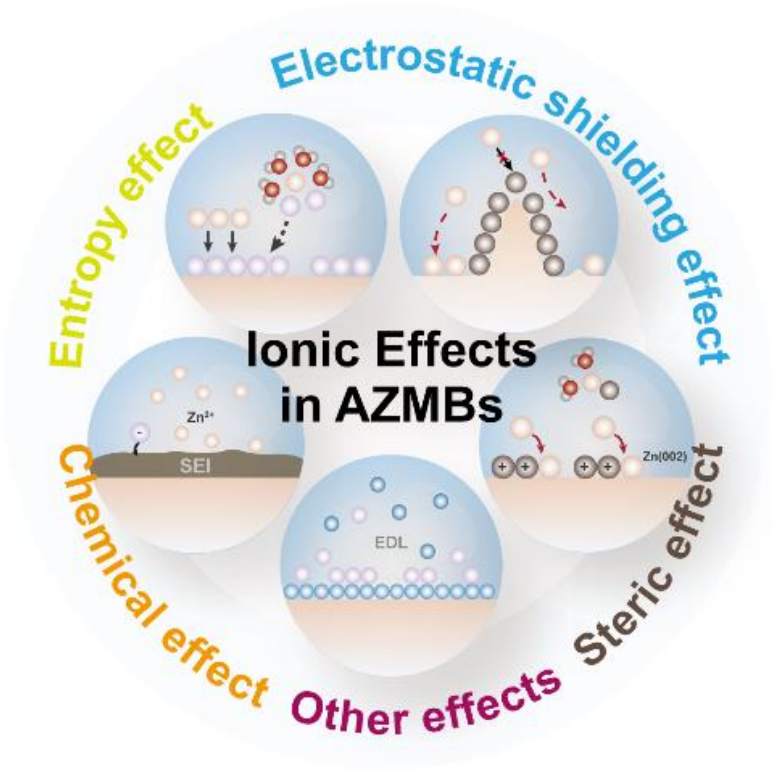
Chun Chen, Zuxin Long, Xiaoyang Du, Liansheng Li, Qinghua Liang,* Dongliang Chao,* and Dan Li*

ABSTRACT

Zn metals anodes (ZMAs) are most attractive for emerging aqueous zinc metal batteries (AZMBs). However, the practical application of AZMBs is still impeded by various formidable issues like uncontrolled Zn dendritic growth, hydrogen evolution reaction, and severe corrosion of ZMAs. This review delves into the pivotal role of interfacial ionic effects in AZMBs. We elucidate how ionic additives can reshape the electric double layer (EDL), thereby mitigating the issues for AZMBs. Given the different influences on the EDL behavior including the water dipoles, local electric field, solvation structure, electrochemical reaction, *etc*, we divide it into five primary interfacial effects of the steric effect, electrostatic shielding effect, entropy effect, chemical effect, and other miscellaneous effects, respectively. Nevertheless, since the EDL is highly inhomogeneous and dynamic, we underscore the tremendous challenge of understanding the exact mechanisms behind these interfacial ionic effects. We thus advocate for the significance of combining advanced Operando characterization techniques and multiscale modelling to uncover the mysteries. Besides, we highlight the development of multifunctional ionic additives and the exploration of interfacial ionic effects in non-aqueous electrolytes. This review arouses the rational design and utilization of ionic additives to design effective electrolytes for more efficient and durable AZMBs.

KEYWORDS: aqueous Zn metal anodes, interfacial ionic effect, Zn-ion batteries, electrical double layer, ionic hydration structures

GRAPHICAL ABSTRACT



1. INTRODUCTION

Zn metal anodes (ZMAs) have attracted significant attention due to their high theoretical capacity (5855 mAh cm^{-3}), low redox potential (–0.76 V vs the standard hydrogen electrode), nontoxicity, substantial abundance, and low cost. As such, ZMAs have been widely used in various promising electrochemical applications, including aqueous batteries,[1–3] hybrid capacitors,[4–6] desalination devices,[7,8] and emerging dynamic windows.[9,10] In particular, ZMAs are commonly considered the optimal choice for anodes in aqueous zinc metal batteries (AZMBs), which are increasingly viewed as a promising alternative to the prevalent lithium-ion batteries due to their affordability and superior safety features. The charging/discharging process of AZMBs is afforded by the electrochemical Zn plating/stripping of ZMAs. As such, the reversibility of ZMAs largely determines the Coulombic efficiency, cycle stability, and overall performance of the AZMBs.[11–13] However, the practical applications of AZMBs are still severely hampered by numerous interfacial issues including the rampant Zn dendritic growth and notorious side reactions like hydrogen evolution reaction (HER) and corrosion on ZMAs because these issues can severely deteriorate the electrochemical stability and reversibility of AZMBs.[14–16] Therefore, understanding the anode electrochemistry of ZMAs is crucial to promoting the development of AZMBs.

As with many other electrochemical processes, the electrochemical Zn plating/stripping of ZMAs in AZMBs mainly occurs at the interface between the ZMA and the aqueous electrolyte, namely, the electric double layer (EDL). Recently, various strategies have been explored to engineer the ZMA interfaces and improve the cycling stability and reversibility of AZMBs by optimizing the chemical composition and structure of the ZMAs.[17] This mainly includes constructing an artificial interfacial layer that provides a stable liquid/solid interface for Zn^{2+} plating and avoids direct contact between the ZMA and aqueous electrolyte;[12] alloying Zn metal which makes ZMA shows better corrosion resistance performance and lower Zn nucleation barrier;[18] designing advanced host substrates which increase the specific surface

area and Zn^{2+} plating sites;[19] reducing local strong electric field for uniform Zn^{2+} plating. This has been widely reviewed in previous reports.[20–24] However, those strategies conducted on the ZMAs are impeded by the easy fragmentation of the artificial interface layer and the collapse of host substrates.[25] The complex fabrication processes (e.g., chemical vapor plating, epitaxial film growth, and 3D printing) can greatly increase the cost for practical application.[26] In contrast, the electrolyte optimization approach offers advantages in feasibility, simplicity, and cost-effectiveness.[27,28]

As an essential component of AZMBs, electrolyte provides a medium environment to transfer charge carriers (ions). The electrolyte composition also plays a pivotal role in the electrochemical process of the ZMAs.[29] For instance, the Zn plating/stripping behavior and surficial side reaction of ZMAs can be readily regulated by simply adjusting the solute and solvent of electrolytes, such as changing the type and concentration of Zn salts,[30–32] introducing effective electrolyte additives,[33] using the deep eutectic solvents or ionic liquid as the solvent,[34,35] and exploring gel or solid-state electrolytes.[36] Among them, the application of various electrolyte additives, including small organic molecules,[37,38] polymers,[39,40] and organic/inorganic salt,[41,42] is particularly appealing. This approach is favored for its significant effectiveness, straightforward preparation, facile preparation, and cost-effectiveness. In particular, various recent studies have demonstrated that ionic additives in electrolytes can positively impact the Zn plating/stripping process by meditating the interfacial EDL behavior of ZMAs.[43,44] Therefore, it is necessary to have an updated and insightful understanding of the working mechanism of different ionic additives affecting the electrochemistry of ZMAs for AZMBs. This will provide useful guidelines for researchers to develop more favorable and effective ionic additives for AZMBs. Yet, there is still a lack of such a systematic discussion of ionic effects on the anode electrochemistry of AZMBs.

Herein, we comprehensively discuss the interfacial ionic effects on the AZMBs. This perspective is structured into four main sections. In the second section, we concisely overview

the fundamentals of aqueous electrolyte ions and EDL formed between ZMA and aqueous electrolytes. Moving on to the third section, based on the different influences on reshaping EDL behaviors, we highlight the recently reported typical examples of harnessing interfacial ionic effects to suppress the Zn dendrite growth and restrain the side reactions of ZMAs for AZMBs by the following aspects: (1) steric effect, (2) electrostatic shielding effect, (3) entropy effect for regulating the ionic hydration structure, (4) chemical effect on the in situ construction of solid electrolyte interphase (SEI), and (5) other miscellaneous effects. Finally, we provide an outlook for the challenges and future efforts in tuning the interfacial ionic effect for promoting the practical applications of AZMBs.

2. THE FUNDAMENTALS OF ION HYDRATION AND EDL

2.1 Ions and Ion hydration

Knowledge about electrolyte ions is vital to understanding the behavior of ions and the ionic effect in the electrochemical process. Ions are defined as the positively or negatively charged atoms or groups of atoms, or both in charge-separated atoms/groups. The charge attribute enables the formation of a strong electric field around ions. The electric field could reach an order of 10^7 V/m, depending on and charge density of the ion and the distance from the ion. Such a strong electric field gives rise to the orientation of water molecules or solvents in its vicinity. This accounts for the ionic hydration in aqueous electrolytes.[45] The charge also enables the ions in dilute aqueous solutions to diminish the permittivity of the solution.

Ionic hydration occurs when an ion is dissolved in water owing to the attractive electrostatic interactions between the ion and dipole of water molecules. As such, hydration is ubiquitous in aqueous electrolytes, and ions in water are unlikely to be bare in electrolytes. The hydration of ions is highly related to the charge of ions and the nature of water. The hydration process gives rise to the formation of a hydration shell around the peripheral region of ions.[46] According to the different interactions between the ion and water molecules, the ionic solvation shell is

composed of chemical and physical solvation shells located near and far away from ions, respectively.[47] The chemical hydration shell is generally rigid and tightly attached to ions owing to the chemical interaction. The physical solvation shell is highly flexible and less rigid because the bonds between the solvation shell and the bare ion are normally much weaker compared to the intramolecular bonds. The time-average number of water molecules residing in the physical hydration shell is usually to describe the solvation numbers of an ion. For instance, multivalent cations are usually hydrated with six water molecules in the physical hydration shell (e.g., for Zn^{2+}),[48] as illustrated in **Figure 1a**. In general, the smaller ions have smaller hydration numbers than the larger ions although the bonding with the smaller ions is more energetically.

Both cations and anions are expected to be hydrated. Owing to the different nature of the electric field around cations and anions, the hydration structure between cations and anions is significantly different. A cation has the water molecules oriented toward it with the oxygen owing to their electron-pair donor. However, an anion in aqueous solutions has the water molecules pointing one of their hydrogen atoms toward it (**Figure 1b**).[49] Notably, the hydration of ions is complex and dynamically changed. Water molecules in the hydration shells of ions do move out from them in exchange with molecules that come in. The hydration strength of an ion usually refers to the rate exchange of water molecules between the hydration shells of ions and bulk water in a bulk aqueous electrolyte.[50] The solvation influences the properties of both ions and water structure. For instance, the water molecules nearest neighbors of the ion will have properties which are distinct from the molecules of bulk water owing to the altered hydrogen bonding between water molecules. Both the cations and anions can disrupt the hydrogen-bond structure of pure water owing to the hydration interaction. In general, cations can promote the formation of hydrogen−bonded water whereas anions may disrupt the hydrogen-bond formation as that in pure water.[51] As such, the arrangement of these bound water molecules is considerably distinct from that of pure water. Accordingly, some ions

enhance the order structure of the water whereas other ions destroy it. Simultaneously, the hydration can significantly increase the ionic size owing to the presence of a hydration shell. In addition, the hydration will impact the electrochemical behaviors of ions since the change of hydration structure may happen during the electrochemical process.[52] The polarization of the water molecules in the physical hydration shell by the charge of anion may remain with the ions as the ions move in the aqueous electrolyte. In addition to interacting with water molecules, ions can also interact with other solutes in the aqueous electrolytes, like other ions and molecules.[53] The addition of other solutes in the aqueous electrolyte can also alter the hydration of ions as well as the electrochemical process (**Figure 1b**).

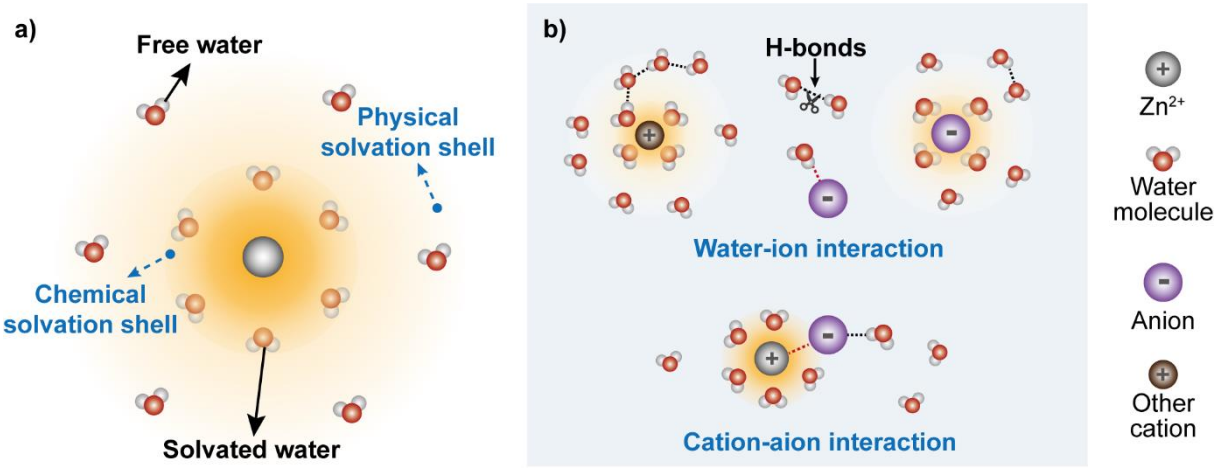


Figure 1. (a) Schematic diagram of the hydrated Zn^{2+} and (b) the effects of hydration between the ions and water in electrolytes.

2.2 The EDL of ZMA

When a Zn metal electrolyte is immersed in an aqueous electrolyte, EDL can be readily formed at the Zn/electrolyte interface owing to their different electrochemical potential. Generally, the EDL formation results in the inhomogeneous distribution of electrolyte ions and molecules near the Zn/electrolyte interface even with constant surface potential owing to the nonuniform surface electric field and electronic charge. Notably, under the charging/discharging of ZMAs, an EDL can afford a potential change of a few volts within such a thin layer (3~5 Å), amounting to a huge electric field (approach 10^8 V/m).[54] Such a huge local electric field can give rise to

highly heterogeneous and dynamic changes in the components and structure of EDL. Furthermore, the strength and distribution of such a huge local electric field are highly related to the applied polarization potential and electrolyte identity since the EDL depends highly on the sign and strength of the polarized voltage and the nature of the electrolyte solution.

The interfacial EDL is generally described by the classical Gouy-Chapman-Stern-Grahame model.[54,55] The EDL is mainly composed of the inter Helmholtz plane (IHP), the outer Helmholtz plane (OHP), and the diffusion plane. As illustrated in **Figure 2**, the interfacial EDL of ZMA is mainly comprised of IHP, OHP, and the diffusion plane DP.[56] The IHP is the interfacial region nearest to the Zn metal at which water dipole is usually present. In addition, there are abundant interfacial water dipoles in IHP. Unlike the free water molecular randomly distributed in the bulk electrolyte, the interfacial water dipoles in IHP tend to be tightly and orderly arranged on the surface of the negatively charged ZMA owing to the high polarity of water molecules and strong interfacial electric field.[57] The orientation of the interfacial water dipoles adjacent to the ZMA is strongly influenced by the magnitude and sign of polarization. The hydrogen atoms of interfacial water molecules generally point toward the ZMA surface at a negative potential while oxygen atoms point toward the surface at potentials above the zero charge potential.[58] The water dipoles in IHP can occupy the active sites for Zn plating. Besides, the water dipoles can cause the HER on ZMAs owing to the lower redox potential of zinc (–0.76 V vs SHE). Furthermore, the water dipoles and free water can be decomposed into H^+ and OH^- under strong polarization. This can cause severe HER and corrosion on ZMAs. As such, decreasing the water dipoles in the IHP is favorable for restricting the side reaction and stabilizing ZMAs in an aqueous electrolyte.

In addition to the water dipoles, in some cases, ions can undergo specific adsorption in IHP through non-electrostatic interaction. The specific-ion adsorption involves the partial removal of the hydrated shell of the solvated ions, followed by their chemical adsorption on the surface of the Zn metal.[59] The specific-ion adsorption process is significantly influenced by the

external polarization, the dehydration energy of electrolyte ions, and the intrinsic adsorption energy of electrolyte ions on Zn metal.[59] The specific-ion adsorption also shows a critical influence on Zn plating on ZMA. For instance, high coverage of the specific adsorption cations can decrease the concentration and arrangement of the water dipole in IHP. This can inhibit the HER and corrosion, thus improving the stability of ZMAs. Besides, the specifically adsorbed cations can homogenize the local electric field near the ZMAs, promoting the uniform Zn plating/stripping and restricting the dendric growth. In addition, since the specific-anions adsorption could attract a higher concentration of Zn^{2+} ions in OHP, the reduction kinetics of Zn^{2+} ions can be improved and the concentration polarization can be also relieved for promoting the rate capability of ZMAs. As such, the specific adsorption of species in IHP is widely explored to improve the electrochemical performance of ZMAs.[60]

The OHP of ZMAs in the aqueous electrolyte is the region composed of a large number of hydrated cations closest to the IHP (**Figure 2**), where the hydrated Zn^{2+} ions could partially lose water molecules and then diffuse toward the IHP.[56] Generally, the dehydration process of Zn^{2+} ions requires overcoming a certain energy barrier, which largely determines the kinetics of specific adsorption and charge transfer. The desolvation energy of Zn^{2+} ions in OHP can be reduced by destroying the original water hydrogen bonding network. Free water and coordinated water can be also present in the OHP. Their scenario can also impact the EDL behaviors and Zn plating/stripping of ZMAs. For example, abundant free water and coordinated water in OHP can also cause HER and side reactions. Therefore, tuning the hydration structure of Zn^{2+} ions and components of OHP by ionic additive is also effective for stabilizing the ZMAs.

