Received: 22 January 2022  |  Revised: 12 February 2022  |  Accepted: 21 February 2022

DOI: 10.1002/sus2.53

REVIEW ARTICLE

Recent progress, mechanisms, and perspectives for crystal and interface chemistry applying to the Zn metal anodes in aqueous zinc-ion batteries

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Funding information
Taishan Scholar Project Foundation of Shandong Province, Grant/Award Number: ts20190908; Natural Science Foundation of Shandong Province, Grant/Award Numbers: ZR2021ZD05, ZR2019MB024; National Natural Science Foundation of China, Grant/Award Numbers: U1764258, 21871164

Abstract
The need for large-scale electrochemical energy storage devices in the future has spawned several new breeds of batteries in which aqueous zinc ion batteries (AZIBs) have attracted great attention due to their high safety, low cost, and excellent electrochemical performance. In the current research, the dendrite and corrosion caused by aqueous electrolytes are the main problems being studied. However, the research on the zinc metal anode is still in its infancy. We think it really needs to provide clear guidelines about how to reasonably configure the system of AZIBs to realize high-energy density and long cycle life. Therefore, it is worth analyzing the works on the zinc anode, and several strategies are proposed to improve the stability and cycle life of the battery in recent years. Based on the crystal chemistry and interface chemistry, this review reveals the key factors and essential causes that inhibit dendrite growth and side reactions and puts forward the potential prospects for future work in this direction. It is foreseeable that guiding the construction of AZIBs with high-energy density and long cycle life in various systems would be quite possible by following this overview as a roadmap.

KEYWORDS
crystal chemistry, interface chemistry, side reaction, Zn dendrites, Zn metal anode

1 | INTRODUCTION

There is no doubt that the growth in energy storage demand as society advances has put forward clear requirements for the development of energy storage technology.1–3 What have been broadly applied to portable electronic devices and electric vehicles are Li-ion batteries considering the nature of their high efficiency and convenience.4 Nonetheless, opposite viewpoints still persist in light of the questions from sustainable development and safety considerations, in which scarce lithium sources and flammable organic electrolytes account for a
It has become the goal of many researchers to find an electrochemical energy storage technology, which is safe, environment friendly, low-cost, and efficient. Accordingly, aqueous zinc-ion batteries (AZIBs) come to prominence in view of the extensive zinc sources (zinc is several times more abundant than lithium in the earth’s crust), tremendous energy density ($820 \text{mAhg}^{-1}, 15851 \text{mAhcm}^{-3}$), and tiny security risk. On the other hand, low redox potential ($-0.762 \text{V vs. standard hydrogen electrode}$) allows Zn metal to be a candidate which could be directly employed as a safe anode in an aqueous metal-ion battery. A weakly acidic zinc salt aqueous solution is non-toxic and environmentally friendly as the electrolyte, permitting the battery to be assembled in the air, which will greatly reduce production costs at the same time. Furthermore, a smaller hydrated radius of Zn ions than other multiple-electron metal elements such as Mg and Al, also promote the dynamics of ion intercalation in the cathode materials.

In a typical ideal model, AZIBs are composed of a cathode, zinc metal anode, and aqueous electrolyte, in which Zn$^{2+}$ ions transfer between the cathode and anode, achieving energy conversion and storage. Unfortunately, the electrochemical reactions and energy storage mechanism of the actual battery system are more complicated. Based on this focal point, many scientists spare no pains to investigate it, as relevant publications are growing rapidly in the past few years. AZIBs and research emphasis of AZIBs component parts are shown in Figure 1A. At present, the emphasis of cathode research is on the excavation of the cathode materials, which usually realize various zinc ions intercalation chemistry depending on the specific structure. Tunnel-type, layer-type, and spinel-type structures are featured with one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D) diffusion channels, respectively, which favor the transportation of zinc ions and are the most broadly explored. For example, vanadium-based oxides, manganese-based oxides, the Na ions superionic conductor (NASICON)-type structure compounds, Prussian blue analogs, organic compounds, polyanion compounds, and chevrel phase compounds are the typical candidates. However, AZIBs have always been bound by unstable Coulombic efficiency (CE) and insufficient cycle life; it is far from a mature industrialization technology. Compared to the cathode, it is the research exploitation of anode and electrolyte that determines the progress of AZIBs into practical application. As with lithium-ion and other battery technologies, anode and electrolyte determine the reversibility of Zn$^{2+}$ plating/stripping and then affect the formation of Zn dendrite on the anode. When the dendrite grows to a certain extent, it will pierce the separator, leading to the short circuit of batteries, always causing the mediocre stability and cycle life of the battery. Meanwhile, if dendrite falls off, the formation of “dead zinc” will result in capacity loss and an increase in battery internal resistance.

Recently, a suite of tactics has been put forward for the optimization of the Zn metal anodes, including structural design, surface modification, and anode-electrolyte interface modification. For structural design, it is mainly focused on constructing 3D Zn anode, which can greatly alleviate the formation of Zn dendrites by increasing active specific surface area. For surface modification, it mainly manifests as various types of protective layers which utilize different mechanisms. For anode-electrolyte
interface modification,\textsuperscript{39,40} it largely depends on the regulation of electrolyte to control and modify the Zn\textsuperscript{2+} stripping/plating behavior on the Zn anode surface. In combination with the research of our research group, the conclusion that was drawn from the above meaningful methods is that interface chemistry and crystal chemistry play significant roles in the optimization of the Zn metal anode.\textsuperscript{41,42} Based on this conclusion, rigorous scientific explanation and deep insight should be put forward systematically to help comprehend the above stabilization strategies, which can not only present as a useful reference for numerous researchers in related fields but also serve as a compass for the future methodical strategy and design.

In this review, we will emphasis on interface chemistry and crystal chemistry to synthetically generalize and summarize the energetic strategies for the Zn metal anode. Starting with the significant published methods, mechanisms of inhibiting zinc dendrite growth or suppressing side reactions have been academically categorized and analyzed. Furthermore, advanced knowledge from other battery techniques, involving accomplishing uniform deposition of lithium ions, and other metal ions has also been utilized so that understanding will be acquired from a variety of perspectives. Finally, a far-reaching vision of future meaningful strategies will be given even though the exploration of the Zn metal anode is still in a infancy. We deem that the successive attempts of the Zn metal anode will not only be beneficial to academic research but also to promote the industrialization and commercialization of the advanced ZIBs.

## 2 | ORIGIN OF METAL DENDRITE FORMATION

It is well acknowledged that uneven deposition of Zn on the metal anode is the main incentive mechanism for zinc dendrites’ growth.\textsuperscript{13,43} At the beginning, the deposition of zinc ions on the zinc surface in the neutral electrolyte environment is not uniform, which leads to the formation of a convex surface of the zinc metal electrode. When zinc continues to be deposited, more and more electrons are inclined to accumulate at the tip of the bulge, so the following zinc ions prefer to deposit over there; that is the “tip effect,” resulting in a vicious circle. Especially for the discharging at high rates, the “tip effect” is more likely to occur because of serious concentration polarization, resulting in severe dendrite growth in large quantities under unchecked conditions.\textsuperscript{44,45}

Likewise, other metal batteries (such as Mg Li and Al) have also suffered from a serious dendrite issue due to irregular metal ions deposition on the anode, making it inclined to reduce the Coulomb efficiency and utilization of metal ions.\textsuperscript{46–48} Zhi et al. compared the Zn dendrite with Li and Al dendrites.\textsuperscript{49} As shown in Figure 1B, the Li dendrite growth was caused by the uneven electric field and heterogeneous solid electrolyte interface (SEI) formed via organic electrolyte decomposition. On the one hand, the body-centered cubic (bcc) matrix of lithium makes lithium dendrites grow along the 1D direction with strong penetration ability.\textsuperscript{50} On the other hand, the distribution of interfacial electric field enables the formation of a branching structure to penetrate the separator from different directions. Finally, it takes on the feature of a 1D branching structure. As for Al dendrites, Al\textsubscript{2}O\textsubscript{3} passivation layer ruptures, and then a large number of nonuniform Al nucleation sites were exposed (Figure 1C).

