

Review

An Overview of Challenges and Strategies for Stabilizing Zinc Anodes in Aqueous Rechargeable Zn-Ion Batteries

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Abstract: Aqueous rechargeable zinc ion batteries (ZIBs) have been revived and are considered a promising candidate for scalable electrochemical energy storage systems due to their intrinsic safety, low cost, large abundance, mature recyclability, competitive electrochemical performance, and sustainability. However, the deployment of aqueous rechargeable ZIBs is still hampered by the poor electrochemical stability and reversibility of Zn anodes, which is a common, inherent issue for most metal-based anodes. This review presents a comprehensive and timely overview of the challenges and strategies of Zn anodes toward durable ZIBs. First, several challenges that significantly reduce the Coulombic efficiency and cycling stability of Zn anodes are briefly discussed including dendrite formation, hydrogen evolution, and corrosion. Then, the mitigation strategies are summarized in terms of modifying the electrode/electrolyte interfaces, designing electrode structures, and optimizing electrolytes and separators. Further, we comprehensively discuss the mechanisms behind these issues and improvement strategies with respect to the anodes, electrolytes, and separators. Lastly, we provide perspectives and critical analyses of remaining challenges, outlook, and future direction for accelerating the practical application of aqueous rechargeable ZIBs.

Keywords: zinc ion batteries; Zn metal anode; dendrite; corrosion; hydrogen evolution



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1. Introduction

Electrochemical energy storage systems that can store energy from green and renewable sources are essential for reducing electricity overconsumption and environmental pollution. Among various forms of electrical energy storage, batteries store energy as chemical potential in the electrodes via redox reactions. One well-known example is the prevailing lithium-ion batteries (LIBs), which have a high energy density, superior cycle life, and low weight making them ideal for powering portable electronics and electric vehicles. Unfortunately, the application of LIBs in grid energy systems is hindered by the potential risk and environmental concerns occurring from highly reactive lithium compounds and flammable organic electrolytes [1–6]. The most significant safety concern associated with LIBs is a thermal runaway, which results in battery rupture and explosion as flammable gases from the battery react with ambient oxygen [7,8]. There are several origins of thermal runaway in batteries, including side reactions involving organic electrolytes, cathodes, and anodes, and interactions between electrode surfaces and Li plating caused by thermal, electrical, and thermal abuse without effective battery management and risk monitoring [9]. Moreover, LIBs often experience different types of improper operation during daily usage, such as overcharging and over-discharging due to variations in cell capacities caused by manufacturing processes, over-heating enabled by poor battery system temperature management, elevated ambient temperature or nearby fire, and physical damage impact [10].

Additionally, the widespread deployment of LIBs for scalable energy storage is restricted by a limited Earth abundance of lithium and other critical metals and difficulty in recycling LIBs [11,12]. Therefore, rechargeable batteries with high safety, long-term stability, low cost, and environmentally benign manufacturing processes are highly desirable for large-scale energy storage [13,14].

Aqueous metal-ion batteries are a promising alternative to traditional LIBs for their higher ionic conductivity, cost-effectiveness, simplified processing, and safety for aqueous electrolytes compared to organic electrolytes [15,16]. Additionally, aqueous metal-ion batteries can be assembled in ambient environments without harsh conditions [17–19]. Diverse aqueous metal-ion batteries have been developed, including aluminum-ion batteries (AIBs), calcium-ion batteries (CIBs), magnesium-ion batteries (MIBs), potassium-ion batteries (KIBs), sodium-ion batteries (SIBs), and zinc-ion batteries (ZIBs) [20]. In contrast to the high reactivity of Ca, K, and Na metal anodes with water and poor reversibility of Al, Zn anodes have a high theoretical capacity of 820 mAh g^{-1} , volumetric capacity of 5854 mAh cm^{-3} , low redox potential of -0.76 V vs. standard hydrogen electrode (SHE), fair redox stability, and relative stability in aqueous solutions [21–23] (Figure 1). From these advantages, ZIBs is considered a suitable energy storage solution for the next generation of electrical energy storage systems. Therefore, the research on ZIBs or Zn anodes has attracted intense interests leading to a trend of continuously increased publications in this field over the past 10 years (Figure 1d).