The diffusion plane of ZMAs is the area from OHP to the bulk electrolyte, and its thickness is related to the surface charge and concentration of the Zn^{2+}-containing electrolyte. The diffusion plan is highly related to the electrodiffusion of ions and mass transfer like the Zn^{2+}

ion flux during the charging/discharging process of ZMA. Thus the components and structure can affect the discharging/charging dynamics of ZMAs.

Notably, any components in the electrolyte can affect the equilibrium and dynamic responses of the interfacial EDL. Although significant progress has been made in recent years in the theoretical modelling of EDL, major challenges remain in understanding the atomic details of the EDL under realistic conditions because the interfacial EDL is highly inhomogeneous and dynamically evolved under external polarization.

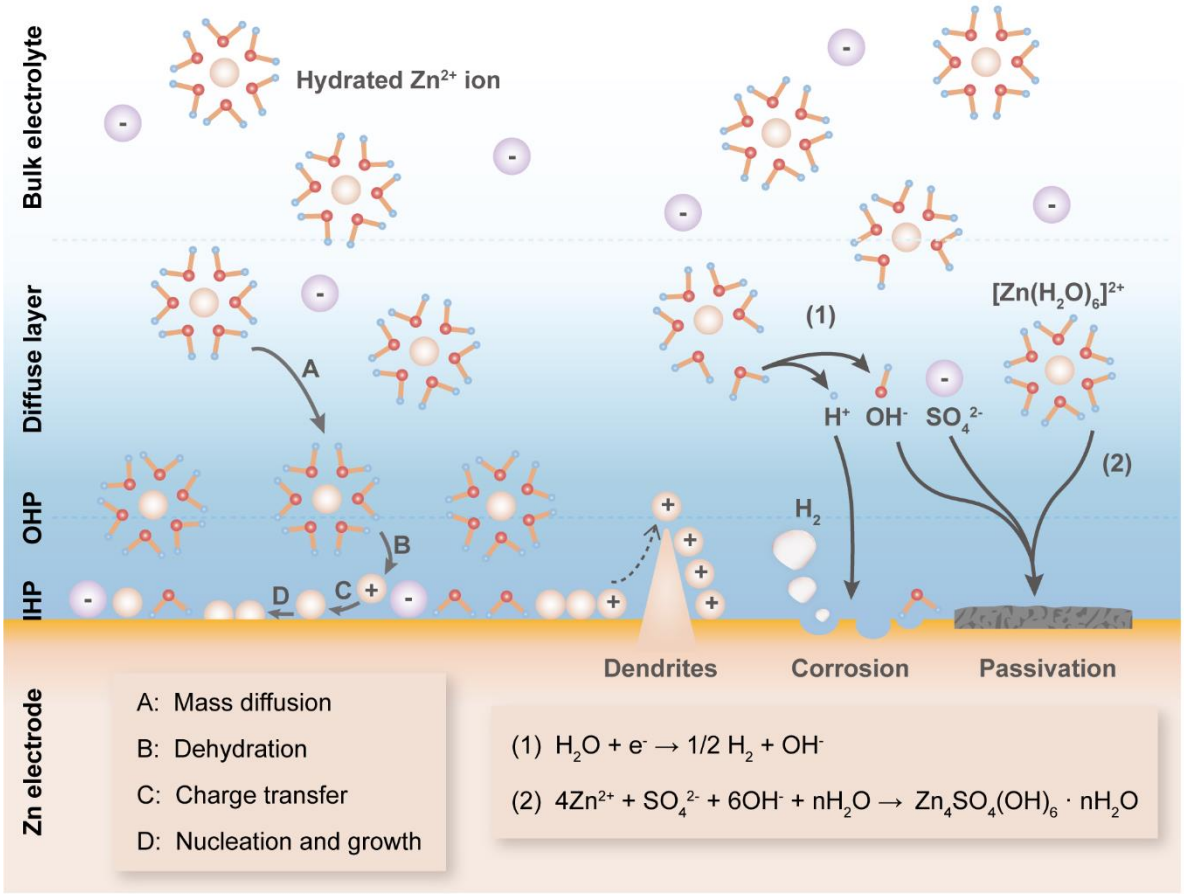


Figure 2. Illustration of the EDL structure of negatively charged ZMAs and the electrochemical process of ZMAs.

3. INTERFACIAL IONIC EFFECTS ON THE ANODE ELECTROCHEMISTRY OF AZMBS

The electrochemical process of ZMAs for AZMBs mainly involves the Zn plating/stripping during the charging/discharging process. The Zn plating process on ZMAs can be generally divided into four steps (**Figure 2**): (1) mass diffusion in the bulk electrolyte, (2) pre-conversion of hydrated Zn^{2+} ions, (3) charge transfer at the interfacial EDL, and (4) Zn nucleation and growth process.[61,62] These four steps could interplay and be highly related to the EDL behavior during the charging/discharging process.[63] During the charging of AZMBs, the hydrated Zn^{2+} ions diffused from the bulk electrolyte to ZMAs could undergo a change of the solvation structure and composition in the IHP. This process can cause the alternation of free H_2O (like the concentration and arrangement) in the IHP, forming a free H_2O-rich EDL that can cause serious HER and corrosion reactions.[15] Under a strong negative polarization, the desolvated Zn^{2+} ions are expected to adsorb onto the surface of ZMAs, where they can be reduced to Zn atoms followed by nucleation and growth.[62] However, the atomic-level irregular surface of commercial Zn metal foil with numerous dislocations, grain boundaries, and kinks could cause an uneven interfacial electric field distribution within the EDL region. Therefore, Zn^{2+} ions preferentially deposit on the protrusion sites owing to the stronger electric field caused commonly known as the "tip effect", leading to the formation of Zn dendrites.[11] In addition, the zinc deposition/stripping process is accompanied by secondary electrochemical processes such as hydrogen evolution reaction, corrosion, passivation, *etc*. (**Figure 2**) These electrochemical processes occurring at the EDL region largely account for the low Coulombic efficiency and poor cycle stability of ZMAs.

Therefore, regulating the interfacial EDL behaviors of ZMA is effective in improving the overall electrochemical performance of AZMBs.[64] For instance, the mass transfer process of Zn^{2+} is affected by the viscosity of the electrolyte, the interaction among various ions and water molecules, and the hydration structure of Zn^{2+} ions. The pre-conversion process of hydrated Zn^{2+} ions is highly related to the desolvation energy and the hydrated structure of hydrated Zn^{2+} ions.[65] The charge transfer process and electrochemical reactions can be highly affected by

the applied polarization and electrolyte composition. For instance, the specifically adsorbed ions in the IHP can influence the concentration of water dipoles and may occupy the active site for Zn^{2+} ion reduction. The structure of hydrated Zn^{2+} ions in OHP will influence the reduction kinetics of Zn^{2+} ions. This will influence the nucleation and growth of the Zn atom at the interfacial EDL region, impacting the final morphology and structure of the electrodeposited Zn layer. The ion distribution within the EDL region can also impact the local electric field and reduction of hydrated Zn^{2+} ions. Besides, the structure and composition of the initially established EDL are also highly related to the formation of SEI. As such, the initial EDL components play a pivotal role in the in-situ construction of SEI which is believed to be significant for the Zn plating/stripping process. In a word, the interfacial EDL plays a dominated role in the electrochemical process of ZMA.[66]

As discussed above, the Zn plating/stripping process on ZMA involves several interfacial issues at the interfacial region, such as Zn dendrite growth, HER, and corrosion. Numerous studies have reported the improvement of AZMBs through the introduction of electrolyte additives owing to the simple operation, cost-effectiveness, sustainability, and variety of ionic additives.[67,68] In particular, the introduction of ionic additives is an effective strategy to improve the stability and reversibility of ZMAs. The ionic additives can affect the EDL behaviors like the water dipole, components, local electric field, solvation structure, and electrochemical redox reactions at the Zn/aqueous electrolyte interface. And even ionic additives show a similar valance state and even ionic radius, these ionic additives show significantly different effects on the electrochemical performance of Zn metal anodes.[69] Accordingly, we divide the currently reported effect of ion additives in the electrolyte, also known as interfacial ionic effects, into five categories based on the specific influence on the EDL behaviors: (1) steric effect in IHP for a free water-poor EDL, (2) electrostatic shielding effect in OHP for tunning the local electric field of EDL, (3) entropy effect in diffusion plane for regulating the hydration structure of EDL, (4) chemical effect in EDL for in situ construction

of favorable solid electrolyte interphase (SEI), and (5) other miscellaneous effects. While not all of these effects are strictly separable, we make this categorization for a concise discussion because the EDL is highly inhomogeneous and dynamically changed during the Zn plating/stripping.

3.1 Steric effect in IHP for a free water-poor EDL

The ionic additives show a great impact on the concentration and reactivity of interfacial water within the EDL of ZMA. The concentration and reactivity of interfacial free water within the EDL are closely tied to the side reactions on the ZMAs. The side reactions are major issues that limit the Coulombic efficiency, longevity, and safety of electrochemical devices based on ZMAs. Although side reactions are related to many factors, such as temperature, applied potential, and electrolyte concentration, the water dipole in the IHP of ZMAs primarily affects the side reaction process. One effective strategy to suppress side reactions involves decreasing the enrichment of free water molecules within the EDL. In the typical aqueous electrolyte of $ZnSO_4$ for AZMBs, the IHP of the negatively charged ZMA is mainly composed of a large number of free water molecules. Accordingly, the water dipoles in EDL can occupy most of the active sites for Zn plating and be decomposed to form adsorbed H^+ and OH^-, which can cause severe HER and side reactions. Tuning the number of free water molecules in EDL can be readily achieved by introducing zincophilic ions, which preferentially adsorb on the ZMA surface. These zincophilic ions isolate water near the Zn surface through steric effect, leading to an H_2O-poor EDL, which in turn suppresses the undesirable HER and side reaction during the Zn plating/stripping process.

Zincophilic ions are typically larger and have significantly lower adsorption energy on Zn metal compared to free water molecules. This allows them to preferentially adsorb on the ZMA and repel H_2O molecules from the surface of the ZMA. For instance, several bulky ions, such as cholinium cation (Ch^+),[70] 1-ethyl-3-methylimidazolium cations ($EMIm^+$),[71] saccharin (Sac^-) anion,[72] and glutamate anion(Glu^-),[73,74] have been incorporated into aqueous Zn-

salt electrolyte to regulate the number of free water molecules near the interfacial EDL for improving the plating/stripping behavior of ZMAs. For example, the Glu^- anions are preferentially adsorbed on the active sites of the Zn anode owing to the much lower adsorption energy of Glu^- than that of free H_2O in different adsorption modes.[73] Without the addition of Glu^- ions in the $ZnSO_4$ electrolytes, free water molecules tend to accumulate near the Zn surface, exacerbating side reactions. When bulky Glu^- ions are present in the $ZnSO_4$ electrolytes, Glu^- can adsorb on the ZMA surface in preference to the water molecule due to the lower adsorption energy than free H_2O in the electrolyte (**Figure 3a**). This approach effectively isolates Zn from contact with water and occupies the active sites, thereby inhibiting HER and side corrosion reactions. Additionally, the adsorbed Glu^- can homogenize Zn^{2+} flux near the ZMA, resulting in more uniform Zn plating (**Figure 3b**). As such, under a current density of 5.0 mA cm^{-2} and 10 mAh cm^{-2}, the Zn//Zn symmetric cell with the Glu^- additive can be steadily cycled for 1700 hours. This is 17-fold in cycling life compared to the cell without Glu^- additives. Similarly, Nie *et al*. reported that adding cholinium (Ch^+) cation into an aqueous $ZnSO_4$ electrolyte enables a spatially compact, dendrite-free, and non-corrosion Zn metal anode.[70] Density functional theory (DFT) calculations and MD simulations were used to analyze the interaction between water molecules and ions. DFT calculations indicated that the significantly lower adsorption energy of the Ch^+ cation on Zn metal, compared to H_2O, results in a preference for Ch^+ cations adsorption over H_2O molecules on the ZMA surface. In addition, MD simulations showed the massive decrease of H-bonds from H_2O-H_2O and the formation of H-bonds between Ch^+ and H_2O. As such, Ch^+ cations can enable an H_2O-poor EDL near the ZMA to inhibit the H_2O-induced side reaction (**Figure 3c**). The Zn anode obtained from Zn//Zn cell after 100 cycles at 1.0 mA cm^{-2} in $ZnSO_4$ electrolytes containing Ch^+ is flatter and more compact than that in bare $ZnSO_4$ electrolyte. As such, the Zn//Zn symmetric cell with Ch^+ additive showed prolonged cycling stability over 2000 h at 1.0 mA cm^{-2} under 1.0 mAh cm^{-2}. More importantly, the steric effect of Ch^+ ions on a ZMA was also found to work for different

zinc electrolytes. Additionally, trisodium nitrilotriacetate (Na_3NTA) was found to be an electrolyte additive that can effectively improve the reversibility of zinc plating/stripping.[75] This is because the preferential adsorption of NTA^{3-} impacts the composition of the EDL structure (**Figure 3d**). The effect of NTA^{3-} anion on Zn^{2+} plating/stripping at the ZMA was also confirmed by the observation of the self-corrosion behavior of ZMAs. After a 10-day immersion in the different electrolytes, the Zn foil in the $ZnSO_4$-Na_3NTA electrolyte remains flat and glossy than that of the $ZnSO_4$ electrolyte (**Figure 3e**). More importantly, a free H_2O-poor EDL is more favourable to the formation of a well-defined (002) texture structure. For example, when the cationic HQA was added to the $ZnSO_4$ electrolyte. The preferentially adsorbed cationic HQA not can only form a water-poor EDL to inhibit HER and promote the uniform distribution of Zn^{2+} ions but also promotes the parallel growth of zinc with a preferred orientation along the (002) plane, thereby achieving dendrite-free deposition (**Figure 3f**).[76]

Additionally, adding large metal cations with better zincophilic properties is beneficial for creating a water-poor EDL structure due to the stronger steric effect.[77] For instance, when the cerium chloride ($CeCl_3$) additive was employed in the aqueous $ZnSO_4$ electrolyte, Ce^{3+} can absorb on the ZMA surface to produce an H_2O-poor EDL owing to the larger size and better zincophilic property.[77] To demonstrate the zincophilicity of Ce^{3+}, the adsorption energy of Ce^{3+}, H_2O, and Zn^{2+} on Zn (002) and (100) surface was revealed by the DFT calculation. The calculation results shows that the binding energies of Ce^{3+} ions on Zn (002) and (100) are –2.74 and –2.98 eV, respectively. These values are substantially lower than those for H_2O and Zn^{2+}. As such, the Ce^{3+} will preferentially adsorb on the ZMA surface, which can not only decrease the H_2O content near the ZMA surface to eliminate side reactions but also promote uniform Zn plating. Therefore, the large-sized ions like bulky anions and large metal cations have stronger steric effects since they could strongly disrupt the H-bond network of water and suppress HER and side reactions. Adding these additives with large ionic sizes into aqueous electrolyte based

on the steric effect prove to be an effective strategy in stabilizing Zn anode electrodes for AZMBs.