## 3 | CRYSTAL CHEMISTRY PERSPECTIVE

When the eyes go back to Zn dendrite, it tends to deposit as 2D hexagonal platelets because of the hexagonal close packing of crystalline Zn to expose (0002) plane achieving a lower thermodynamic free energy.\textsuperscript{51} Even though the edge size varies with charge and discharge conditions and electrolyte composition, uniform deposition of Zn\textsuperscript{2+} would be realized by epitaxial growth at the coherent interface, which is supported by the heteroepitaxial nucleation mechanism. The above concept was first put forward by Archer et al. in 2019 and has become one roadmap for studies on controlling the exposed crystal plane orientation to make the uniform deposition of Zn ions (Figure 2A).\textsuperscript{52} Specifically, it is the substrate for Zn deposition that plays an important role in the uniform Zn plating by regulating the orientation of crystal growth. In the process of epitaxial electrodeposition, a matched interface between the first deposited Zn layer and substrate (i.e., graphene) is formed driven by the maximum crystal lattice match and minimal strain; the Zn-graphene interface is parallel to the graphene. Subsequently, this coherent (or semicoherent) interface promotes the Zn ion plating in a parallel way to the graphene substrate, revealing the next homoepitaxial growth layer stacking on top of the existing interface. Finally, more homoepitaxial growth layers above comprise the flat and compact hexagonal zinc deposit stacking along the special crystal orientation.

### 3.1 | Modified Zn substrate

Stimulated by this significant epitaxy regulation growth concept, many efforts have been made to moderate the undesirable inhomogeneity of Zn crystal growth. Recently, profuse materials have been developed, which take advan-
For example, Wang et al. coated the commercial Zn foil with (001) faceted TiO$_2$, which was prepared via a simple hydrothermal reaction (Figure 2B). As applied in the rechargeable aqueous zinc-ion batteries, stable Zn ions stripping/plating performance with a long electrochemistry lifespan is exhibited because of the highly exposed (001) plane of TiO$_2$. Fu et al. built a modified Zn–metal anode surface via Sn flakes retexturing as shown in Figure 2C. Compared to the Zn/Sn(101) and the bare Zn, the preferential orientation of Zn/Sn(200) not only contributes to the lower deposition energy barrier, which promotes Zn deposition kinetics but also induces the lateral growth of Zn crystals. Benefiting from the strong points, the Zn/Sn(200) shows lower voltage hysteresis of about 20 mV, as well as a better cycle lifetime over 500 h at 1 mA cm$^{-2}$ with the restrained Zn dendrite formation. At the same time, the full battery constructed by dendrite-free Zn/Sn(200) anode and V$_2$O$_5$ cathode exhibited a surpassing rate capability and grander-specific capacity.

If the Zn anode was prepared with a preferred crystal orientation surface, it can also handle the terrible issue of Zn dendrites. Zhou et al. produced two kinds of the Zn anode which were distinguished through crystal orientation with Zn(002) and Zn(100) plane exposed by the method of large rolling deformation (Figure 3A). By means of density functional theory (DFT) calculations, Zn(002) presented...
a smooth equipotential surface and homogeneous interfacial charge density distribution, which was attributed to more even nucleation site formation along the parallel direction in the initial Zn deposition. Besides, the specific sites of the Zn(002) surface possess the stronger adsorption energy with the plating Zn atoms and render them deposit parallel to the Zn(002) surface via an epitaxial mechanism during the subsequent cycling. Wang et al. engineered the Zn surface texturing extent via different acid etching, in which the phosphoric acid etching presents the most Zn(002) planes exposed as shown in Figure 3B–D. Specifically, the product of zinc phosphate was the interface species to regulate interfacial charge distribution and enable the fast ion kinetics, mainly resulting from a superior crystal texture and closely packed layer. More importantly, zinc phosphate acts as not only a selective crystal plane interface layer but also a greater corrosion resistance durable layer because of the low electrochemical activity towards electrolytes. This zinc phosphate@Zn (PPZ@Zn) electrode endows reversible Zn stripping/plating over 3000 h at 1 mA cm\(^{-2}\). Furthermore, the LiFePO\(_4\)/C||PPZ@Zn hybrid battery exhibits a high stable capacity of 155 mAh g\(^{-1}\) at the current density of 0.1 A g\(^{-1}\) and the Carbon nanotubes (CNT)/MnO\(_2\)||PPZ@Zn full cell delivers a reversible capacity of 213 mAh g\(^{-1}\) at the current density of 1 A g\(^{-1}\) after 1250 cycles. The method also gave rise to new Zn anodes, such as zinc foil and Zn powder, which possess advantages of superior processability and tunability and low cost. Lately, Zhi et al. chose 2D-layered Ti\(_3\)C\(_2\)Tx MXene which succeed in the low mismatch crystalline lattice to the electrodeposited Zn from its MAX precursor, as the dendrite growth regulator to achieve a highly reversible Zn stripping/plating. As shown in Figure 3E–G, an initial heterogeneous seed interface formed between the (0002) facet of deposited Zn and the (0002) facet of MXene so that uniform Zn deposition can be achieved afterwards. Moreover, the coherent layer on the Ti\(_3\)C\(_2\)Tx MXene enables subsequent deposition of Zn ions faster and facilitates electrons flowing on the great conductive MXene framework. In this way, the smaller nucleation barrier and polarization potential of Zn ions and CE (about 98%) prove that the modified Zn powder anode possesses a promoting kinetic performance and durability compared to the most studied Zn foil anode. At the same time, the assembled FeHCF//MXene@Zn full battery with improved cycle life, CE, and capacity retention demonstrated superior electro-

**FIGURE 3** (A) Zn anode with (002) texture shows even nucleation site formation along the parallel direction in the initial process of Zn deposition. Reproduced with permission. Copyright 2021, Wiley. (B–D) The phosphoric acid etching exposes the most Zn (002) planes among different acid etchings. Reproduced with permission. Copyright 2021, Wiley. (E) coherent layer on the Ti\(_3\)C\(_2\)Tx MXene enabling even deposition of Zn ions. (F–G) SEM images of MXene@Zn powders before and after deposition. Reproduced with permission. Copyright 2021, American Chemical Society
chemical performance, benefiting from the efficiently suppressed dendrite growth and the role of MXene as electrons/ions redistributor.

3.2 Modified separators and electrolytes

Heteroepitaxial nucleation is a significant way that can be not only used in anode but also applied to a novel separator and electrolyte solution. Zhang et al. applied graphene oxide (GO) as a modified material to glass fiber (GF) separator,\textsuperscript{38} which helped in obtaining a stable and dendrite-free Zn anode (Figure 4A). With this modified separator, a Zn/Zn symmetrical battery demonstrates an excellent cycle performance, no matter at the low current density or high. At the same time, the Zn//MnO\textsubscript{2} full battery displays a better specific capacity, power density, and energy density compared to the counterpart using the original GF separator (Figure 4B). Besides glass fiber, the cellulose nanofiber separator can also be optimized by adjusting the preferred crystal orientation. Zhang et al. reported a cellulose separator modified by cellulose/graphene oxide (CG),\textsuperscript{59} which helped the initial epitaxial electrodeposition of Zn ions because of a low lattice mismatch between (002) planes of GO and electrodeposited Zn (Figure 4C,D). Profiting from the crystal orientation manipulation, the resultant symmetric batteries with the CG separator exhibited excellent Zn plating/stripping performance with a low nucleation overpotential (82 mV) and stable Coulombic efficiency (98.69\%) and long-term cycle life (over 1750 h) as shown in Figure 4E. Meanwhile, the remarkable improvement in the electrochemical performance of the assembled full batteries as well as the flexible soft-packaged batteries with this CG separator can significantly testify to the feasibility of a high crystal-plane-selective method, which shows huge potential in the practical use for large-scale energy storage systems.