The performance and lifespan of batteries are strongly influenced by the anodes. A similar problem occurs with ZIBs such as lithium metal batteries, where the inhomogeneous Zn stripping/plating leads to dendritic growth of the Zn anodes [24]. The uncontrolled growth of zinc dendrites can negatively impact the Coulombic efficiency (CE) and cycling lifetime of ZIBs, piercing the separator, and resulting in a short circuit [25]. In addition, weakly acidic electrolytes provide a more corrosive environment for the thermodynamically favored hydrogen evolution and anode corrosion than traditional alkaline electrolytes [26,27]. In the entire pH range, $\text{H}_2\text{O}/\text{H}_2$ has a higher equilibrium potential than Zn^{2+}/Zn , indicating spontaneous hydrogen evolution and corrosion on the anode. In turn, the increase in pH value of electrolytes and the residual OH^- ions will result in the formation of by-products, including zinc hydroxide sulfate (ZHS) and other Zn compounds, which interfere with ion/electron diffusion and lead to the negative effect on Zn reversibility. Additionally, these by-products firmly bind zincate complexes, further promoting Zn dendrite formation. ZIBs are often prone to rapid failure due to the above-mentioned issues. Consequently, it is challenging to translate academic knowledge into industrial or commercial applications for ZIBs. Therefore, an overview of Zn anodes problems and mitigation strategies is needed to realize high-capacity and durable ZIBs for practical application.

The issues of zinc anodes have been usually addressed in two kinds of methods, including (i) anode tailoring with the introduction of a protective layer on Zn foil, design of a three-dimensional Zn structure and use of Zn alloy, and (ii) electrolyte modification. Several review articles have highlighted these strategies [28–32]. For example, Tao and co-workers discussed different methods for introducing protective layer strategies on the surface of the Zn anodes [28]. On the other hand, Liu et al. summarized the electrolyte optimization regarding the procedure for stabilizing Zn anodes [32]. Furthermore, Li et al. discussed and outlined the optimization strategies of ZIBs in two aspects: anode modification and electrolyte tuning [33]. However, little attention is paid to the separator construction, which also plays a vital role in the performance of ZIBs together with anode structure and electrolyte. Thus, it is crucial to provide a broad and up-to-date overview of the anode challenges, mitigation strategies in terms of the anode design, electrolyte component, separator fabrication, and critical perspectives as well as analyses.

This review aims to provide a comprehensive and timely overview of challenges and various mitigation strategies developed in recent years for Zn anodes. The existing issues in Zn anodes are summarized, including the dendrite growth, hydrogen evolution reaction (HER), corrosion, and their interplay. Then, several emerging strategies for improving Zn

electrochemistry are categorized and mapped out, including surface modification, rational design of anode architectures, electrolyte optimization, and separator design (Figure 2). Last, the remaining Zn anode challenges and future opportunities for developing stable Zn anodes in practically viable ZIBs are highlighted. This review will provide guidance and a new understanding of Zn electrochemistry for promoting the application of rechargeable aqueous ZIBs in large-scale energy storage.