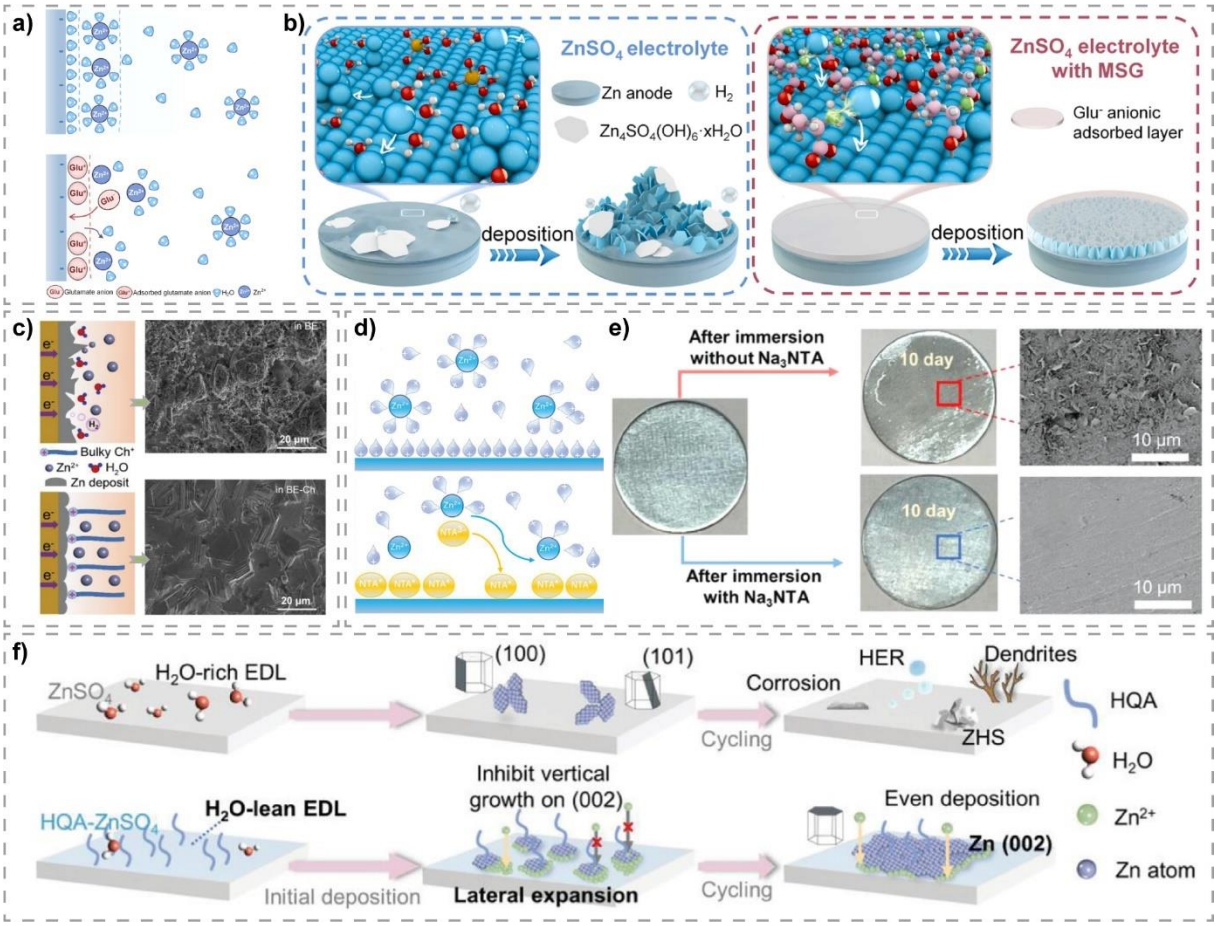


Figure 3. Examples of the steric effect in IHP for a free water-poor EDL. (a) Schematic illustration of EDL structure in electrolyte without and with glutamate anion (b) Schematic of Zn/electrolyte interface behaviors during Zn deposition in $ZnSO_4$ and $ZnSO_4$ electrolyte with Glu^-. Reproduced with permission from ref.[73] Copyright 2022, Elsevier. (c) Schematically illustrating the Zn interface chemistry and SEM images of the cycled Zn electrodes (recovered from Zn//Zn cells) in BE and BE-Ch^+. Reproduced with permission from ref.[70] Copyright 2022, Wiley. (d) Schematic of EDL structure and (e) Optical images and SEM images of polished Zn before and after 10-day immersion in $ZnSO_4$ electrolytes with/without Na_3NTA. Reproduced with permission from ref.[75] Copyright 2023, Wiley. (f) Schematic illustration of zinc deposition mechanism in $ZnSO_4$ electrolytes with and without cationic HQA. Reproduced with permission from ref.[76] Copyright 2023, Wiley.

3.2 Electrostatic shielding effect in OHP for tunning the local electric field of EDL

The OHP plays an important role in the Zn plating/stripping of ZMAs since any component of OHP could participate in the electrochemical process of Zn plating/stripping. In particular, the OHP can be affected by the ionic additives through the electrostatic shielding effect enabled by the charge attribute of ionic additives. The electrostatic shielding effect, a prevalent cationic phenomenon, results from the preferential adsorption of cationic additives in the Helmholtz plane of ZMA.[78] This gives rise to the formation of a cationic screen layer that affects the composition of EDL and homogenizes the electric field strength near the ZMA. The electrostatic shielding effect can efficiently inhibit the growth of Zn dendrites and suppress side reactions of ZMAs. Recently, numerous metal cation additives introduced into aqueous $ZnSO_4$ electrolytes, including Li^+,[79] Mg^{2+},[80] Mn^{2+}, La^{3+},[81] Ce^{3+},[82] Y^{3+},[83] Sc^{3+},[84] and Al^{3+} ions,[85] have been reported to improve the stability and reversibility of ZMAs through the electrostatic shielding effect.

Generally, the surface of commercial zinc metal foil is irregular at the atomic level. Many defects such as dislocations, grain boundaries, cracks, and residual stresses result in the Zn foil with a higher surface energy. When the Zn metal is in contact with the aqueous electrolyte, these locations are more likely to be corroded. This will aggravate the irregularity of the ZMA surface and cause an uneven electric field distribution at the interfacial EDL.[86] When the irregular ZMA surface is exposed to a non-uniformly distributed electric field, Zn^{2+} ions preferentially deposit on the original protrusions because of the more favorable reduction thermodynamics. This can give rise to the formation of numerous dendrites during the initial Zn plating stage.[87] Furthermore, the surface passivation layer including the $Zn_4SO_4(OH)_6 \cdot xH_2O$, $Zn(OH)_2$, and ZnO produced from the reaction of active Zn and the aqueous electrolyte at the EDL region is insulating and loose. Such a passivated layer accumulated on the ZMA surface can increase the roughness, resulting in a more uneven surface electric field and Zn ions flux that triggers the formation of Zn dendrites. The electrostatic

shielding layer formed by the cationic additive can fundamentally alter the interfacial EDL by optimizing electric field distribution during Zn plating/stripping. For instance, as shown in **Figure 4a**, the ZMA shows obvious dendrite growth in the common aqueous $ZnSO_4$ electrolyte during the repeated charging/discharging process owing to the irregular Zn nucleation and dendritic growth on the ZMAs caused by the uneven surface electric field. The uneven surface electric field will also result in a serious side reaction because the Zn dendrites have a higher surface energy. Besides, the strong electric field at the tips can also accelerate the growth of initially formed dendrites. However, when Mg^{2+} ions are added to the $ZnSO_4$ electrolyte, Mg^{2+} ions can accumulate around the Zn dendrites to form an electrostatic shield layer. This effectively reduces the local strong electric field, resulting in a more uniform electric field distribution that can suppress Zn dendrites formation.[80] Furthermore, the diffusion barrier of Zn^{2+} ions around these adsorbed Mg^{2+} ions is higher than the region of the low electric field. As such, Zn^{2+} ions will not continue to accumulate at the dendrite but instead will deposit on the adjacent flat surfaces. This reduces the concentration of Zn^{2+} ions around Zn dendrites and inhibits dendrite growth. As a result, the ZMA in the aqueous $ZnSO_4$ electrolyte with Mg^{2+} ions shows a flat morphology after the repeated charging/discharging process.

The electrostatic shielding effect enables some trivalent metal cation additives to be more effective in improving the reversibility of ZMAs for AZMBs due to the higher charge density. For example, Li *et al.* found that introducing $Ce_2(SO_4)_3/La_2(SO_4)_3$ into an aqueous $ZnSO_4$ electrolyte can significantly improve the cycling stability of ZMAs.[82] They proposed a new mechanism to explain the zinc nucleation and plating on ZMAs owing to the electrostatic shielding effect of Ce^{3+}/La^{3+} ions. As presented in **Figure 4b**, the high charge density enables the Ce^{3+}/La^{3+} ions to first occupy the active sites for Zn nucleation. The latent sites distributed on unstripped areas will be more active. As such, the zinc, therefore, nucleation and growth at other relatively inert areas. As plating goes by, Ce^{3+}/La^{3+} tend to occupy the active sites with a stronger electric field formed during the deposition process. This promotes zinc nucleation from

instantaneous nucleation to progressive nucleation. Such nucleation can not only effectively suppress strong electric fields on Zn tips but also guide the uniform Zn plating/stripping. In addition, Hu *et al*. reported that the introduction of $CeCl_3$ into the $ZnSO_4$ electrolyte can effectively inhibit Zn dendrite growth and HER.[77] The Ce^{3+} additive can preferentially and selectively adsorb on the surface of the ZMAs to form a dynamic electrostatic shielding layer. This functional layer significantly reduces the charge transfer resistance of Zn plating and HER rate, enabling Zn^{2+} to be deposited on the smooth region of ZMA (**Figure 4c**). The ZMA cycled in the presence of Ce^{3+} showed a smoother surface than that cycled in bare $ZnSO_4$ electrolytes (**Figure 4d**). Notably, the Zn||Zn cell assembled with Ce^{3+}-modified $ZnSO_4$ electrolyte exhibit excellent cycle stability of 170 h at a current density of 40 mA cm^{-2} under a high capacity of 10 mAh cm^{-2} (**Figure 4e**). Recently, a Y^{3+}-modified $ZnSO_4$ electrolyte ($ZnSO_4/Y^{3+}$) was investigated to show the electrostatic shielding effect of Y^{3+} ions. The Y^{3+} ions with a lower reduction potential and can selectively occupy the active sites on the surface of ZMAs (**Figure 4f**).[83] As shown in **Figure 4g**, the Y^{3+} ions can be aggregated on the protuberance of ZMAs in the $ZnSO_4/Y^{3+}$ electrolyte. The adsorbed Y^{3+} causes a strong electrostatic shield effect on ZMA, enabling Zn^{2+} to deposit at the region with a weak electric field. Consequently, the electrostatic shielding effect of Y^{3+} promotes Zn deposition with a flat and dense deposition morphology.

In addition, some nonmetallic cation additives, such as NH_4^+,[88,89] and TBA^+ (tetrabutylammonium)[90] also show an obvious electrostatic shielding effect on improving Zn plating/stripping on ZMAs. These ions can preferentially adsorb on the ZMA than Zn^{2+} and form an electrostatic shielding layer. For example, the NH_4I,[89] NH_4OAc,[88] and tetrabutylammonium sulfate (TBA_2SO_4)[90] have been also employed as effective additives in aqueous electrolytes to improve Zn plating/stripping through the electrostatic shielding effect. However, not every cationic additive offers effective electrostatic shielding or enhances the lifespans of the ZMAs. The efficacy of the electrostatic shielding effect is closely related to the

valence state, size, solvation structure of the ions and adsorption energy on Zn metal. Previous studies indicated that metal cations with higher valence, lower adsorption energy, and lower standard redox potential than Zn/Zn^{2+} are more favorable through an electrostatic shield effect. A higher valence state would repel coming Zn^{2+} more effectively (**Figure 4h**). A lower bonding energy would preferentially adsorb on the active sites of ZMAs. Therefore, the cation additives with the above-mentioned features, such as Mg^{2+}, Y^{3+}, and Ce^{3+} enable favorable Zn plating with a denser and more uniform structure. Besides, metal cations with a rigid solvation shell general show a stronger electrostatic shielding effect.[85] The shell rigidity can be quantified by the rate constant of the exchange reaction (k_{ex}). As shown in **Figure 4i**, a labile solvation shell (high k_{ex}) could be easily perturbed by foreign components. However, a rigid solvation shell (low k_{ex}) is more effective to prevent Zn ions from being deposited on the protruding tips from the surface of the ZMAs (**Figure 4j**). This is favorable for alleviating the dendritic growth and modulating Zn plating/stripping. Therefore, the introduction of higher valence, larger size, and rigid solvation shell cations into the electrolyte provides effective electrostatic shielding that can give rise to the denser and more uniform Zn deposition on the ZMAs.

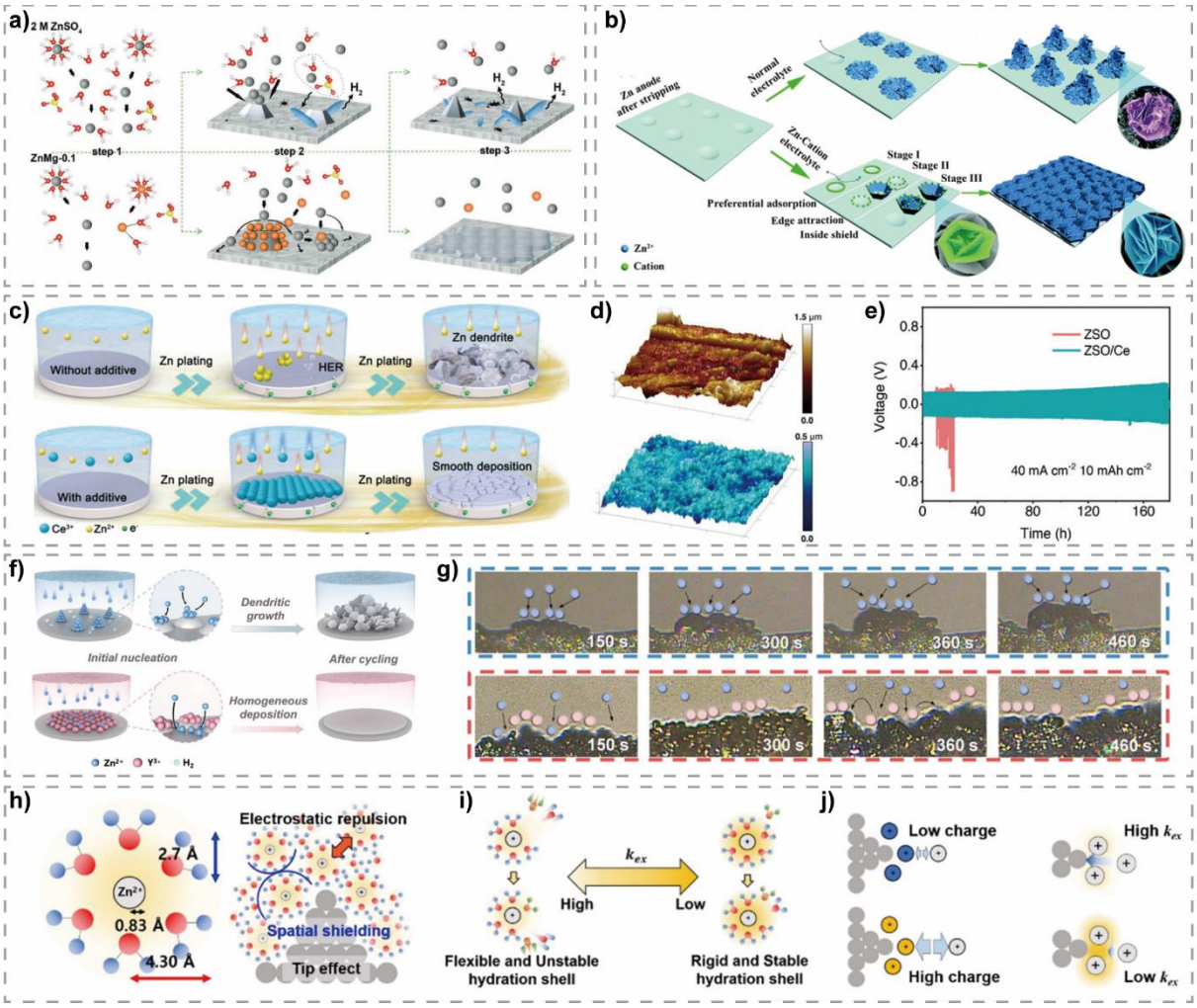


Figure 4. Examples of electrostatic shielding effect in OHP for tunning the local electric field of EDL. (a) Schematics of the Zn plating process in the 2.0 M $ZnSO_4$ (top row) and ZnMg-0.1 (bottom row) electrolyte. Reproduced with permission from ref.[80] Copyright 2021, Wiley VCH. (b) Schematic illustration of zinc deposition on the zinc foil after stripping in normal and Zn-Ce electrolytes. Reproduced with permission from ref.[82] Copyright 2021, RSC. (c) Schematic illustration of the effect of $CeCl_3$ additive on the Zn deposition process. (d) AFM images of the cycled Zn in the ZSO electrolyte and ZSO/Ce electrolyte. (e) Galvanostatic voltage profiles of a Zn–Zn symmetric cell cycled in ZSO electrolyte and ZSO/Ce electrolyte for plating/stripping 10 mAh cm^{-2} per cycle at current densities of 40 mA cm^{-2}. Reproduced with permission from ref.[77] Copyright 2022, Wiley VCH. (f) Schematic illustration of the effect of Y^{3+} ions additive on the Zn deposition process. (g) In situ microscopy images of Zn plating process in ZSO and ZSO/Y^{3+} electrolytes. Reproduced with permission from ref.[83]

Copyright 2023, Elsevier. (h-j) Effect of key parameters of redox-inactive cationic additives on electrostatic shielding effect. Reproduced with permission from ref.[85] Copyright 2022, Wiley.