As for electrolyte solution, Archer et al. came up with a reversible electrodeposition method which made crystal growth stabilization through the usage of salt and molecular additives.\textsuperscript{60} They regulated the initial crystal growth orientation and reshaped the morphological shape of metal nano-electrodeposits. Polyethylene glycol (PEG)-Zn\textsuperscript{2+}-al\textsuperscript{−} (α = 1,2,3) is the most powerful polymer–salt complex system to facilitate the growth of preferential crystalline (002) facet and the formation of hexagonal platelet electrodeposits as shown in Figure 5A. When applying this strategy in a coin cell and a single flow battery, they both display superior areal capacity and stable Coulombic efficiency at a certain current density. In addition to the above polymer, inorganic salts could also be utilized as additives to limit the harmful growth of zinc crystals. For instance, Wang et al. discovered a new crystal growth mechanism via the addition of cations (Ce\textsuperscript{3+} and La\textsuperscript{3+}) to prevent the formation of Zn dendrite.\textsuperscript{61} It has been demonstrated that these cation additives would occupy the initial preferential plating sites and then confine the following Zn\textsuperscript{2+} nucleation as well as growth in a relatively limited scope. These active sites tend to improve the above process in nature. Specifically, the cation additives could construct lots of preoccupied electric fields that would be more active for the continuous deposition process, guiding the process of Zn\textsuperscript{2+} progressive nucleation rather than instantaneous nucleation in the absence of cations (Figure 5B). At the same time, Chen et al. have enquired about the influence of kinds of surfactants on the process of zinc deposition (Figure 5C).\textsuperscript{62} They carried out the interface engineering on the commercial Zn foils where surfactant played a key role in the process of electroplating, thus producing a novel zinc metal interface with different strong orientations. The results verify that in the case of modified Zn surface with (002) and (103) planes exposed most, the growth of dendrite would be less possible (Figure 5D). On the contrary, if (100) and (110) crystal planes dominate the surface of the zinc anode, zinc dendrites would be likely to form to a large extent. In conclusion, the surface morphology can be regulated by the additional surfactants, which influenced the surface energy of diverse planes so that the plating of Zn\textsuperscript{2+} would be along a particular crystallographic orientation.

3.3 Application of crystal orientation in lithium batteries

In the case of preferred crystal orientation, Zn metal anodes show the uniform electrodeposition performance, which could be extended in analogous fields of other metal ions plating.\textsuperscript{63–65} For example, Ishikawa et al. investigated the relationship between the crystal orientation of Cu collectors and the interfacial electrodeposition of the Li metal anode.\textsuperscript{65} As the evidence from electrochemical and interfacial characterization given, the SEI layer formed on the single-crystal Cu(111) not only displayed the lowest resistance but also presented the thinnest thickness compared to those on Cu with other orientations. Remarkably, this correlation is consistent with the least surface energy of Cu(111) among Cu crystal planes, indicating that the construction of the SEI layer depends a lot on the chemical activity of crystal planes. In addition, the traditional polycrystalline Cu collector tended to damage interfacial stability because of the uneven formed SEI layer. The crystal orientation of Cu current collectors contributes to the uniform SEI engineering for inhibiting the lithium dendrites growth. This tactic that aims to find the best current collector could generalize to other fields such as optimizing electrolyte and separator. We believe that numerous challenges
FIGURE 4  (A) XRD pattern of GO modified glass fiber (GF) separator. (B) The schematic illustration of full Zn//MnO$_2$ batteries with a GO-modified GF separator. Reproduced with permission.\textsuperscript{[58]} Copyright 2020, Royal Society of Chemistry. (C) XRD pattern of cellulose composite separator (CG) modified by GO. (D) The schematic diagram of low lattice mismatch between (002) planes of GO and electrodeposited Zn. (E) The schematic legend of excellent Zn plating/stripping performance using CG separator. Reproduced with permission.\textsuperscript{[59]} Copyright 2021, Wiley
in the topic of controlling dendrite growth will come to a solution relying on crystal chemistry principles, especially preferred crystal orientation. The exploration and engineering of lattice plane and epitaxial growth about various metal dendrite growth could efficaciously lighten each other which helps in understanding and building stable energy storage systems.

3.4 | Summary

In a typical way, the lattice mismatch between deposited Zn and substrate, which is mainly related to the lattice structure and atomic arrangements, has a critical effect on regulating the process of dendrite nucleation and growth. Detailedly, the mismatch of the lattice makes against the combination of two crystal components, leading to the increase of diffusion barrier and nucleation overpotential of Zn ions. The above limits cause tremendous resistance for the deposition and the local accumulation of Zn ions, which may promote the “tip effect” on the initial electrodeposition sites and ultimately lead to the growth of zinc dendrites. As an effective measure, the preferential crystal orientation of deposited Zn can be obtained by decreasing the lattice mismatch so that the uniform deposition would be realized usually along the Zn closest packing (0002) plane.
Consequently, the analysis of crystal plane and binding energy of zinc ions with facets is quite necessary to be performed at the nanodimension and atomic level by means of the following approaches:

1. The X-ray diffraction (XRD) patterns: The use of X-ray diffraction in crystal diffraction phenomenon helps to obtain the signal characteristics and spectogram after processing. The obtained information can not only determine the phase as a conventional microscope but also have a “perspective eye” to see whether there are dislocations and lattice defects in the crystal. Because the arrangement of atoms inside each crystal is unique, the corresponding diffraction pattern is unique, similar to a human fingerprint. In the diffraction pattern, the distribution of diffraction lines is determined by the size, shape, and orientation of crystal cells, which is a powerful instrument to choose the most favorable plane exposed texture.

2. The scanning electron microscopy (SEM): A large analytical instrument, which is widely used to observe the 3D morphology and composition of the solid surface ultrastructure. The instrument with a high resolution can observe the details of the sample surface at about 6 nm through the secondary electron image, monitoring the microstructure of deposited Zn to check whether it is homogeneous deposition. On the other hand, sample preparation is simple, so it is closer to the natural state of the material.

3. Theoretical analysis: The combination of theoretical calculation and experiment has become the most mainstream research method, especially in the aspect of mechanism analysis, theoretical calculation is almost indispensable. The crystal preference orientation and lattice matching of materials can be realized by a simple calculation process. The calculation of adsorption energy between materials is more complicated, but it can indicate the binding state between different components, which is very important. The diffusion of ions is also very meaningful for zinc ions batteries and all kinds of new battery systems because it is the control step of dynamics. Therefore, it is of great significance to characterize the diffusion properties of materials to ions through theoretical calculation.

4. INTERFACE CHEMISTRY PERSPECTIVE

In the definition of physical chemistry, an interface is a transition zone between two different phases in contact. The thickness of an interface is usually at the molecular scale. In the research of battery systems, the SEI formed between the electrode and electrolyte is studied most, especially in lithium-ion batteries, which have mainly focused on the formation and structure of SEI as well as the way that metal ions go across it. The electrochemical plating of metal ions is an interfacial reaction. Moreover, the nucleation and the corrosion of metal anode all take place on the SEI. Based on this reason, remodeling the SEI of Li metal anodes is an effective method to build stable and dendrite-free character, which is a time-honored subject. Successful experiences have been summed up based on numerous meticulous studies, including the establishment of various models, an array of modified strategies, and necessary design criteria. Distinct from the lithium-ion batteries, Zn metal hits an obstacle to weave a dense SEI on its surface because of the thermodynamically preferred reaction between Zn anode and aqueous electrolyte, which causes water decomposition and hydrogen evolution. The reaction at the interphase constantly went on, which resulted in the violent corrosion of Zn metal and an uneven electric field distribution, contributing to the dendrite growth. Therefore, constructing an artificial SEI is a promising strategy to suppress the hydrogen evolution reaction and regulate the Zn dendrite growth. To this end, what can be inferred is that the criteria of the advanced SEI for AZIBs need to fulfill various tough conditions, which threw down the gauntlet of the interface adjustment. Intelligent researchers could draw on their experience on the lithium metal anode which involves the key factors of improving the CE, inhibiting dendrite growth, and expanding the lifespan of Li metal anode. Up to date, multiple efforts have been made so that diverse SEI has been reported which combines chemical stability and high Zn$^{2+}$ conductivity. According to several classic studies, this favorable strategy can be applied to three main categories: an artificial protective layer on the Zn anode and separator surface, and electrolyte regulation.

4.1 Artificial protective layer

The artificial protective layer can be divided into two kinds according to the construction methods of protecting layer: ex situ or in situ, which alleviates dendrites growth via various chemical effects. At the beginning stage of the artificial protective layer research, the ex situ coating method contributed a lot because this method is very convenient and ready to use. Inorganic materials (such as clay minerals and ZrO$_2$) could be cast directly on the surface of Zn metal as the most general method for the cathode preparation, which is based on innumerable studies. The second method more ingenious that manages the surface by various treatments so that the protective layer would be in situ formed on the Zn surface.
This approach could make up the short board that ex situ method might result in inhomogeneous coating and local contact, contributing to the reaction between the electrolyte and Zn metal surface. According to the above two formation approaches, we have combined the reported tactics to analyze modification mechanisms, which guide the homogeneous deposition of Zn\(^{2+}\) by all kinds of fancy ideas.

### 4.1.1 Ex situ coating approach

Interface engineering by means of the ex situ coating approach is mainly revolved around inorganic materials, which serve as physical isolation between the zinc metal anode and electrolyte. In the experience of the pioneers, nano-CaCO\(_3\), TiO\(_2\), ZrO\(_2\) have been successful models of the insulating material layer.\(^{38,73,77}\) For example, Xia et al. made use of ZrO\(_2\) (Figure 6A), which inhibited the hydrogen evolution reaction because the immediate contact between the Zn metal anode and the aqueous electrolyte could be blocked.\(^{78}\) What’s more, ZrO\(_2\) is a representative of ceramic materials with a high dielectric constant, to govern the Zn plating/stripping because of the advantageous Maxwell–Wagner polarization which induces the separation of positive and negative charges. This beneficial effect could help the distribution of uniform Zn\(^{2+}\) nucleation sites and improve the stability of the Zn anode. Consequently, experimental results verify the ZrO\(_2\)-coated Zn anode could be capable of working in high-performance rechargeable Zn-based batteries, which display ultra-long cycle life and stable Coulombic efficiency.

Several kinds of clay minerals, phyllosilicate in particular, have attracted the higher attention of researchers lately. A phyllosilicate is one of the silicate minerals according to its layer crystal structure.\(^{74,75}\) In its complex ions, 2D and infinitely extended silicon–oxygen tetrahedral layers could be formed by connecting with each other and sharing 3/4 of the vertexes usually. Inside the layer, the residual oxygen of tetrahedra, which is not shared, has a more negative charge so that it can coordinate with metal cations such as Na\(^+\), K\(^+\), and Fe\(^{2+}\). Sometimes, the silicon-oxygen layer could be replaced by the aluminum–oxygen tetrahedra, leading to the formation of sandwiched structures. The interlamellar space opens a gate to the migration of Zn\(^{2+}\), creating a favorable Zn ion transportation layer. Montmorillonite and kaolin, on behalf of the phyllosilicate, have been reported to alleviate the issues of zinc dendrites as shown in Figure 6B, C. The cast layer on the Zn anode surface presents the characteristics of uniformity, porosity as well as, cation transportation functionality. On the one hand, the dense phyllosilicate coating layer displays the resistance of the self-corrosive reaction between Zn metal and electrolyte. On the other hand, nanoconfinement is proposed by the restriction effect at the nanoscale in a 3D structure such as a tube, pore, and hole. It also appears with the confinement of nanomaterials with a 2D surface. This effect palys an important role that provides a constrained environment for the reaction system at the nanoscale, so as to achieve precise regulation of chemical performance and make the reaction fast and controlled.\(^{78}\) This interlamellar channel could confine the Zn\(^{2+}\) migration due to O–H and Si–O bonds providing plentiful adsorption sites, which makes the Zn\(^{2+}\) uniform absorption on the metal surface and therefore regulates the deposition process.

In addition, layered double hydroxide (LDH) has also been introduced to construct the functional protective layer, similar to the montmorillonite cationic clay in structure, and their layer spacing can be adjusted by filling anions with different ion radii. At the same time, LDH has a certain intrinsic stability, which originates from a strong covalent bond interaction within layers and electrostatic attraction between layers.\(^{77}\) Other weak interaction between layers, such as hydrogen bonds, could also contribute to mechanical stability. Based on these above characteristics, the LDH film has the potential to realize a high stable Zn–ion flux and reversible Zn\(^{2+}\) plating/stripping behavior (Figure 7A). Recently, Li et al. exploit the Mg–Al LDH, that is, \([(\text{Mg}_{0.667}\text{Al}_{0.333})(\text{OH})_{2}(\text{CO}_3)_{0.167}(\text{H}_2\text{O})_{0.5}]\), as an artificial protective SEI on the surface of the Zn metal anode, which manifests multifunctional integration as an optimal SEI.\(^{78}\) This Mg–Al LDH is in consonance with the criteria of a superior SEI model, which possesses low electron transference and high ion conductivity. In addition, ideal mechanical strength could effectively improve the stability of the Zn@LDH electrode in aqueous electrolytes, contributing to the inhibition of the H\(_2\)O decomposition reaction in the process of electrochemical cycling.

Besides inorganic materials, solid-state polymers, such as polyamide (PA)\(^{79}\) and polypyrrole,\(^{80}\) can also play an absorbing role in the ex situ protective layer. These multifunctional polymer coatings could be engineered as brighteners that have forceful coordination with Zn\(^{2+}\), facilitating the construction of a Zn\(^{2+}\) diffusion layer on anode metal substrates. Polymers have many unique advantages, including high mechanical flexibility, low cost, and good compatibility, so they will have important applications in electronic device systems. Conductive polymers combine the inherent properties of traditional polymers with the unique electrical properties of metals. They have attracted great interest over the past decade because of their high electrical conductivity, robustness and flexibility, ease of manufacture, and cost-effectiveness. Some conductive polymers also have well-defined nanostructures or microstructures, high specific surface areas, more
exposed reaction sites, and significantly enhanced activity. These attractive properties have led to applications such as energy storage and conversion devices. The polymer coating should meet the following requirements. First, the ideal polymer should possess superior ionic conduction and poor electronic conduction so that it would coordinate with metal ions strongly. Second, the polymer coating should present strong hydrogen bonding frameworks dense enough to isolate the aqueous electrolyte, leading to stable mechanical properties. Third, the researched polymers should be in common use and studied thoroughly, which are cost-effective and easy to carry out follow-up studies with other researchers. Cui et al. arranged the interface chemistry through polymeric engineering by PA. As shown in Figure 7B, the PA coating layer effectively confines the nucleation process by means of elevating the nucleation over potential and increasing the nucleation density via restricting Zn^{2+} 2D diffusion, leading to a dense and smooth Zn deposition. As a physical layer, it could efficiently block the contact of aqueous electrolyte and Zn anode, inhibiting the adverse side reactions sharply (Figure 7C). The method to modify the Zn electrode with mature and commercialized polymer is cost-efficient and easy to operate. All these attractive choices make the com-

**FIGURE 6** (A) Performance during cycling of the Zn anode with and without ZrO_2 coating. Reproduced with permission. Copyright 2021, Wiley. (B–C) The schematic diagram of montmorillonite and kaolin coating contributing to the Zn^{2+} nucleation process. Reproduced with permission. Copyright 2021, Wiley.
bination of classical polymers and low-cost Zn anode, which hopefully improves the superior electrochemistry performance and practical industrial potential of environmentally friendly AZIBs. Besides, this strategy could also be applied in other metal anodes, which face the same issue of dendrite growth, taking a solid step towards their application in large-scale energy storage.79

4.1.2  In situ coating approach

Ex situ methods proceed always by spraying or coating the as-prepared materials on the substrates. So the interaction is frequently established at the interface that makes the weak adhesion of artificial layers which tend to detach from the Zn anode surface in the process of cycling resulting from the volume changes. Moreover, the artificial layers constructed by ex situ methods are likely to be inhomogeneous and leaky due to the intrinsic synthesis disadvantages, triggering the contact of aqueous electrolyte and the Zn anode surface.