3.3 Entropy effect in DP for regulating the hydration structure of EDL

The electrochemical Zn plating/stripping on ZMAs is highly related to the hydration structure of Zn^{2+} ions. Generally, the ionic additives in the bulk aqueous matrix electrolyte will interact with the Zn^{2+}, water, and anions as well owing to the entropy effect. This could alter the hydration structure of Zn^{2+} ions and influence interfacial EDL behaviors like ionic distribution, charge transfer, and phase transition. For instance, during the Zn plating process, the hydration structure of $[Zn(H_2O)_6]^{2+}$ will change, including the rearrangement or partial/complete removal of the hydration shell process. These processes not only affect the thermodynamics of the charge transfer kinetics of $[Zn(H_2O)_6]^{2+}$ but also cause the change of free water within the interfacial EDL.[38,91]

Previous reports suggest that certain ionic additives significantly influence the Zn^{2+} solvation structure. These ions can alter the water molecules in the $[Zn(H_2O)_6]^{2+}$ solvation shell, weaken the Zn^{2+} solvation effect, and promote desolvation kinetics. Consequently, the regulated Zn^{2+} solvation structure gives rise to the Zn plating with improved Coulombic efficiency and cycling stability. In particular, introducing metal cations (e.g., Mg^{2+} and Li^{+} ions) with a high affinity for water molecules into the aqueous $ZnSO_4$ electrolyte can also influence the Zn^{2+} solvation structure. These cations can influence the solvation structure of Zn^{2+} ions by sharing the surrounding solvated H_2O and SO_4^{2-}. For instance, when LiCl is introduced as an additive into the $ZnCl_2$ electrolyte, the Li^{+} can capture part of the H_2O molecules and decrease the solvation degree of Zn^{2+} ions. This will decrease the concentration of free water within the EDL region. This will inhibit the HER and induce uniform Zn plating on ZMAs (**Figure 5a**).[92] Another study reported that when $MgSO_4$ was introduced into the $ZnSO_4$ electrolyte, the Mg^{2+} and Zn^{2+}

ions share the surrounding solvated H_2O and SO_4^{2-} because Mg^{2+} ions have a much stronger binding interaction with water molecules than Zn^{2+} ions (**Figure 5b**).[80] As a result, water molecules can be easily removed from the solvation shell of the hydrated Zn^{2+} ions. This is beneficial for promoting the electrochemical reduction kinetics and suppressing side reactions on ZMA for improving the Coulombic efficiency and stability of ZMAs.

The species and concentration of anions can also significantly influence the solvation structure of Zn^{2+} ions owing to the different ion correlations and interactions with water. previous reports indicate that bulky salt anions with electro-withdrawing groups in electrolytes can effectively reduce the number of hydration water molecules in the $[Zn(H_2O)_6]^{2+}$ structure. This disrupts the original hydrogen bond network, resulting in the passivated water molecules, and suppressed HER and corrosion reactions.[93] For example, when different zinc salts were used as electrolytes, the ZMA showed a longer cycle life and higher Coulombic efficiency in aqueous $Zn(CF_3SO_3)_2$ electrolytes than in aqueous $ZnSO_4$, $ZnNO_3$, and $ZnCl_2$ electrolytes.[94] This is because $CF_3SO_3^-$ interacts more strongly with water molecules compared to SO_4^{2-}, NO_3^-, and Cl^-, thereby weakening the interaction between Zn^{2+} and hydrated water molecules. Additionally, partial hydrated water in $[Zn(H_2O)_6]^{2+}$ structure can be replaced by the $CF_3SO_3^-$ owing to a strong interaction of $CF_3SO_3^-$-Zn^{2+} coordination compared to that of H_2O-Zn^{2+} (**Figure 5c**). This can reduce the number of water molecules owing to the desolvation process of $[Zn(H_2O)_6]^{2+}$, thereby inhibiting the side reactions involved with water molecules.[44] Similarly, the solvation structures of Zn^{2+} and the hydrogen bonding network of H_2O molecules in the $Zn(TFSI)_2$ electrolyte differ significantly from those in the aqueous $ZnSO_4$ electrolyte.[95] In the typical aqueous $ZnSO_4$ electrolyte, Zn^{2+} ions are coordinated by water molecules through Zn-O bonds, forming $[Zn(H_2O)_6]^{2+}$ solvation structure. The SO_4^{2-} anions do not participate in the interior coordination shell of Zn^{2+} ions but reinforce the hydrogen bonding network of H_2O. While in $Zn(TFSI)_2$ electrolyte, the bulky $TFSI^-$ anions and H_2O molecules both exhibit strong bonding strength with Zn^{2+} ions (**Figure 5d**). The N and O atoms in the

$TFSI^-$ anion can bond directly with partially solvated Zn^{2+} ions, reducing the number of hydrated H_2O molecules in the Zn^{2+} solvation shell. Additionally, $TFSI^-$ anions, with a more even charge distribution, exhibit weaker bonding energy for Zn^{2+} in aqueous electrolytes, facilitating the Zn^{2+} desolvation process.[40]

In addition to bulky organic anions, halogen ions (Cl^-, Br^-, and I^-) have been shown to affect the Zn^{2+} hydration structure.[96] Halogen ions can replace the water molecule in $Zn(H_2O)_6^{2+}$ to form a Zn^{2+} solvation shell containing halogen ions due to their stronger coordination ability with Zn^{2+} ions. For example, a reported chloride salt with bulk cation (ethyl-3-methylimidazolium chloride) additive in $ZnSO_4$ electrolytes can release the bound water in $Zn(H_2O)_6^{2+}$ and form an anion-type solvation structure $ZnCl_4^{2-}$ (**Figure 5e**).[71] Compared to solvated Zn^{2+} ions in the $ZnSO_4$ electrolyte (**Figure 5f**), owing to the electrostatic repulsion between Zn tips and anion-type solvation structure $ZnCl_4^{2-}$, the plated Zn showed a uniform and flat morphology. Furthermore, Zhang *et al.* found that the electron-donation anion I^- and Br^- in aqueous electrolytes can coordinate with Zn^{2+} to form halogen ions participating in solvation structure $ZnI(H_2O)_5^+$ and $ZnBr(H_2O)_5^+$, respectively.[89] The negatively charged I^- and Br^- can transfer electrons into Zn^{2+}, which reduces the electron loss of water molecules and improves the stability of water molecules (**Figure 5g**). As a result, in the electrolyte with I^- or Br^-, Zn plating shows an evenly distributed and smooth structure on the Cu substrate, and the Coulombic efficiency of Zn plating/stripping reaches 99.8% after several cycles and remains stable over 100 cycles. This indicates the high stability and reversibility of Zn plating/stripping in the presence of halogen ionic additives.

The entropy effect can enhance the homogeneous Zn^{2+} diffusion and the suppressed direct contact of active water with Zn anodes owing to the changed solvation structure of Zn^{2+} enabled by the entropy increase in the presence of ionic electrolyte additive. It is worth noting that the entropy effect can be related to the concentration of electrolyte salts or additives. As the concentration of ionic electrolyte additive increases, the solvation shell of anions and cations

can highly interplay, resulting in the formation of anion-involved solvation structure. However, a high concentration of electrolyte additive may cause negative effects because of the completely changed solvation structure of the intrinsic electrolyte. Besides, a high concentration of additives increases the cost and may cause environmental issues, making them unsuitable for large-scale practical applications. Therefore, it is necessary to quantify the influence of moderate ionic additives on the solvation structures of bulk electrolytes.

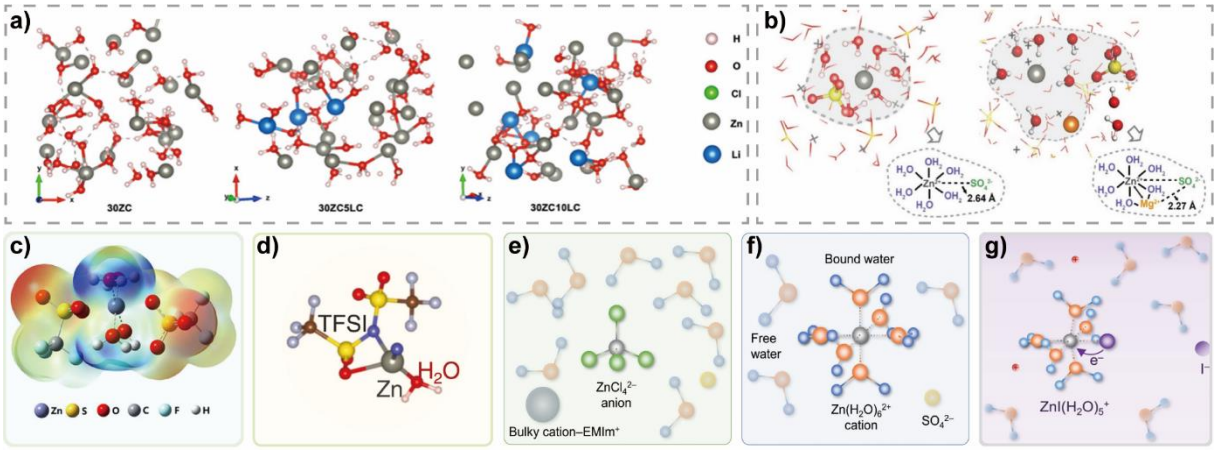


Figure 5. Entropy effect in diffusion plane for regulating the hydration structure of EDL. a) Ab initio molecular dynamics simulation studies. Reproduced with permission from ref.[92] Copyright 2020, Wiley. b) Molecular dynamics simulations of 2.0 M $ZnSO_4$ (left) and ZnMg-0.1(right). Reproduced with permission from ref.[80] Copyright 2021, Wiley-VCH GmbH. c) Molecular electrostatic potential map of $Zn(OTf)_2(H_2O)_4$ formed in the aqueous $Zn(OTf)_2$ electrolyte based on DFT calculations. Reproduced with permission from ref.[44] Copyright 2020, Wiley. d) Solvation structures of Zn^{2+} ions and neighbouring $TFSI^-$ anions. Reproduced with permission from ref.[40] Copyright 2021, Elsevier. e) The anion-type water-free Zn^{2+} solvation structure in the electrolyte containing $EMIm^+$ and Cl^- (right). f) The solvation structure of Zn^{2+} in the conventional $ZnSO_4$ electrolyte. Reproduced with permission from ref.[71] Copyright 2021, Wiley-VCH GmbH. g) In the I^- participating solvation structure electrolyte, the I^- injects electrons to stabilize the solvation structure. Reproduced with permission from ref.[89] Copyright 2022, American Chemical Society.

3.4 Chemical effect in EDL for in situ construction of favorable SEI

Similar to Li-ion batteries, the solid electrolyte interphase (SEI), in situ produced from the reaction between the ZMA and the aqueous electrolyte during the initial charge and discharge, plays a critical role in the electrochemical performance of ZMAs.[97] Since the EDL forms before the in-situ formation of SEI at the interface between the ZMA and the aqueous electrolyte, the initial EDL structure and composition play a critical role in the interface chemistry of SEI. Generally, SEI acts as a proficient ionic conductor and an electrical insulator, preventing direct contact between the ZMA and the electrolyte. As such, SEI has the dual function of protecting the ZMA from corrosion and inducing uniform Zn plating, which plays a crucial role in stabilizing the metal electrode/electrolyte interface. [98]

Generally, the pristine SEI formed on ZMAs is loose, unstable, and prone to degradation, which hinders uniform Zn plating.[99] Hence, constructing an artificial SEI is an effective strategy to protect the ZMA.[100] The strategy of in situ construction of an artificial SEI using electrolyte additives has attracted increasing attention. The competitive adsorption of ionic additives in IHP is highly related to the composition and structure of SEI. As such, the in-situ formation of a favorable SEI layer can be facilitated by the decomposition of additives ions in electrolytes. For example, when saccharin (Sac) is introduced into $ZnSO_4$ electrolytes, Sac anions can chemically adsorb on the ZMA surface and be decomposed during the charging/discharging process to form an SEI composed of ZnS and $ZnSO_4$. The resultant SEI prevents H_2O from coming into contact with the ZMA and restricts the random diffusion of Zn^{2+} ions on the ZMA. Such SEI enables the Zn//Zn symmetric cell to achieve an ultra-long cycle life of 550 h at a current density of 10 mA cm^{-2} with a capacity of 10 mAh cm^{-2}.[72]

In addition, a favorable SEI layer can be in situ formed from the reactions between Zn^{2+} ions and ionic additives in the electrolyte. For example, when 20 mM $Zn(NO_3)_2$ additive was introduced into an aqueous 3.0 M $Zn(OTF)_2$ electrolyte, an electrically and ionically resistive $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ passivation layer was formed on ZMA through the reaction with NO_3^-

and OH^-.[101] This passivation layer can restrain water decomposition by isolating active H_2O from ZMA. During the subsequent cycling process, the $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ passivation layer gradually transitions into a Zn-ion conducting $Zn_5(CO_3)_2(OH)_6$ layer (**Figure 6a**). This transformation effectively suppresses HER and corrosion while facilitating the reversible Zn plating/stripping. In another study, introducing a small amount of $Zn(H_2PO_4)_2$ salt into $Zn(CF_3SO_3)_2$ can promote the formation of a dense and uniform SEI layer of $Zn_3(PO_4)_2 \cdot 4H_2O$ that can effectively protect the Zn anode from corrosion.[102] This SEI layer of $Zn_3(PO_4)_2 \cdot 4H_2O$ formed from the reaction among Zn^{2+}, OH^-, and $H_2PO_4^-$ has high interfacial stability, a high Zn^{2+} transference number, and high Zn^{2+} ion conductivity (**Figure 6b**). Thus, such SEI not only helps reduce the locally high concentrations of OH^-, mitigating corrosion but also ensures uniform and rapid Zn^{2+} transport kinetics, inhibiting the growth of Zn dendrites. Similarly, by using KPF_6 as an aqueous electrolyte additive, a hybrid SEI composed of $Zn_3(PO_4)_2$ and ZnF_2 was produced in situ on the ZMA.[103] PF_6^- is thermodynamically unstable in water and easily generates reactive acidic compounds. Thus, the ZMA can spontaneously react with the PF_6^--derived reactive acidic compounds to form the hybrid SEI (**Figure 6c**). This hybrid SEI significantly reduces the nucleation overpotential, suppresses HER and corrosion, and promotes uniform Zn^{2+} distribution and plating/stripping. Overall, the chemical effects regulate the composition and structure of SEI through the competitive chemically adsorption of ionic additives on the ZMA surface or the chemical reaction between ions, forming a dense, stable and uniform SEI to protect ZMA from corrosion and ensure the excellent electrochemical performance of the AZMBs.

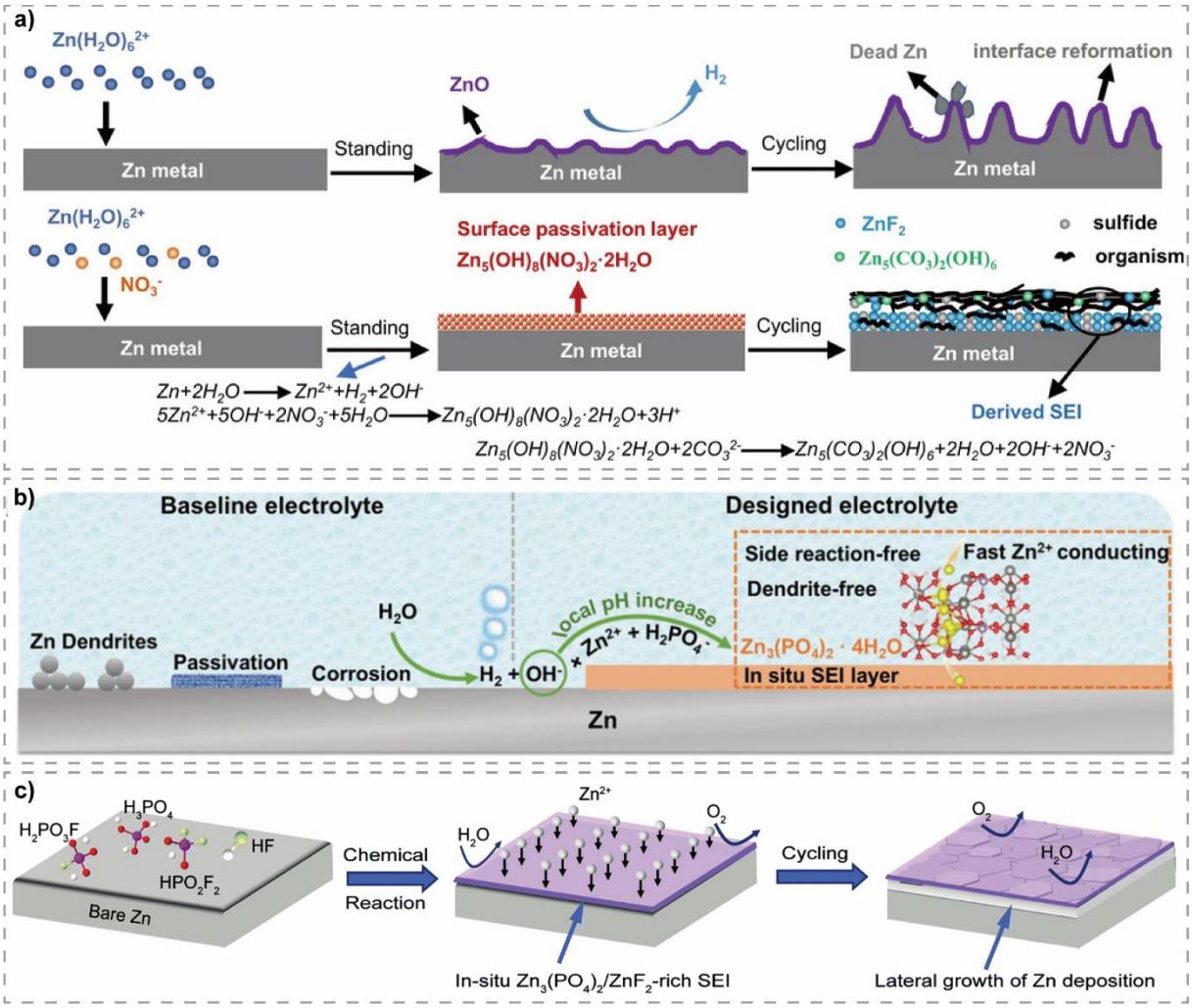


Figure 6. Examples for illustrating the chemical effect in EDL for the in-situ formation of favorable SEI on ZMAs. a) Illustration of surface evolution mechanism. Reproduced with permission from ref.[101] Copyright 2021, Wiley. b) Schematic illustration of Zn surface evolution and the SEI formation mechanism. Reproduced with permission from ref.[102] Copyright 2021, Wiley. c) Schematic illustration of the in-situ formation process of the $Zn_3(PO_4)_2$ and ZnF_2 interphase and its effect on Zn plating. Reproduced with permission from ref.[103] Copyright 2021, RSC.

3.5 Other miscellaneous effects on ZMAs

While the previously mentioned four ionic effects are categorized based on their influence on the interfacial EDL, they are not mutually exclusive, and even some multifunctional ions can achieve multiple ionic effects simultaneously.[104] These multifunctional ions are referred to

as other miscellaneous effects, often exhibiting unique properties that render them valuable in electrolyte optimization. For example, on the one hand, some ions with double function can enter the solvation shell of Zn^{2+} ions, weakening the strong interaction between Zn^{2+} ions and solvated water molecules, thus being conducive to alleviating corrosion and side reactions. On the other hand, these zinc ions can also preferentially adsorb on the zinc anode surface to guide the deposition direction of Zn on the (002) plane (**Figure 7a**) or decompose to form an in-situ SEI layer to protect the zinc anode from corrosion and homogenize ion flux (**Figure 7b**).[105–107] Therefore, the ZMA exhibits better cycling stability and higher reversibility in the electrolyte containing multifunctional ions even under more stringent testing conditions of high current density and high capacity density (**Figure 7c-7d**). Beyond the aforementioned ionic effects on ZMA electrochemistry, certain ionic additives have demonstrated specific positive effects on other aspects such as the crystal orientation of deposited Zn and the plating site for Zn^{2+}. For instance, a previous study has demonstrated that the preferential growth of specific crystal planes, such as (105), (103), and (002), of the deposited Zn can lead to the formation of a denser and smoother plating layer, which inhibits corrosion and HER to some extent.[108] However, promoting Zn plating with more exposed (002) crystal facets is intricate, necessitating pre-deposition of Zn with (002) crystal planes at a specific high current density.[86] Compared to these methods, adjusting the crystal plane orientation and texture of the deposited metallic Zn by changing the electrolyte ions is simpler and more cost-effective. For instance, in an aqueous $ZnSO_4$ electrolyte, the growth of (101) planes is predominant. However, in the $Zn(OTF)_2$ electrolyte, the dominant intensity of Zn (002) diffraction is over the highly depressed (100) and even far over that of (101) diffraction, indicating that the $Zn(OTF)_2$ electrolyte is more conducive to the growth of (002) crystal planes (**Figure 7e**).[44] In addition, several ionic additives were reported to have a great influence on the crystal orientation during the Zn plating/stripping process. For instance, Zhang and co-workers found that adding 1-butyl-3-methylimidazolium cation to 2.0 M $ZnSO_4$ promotes the preferential

growth of Zn exposed with (002) crystal plane.[109] In the $ZnSO_4$ electrolyte, Zn^{2+} ions are deposited on some tips composed of (100) and (101) crystal facets without ionic additives. The Zn dendrites are easily produced in this plating mode. However, when $BMIm^+$ cations were added to the electrolyte, they preferentially adsorb on unstable crystal faces such as (100) and (101) during the Zn plating process. This enables the Zn^{2+} ions to be deposited towards the (002) crystal plane, thereby inducing the preferential growth of (002) crystal faces of Zn and forming a dense and flat plating layer (**Figure 7f**). Wei *et al*. also proposed that when adding disodium maleate (DMA) into the traditional $ZnSO_4$ electrolyte, the adsorbed MA^{2-} anions at the ZMA surface can control the Zn texture during the electrodeposition process.[104] Benefiting from the preferential adsorption of MA^{2-} anions on the (002) plane, the MA^{2-} anions can restrain the Zn^{2+} plating along the [002] direction and promote the Zn ions to diffuse along the [100] and [101] direction, enabling the preferred (002) plane landscape orientation growth (**Figure 7g**). The deposited Zn was constructed by the hexagon-shaped Zn plate that is parallel to the substrate is a characteristic of the Zn(002) crystal plane. Notably, an increasing number of functional ions have been investigated to construct adaptive ions-influenced tunable EDL on the Zn anode interface.[107,110] The AZMBs constructed with these multifunctional ions deliver excellent cycling stability and reversibility.

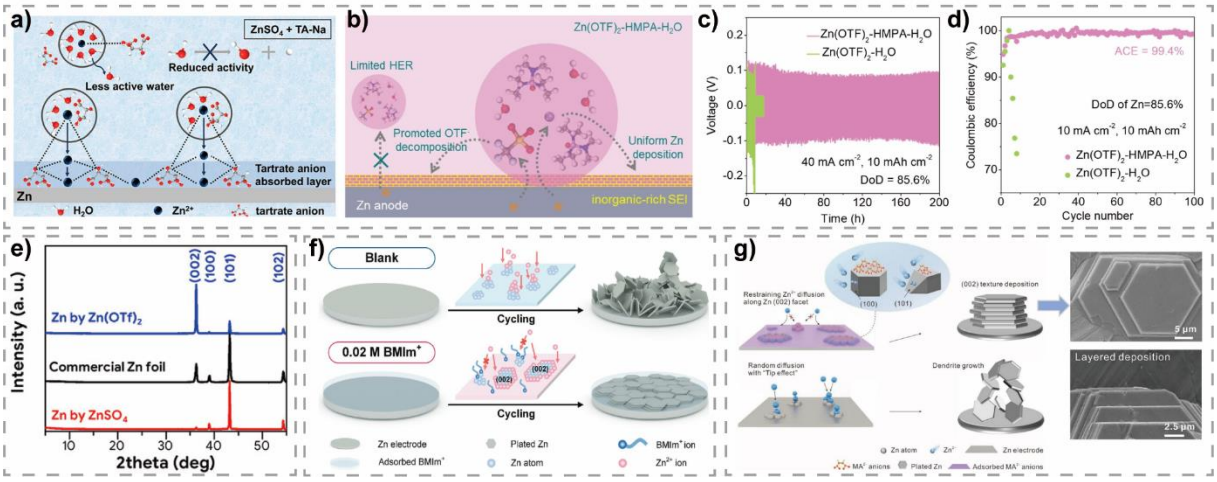


Figure 7. Examples for illustrating the other miscellaneous effects on ZMAs. a) Schematic illustration of the Zn^{2+} solvation structure and the interfacial reaction between the Zn anode and the electrolyte $ZnSO_4$ with TA-Na electrolyte. Reproduced with permission from ref.[106] Copyright 2023, ACS. b) Schematic illustration about the OTF- decomposition to form SEI. c) Cycling performance of Zn-Zn cells using $Zn(OTF)_2$ and $Zn(OTF)_2$/HMPA electrolyte at a current density of 40 mA cm^{-2} with a capacity 10 mAh cm^{-2}. d) Cycling performance of Zn-Cu cells using $Zn(OTF)_2$ and $Zn(OTF)_2$/HMPA electrolyte at 10 mA cm^{-2} of a capacity 10 mAh cm^{-2}. Reproduced with permission from ref.[105] Copyright 2023, Wiley-VCH GmbH. e) XRD spectra comparing the metallic zinc products by electroplating in 2M $Zn(OTf)_2$ and 2M $ZnSO_4$ aqueous electrolytes, with reference to the commercial Zn foil. Reproduced with permission from ref.[44] Copyright 2020, Wiley-VCH GmbH. f) Schematic of preferential growth of (002) plane induced by $BMIm^+$ ion during cycling of AZIBs; Reproduced with permission from ref.[109] Copyright 2020, Wiley-VCH GmbH. g) The schematic diagrams for Zn deposition in the electrolytes with MA^{2-}. Reproduced with permission from ref.[104] Copyright 2023, Wiley-VCH GmbH.

3.6 Design principles of ionic electrolyte additives based on the interfacial ionic effects

Herein, we briefly classify existing results from the perspective of interfacial effects on aqueous ZMAs. This classification is beneficial for gaining a deeper understanding of ion effects and screening electrolyte additives based on these effects (Table 1). However, it remains a challenge

to accurately design electrolyte additives based on interface ion effects. Based on the above discussion, we propose three potential principles for screening electrolyte additives based on ion effects, including the interaction between ions (electrostatic repulsion, electrostatic attraction), the interaction between ions and molecules (hydration effect), and the interaction between ions and the Zn anode (adsorption and electrostatic force).

The interaction between ions is a prerequisite for the electrostatic shielding effect and Steric effect. The electrostatic shielding effect arises from the mutual repulsion between cations, and a strong electrostatic repulsion force corresponds to strong electrostatic shielding effects.[111] The aggregation state and solvation structure of ions in an aqueous electrolyte are influenced by the interaction between cations and anions. The solvent-separated ion pair (SSIP) can be converted into a contact ion pair (CIP) through the strong electrostatic attraction between cations and anions.[112] Meanwhile, the partly solvated water molecules of Zn^{2+} can be replaced by anions to form different solvated structures.

The interaction between ions and water molecules could be a screening basis for designing ionic electrolyte additives with an entropy effect. The hydration structure of ions depends highly on the interaction with water molecules. A stronger hydration interaction indicates the requirement of higher energy for dehydration.[113] On the contrary, the weak hydration interaction indicates the prone of ions to be desolvated. Therefore, when ionic additives with strong interactions with water molecules are introduced into the electrolyte, the ionic additives can more easily alter the Zn^{2+} solvation structure.[114]

The interaction between ions and ZMAs is related to the adsorption energy of ions on ZMAs, which can be a screening basis for additives with electrostatic shielding effect, steric effect, and chemical effect. The inert cations with low adsorption energy can preferentially adsorb onto the ZMAs to form an electrostatic shielding layer or steric effect.[115] The intrinsically chemical-active ions with low adsorption energy adsorbed on the Zn anode may be prone to participate in chemical/electrochemical reactions and produce an in-situ SEI.[116] Although the strength

of these interactions can serve as a criterion for selecting ionic electrolyte additives, quantifying these interactions is still a challenge for experiments. Therefore, computational methodologies will be favorable for the effective screening of electrolyte additives.

Table 1 Summary of electrolyte additives, corresponding ionic effects and electrochemical performance.

Additive and ions	Base electrolyte	Ionic effect	Average CE in Zn//Cu cell (cycles, mA cm^{-2}, mAh cm^{-2})	Cycling lifespan in Zn//Zn cell (mA cm^{-2}, mAh cm^{-2})	Refs.
4.5 M choline chloride (Ch^+)	1 M $ZnSO_4$	Steric effect	99.6% (300, 0.5, 0.5)	2000 h (1.0, 1.0)	[70]
4 M 1ethyl-3-methylimidazolium chloride ($EMIm^+$)	1 M $ZnSO_4$	Steric effect	99.9% (90, 1.0, 1.0)	500 h (1.0, 1,0)	[71]
0.5g L^{-1} Saccharin (Sac^-)	2 M $ZnSO_4$	Steric effect	99.6% (50, 10, 10)	550 h (10, 10)	[72]
0.1 M Monosodium glutamate (Clu^-)	2 M $ZnSO_4$	Steric effect	99.75% (1700, 2.0, 1.0)	2200 h (2.0, 2.0)	[73]
0.01 Glucose (Glu^-)	1 M $ZnSO_4$	Steric effect	97.72% (200, 1.0, 0.5)	2000 h (1.0, 1.0)	[74]
0.005 M trisodium nitrilotriacetate (NTA^-)	2M $ZnSO_4$	Steric effect	99.75% (600, 1.0, 0.5)	3000 h (1.0, 1.0)	[75]
0.78 mM hydrophobic hyamine (HQA^-)	2 M $ZNSO_4$	Steric effect	99.7% (700, 1.0, 1.0)	1600 h (1.0, 1.0)	[76]
0.3 g L^{-1} $CeCl_3$ (Ce^{3+})	2 M $ZnSO_4$	Steric effect	99.7% (50, 10, 10)	2600 h (2.0, 1.0)	[77]
0.1 M $MgSO_4$ (Mg^+)	2 M $ZnSO_4$	Electrostatic shielding effect	/	600 h (1.0, 0.25)	[80]
8.5 mM $La(NO_3)_3$ (La^{3+})	2 M $ZnSO_4$	Electrostatic shielding effect	99.9% (2100, 2.0, 1.0)	1200 h (1.0, 1.0)	[81]
0.01 M $Ce_2(SO_4)_3$ (Ce^{3+})	1 M $ZnSO_4$	Electrostatic shielding effect	/	400 h (1.0, 1.0)	[82]
0.05 M $Y_2(SO_4)_3$ (Y^{3+})	3 M $ZnSO_4$	Electrostatic shielding effect	99.6% (300, 1.0, 1.0)	1200 h (2.0, 2.0)	[83]

0.01 M $Sc_2(SO_4)_3$ (Sc^{3+})	2 M ZnSO4	Electrostatic shielding effect	99.81% (2000, 2.0, 1.0)	2000 h (5.0, 1.0)	[84]
0.05 M NH_4OAc (NH_4^+)	2 M $ZnSO_4$	Electrostatic shielding effect	99.7% (1800, 1.0, 0.5)	3500 h (1.0, 1.0)	[88]
4 M NH_4I. (NH_4^+)	1 M $ZnAc_2$	Electrostatic shielding effect	99.8% (100, 1.0, 1.0)	/	[89]
0.05 mM tetrabutylammonium sulfate (TBA^+)	2 M $ZnSO_4$	Electrostatic shielding effect	/	300 h (2.0, 2.0, 2.0)	[90]
5 M LiCl (Li^+, Cl^-)	30 M $ZnCl_2$	Entropy effect	/	2000 h (2.0, 4.0)	[92]
0.1 M Citrate anion (Cit^{3-})	1 M $ZnSO_4$	Entropy effect	/	100 h (5.0, 1.25)	[93]
20 M LiTFSI (Li^+, $TFSI^-$)	1 M $Zn(TFSI)_2$	Entropy effect	99.7% (200, 1.0, 0.15)	170 h (0.2, 0.3)	[95]
20 mM $Zn(NO_3)_2$ (NO_3^-, OTF^-)	3 M $Zn(OTF)_2$	Chemical effect	99.4% (200, 1.0, 0.5)	1200 h (0.5, 0.5)	[101]
0.025 M $Zn(H_2PO_4)_2$ (HPO_4^-)	1 M Zn $(CF_3SO_3)_2$	Chemical effect	99.4% (400, 1.0, 3.0)	1200 h (1.0, 1.0)	[102]
0.05 M KPF_6 (PF_6^-)	2 M $ZnSO_4$	Chemical effect	99.37% (90, 4.0, 2.0)	1200 h (2.0, 4.0)	[103]
0.02 M Disodium maleate (MA^-)	2 M $ZnSO_4$	Other miscellaneous effects	99.81% (3000, 1.0, 0.5)	3200 h (1.0, 1.0)	[104]
0.01M sodium tartrate (Na^+, TA^-)	1 M $ZnSO_4$	Other miscellaneous effects	99.3% (1000, 0.2, 0.1)	1500 h (0.5, 0.25)	[106]
0.1 M YCl_3 (La^{3+}, Cl^-)	2 M $ZnSO_4$	Other miscellaneous effects	99.9% (3500, 5.0, 1.0)	3200 h (5.0, 1.0)	[115]
0.4 M zinc pyrrolidone carboxylate (PCA^-)	2 M $ZnSO_4$	Other miscellaneous effects	99.43% (700, 1.0, 1.0)	1700 h (1.0, 1.0)	[117]
0.05 M sodium gluconate (Na^+, SG^-)	2 M $ZnSO_4$	Other miscellaneous effects	99.27% (400, 0.5, 0.5)	800 h (5.0, 1.0)	[118]
volume ratios of $Zn(OTf)_2$:EMIm(OTf) =7:3 (OTF^-, $EMIm^+$)	3 M $Zn(OTF)_2$	Other miscellaneous effects	99.15% (600, 1.0, 1.0)	3000 h (1.0, 1.0)	[119]
25 mM $NH_4(H_2PO_4)$ (NH_4^+, $H_2PO_4^-$)	1 M $ZnSO_4$	Other miscellaneous effects	99.4% (1000, 1.0, 0.5)	2100 h (1.0, 1.0)	[120]

4. SUMMARY AND OUTLOOK

In conclusion, this review has provided insights into the significant role of interfacial ionic effects in the anode electrochemistry of AZMBs. We highlighted how ionic additives positively impact Zn plating/stripping behavior and reduce side reactions in the ZMAs. These effects manifest through alternations in the interfacial EDL behaviors, encompassing aspects such as water dipoles, local electric field distribution, ionic distribution and solvation structure, and SEI. As shown in **Figure 8**, we have identified five key interfacial ionic effects that regulate the EDL behavior and improve the electrochemical performance of AZMBs. These include the steric effect in IHP, the electrostatic shielding effect in OHP, the entropy effect in the diffusion plane, the chemical effect for in situ SEI construction, and various other mechanisms. These ionic additives have shown remarkable potential in promoting dendrite-free and stable Zn plating/stripping, pivotal for the practical applications of AZMBs.