On the contrary, in situ methods can apply the alien layers directly on the zinc substrates via growth reaction. Compared to ex situ assembly tactics, the layers constructed via in situ fabrication methods afford a promising way to build hopeful protective layer nano-level in thickness, which shows the strong capability to restrain the dendrite growth and suppress side reactions simultaneously. A
series of such fabrication approaches have been developed, involving the vapor–solid method on the Zn anode surface and the liquid–solid method at the Zn metal–electrolyte interface. Different synthesis conditions were tried, and the greatest degree of homogeneous layers is expected to realize with no effort. Recently, a series of ZnX (X = O, F, S, Se, ...)\(^{81–83}\) have been directly formed on the surface of the Zn metal anode for advanced AZIBs, which plays a key point in restraining the growth of Zn dendrite. As expected, they could control the side reactions for the reason that the contact and reaction between Zn electrode and electrolyte would be inhibited severely.

There is a construction method that takes a simple gas–solid reaction. Generally, the raw materials and Zn metal foils are placed in a furnace together and heated under the optimal temperature and gas atmosphere/flow. A compact and homogeneous film will be finally harvested and plays a crucial role in preventing capacity reduction and battery malfunction. For instance, Guo et al. bring in a homogeneous ZnS protective layer on the bare Zn metal foil,\(^{81}\) which is regulated by the gas–solid reaction to present the dense and robust characteristic (Figure 8A). The layer displays strong bonding interaction between S atoms and Zn metal crystal, leading to the forceful adhesion and excellent mechanical strength, confirmed by various characterizations. In ZnSO\(_4\) electrolyte, this ZnS layer has been proved to be greatly stable, contributing to enhance reversibility of Zn plating/stripping by boosting the diffusion of Zn ions and inhibiting the side reactions induced by the aqueous environment. Moreover, it could overcome the sensitive issue that most previous reported layers undergo with inferior transference numbers of Zn\(^{2+}\). This method has also been expanded to other elements, such as ZnF\(_2\) and ZnSe (Figure 8B), which in situ creates the multifunctional layers.\(^{82,83}\) The DFT is a good proof to support the mechanism which concentrates on the adsorption energy and charge distribution of the interface between the protective layer and the Zn metal surface (Figure 8C). The high adsorption energy indicates the Zn atoms could be seized easily because of the intense zincophilicity. The interaction at the interface could be speculated by the imbalanced charge distribution which is reflected by the accumulated positive charge around the Zn layer and negative charge around ZnF\(_2\) bonds. What’s more is that the diffusion energy barrier of Zn\(^{2+}\) obtained from theoretical calculation reveals the lower barrier at the modified Zn metal than the bare one, accounting for the acceleration of the Zn ions diffusion kinetics.

This in situ SEI growth could also be operated in an aqueous solution, which needs additional conditions to drive this reaction. Li et al.\(^{84}\) prepared a 3D-connected ZnF\(_2\) layer on a Zn foil surface in an NH\(_4\)F aqueous solution via the potentiostatic electrodeposition as shown in Figure 9A. In the process, plenty of Zn\(^{2+}\) is generated through the anodic reaction at the inner Helmholtz plane at a constant voltage applied to the electrolytic tank system. The electrostatic attraction renders F\(^{−}\) and Zn\(^{2+}\) ions approach each other and react into a ZnF\(_2\) 3D network on the Zn substrate. Additionally, the thickness of ZnF\(_2\) SEI can be readily adjusted by regulating the reaction duration. The as-constructed ZnF\(_2\) SEI could not only reallocate the flow of Zn\(^{2+}\) ion but also promote the Zn deposition kinetics in a stable and facile direction. The in situ characterization results and analyses demonstrate that the introduction of the in situ SEI layer can effectively suppress the growth of dendrites, inhibit the side reactions, and enhance Zn\(^{2+}\) plating/stripping reversibility.

As shown in Figure 9B, Zhou et al. have also equipped the 3D zinc oxide with a thickness of 5 mm on the surface of Zn substrate by means of one-step liquid–solid interphase deposition. The special 3D framework of ZnO could form a steady and homogeneous layer adhering to the surface of Zn metal, alleviating the tip effect. More importantly, this homogeneous structure and inert coating could promote the transference dynamics of Zn ions and decrease the electronic conduction. Particularly, the desolvation and extraction of Zn\(^{2+}\) at the interface would be improved by adjusting the solvation sheath configuration of electric double layers (EDLs), which regulate the activation energies and contribute to the excellent transference dynamics. The results of DFT also demonstrate that electrostatic attraction tends to happen with the individual Zn\(^{2+}\) rather than hydrated one, avoiding the energy expense for unlocking the compact and strong solvation sheath structure. As a consequence, the hydrogen evolution reaction could be efficiently avoided by reducing the free water close to the Zn@ZnO SEI; thus the reversibility of Zn\(^{2+}\) plating/stripping would become more stable with Coulombic efficiency of 99.55% and the morphology of the anode remains well preserved.\(^{85}\)

### 4.2 Separator

The separator could assist to build the SEI that efficiently facilitates the homogeneous electric field distribution and Zn ion flux, which restrains the dendrite growth and prolongs cycle life. There is also another question that the morphology of the Zn metal anode after a cycle cannot be easily determined via microscopic techniques. This issue mainly originates from the most used separator made by glass fiber, thus a few glass fibers might detach and adhere to the Zn metal surface in the process of cycling life. From this sight, modified separators should be developed to face the challenge of surface construction as well as Zn anode observations.
Based on the above views, Zhang et al. provide a strategy that prepared a fresh separator by a conductive and high zinc-affinity coating layer, which not only enables the homogeneous distribution of electric field but also induces the Zn deposition on the Sn-modified separator (Figure 10A). Sn is chosen as it displays the most excellent zinc affinity as well as electrochemical stability after checking several candidate elements by means of theoretical simulation. In addition, the superior electrical conductivity enables smooth electron flow on the surface of the Zn anode. As revealed by the performance of cycling and morphology of Zn deposition, the regulation of Zn dendrite growth can essentially promote the smooth deposition between the anode and separator. Consequently, this modified MnO₂/Zn full cell shows a highly prolonged cycle life at different current densities, without short circuit happening as in the other general AZIBs system.⁸⁶

A Janus structure refers to the integration of two chemically discrepant composites into one structure system. To design a Janus separator, it is common to modify the sep-
**FIGURE 9**  (A) The schematic legend of in situ formations of ZnF$_2$ on Zn metal foils in an aqueous environment. Reproduced with permission. [84] Copyright 2021, Wiley. (B) The schematic diagram of in situ formations of ZnO on Zn metal foils and its working principle. Reproduced with permission. [85] Copyright 2021, Royal Society of Chemistry

**FIGURE 10**  (A) The schematic diagram of inducing the Zn deposition on the Sn-modified separator. Reproduced with permission. [86] Copyright 2021, Springer Nature. (B) The schematic legend of the designed Janus separator with 3D conductive skeleton graphene. (C) Electric field distribution of the designed Janus separator. Reproduced with permission. [87] Copyright 2020, Wiley
ator surface with a layer of ceramic or carbon material, able to improve the safety and electrochemical performance of the battery. However, it often increases the overall mass and volume of the battery obviously so that the energy density might be sacrificed, which cannot meet the current requirements of lightweight and flexible wearable devices. Sun et al. employ a subtle chemical vapor deposition technology, which implements an ultra-thin layer of vertical graphene to grow on the commercial glass fiber membrane directly, meeting the premise of no increase in overall quality or volume of Janus separator. As shown in Figure 10B,C, vertical graphene as a 3D conductive skeleton structure, plays a critical role that realizing the extension of zinc metal anode surface. 3D space could effectively reduce the local current density to slow down the dendrite formation, while the graphene skeleton provides a uniformly distributed electric field, thus enabling homogeneous Zn$^{2+}$ plating/stripping.