Despite significant advancements, current research is still in its nascent stages. Current studies have been limited in scope and there's a need for a deeper understanding of the exact mechanisms since the EDL is highly heterogeneous and dynamic. Future great efforts are expected to be imperatively devoted to further understanding and harnessing the ionic effects in AZMBs by the following aspects.

(1) Probing EDL structure and dynamics at the atomic level: A more nuanced exploration of the dynamic EDL evolution at the atomic level is needed to reveal the exact mechanism. Although the interfacial ionic effect is effective for relieving dendritic growth and side reactions on ZMAs, understanding the exact mechanism at the atomic level remains unclear. Since any ionic additive can influence the ionic structure and EDL behaviors, more future efforts are expected to reveal how the ionic additives affect the interfacial EDL structure and composition of the ZMAs at the atomic level. Advanced characterization techniques like Operando Fourier transform infrared spectroscopy, nuclear magnetic resonance spectroscopy, and X-ray absorption fine structure spectroscopy, could be explored to probe the microscopic details of

the interfacial EDL under realistic conditions. In addition, the interfacial EDL and Zn plating/stripping behavior show dynamic changes during the charging/discharging process of AZMBs. It will be necessary to reveal the time-dependent EDL structure/composition and electrochemical process of AZMBs by Operando electroanalytical and spectroscopic methods with a high temporal-spatial resolution like electrochemical impedance spectroscopy.[121] Various multiscale theoretical calculations such as DFT calculations and MD simulations, finite element methods, and machine learning are also expected to be further explored and combined to gain a comprehensive understanding of the atomic details of interfacial EDL the underlying mechanisms of electrolyte regulation from the theoretical modeling aspect. Moreover, the combined experimental characterizations and theoretical calculations will be instrumental in this pursuit as this provides a more profound comprehension of the interplay of ionic additives with the EDL structure and composition and the electrochemical performance of AZMBs.

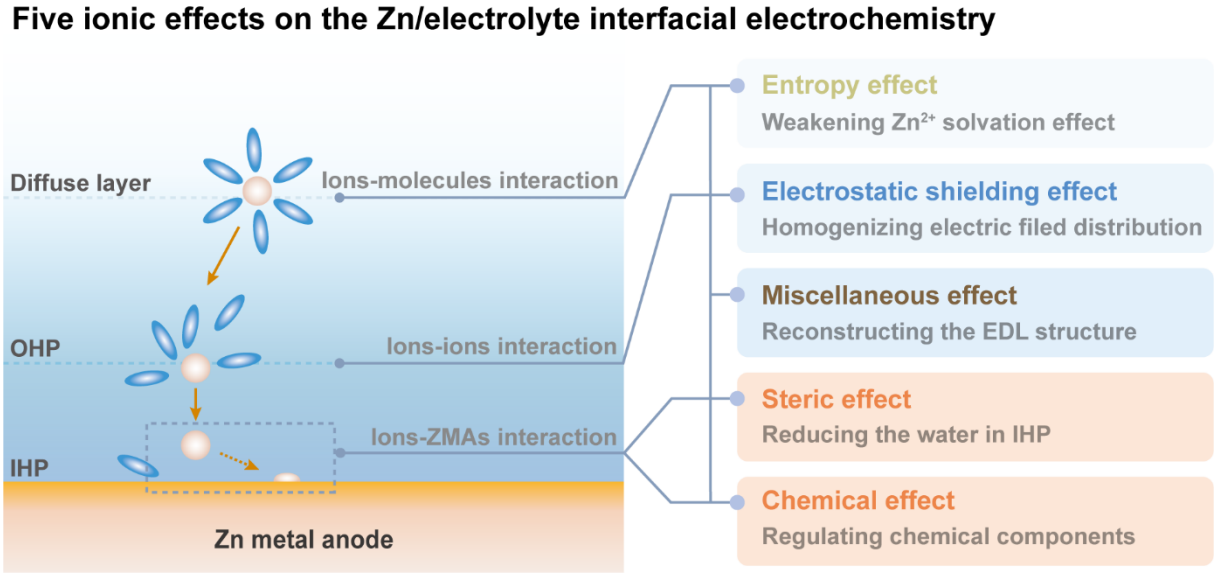


Figure 8. Summary of the interfacial ionic effects on the anode electrochemistry for AZMBs.

(2) Developing multifunctional ionic additives: Future studies should also aim at developing multifunctional ionic additives that provide synergistic effects. The ionic additives in the electrolyte are also expected to influence the properties of bulk electrolytes and the overall electrochemical performance of AZMBs. Previous studies indicated that the synergistic effects

among ionic additives and bulk electrolytes can give rise to the much better electrochemical performance of ZMAs. For instance, Wang *et al*. demonstrated the synergistic effect of cation additives and anions in breaking the hydrogen bond network of primordial water molecules. They developed a mixed aqueous electrolyte of 3.5 M $Mg(ClO_4)_2$ and 1.0 M $Zn(ClO_4)_2$ for ZMAs. The presence of the oxygen ligand (Mg^{2+}) and the hydrogen ligand (ClO_4^-) significantly reduces the proportion of hydrogen bonds in water molecules and lowers the freezing point of electrolyte to –121 °C, enabling the AZMBs to stably work under extreme temperatures.[122] In addition, we need to systematically optimize various parameters such as solubility, pH, chemical/electrochemical stability, cost, volatileness, toxicity, flammability, the concentration of ionic additives, and compatibility with the cathode of the AZMBs. Notably, the volatile, toxic, flammable, and expensive reagents should be avoided from being used as electrolyte additives. Theoretical modelling and machine learning can accelerate the discovery of such additives.

(3) Exploring ionic effect in non-aqueous ZMBs: The interfacial ionic effect in non-aqueous ZMBs warrants exploration, given their wider voltage windows and similar challenges as aqueous systems. Since the Zn plating/stripping process on ZMAs in the non-aqueous electrolyte is also mediated by interfacial EDL, the above-mentioned ionic effect on the anode electrochemistry of non-aqueous ZMBs could also work. Therefore, systematic studies on ionic effects in such environments could lead to significant improvements in ZMB performance. For example, Raze *et al*. report N, N-dimethyl formamide (DMF) based non-aqueous electrolyte containing Cu^{2+} ions as an additive (Cu^{2+}-DMF) for ZMA with improved performance.[123] However, the electrochemical process, the interfacial EDL behavior, and the electrochemical thermodynamics and kinetics in non-aqueous electrolytes could be much more complicated. Only a few studies reported the use of ionic additives to promote Zn plating/stripping of ZMAs in non-aqueous ZMBs. Thus, more exploration of ionic effects for non-aqueous ZMBs is expected in future studies.

(4) Advancing ZMA and ZMB design: The development of advanced ZMAs and ZMBs can be incorporated with the interfacial ionic effect. Since the interfacial EDL is also highly related to the structure and composition of the ZMA, the design of advanced ZMAs also enables us to better understand the ionic effects on the interfacial EDL behavior. For instance, incorporating other emerging materials like graphene, metal-organic framework, and covalent organic framework as an external functional framework to construct advanced Zn-based composite anodes, the nanoconfined electrolyte environment created by those materials could also dramatically change the EDL behaviors and ionic effects due to the magnified short-range interactions between ion-ion, ion-solvent, and ion-electrode.[124,125] This could enable more favorable material platforms to study and expand the ionic effects on ZMAs. Furthermore, the construction of novel ZMBs based on ZMAs could be a promising strategy to delve into interfacial ionic effects. For example, the Zn-air desalination device not only allows energy-efficient removal of ions from seawater but also shows promising applications for studying ionic effects on ZMAs.[126] The ionic effect has been demonstrated to improve the overall electrochemical performance of electrochemical devices based on ZMAs. This also enables us to probably design new electrochemical devices based on ZMAs by coupling the specific function of ionic additives. For example, the stability of Zn-air batteries can be suppressed by the addition of alcoholic and ionic ligands, giving rise to longer cycling life.[127] The ZMAs have also been explored for efficient electrochemical desalination and desalination batteries and desalination fuel cells.[113] The ionic effect can be further harnessed to improve the overall performance of these new electrochemical devices. Works in this field are still in progress, and more innovative efforts and rational designs are highly required in future studies.

In summary, while progress has been made in understanding and harnessing interfacial ionic effects in AZMBs, the field remains ripe for further exploration and innovation. Addressing these challenges will be significant to advancing the practical application of ZMBs.

ACKNOWLEDGEMENTS

The authors thank the financial support from the Natural Science Foundation of Jiangxi province (No. 20232ACB214001), Research Projects of Ganjiang Innovation Academy (No. E355F003) of the Chinese Academy of Sciences, and the Research fund from the Chinese Academy of Sciences. The authors also thank the Australian Research Council for financial support (FL180100029 and DE190100445).

REFERENCES

[1] Q. Cao, H. Gao, Y. Gao, J. Yang, C. Li, J. Pu, J. Du, J. Yang, D. Cai, Z. Pan, C. Guan, W. Huang, Regulating Dendrite-Free Zinc Deposition by 3D Zincopilic Nitrogen-Doped Vertical Graphene for High-Performance Flexible Zn-Ion Batteries, Adv. Funct. Mater. 31 (2021) 2103922. https://doi.org/10.1002/adfm.202103922.

[2] Z. Zhao, J. Zhao, Z. Hu, J. Li, J. Li, Y. Zhang, C. Wang, G. Cui, Long-life and deeply rechargeable aqueous Zn anodes enabled by a multifunctional brightener-inspired interphase, Energy Environ. Sci. 12 (2019) 1938–1949. https://doi.org/10.1039/C9EE00596J.

[3] K. Jiang, X. Wen, Y. Deng, Z. Zhou, Q. Weng, Integration of all-printed zinc ion microbattery and glucose sensor toward onsite quick detections, SusMat 2 (2022) 368–378. https://doi.org/10.1002/sus2.59.

[4] L. Han, H. Huang, J. Li, X. Zhang, Z. Yang, M. Xu, L. Pan, A novel redox bromide-ion additive hydrogel electrolyte for flexible Zn-ion hybrid supercapacitors with boosted energy density and controllable zinc deposition, J. Mater. Chem. A 8 (2020) 15042–15050. https://doi.org/10.1039/D0TA03547E.

[5] N. Chang, T. Li, R. Li, S. Wang, Y. Yin, H. Zhang, X. Li, An aqueous hybrid electrolyte for low-temperature zinc-based energy storage devices, Energy Environ. Sci. 13 (2020) 3527–3535. https://doi.org/10.1039/D0EE01538E.

[6] J. Eskusson, T. Thomberg, E. Lust, A. Jänes, Electrochemical Characteristics of Zn-Ion Hybrid Supercapacitors Based on Aqueous Solution of Different Electrolytes, J. Electrochem. Soc. 169 (2022) 020512. https://doi.org/10.1149/1945-7111/ac4d68.

[7] P. Srimuk, L. Wang, Ö. Budak, V. Presser, High-performance ion removal via zinc–air desalination, Electrochem. Commun. 115 (2020) 106713. https://doi.org/10.1016/j.elecom.2020.106713.

[8] L. Wang, Y. Zhang, K. Moh, V. Presser, From capacitive deionization to desalination batteries and desalination fuel cells, Curr. Opin. Electrochem. 29 (2021) 100758. https://doi.org/10.1016/j.coelec.2021.100758.

[9] S.M. Islam, C.J. Barile, Dynamic Windows Using Reversible Zinc Electrodeposition in Neutral Electrolytes with High Opacity and Excellent Resting Stability, Adv. Energy Mater. 11 (2021) 2100417. https://doi.org/10.1002/aenm.202100417.

[10] W. Zhang, H. Li, W.W. Yu, A.Y. Elezzabi, Emerging Zn Anode-Based Electrochromic Devices, Small Sci. 1 (2021) 2100040. https://doi.org/10.1002/smsc.202100040.

[11] Q. Yang, Q. Li, Z. Liu, D. Wang, Y. Guo, X. Li, Y. Tang, H. Li, B. Dong, C. Zhi, Dendrites in Zn-Based Batteries, Adv. Mater. 32 (2020) 2001854. https://doi.org/10.1002/adma.202001854.
[12] P. He, J. Huang, Chemical Passivation Stabilizes Zn Anode, Adv. Mater. 34 (2022) 2109872. https://doi.org/10.1002/adma.202109872.
[13] C. Li, X. Xie, S. Liang, J. Zhou, Issues and Future Perspective on Zinc Metal Anode for Rechargeable Aqueous Zinc-ion Batteries, Energy Environ. Mater. 3 (2020) 146–159. https://doi.org/10.1002/eem2.12067.
[14] Y. Yang, G. Qu, H. Wei, Z. Wei, C. Liu, Y. Lin, X. Li, C. Han, C. Zhi, H. Li, Weakly Solvating Effect Spawning Reliable Interfacial Chemistry for Aqueous Zn/Na Hybrid Batteries, Adv. Energy Mater. 13 (2023) 2203729. https://doi.org/10.1002/aenm.202203729.
[15] M. Li, Z. Li, X. Wang, J. Meng, X. Liu, B. Wu, C. Han, L. Mai, Comprehensive understanding of the roles of water molecules in aqueous Zn-ion batteries: from electrolytes to electrode materials, Energy Environ. Sci. 14 (2021) 3796–3839. https://doi.org/10.1039/D1EE00030F.
[16] Q. Zhang, Z. Yang, H. Ji, X. Zeng, Y. Tang, D. Sun, H. Wang, Issues and rational design of aqueous electrolyte for Zn-ion batteries, SusMat 1 (2021) 432–447. https://doi.org/10.1002/sus2.20.
[17] Y. Zhang, M. Li, S. Liang, G. Fang, Advances on new configuration of zinc anode towards high-performance emerging zinc-based electronic devices, Energy Mater. Devices 1 (2023) 9370018. https://doi.org/10.26599/EMD.2023.9370023.
[18] Z. Cai, Y. Ou, J. Wang, R. Xiao, L. Fu, Z. Yuan, R. Zhan, Y. Sun, Chemically resistant Cu–Zn/Zn composite anode for long cycling aqueous batteries, Energy Storage Mater. 27 (2020) 205–211. https://doi.org/10.1016/j.ensm.2020.01.032.
[19] Z. Kang, C. Wu, L. Dong, W. Liu, J. Mou, J. Zhang, Z. Chang, B. Jiang, G. Wang, F. Kang, C. Xu, 3D Porous Copper Skeleton Supported Zinc Anode toward High Capacity and Long Cycle Life Zinc Ion Batteries, ACS Sustain. Chem. Eng. 7 (2019) 3364–3371. https://doi.org/10.1021/acssuschemeng.8b05568.
[20] N. Guo, W. Huo, X. Dong, Z. Sun, Y. Lu, X. Wu, L. Dai, L. Wang, H. Lin, H. Liu, H. Liang, Z. He, Q. Zhang, A Review on 3D Zinc Anodes for Zinc Ion Batteries, Small Methods 6 (2022) 2200597. https://doi.org/10.1002/smtd.202200597.
[21] H. Li, S. Guo, H. Zhou, Recent advances in manipulating strategy of aqueous electrolytes for Zn anode stabilization, Energy Storage Mater. 56 (2023) 227–257. https://doi.org/10.1016/j.ensm.2023.01.027.
[22] Y. Xu, G. Zhang, J. Liu, J. Zhang, X. Wang, X. Pu, J. Wang, C. Yan, Y. Cao, H. Yang, W. Li, X. Li, Recent Advances on Challenges and Strategies of Manganese Dioxide Cathodes for Aqueous Zinc-Ion Batteries, ENERGY Environ. Mater. 6 (2023) e12575. https://doi.org/10.1002/eem2.12575.
[23] Z. Zhang, B. Xi, X. Ma, W. Chen, J. Feng, S. Xiong, Recent progress, mechanisms, and perspectives for crystal and interface chemistry applying to the Zn metal anodes in aqueous zinc-ion batteries, SusMat 2 (2022) 114–141. https://doi.org/10.1002/sus2.53.
[24] X. Wang, C. Sun, Z.-S. Wu, Recent progress of dendrite-free stable zinc anodes for advanced zinc-based rechargeable batteries: Fundamentals, challenges, and perspectives, SusMat 3 (2023) 180–206. https://doi.org/10.1002/sus2.118.
[25] L. Kang, M. Cui, F. Jiang, Y. Gao, H. Luo, J. Liu, W. Liang, C. Zhi, Nanoporous CaCO3 Coatings Enabled Uniform Zn Stripping/Plating for Long-Life Zinc Rechargeable Aqueous Batteries, Adv. Energy Mater. 8 (2018) 1801090. https://doi.org/10.1002/aenm.201801090.
[26] Y. Zhou, X. Wang, X. Shen, Y. Shi, C. Zhu, S. Zeng, H. Xu, P. Cao, Y. Wang, J. Di, Q. Li, 3D confined zinc plating/stripping with high discharge depth and excellent high-rate

reversibility, J. Mater. Chem. A 8 (2020) 11719–11727. https://doi.org/10.1039/D0TA02791J.
[27] Y. Wang, Z. Wang, F. Yang, S. Liu, S. Zhang, J. Mao, Z. Guo, Electrolyte Engineering Enables High Performance Zinc-Ion Batteries, Small 18 (2022) 2107033. https://doi.org/10.1002/smll.202107033.
[28] M. Liu, P. Wang, W. Zhang, H. He, G. He, S. Xu, L. Yao, T.S. Miller, Strategies for pH regulation in aqueous zinc ion batteries, Energy Storage Mater. 67 (2024) 103248. https://doi.org/10.1016/j.ensm.2024.103248.
[29] Y. Liang, M. Qiu, P. Sun, W. Mai, Comprehensive Review of Electrolyte Modification Strategies for Stabilizing Zn Metal Anodes, Adv. Funct. Mater. 33 (2023) 2304878. https://doi.org/10.1002/adfm.202304878.
[30] Y. Shang, P. Kumar, T. Musso, U. Mittal, Q. Du, X. Liang, D. Kundu, Long-Life Zn Anode Enabled by Low Volume Concentration of a Benign Electrolyte Additive, Adv. Funct. Mater. 32 (2022) 2200606. https://doi.org/10.1002/adfm.202200606.
[31] X. He, Y. Cui, Y. Qian, Y. Wu, H. Ling, H. Zhang, X.-Y. Kong, Y. Zhao, M. Xue, L. Jiang, L. Wen, Anion Concentration Gradient-Assisted Construction of a Solid–Electrolyte Interphase for a Stable Zinc Metal Anode at High Rates, J. Am. Chem. Soc. 144 (2022) 11168–11177. https://doi.org/10.1021/jacs.2c01815.
[32] S. Chen, R. Lan, J. Humphreys, S. Tao, Salt-concentrated acetate electrolytes for a high voltage aqueous Zn/MnO2 battery, Energy Storage Mater. 28 (2020) 205–215. https://doi.org/10.1016/j.ensm.2020.03.011.
[33] G. Chang, S. Liu, Y. Fu, X. Hao, W. Jin, X. Ji, J. Hu, Inhibition Role of Trace Metal Ion Additives on Zinc Dendrites during Plating and Striping Processes, Adv. Mater. Interfaces 6 (2019) 1901358. https://doi.org/10.1002/admi.201901358.
[34] J. Wu, Q. Liang, X. Yu, Q. Lü, L. Ma, X. Qin, G. Chen, B. Li, Deep Eutectic Solvents for Boosting Electrochemical Energy Storage and Conversion: A Review and Perspective, Adv. Funct. Mater. 31 (2021) 2011102. https://doi.org/10.1002/adfm.202011102.
[35] L. Zhang, G. Wang, J. Feng, Q. Ma, Z. Liu, X. Yan, Designing a Zn(BF4)2-Based Ionic Liquid Electrolyte to Realize Superior Energy Density in a Carbon-Based Zinc-Ion Hybrid Capacitor, ChemElectroChem 8 (2021) 1289–1297. https://doi.org/10.1002/celc.202100003.
[36] C. Liu, X. Xie, B. Lu, J. Zhou, S. Liang, Electrolyte Strategies toward Better Zinc-Ion Batteries, ACS Energy Lett. 6 (2021) 1015–1033. https://doi.org/10.1021/acsenergylett.0c02684.
[37] W. Deng, Z. Xu, X. Wang, High-donor electrolyte additive enabling stable aqueous zinc-ion batteries, Energy Storage Mater. 52 (2022) 52–60. https://doi.org/10.1016/j.ensm.2022.07.032.
[38] R. Qin, Y. Wang, M. Zhang, Y. Wang, S. Ding, A. Song, H. Yi, L. Yang, Y. Song, Y. Cui, J. Liu, Z. Wang, S. Li, Q. Zhao, F. Pan, Tuning Zn2+ coordination environment to suppress dendrite formation for high-performance Zn-ion batteries, Nano Energy 80 (2021) 105478. https://doi.org/10.1016/j.nanoen.2020.105478.
[39] G. Ji, R. Hu, Y. Wang, J. Zheng, High energy density, flexible, low temperature resistant and self-healing Zn-ion hybrid capacitors based on hydrogel electrolyte, J. Energy Storage 46 (2022) 103858. https://doi.org/10.1016/j.est.2021.103858.
[40] M. Yan, C. Xu, Y. Sun, H. Pan, H. Li, Manipulating Zn anode reactions through salt anion involving hydrogen bonding network in aqueous electrolytes with PEO additive, Nano Energy 82 (2021) 105739. https://doi.org/10.1016/j.nanoen.2020.105739.
[41] Z. Wang, M. Zhou, L. Qin, M. Chen, Z. Chen, S. Guo, L. Wang, G. Fang, S. Liang, Simultaneous regulation of cations and anions in an electrolyte for high-capacity, high-

stability aqueous zinc–vanadium batteries, eScience 2 (2022) 209–218. https://doi.org/10.1016/j.esci.2022.03.002.
[42] X. Guo, Z. Zhang, J. Li, N. Luo, D. Han, G. He, I.P. Parkin, Alleviation of Dendrite Formation on Zinc Anodes via Electrolyte Additives, ACS Energy Lett. 6 (2021) 395–403. https://doi.org/10.1021/acsenergylett.0c02371.
[43] R. Yao, L. Qian, Y. Sui, G. Zhao, R. Guo, S. Hu, P. Liu, H. Zhu, F. Wang, C. Zhi, C. Yang, A Versatile Cation Additive Enabled Highly Reversible Zinc Metal Anode, Adv. Energy Mater. 12 (2022) 2102780. https://doi.org/10.1002/aenm.202102780.
[44] D. Yuan, J. Zhao, H. Ren, Y. Chen, R. Chua, E.T.J. Jie, Y. Cai, E. Edison, W. Manalastas Jr., M.W. Wong, M. Srinivasan, Anion Texturing Towards Dendrite-Free Zn Anode for Aqueous Rechargeable Batteries, Angew. Chem. Int. Ed. 60 (2021) 7213–7219. https://doi.org/10.1002/anie.202015488.
[45] R. Friedman, Electrolyte Solutions and Specific Ion Effects on Interfaces, J. Chem. Educ. 90 (2013) 1018–1023. https://doi.org/10.1021/ed4000525.
[46] J. Peng, D. Cao, Z. He, J. Guo, P. Hapala, R. Ma, B. Cheng, J. Chen, W.J. Xie, X.-Z. Li, P. Jelínek, L.-M. Xu, Y.Q. Gao, E.-G. Wang, Y. Jiang, The effect of hydration number on the interfacial transport of sodium ions, Nature 557 (2018) 701–705. https://doi.org/10.1038/s41586-018-0122-2.
[47] W.R. Fawcett, Acidity and basicity scales for polar solvents, J. Phys. Chem. 97 (1993) 9540–9546. https://doi.org/10.1021/j100139a045.
[48] M. Hartmann, T. Clark, R. van Eldik, Hydration and Water Exchange of Zinc(II) Ions. Application of Density Functional Theory, J. Am. Chem. Soc. 119 (1997) 7843–7850. https://doi.org/10.1021/ja970483f.
[49] J.D. Bernal, R.H. Fowler, A Theory of Water and Ionic Solution, with Particular Reference to Hydrogen and Hydroxyl Ions, J. Chem. Phys. 1 (1933) 515–548. https://doi.org/10.1063/1.1749327.
[50] S.F. Lincoln, Mechanistic Studies of Metal Aqua Ions: A Semi-Historical Perspective, Helv. Chim. Acta 88 (2005) 523–545. https://doi.org/10.1002/hlca.200590036.
[51] P. Sebastián-Pascual, Y. Shao-Horn, M. Escudero-Escribano, Toward understanding the role of the electric double layer structure and electrolyte effects on well-defined interfaces for electrocatalysis, Curr. Opin. Electrochem. 32 (2022) 100918. https://doi.org/10.1016/j.coelec.2021.100918.
[52] K. Kiyohara, Y. Kawai, Hydration of monovalent and divalent cations near a cathode surface, J. Chem. Phys. 151 (2019) 104704. https://doi.org/10.1063/1.5113738.
[53] D. Paschek, R. Ludwig, Specific Ion Effects on Water Structure and Dynamics beyond the First Hydration Shell, Angew. Chem. Int. Ed. 50 (2011) 352–353. https://doi.org/10.1002/anie.201004501.
[54] D.C. Grahame, The Electrical Double Layer and the Theory of Electrocapillarity., Chem. Rev. 41 (1947) 441–501. https://doi.org/10.1021/cr60130a002.
[55] J. Wu, Understanding the Electric Double-Layer Structure, Capacitance, and Charging Dynamics, Chem. Rev. 122 (2022) 10821–10859. https://doi.org/10.1021/acs.chemrev.2c00097.
[56] G. Gonella, E.H.G. Backus, Y. Nagata, D.J. Bonthuis, P. Loche, A. Schlaich, R.R. Netz, A. Kühnle, I.T. McCrum, M.T.M. Koper, M. Wolf, B. Winter, G. Meijer, R.K. Campen, M. Bonn, Water at charged interfaces, Nat. Rev. Chem. 5 (2021) 466–485. https://doi.org/10.1038/s41570-021-00293-2.
[57] L. Li, Y.-P. Liu, J.-B. Le, J. Cheng, Unraveling molecular structures and ion effects of electric double layers at metal water interfaces, Cell Rep. Phys. Sci. 3 (2022) 100759. https://doi.org/10.1016/j.xcrp.2022.100759.
[58] A. Schlaich, A.P. dos Santos, R.R. Netz, Simulations of Nanoseparated Charged Surfaces Reveal Charge-Induced Water Reorientation and Nonadditivity of Hydration and Mean-

Field Electrostatic Repulsion, Langmuir 35 (2019) 551–560. https://doi.org/10.1021/acs.langmuir.8b03474.
[59] M.M. Waegele, C.M. Gunathunge, J. Li, X. Li, How cations affect the electric double layer and the rates and selectivity of electrocatalytic processes, J. Chem. Phys. 151 (2019) 160902. https://doi.org/10.1063/1.5124878.
[60] H. Yang, D. Chen, R. Zhao, G. Li, H. Xu, L. Li, X. Liu, G. Li, D. Chao, W. Han, Reunderstanding aqueous Zn electrochemistry from interfacial specific adsorption of solvation structures, Energy Environ. Sci. 16 (2023) 2910–2923. https://doi.org/10.1039/D3EE00658A.
[61] W. Du, J. Yan, C. Cao, C.C. Li, Electrocrystallization orientation regulation of zinc metal anodes: strategies and challenges, Energy Storage Mater. 52 (2022) 329–354. https://doi.org/10.1016/j.ensm.2022.07.046.
[62] F. Hao, A. Verma, P.P. Mukherjee, Electrodeposition stability of metal electrodes, Energy Storage Mater. 20 (2019) 1–6. https://doi.org/10.1016/j.ensm.2019.05.004.
[63] K. Kiyohara, Y. Kawai, Hydration of monovalent and divalent cations near a cathode surface, J. Chem. Phys. 151 (2019) 104704. https://doi.org/10.1063/1.5113738.
[64] X. Xie, S. Liang, J. Gao, S. Guo, J. Guo, C. Wang, G. Xu, X. Wu, G. Chen, J. Zhou, Manipulating the ion-transfer kinetics and interface stability for high-performance zinc metal anodes, Energy Environ. Sci. 13 (2020) 503–510. https://doi.org/10.1039/C9EE03545A.
[65] M. Zhou, Y. Chen, G. Fang, S. Liang, Electrolyte/electrode interfacial electrochemical behaviors and optimization strategies in aqueous zinc-ion batteries, Energy Storage Mater. 45 (2022) 618–646. https://doi.org/10.1016/j.ensm.2021.12.011.
[66] L. Jiang, D. Li, X. Xie, D. Ji, L. Li, L. Li, Z. He, B. Lu, S. Liang, J. Zhou, Electric double layer design for Zn-based batteries, Energy Storage Mater. 62 (2023) 102932. https://doi.org/10.1016/j.ensm.2023.102932.
[67] Y. Du, Y. Li, B.B. Xu, T.X. Liu, X. Liu, F. Ma, X. Gu, C. Lai, Electrolyte Salts and Additives Regulation Enables High Performance Aqueous Zinc Ion Batteries: A Mini Review, Small 18 (2022) 2104640. https://doi.org/10.1002/smll.202104640.
[68] Y. Geng, L. Pan, Z. Peng, Z. Sun, H. Lin, C. Mao, L. Wang, L. Dai, H. Liu, K. Pan, X. Wu, Q. Zhang, Z. He, Electrolyte additive engineering for aqueous Zn ion batteries, Energy Storage Mater. 51 (2022) 733–755. https://doi.org/10.1016/j.ensm.2022.07.017.
[69] J. Wu, Understanding the Electric Double-Layer Structure, Capacitance, and Charging Dynamics, Chem. Rev. 122 (2022) 10821–10859. https://doi.org/10.1021/acs.chemrev.2c00097.
[70] S. Shen, N. Zhang, Cholinium Cations Enable Highly Compact and Dendrite-Free Zn Metal Anodes in Aqueous Electrolytes, Adv. Funct. Mater. 32 (2022) 2203905. https://doi.org/10.1002/adfm.202203905.
[71] Q. Zhang, Y. Ma, Y. Lu, X. Zhou, L. Lin, L. Li, Z. Yan, Q. Zhao, K. Zhang, J. Chen, Designing Anion-Type Water-Free Zn2+ Solvation Structure for Robust Zn Metal Anode, Angew. Chem. Int. Ed. 60 (2021) 23357–23364. https://doi.org/10.1002/anie.202109682.
[72] C. Huang, X. Zhao, S. Liu, Y. Hao, Q. Tang, A. Hu, Z. Liu, X. Chen, Stabilizing Zinc Anodes by Regulating the Electrical Double Layer with Saccharin Anions, Adv. Mater. 33 (2021) 2100445. https://doi.org/10.1002/adma.202100445.
[73] Y. Zhong, Z. Cheng, H. Zhang, J. Li, D. Liu, Y. Liao, J. Meng, Y. Shen, Y. Huang, Monosodium glutamate, an effective electrolyte additive to enhance cycling performance of Zn anode in aqueous battery, Nano Energy 98 (2022) 107220. https://doi.org/10.1016/j.nanoen.2022.107220.
[74] P. Sun, L. Ma, W. Zhou, M. Qiu, Z. Wang, D. Chao, W. Mai, Simultaneous Regulation on Solvation Shell and Electrode Interface for Dendrite-Free Zn Ion Batteries Achieved