### 4.3 Functional electrolyte

As the “E” in “SEI,” the electrolyte is definitely a pivotal component to adjust the interface chemistry of the Zn anode. Decreasing the number of free waters, which would cause H$_2$ evolution and corrosion on the Zn anode, is an effective way to promote the Coulombic efficiency of Zn plating/stripping. The “water-in-salt” electrolyte model is the most noted because of the high concentration electrolyte validly reducing the free water content around the Zn anode surface as well as facilitating the homogeneous Zn$^{2+}$ deposition. Remarkably, an exquisite ultrahigh concentration electrolyte with 1 M bis(trifluoromethanesulfonyl)imide zinc(II) ($\text{Zn(TFSI)}_2$) and 21 M bis(trifluoromethane)sulfonimide lithium salt ($\text{LiTFSI}$) has been applied in the form of the “water-in-salt” model, in which a powerful TFSI$^-$ solvation sheath would be constructed because of the heavy interaction between lithium ions and a large proportion of water molecules (Figure 11A). More importantly, this novel model not only improves the Zn$^{2+}$ transference capacity and viscosity of the electrolyte but also reduces the water molecules, which strive against the growth of Zn dendrite so that the uniform Zn$^{2+}$ plating at the SEI can proceed. Similarly, ionic liquid (IL) compact gels with excellent ion-conducting properties have been fabricated by TFSI$^-$ as a kind of hydrophobic protective method for the Zn metal anode. As shown in Figure 11B, this IL skinny gel is straightly fabricated on the Zn metal foil via spin coating, and then UV curing is employed to solidify the gel rather than utilizing any other solvent, realizing the elimination of tedious steps and saving consumption at the same time. Thanks to the IL skinny gel, the probability of harmful side reactions towards the Zn anode surface, would be greatly reduced in the deposition process. In the issue, the IL skinny gel forcefully could inhibit water decomposition occurring on the interface including creating H$_2$ gas and corrosion secondary products on the Zn metal anode. What comes to the result is that the reversibility of Zn ion plating/stripping could achieve high reversion even as suffering from severe testing conditions like 90% depth of discharge, indicating that this work presents superior promise with high achievability (Figure 11C).

Recently, numerous functional electrolyte additives with a number of strengths have also assisted to regulate the interface chemistry of zinc electrolyte, which realizes reversible Zn$^{2+}$ plating/stripping by controlling the adsorption of zinc ions on the metal anode surface. Some effort has been taken to control the dendrite growth of Zn, attributed to the employment of several water-soluble organic additives. What they could do is to prepare a stable zinc metal anode surface by means of absorption, restricting the plating behavior, and influencing the interface between the anode and electrolyte. For example, Xu et al. utilized a few quantities of diethyl ether ($\text{Et}_2\text{O}$) as the electrolyte additive which greatly constricts the growth of protrusions on the Zn metal surface. To be specific, small-size zinc ions are gathered on the Zn metal surface at the initial stage of Zn$^{2+}$ plating, which displays the highly locally intensive electric field. The $\text{Et}_2\text{O}$ molecules with high polarization in the aqueous electrolyte tend to selectively adsorb on the uneven Zn protrusion, acting as an electrostatic shield layer so that the most likely occurrence of “tip effect” would be inhibited (Figure 12A). The Zn$^{2+}$ ions would deposit more possibly on flat areas with few $\text{Et}_2\text{O}$ molecules adsorbed then maintain an even smooth surface in the following plating/stripping.

Wang et al. have applied the polyacrylamide (PAM) as an electrolyte additive to prevent the growth of dendrites, which could adhere to the metal anode surface first and then the Zn$^{2+}$ in electrolyte would transfer to the anode surface via acyl groups in the polymer chains of PAM (Figure 12B). Specially, PAM is a common multifunction polymer containing countless acyl groups which have a heavy effect on adsorption towards zinc ions. The modified anode surface would bind the Zn$^{2+}$ via acyl groups to acquire even ion distribution so that the growth of dendrite is primarily suppressed. In a word, the application of PAM and $\text{Et}_2\text{O}$ as ion-oriented guiding additives probably figures out a new solution to suppress the formation of dendrite by means of regulating the zinc ions flux between the Zn metal anode and electrolyte interface.

The addition of a zeolite molecular sieve in the aqueous electrolyte could efficiently decrease the active free water and suppress the occurrence of side reactions (Figure 13A). Raman spectroscopy results prove that zeolite would
change the environment of electrolyte filling with strongly polar solvation sheath and obviously tighten the water molecules, contributing to the space confinement and complete interaction attraction in zeolite pores. The simulation results reveal that zeolite molecules empower a uniform current density field which has a more delicate concentration gradient and less hydrogen evolution reaction (HER) possibility. What benefits from the minor water decomposition ignited by zeolite-doped electrolyte is that few products would form on the surface. More importantly, the morphology of thickset Zn deposition is observed clearly rather than the distinct flake or protrusion dendrites on the Zn anode, demonstrating the superior reversibility of the Zn plating/stripping process.

Contact between two different phases would produce an electric potential, which is caused by the separation of charges. The excess charge existing in two phases has an equal amount of positive and negative charge which attracts each other and finally forms a double electric layer. There is an electric potential at the metal–electrolyte two-phase interface of the electrode, which also generates a double electric layer with a total thickness of about 0.2–20 nm. The metal phase of the electrode is a good conductor, and the excess charge is concentrated on the metal surface. The resistance of electrolytes is large, and the excess charge is only partly close to the phase interface, which is called a tight double layer. The core step of electrode reaction takes place in the tight layer, and the adsorption process which affects the electrode reaction also takes place in this double layer. The EDL structure on the Zn metal surface could greatly contribute to constructing a steady SEI before cycling to stabilize the Zn anode initially by means of adjusting the electrolyte component. Chen et al. have proposed a subtle idea of regulating the EDL structure, which also reveals the influence of the EDL structure theoretically and experimentally. The introduction of saccharin (Sac) additive could realize the characteristic adsorption between Sac-derived anions and initial EDL structure because of its great affinity to Zn, which prevents the direct contact between some water molecules and zinc, thus the proportion of water molecules in the EDL structure would be reduced. As shown in Figure 13B, this aformed water-poor EDL structure has a significant impact on the formation of SEI near the zinc anode interface, inhibiting the side reaction between the zinc anode and electrolyte. Meanwhile, in the process of zinc deposition, Sac-derived anions would decompose into the organic–inorganic mixed solid electrolyte phase, which regulates
FIGURE 12  (A) The schematic illustration of diethyl ether (Et2O) as the electrolyte additive which greatly constricts the growth of protrusions on the Zn metal surface. Reproduced with permission. Copyright 2019, Elsevier. (B) The schematic diagram of PAM as an electrolyte additive to prevent the growth of dendrites. Reproduced with permission. Copyright 2019, Wiley.

the diffusion of zinc ions and inhibits the formation of zinc dendrites. Based on the Sac/ZnSO4 electrolyte, the Coulomb efficiency of the Zn–Cu half-cell is as high as 99.6%, indicating that the Zn2+-plating/stripping process possesses excellent reversibility.95

4.4 Research progress of SEI in other batteries

The SEI investigations in lithium-ion batteries (LIBs) have been very extensive and have a good incentive effect in which related research in magnesium ion batteries (MIBs) and other new ion batteries have become very attractive.69,96,97 The advanced SEI shows great potential in LIB materials no matter in graphite, silicon, and lithium metal anode. When suitable strategies are employed, adequate SEI can be obtained well in composition, stability, and so on. As shown in Figure 14A,B, the SEI modification in the Mg metal anode is a fledging field of investigation that combines artificial engineering, the exploitation of improving ionic conductivity, and deep comprehension of interface chemistry by various characterizations.96 Similar to MIBs, the development of aluminum ion batteries is in the “first-generation” stage at the current moment, which is bound up with the decomposition of the Al2O3 passivation layer on the initial Al metal anode. Conductive carbon materials and Al alloy are emerging methods
for stabilizing the SEI, which avoids tip-growth behavior and realizes uniform Al plating in the process of charging. All in all, the development of SEI science is of great significance for various metal anodes which not only figure out the ion’s electrodeposition in microscale but also batteries have practical applications. Furthermore, the mechanism and manufacture gap could also be bridged by harmonizing the research of different metal anodes when one fancy creation work may solve the above problems. 97

4.5 | Summary

As a typical and efficacious protection method, the SEI layer has been widely reported in recent studies in the field of inhibiting dendritic growth in AZIBs. Thanks to the construction of SEI, the Coulombic efficiency, and cyclic stability of AZIBs could be improved to a certain extent. More importantly, it has produced a primary prototype after general consensus on the standard of excellent SEI. First of all, the components of the protective layer should have high chemical stability in the aqueous electrolytes, which should also be dense enough to prevent an electrolyte from contacting the zinc electrode directly, guarding against side reactions in the exposed areas. Second, the SEI should ensure strong affinity with zinc ions and high ionic conductivity which enables Zn$^{2+}$ to uniformly adsorb on the SEI then pass through the interface smoothly. In addition, the SEI layer should be flexible to assure its integrity under repeated volume changes in a long cycle. There is a critical challenge that convincing models have not been established in contrast to the evolution of the typical SEI model in the Li metal anode. Specifically, a mosaic model is considered a mainstream detailed one of the SEI in the Li
metal anode. On the one hand, it inherits the hypothesis of the two-layer model; on the other hand, it is assumed that each component constitutes a pure microphase, and the SEI is a mosaic assemblage of different microphases. We believe that the SEI model in the pristine Zn metal anode would evolve with the development of characterization technologies, which is fine guidance for the next stage that works towards the establishment of stable SEI in Zn metal anodes.

5 | ADVANCED CHARACTERIZATION METHODS

Advanced characterization techniques play important roles in determining whether Zn\(^{2+}\) ions experience uniform electrodeposition or not. In another word, acquiring insight into the dendrite growth manner or uniform Zn\(^{2+}\) plating performance should be monitored carefully to find the beneficial rule. At the same time, they could also verify how multifunction methods protect the metal Zn anodes. These advanced characterization methods are helpful in exploring the inherent crystal structures and chemical properties of the artificially modified surface and optimized electrolyte systems, making sure the stability and integrity in the case of extreme current densities and ultra-long cycling at the same time. The following technologies are highlighted in this section: (1) electrochemistry characterization techniques; (2) computational simulation techniques; (3) phase characterization techniques. Beyond those, there are still various methods. For example, mechanical properties should be tested by measuring the tolerance of stretch and press. In addition, the pH or concentration of the aqueous electrolytes should also be in situ investigated for the change and the optimal solution.

5.1 | Electrochemistry characterization techniques

In order to promote the practical application of Zn metal in aqueous batteries directly, any unplanned breaking down during usage should avoid, which triggers the vitality of zinc metal anode protection. The excellent performance of electrochemical properties is the most critical in practical application. However, it is worth mentioning that soft short circuits should be paid attention based on the assumption that this phenomenon leads to an overrated stable symmetric cell performance via the normal galvanostatic cycling characterization. The soft short circuit refers to the microcontact between dendrites which decreases the voltage so that the misjudgment of the validity of the modified method. Recently, Zhi et al. proposed a method that minimizes this effect by an instant electrochemical impedance spectroscopy (EIS) examination after several cycles to avoid inaccuracy. By checking the impedance distinction after different current density experiments, the battery internal state could be preliminarily estimated: an obvious difference between initial and test-in-process charge transfer resistance could be speculated that the cells might be in the soft short circuit. There are three main indicators in electrochemical characterization to measure the effectiveness of zinc metal anode protection strategies, including (a) Coulomb efficiency and cycle life, (b) nuclear potential and polarization voltage, and (c) full cell performance. Detailed standards for evaluating the effectiveness of each optimized strategy by electrochemical methods are not consolidated and mature. However, rough standard models have been established through numerous previous studies and industrial usage requirements.

5.2 | Computational simulation techniques

In the published studies, a theoretical simulation that reveals the reason for suppressing Zn dendrite growth mainly focuses on finite element modeling, DFT calculation, and molecular dynamics (MD) simulation. Based on the existing advancements, these three methods complement each other in their respective scales, which contributes a lot to the critical issue of homogeneous electrodeposition of Zn\(^{2+}\). The main function of finite element modeling is imitating the electric field distribution, which could speculate the plane distribution on the nucleation layer. For the investigation of inhibiting dendrite, finite element modeling indicates the achievement of surface functionalization at a relative macroscale (Figure 15A). DFT calculation is an effective method to get the energy of chemical interaction between Zn\(^{2+}\) and modified substrates. The diffusion barrier of Zn\(^{2+}\) on the surface of substrates could be obtained simultaneously. The energy barrier of Zn\(^{2+}\) towards the substrate could clearly demonstrate the ability of the ions diffusion as well as the difficulty level in the views of electrostatic attraction with Zn\(^{2+}\). The above two viewpoints are very helpful to explain the deposition barrier in terms of fast kinetics in the atomic aspect. These simulation studies are dedicated to disclosing the origination of uneven Zn\(^{2+}\) plating from the perspective of atomic scale, which has been employed in the AZIBs cathode (Figure 15B). Moreover, the electrostatic potential could be obtained in order to express the total electrostatic repulsion of Zn\(^{2+}\) and solvation sheath, conducing to evaluate the ability of the fast transportation (Figure 15C).
tion is intended to analyze the interaction between zinc ions and solvent molecules, which tend to form the solvation sheath structure. In the modified electrolyte, the Zn$^{2+}$ might have a more combination with functional additives instead of H$_2$O molecules proved by MD simulation strongly (Figure 15D). In addition, there are still other computational simulation methods that have also been applied in the demonstration of strategic advantages. For example, the mean-squared displacement, which is an extent of the deviation of particles' location over time compared to their reference location, is used to assess the diffusion coefficient of zinc ions in various aqueous electrolyte systems (Figure 15E,F). It can be confirmed that theoretical simulation helps to investigate the mechanism of zinc dendrite formation at different scales which facilitates both basic chemistry research and electrochemical performance improvement.

5.3 Phase characterization techniques

Phase characterization mainly concentrates on two issues: crystal structure and chemical bonds. These two points are mandatory for evaluating the effectiveness of crystal chemistry and interfacial chemistry modification strategies.