by a Low-Cost Glucose Additive, Angew. Chem. Int. Ed. 60 (2021) 18247–18255. https://doi.org/10.1002/anie.202105756.
[75] Z. Jiao, X. Cai, X. Wang, Y. Li, Z. Bie, W. Song, Trace Amount of Nitrilotriacetate Induced Electrolyte Evolution and Textured Surface for Stable Zn Anode, Adv. Energy Mater. 13 (2023) 2302676. https://doi.org/10.1002/aenm.202302676.
[76] S. Cai, J. Hu, Y. Luo, P. Zhu, T. He, G. Zou, H. Hou, X. Ji, Hydrophobic Hyamine-Mediated Water-Lean Electric Double Layer Boosting Reversible Dendrite-Free Zinc Metal Anodes, Adv. Funct. Mater. 34 (2023) 2309667. https://doi.org/10.1002/adfm.202309667.
[77] Z. Hu, F. Zhang, Y. Zhao, H. Wang, Y. Huang, F. Wu, R. Chen, L. Li, A Self-Regulated Electrostatic Shielding Layer toward Dendrite-Free Zn Batteries, Adv. Mater. 34 (2022) 2203104. https://doi.org/10.1002/adma.202203104.
[78] Y. Yuan, S.D. Pu, M.A. Pérez-Osorio, Z. Li, S. Zhang, S. Yang, B. Liu, C. Gong, A.S. Menon, L.F.J. Piper, X. Gao, P.G. Bruce, A.W. Robertson, Diagnosing the Electrostatic Shielding Mechanism for Dendrite Suppression in Aqueous Zinc Batteries, Adv. Mater. 36 (2023) 2307708. https://doi.org/10.1002/adma.202307708.
[79] X. Guo, Z. Zhang, J. Li, D. Han, Z. Weng, G. He, I.P. Parkin, Alleviation of Dendrite Formation on Zinc Anodes via Electrolyte Additives, ACS Energy Lett. 6 (2021) 395–403. https://doi.org/10.1021/acsenergylett.0c02371.
[80] P. Wang, X. Xie, Z. Xing, X. Chen, G. Fang, B. Lu, J. Zhou, S. Liang, H.J. Fan, Mechanistic Insights of Mg^{2+} -Electrolyte Additive for High-Energy and Long-Life Zinc - Ion Hybrid Capacitors, Adv. Energy Mater. 11 (2021) 2101158. https://doi.org/10.1002/aenm.202101158.
[81] R. Zhao, H. Wang, H. Du, Y. Yang, Z. Gao, L. Qie, Y. Huang, Lanthanum nitrate as aqueous electrolyte additive for favourable zinc metal electrodeposition, Nat. Commun. 13 (2022) 3252. https://doi.org/10.1038/s41467-022-30939-8.
[82] Y. Li, P. Wu, W. Zhong, C. Xie, Y. Xie, Q. Zhang, D. Sun, Y. Tang, H. Wang, A progressive nucleation mechanism enables stable zinc stripping–plating behavior, Energy Environ. Sci. 14 (2021) 5563–5571. https://doi.org/10.1039/D1EE01861B.
[83] Y. Ding, X. Zhang, J. Zhou, S. Liang, A dynamic electrostatic shielding layer toward highly reversible Zn metal anode, Energy Storage Mater. 62 (2023) 102949. https://doi.org/10.1016/j.ensm.2023.102949.
[84] C. Chen, L. Li, Z. Long, Q. Liang, Trace Sc3+-electrolyte additive enabling stable Zn metal anodes for aqueous zinc-ion batteries, Chem. Commun. 59 (2023) 13363–13366. https://doi.org/10.1039/D3CC04476A.
[85] M.K. Kim, S.-J. Shin, J.M. Lee, Y.B. Park, Y.M. Kim, H.J. Kim, J.W. Choi, Cationic Additive with a Rigid Solvation Shell for High-Performance Zinc Ion Batteries, Angew. Chem. Int. Ed. 61 (2022) e202211589. https://doi.org/10.1002/anie.202211589.
[86] Q. Li, A. Chen, D. Wang, Y. Zhao, X. Wang, X. Jin, B. Xiong, C. Zhi, Tailoring the metal electrode morphology via electrochemical protocol optimization for long-lasting aqueous zinc batteries, Nat. Commun. 13 (2022) 1–9. https://doi.org/10.1038/s41467-022-31461-7.
[87] H. Tang, H. Liang, R. Jia, Y. Liu, J. Wang, M. Zhou, P. Luo, Q. An, Homogenization of electric field distribution facilitating the Zn anode reversibility, Chem. Commun. 58 (2022) 13648–13651. https://doi.org/10.1039/D2CC05532E.
[88] Z. Weng, Q. Yang, A Self-Regulated Interface toward Highly Reversible Aqueous Zinc Batteries, Adv. Energy Mater. 12 (2022) 2102982. https://doi.org/10.1002/aenm.202102982.
[89] Q. Zhang, Y. Ma, Y. Lu, Y. Ni, L. Lin, Z. Hao, Z. Yan, Q. Zhao, J. Chen, Halogenated Zn2+ Solvation Structure for Reversible Zn Metal Batteries, J. Am. Chem. Soc. 144 (2022) 18435–18443. https://doi.org/10.1021/jacs.2c06927.

[90] A. Bayaguud, X. Luo, Y. Fu, C. Zhu, Cationic Surfactant-Type Electrolyte Additive Enables Three-Dimensional Dendrite-Free Zinc Anode for Stable Zinc-Ion Batteries, ACS Energy Lett. 5 (2020) 3012–3020. https://doi.org/10.1021/acsenergylett.0c01792.
[91] J. Hao, X. Li, X. Zeng, D. Li, J. Mao, Z. Guo, Deeply understanding the Zn anode behaviour and corresponding improvement strategies in different aqueous Zn-based batteries, Energy Environ. Sci. 13 (2020) 3917–3949. https://doi.org/10.1039/D0EE02162H.
[92] C. Zhang, W. Shin, L. Zhu, C. Chen, J.C. Neuefeind, Y. Xu, S.I. Allec, C. Liu, Z. Wei, A. Daniyar, J.-X. Jiang, C. Fang, P. Alex Greaney, X. Ji, The electrolyte comprising more robust water and superhalides transforms Zn-metal anode reversibly and dendrite-free, Carbon Energy 3 (2021) 339–348. https://doi.org/10.1002/cey2.70.
[93] N. Wang, S. Zhai, Y. Ma, X. Tan, K. Jiang, W. Zhong, W. Zhang, N. Chen, W. Chen, S. Li, G. Han, Z. Li, Tridentate citrate chelation towards stable fiber zinc-polypyrrole battery with hybrid mechanism, Energy Storage Mater. 43 (2021) 585–594. https://doi.org/10.1016/j.ensm.2021.10.004.
[94] S. Wu, Y. Chen, T. Jiao, J. Zhou, J. Cheng, B. Liu, S. Yang, K. Zhang, W. Zhang, An Aqueous Zn-Ion Hybrid Supercapacitor with High Energy Density and Ultrastability up to 80 000 Cycles, Adv. Energy Mater. 9 (2019) 1902915. https://doi.org/10.1002/aenm.201902915.
[95] F. Wang, O. Borodin, T. Gao, X. Fan, W. Sun, F. Han, A. Faraone, J.A. Dura, K. Xu, C. Wang, Highly reversible zinc metal anode for aqueous batteries, Nat. Mater. 17 (2018) 543–549. https://doi.org/10.1038/s41563-018-0063-z.
[96] C. Wang, Z. Pei, Q. Meng, C. Zhang, X. Sui, Z. Yuan, S. Wang, Y. Chen, Toward Flexible Zinc-Ion Hybrid Capacitors with Superhigh Energy Density and Ultralong Cycling Life: The Pivotal Role of $ZnCl_2$ Salt-Based Electrolytes, Angew. Chem. Int. Ed. 60 (2021) 990–997. https://doi.org/10.1002/anie.202012030.
[97] X. Wang, X. Li, H. Fan, L. Ma, Solid Electrolyte Interface in Zn-Based Battery Systems, Nano-Micro Lett. 14 (2022) 205. https://doi.org/10.1007/s40820-022-00939-w.
[98] R. Chen, W. Zhang, C. Guan, Y. Zhou, I. Gilmore, H. Tang, Z. Zhang, H. Dong, Y. Dai, Z. Du, X. Gao, W. Zong, Y. Xu, P. Jiang, J. Liu, F. Zhao, J. Li, X. Wang, G. He, Rational Design of an In-Situ Polymer-Inorganic Hybrid Solid Electrolyte Interphase for Realising Stable Zn Metal Anode under Harsh Conditions, Angew. Chem. Int. Ed. 63 (2024) e202401987. https://doi.org/10.1002/anie.202401987.
[99] Q. Zhang, Y. Su, Z. Shi, X. Yang, J. Sun, Artificial Interphase Layer for Stabilized Zn Anodes: Progress and Prospects, Small 18 (2022) 2203583. https://doi.org/10.1002/smll.202203583.
[100] K. Wu, J. Yi, X. Liu, Y. Sun, J. Cui, Y. Xie, Y. Liu, Y. Xia, J. Zhang, Regulating Zn Deposition via an Artificial Solid–Electrolyte Interface with Aligned Dipoles for Long Life Zn Anode, Nano-Micro Lett. 13 (2021) 79. https://doi.org/10.1007/s40820-021-00599-2.
[101] D. Li, L. Cao, T. Deng, S. Liu, C. Wang, Design of a Solid Electrolyte Interphase for Aqueous Zn Batteries, Angew. Chem. Int. Ed. 60 (2021) 13035–13041. https://doi.org/10.1002/anie.202103390.
[102] X. Zeng, J. Mao, J. Hao, J. Liu, S. Liu, Z. Wang, Y. Wang, S. Zhang, T. Zheng, J. Liu, P. Rao, Z. Guo, Electrolyte Design for In Situ Construction of Highly Zn2+-Conductive Solid Electrolyte Interphase to Enable High-Performance Aqueous Zn-Ion Batteries under Practical Conditions, Adv. Mater. 33 (2021) 2007416. https://doi.org/10.1002/adma.202007416.
[103] Y. Chu, S. Zhang, S. Wu, Z. Hu, G. Cui, J. Luo, In situ built interphase with high interface energy and fast kinetics for high performance Zn metal anodes, Energy Environ. Sci. 14 (2021) 3609–3620. https://doi.org/10.1039/D1EE00308A.

[104] T. Wei, H. Zhang, Y. Ren, L. Mo, Y. He, P. Tan, Y. Huang, Z. Li, D. Zhu, L. Hu, Building Near-Unity Stacked (002) Texture for High-Stable Zinc Anode, Adv. Funct. Mater. 34 (2024) 2312506. https://doi.org/10.1002/adfm.202312506.
[105] D. Wang, D. Lv, H. Peng, C. Wang, H. Liu, J. Yang, Y. Qian, Solvation Modulation Enhances Anion-Derived Solid Electrolyte Interphase for Deep Cycling of Aqueous Zinc Metal Batteries, Angew. Chem. Int. Ed. 62 (2023) e202310290. https://doi.org/10.1002/anie.202310290.
[106] J. Wan, R. Wang, Z. Liu, L. Zhang, F. Liang, T. Zhou, S. Zhang, L. Zhang, Q. Lu, C. Zhang, Z. Guo, A Double-Functional Additive Containing Nucleophilic Groups for High-Performance Zn-Ion Batteries, ACS Nano 17 (2023) 1610–1621. https://doi.org/10.1021/acsnano.2c11357.
[107] C. Lin, L. He, P. Xiong, H. Lin, W. Lai, X. Yang, F. Xiao, X.-L. Sun, Q. Qian, S. Liu, Q. Chen, S. Kaskel, L. Zeng, Adaptive Ionization-Induced Tunable Electric Double Layer for Practical Zn Metal Batteries over Wide pH and Temperature Ranges, ACS Nano 17 (2023) 23181–23193. https://doi.org/10.1021/acsnano.3c09774.
[108] H. Liu, Y. Zhang, C. Wang, J.N. Glazer, Z. Shan, N. Liu, Understanding and Controlling the Nucleation and Growth of Zn Electrodeposits for Aqueous Zinc-Ion Batteries, ACS Appl. Mater. Interfaces 13 (2021) 32930–32936. https://doi.org/10.1021/acsami.1c06131.
[109] H. Zhang, Y. Zhong, J. Li, Y. Liao, J. Zeng, Y. Shen, L. Yuan, Z. Li, Y. Huang, Inducing the Preferential Growth of Zn (002) Plane for Long Cycle Aqueous Zn-Ion Batteries, Adv. Energy Mater. 13 (2023) 2203254. https://doi.org/10.1002/aenm.202203254.
[110] Y. Onabuta, M. Kunimoto, S. Wang, Y. Fukunaka, H. Nakai, T. Homma, Effect of Li+ Addition during Initial Stage of Electrodeposition Process on Nucleation and Growth of Zn, J. Electrochem. Soc. 169 (2022) 092504. https://doi.org/10.1149/1945-7111/ac8c03.
[111] J. Xu, H. Li, Y. Jin, D. Zhou, B. Sun, M. Armand, G. Wang, Understanding the Electrical Mechanisms in Aqueous Zinc Metal Batteries: From Electrostatic Interactions to Electric Field Regulation, Adv. Mater. 36 (2024) 2309726. https://doi.org/10.1002/adma.202309726.
[112] L. Miao, Z. Guo, L. Jiao, Insights into the design of mildly acidic aqueous electrolytes for improved stability of Zn anode performance in <InlineParagraph>zinc-ion</InlineParagraph> batteries, Energy Mater. 3 (2023) null-null. https://doi.org/10.20517/energymater.2022.89.
[113] K.D. Collins, M.W. Washabaugh, The Hofmeister effect and the behaviour of water at interfaces, Q. Rev. Biophys. 18 (1985) 323–422. https://doi.org/10.1017/S0033583500005369.
[114] X. Zhang, Z. Deng, C. Xu, Y. Deng, Y. Jia, H. Luo, H. Wu, W. Cai, Y. Zhang, Electrolyte Engineering via Competitive Solvation Structures for Developing Longevous Zinc Ion Batteries, Adv. Energy Mater. n/a (n.d.) 2302749. https://doi.org/10.1002/aenm.202302749.
[115] Y. Chen, S. Zhou, J. Li, J. Kang, S. Lin, C. Han, H. Duan, S. Liang, A. Pan, Non-Expendable Regulator Enables Durable and Deep Cycling Aqueous Zinc Batteries, Adv. Energy Mater. (n.d.) 2400398. https://doi.org/10.1002/aenm.202400398.
[116] K. Wang, T. Qiu, L. Lin, H. Zhan, X.-X. Liu, X. Sun, Solvation Sheath Regulation to Induce Sulfide Solid–Electrolyte Interphase on Zn Metal Anode, ACS Energy Lett. 9 (2024) 1000–1007. https://doi.org/10.1021/acsenergylett.4c00318.
[117] M. Yang, J. Zhu, S. Bi, R. Wang, H. Wang, F. Yue, Z. Niu, The Construction of Anion-Induced Solvation Structures in Low-concentration Electrolyte for Stable Zinc Anodes, Angew. Chem. Int. Ed. 63 (2024) e202400337. https://doi.org/10.1002/anie.202400337.
[118] H. Tang, N. Hu, L. Ma, H. Weng, D. Huang, J. Zhu, H. Yang, Z. Chen, X. Yin, J. Xu, H. He, Interfacial Dual-Modulation via Cationic Electrostatic Shielding and Anionic

Preferential Adsorption toward Planar and Reversible Zinc Electrodeposition, Adv. Funct. Mater. (n.d.) 2402484. https://doi.org/10.1002/adfm.202402484.
[119] C. Ma, X. Wang, W. Lu, K. Yang, N. Chen, H. Jiang, C. Wang, H. Yue, D. Zhang, F. Du, Dual-Parasitic Effect Enables Highly Reversible Zn Metal Anode for Ultralong 25,000 Cycles Aqueous Zinc-Ion Batteries, Nano Lett. 24 (2024) 4020–4028. https://doi.org/10.1021/acs.nanolett.4c00873.
[120] W. Zhang, Y. Dai, R. Chen, Z. Xu, J. Li, W. Zong, H. Li, Z. Li, Z. Zhang, J. Zhu, F. Guo, X. Gao, Z. Du, J. Chen, T. Wang, G. He, I.P. Parkin, Highly Reversible Zinc Metal Anode in a Dilute Aqueous Electrolyte Enabled by a pH Buffer Additive, Angew. Chem. Int. Ed. 62 (2023) e202212695. https://doi.org/10.1002/anie.202212695.
[121] X. Wang, Q. Liang, W.-J. Jiang, P. Wang, J. Liao, Z. Xiong, D. Li, Probing Nanoconfined Ion Transport in Electrified 2D Laminate Membranes with Electrochemical Impedance Spectroscopy, Small Methods 6 (2022) 2200806. https://doi.org/10.1002/smtd.202200806.
[122] T. Sun, S. Zheng, H. Du, Z. Tao, Synergistic Effect of Cation and Anion for Low-Temperature Aqueous Zinc-Ion Battery, Nano-Micro Lett. 13 (2021) 204. https://doi.org/10.1007/s40820-021-00733-0.
[123] B. Raza, A. Naveed, J. chen, H. Lu, T. Rasheed, J. Yang, Y. NuLi, J. Wang, Zn anode sustaining high rate and high loading in organic electrolyte for rechargeable batteries, Energy Storage Mater. 46 (2022) 523–534. https://doi.org/10.1016/j.ensm.2022.01.043.
[124] D. Liu, Z. Xiong, P. Wang, Q. Liang, H. Zhu, J.Z. Liu, M. Forsyth, D. Li, Ion-Specific Nanoconfinement Effect in Multilayered Graphene Membranes: A Combined Nuclear Magnetic Resonance and Computational Study, Nano Lett. 23 (2023) 5555–5561. https://doi.org/10.1021/acs.nanolett.3c00877.
[125] M. Seo, T.D. Chung, Nanoconfinement effects in electrochemical reactions, Curr. Opin. Electrochem. 13 (2019) 47–54. https://doi.org/10.1016/j.coelec.2018.10.011.
[126] P. Srimuk, L. Wang, Ö. Budak, V. Presser, High-performance ion removal via zinc–air desalination, Electrochem. Commun. 115 (2020) 106713. https://doi.org/10.1016/j.elecom.2020.106713.
[127] J. Lee, B. Hwang, M.-S. Park, K. Kim, Improved reversibility of Zn anodes for rechargeable Zn-air batteries by using alkoxide and acetate ions, Electrochimica Acta 199 (2016) 164–171. https://doi.org/10.1016/j.electacta.2016.03.148.
[128] J. Dai, J. Wang, X. Hou, Q. Ru, Q. He, P. Srimuk, V. Presser, F. Chen, Dual-Zinc Electrode Electrochemical Desalination, ChemSusChem 13 (2020) 2792–2798. https://doi.org/10.1002/cssc.202000188.