On the one hand, identification of the crystal structure contributes greatly to the crystal plane matching and the crystal type of zinc dendrite. Based on the above targets, transmission electron microscopy (TEM) and XRD are selected as the two most precise methods according to the validation of countless works. TEM and its advanced version such as high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) could be helpful in gaining knowledge of researched objects at an atomic resolution. In addition, TEM and its standard card database have become the most typical approaches to identify the crystallographic texture such as characteristic peak and crystallographic point group, which are based on previous work (Figure 16D–F). On the other hand, the detection of chemical bonds sheds light on the valence state and chemical environment of elements in the chemical compound. Especially in the investigation of SEI, it is the change of chemical interaction that must be monitored qualitatively or quantitatively to determine the efficacy of SEI modification tactics. As a result, the chemical bonds whether before or after modifications should be precisely inquired by means of various characterization techniques. As shown in Figure 17A–C, several techniques should be noticed for a long time, for example, X-ray photoelectron spectroscopy (XPS), which figures out the valence states and chemical environments of molecules in the battery system, and Raman spectroscopy which is based on the inherent chemical interaction to identify the chemical bond character. Additionally, Fourier transform infrared (FTIR)
spectroscopy reveals the chemical bonds or functional groups in molecules that could deliver different vibration and absorption frequencies under infrared excitation. The information of chemical bonds or functional groups in the molecule would be obtained according to the different bands in the FTIR spectrum. However, among many detection techniques, microscopy techniques are the most direct detection of zinc dendrites because they vividly describe the topological evolution of the Zn deposit. The morphology evolution in the process of stripping/plating on the Zn metal anode has a very crucial research value, indicating whether uniform electrodeposition occurs stably and reversibly. Besides, the regularity of dendrite in terms of growth direction and rate would also count for much which could be detected by various visualization techniques (Figure 17D,E).

5.4 Summary

There is no doubt that advanced characterization methods contributed a lot to the development of the stable Zn anode. In the future, more precise methods such as in situ technologies would come in handy to monitor the evolution of the crystal phase or the property of the as-formed SEI, which accurately records the zinc plating/stripping in the process of charge and discharge. For example, in situ Raman and in situ XRD are powerful technologies that dynamically detect the structure during charge and discharge, monitoring the metal ions intercalation. At the same time, the chemical bonds and phase composition on the basis of the ex situ method with more sensitivity are able to be present accurately and truthfully. In particular, layered structures and carbon materials which have an obviously characteristic peaks transform more obviously during striping/plating. The information could also determine by-product formation, reaction reversibility, and other key issues. Moreover, it does not only prove a valid evidence that the implemented strategy is efficacious but also give direct guidance for designing the protective methods in the next step.

6 PERSPECTIVE

Until now, the key points of AZIBs have been shifted from the cathode to the Zn anode, which mainly revolves around
the formation of Zn dendrite. In order to settle the issues of the battery system and basic science, a variety of investigations have been developed to respond to bad lifetime and serious irreversibility, focusing on interface chemistry and crystallization chemistry. This review aims to make contributions to present integrated discussion including retrospect excellent works and scientific principles. To summarize these strategies, three modified aspects around the Zn metal substrate, electrolyte additives, and separator are performed so that the electrochemistry of aqueous Zn batteries and the science questions on the metal anode both receive the result. For the modification, the criteria for constructing a superior performance metal anode should satisfy at least one of the following: (1) nucleation layers need to possess a low mismatch with the first Zn deposition layer; (2) protective layers need to be dense and uniform; (3) as-formed SEI needs to have a strong affinity for zinc ions; (4) the amount of free water near the SEI should be decreased to suppress the water decomposition by means of protective layers or electrolyte additives. To give identification and foresight of the efficacy of the tactics for homogeneous zinc deposits and infinitesimal side reactions, miscellaneous advanced characterization measurements including electrochemical experiments, theoretical simulations, and phase representation, have risen in response to the proper time and conditions. At the same time, there are still several perspectives to be a real boon in the future, which offer guidelines for exploiting the fields both on the basic theory research and industrial application:

1. In the aspect of as-constructed protective layers, especially via ex situ methods, the disadvantage of poor adhesion might create serious problems. However, the in situ methods are relatively limited to the applicable compounds. The basic principle of the in situ method is the chemical reaction between different elements or compounds under certain conditions and the formation of one or several other phases in the matrix, improving the performance of a single substrate. In the composites prepared by this method, the reinforcer nucleates and grows spontaneously in the matrix. Therefore, the surface of the reinforcer is pollution-free, the matrix and reinforcer contain well, and the interface bond strength is high. At the same time, unlike other composites, the complex reinforcement pretreatment process is eliminated and the preparation process is simplified. Therefore, new methods and devices should be developed to form a dense and uniform interface with long service life.
2. Based on the high electric charge as well as the big radius of Zn$^{2+}$, the problem might be caused for the high diffusion energy barrier. In addition, the conductance of Zn$^{2+}$ would be distinctly cut down when adding high-concentration salt in the electrolyte, which negates the electrochemistry performance of battery systems. Therefore, the balance should be found for the rational proportion of salt to solvent, contributing to the high ionic conductivity in the aqueous electrolyte and SEI.\textsuperscript{89,118,119}

3. The advantages of theoretical simulation should be made full use of, especially artificial intelligence, data mining, and machine learning, which have gained great attention recently.\textsuperscript{120–122} These tools are increasingly becoming a treasure for researchers in a variety of science and technology facilitating interdisciplinary collaboration, and advanced theoretical simulation is helping to improve the efficiency of joint work. For example, we believe that thousands of experiences on key aspects of metal anode stability could be extracted from the various works, including references to crystal chemistry and interface chemistry that are essential for practical applications of metal anodes.\textsuperscript{123,124} The analyses of the relationship between the prone problems and the protection strategy show that the development of one or more heuristic models will achieve a wider improvement for the research in the future. Researchers should provide predictive models through machine learning (i.e., deep learning and artificial neural network) to achieve a flexible and robust strategy model mainly based on crystal plane matching and reversible SEI.\textsuperscript{121,125} These well-trained models predict two orders of magnitude faster than traditional screening techniques via experiments.

4. In the case of practical or industrial application, things get complicated because the current studies remained in the stage of the basic academy. When the conditions of practicality are met, side reactions, especially hydrogen evolution would become the major issues of overall significance that must be faced, ascribed to the aggrandizement of the area of the zinc metal anode. In response to this problem, an electrolyte is the most effective measure which links cathode and anode to avoid potential safety hazards. Considering the cost, the current high-concentration salt strategy is not valid for industrialization and extensive commercialization. By contrast, electrolyte additives and gel electrolytes are more reasonable choices so that this exploration could satisfy the command of the large-scale energy storage.\textsuperscript{126–128} On the one hand, the free water molecules could be regulated by these methods in an electrolyte which suppress H$_2$ generation and Zn corrosion at the SEI validly. On the other hand, flexible devices call for the development of this quasi-solid electrolyte technology to a higher degree, which is a crucial step from the lab to the assembly line. With the development of science and technology, flexible electronic devices gradually enter the public’s vision. At present, many electronic devices on the market need flexible batteries to match, so the development of flexible batteries has become a frontier subject in the battery field. Flexible batteries are not hard to understand in the literal sense, that is, they can withstand bending, stretching, twisting, and even folding, and they come in different sizes, shapes, and excellent mechanical properties. Now all-solid-state battery has become a new direction of secondary battery development; flexible battery is no exception. The size and shape of flexible batteries are limited by traditional electrolytes because of their fluidity. It is particularly important to choose suitable solid or gel electrolytes so that the current disadvantages could be overcome.\textsuperscript{129,130}

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial supports provided by the National Natural Science Foundation of China (U1764258, 21871164), the Taishan Scholar Project Foundation of Shandong Province (ts20190908), and the Natural Science Foundation of Shandong Province (ZR2021ZD05, ZR2019MB024).

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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How to cite this article: Zhang Z, Xi B, Ma X, Chen W, Feng J, Xiong S. Recent progress, mechanisms and perspectives for crystal and interface chemistry applying to the Zn metal anodes in aqueous zinc-ion batteries. SusMat. 2022;2:114–141. https://doi.org/10.1002/sus2.53