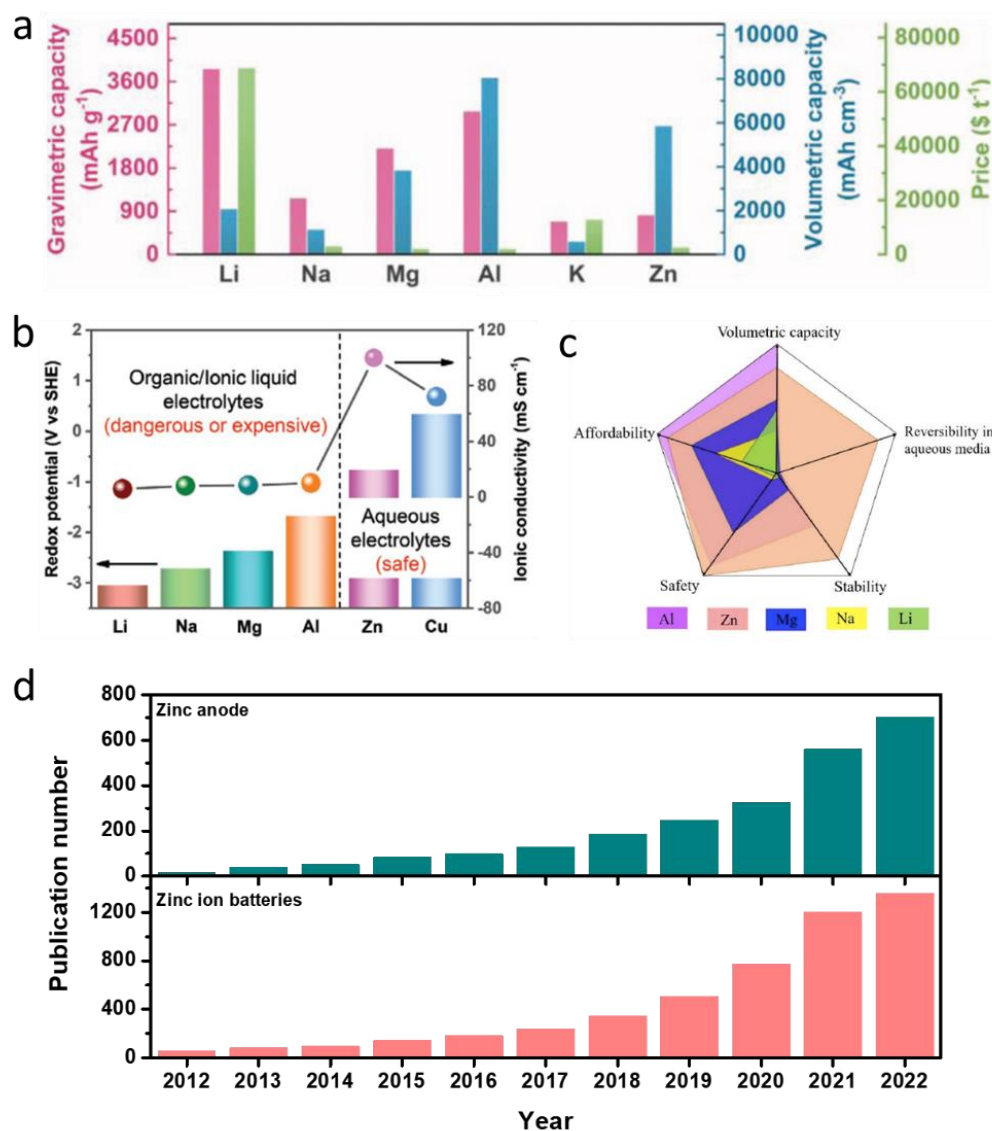


Figure 1. (a) Comparison of the gravimetric capacity, volumetric capacity, and price for typical anode metals (Reproduced with permission [34] Copyright 2021, John Wiley & Son). (b) Comparison of the redox potential and ionic conductivity for Zn and other metal anodes (Reproduced with permission [35] Copyright 2020, John Wiley & Son). (c) Radar plot of performance properties of selected metal anodes (Reproduced with permission [22] Copyright 2019, Elsevier). Compared to other metals, Zn shows balanced kinetics and a high level of stability in an aqueous solution. The fair reversibility of plating and stripping for Zn in aqueous media makes it an ideal material for aqueous energy storage systems. (d) The number of publications with keywords of zinc ion batteries or zinc anode over the past 10 years (data were collected from Clarivate Web of Science database as of December 2022).

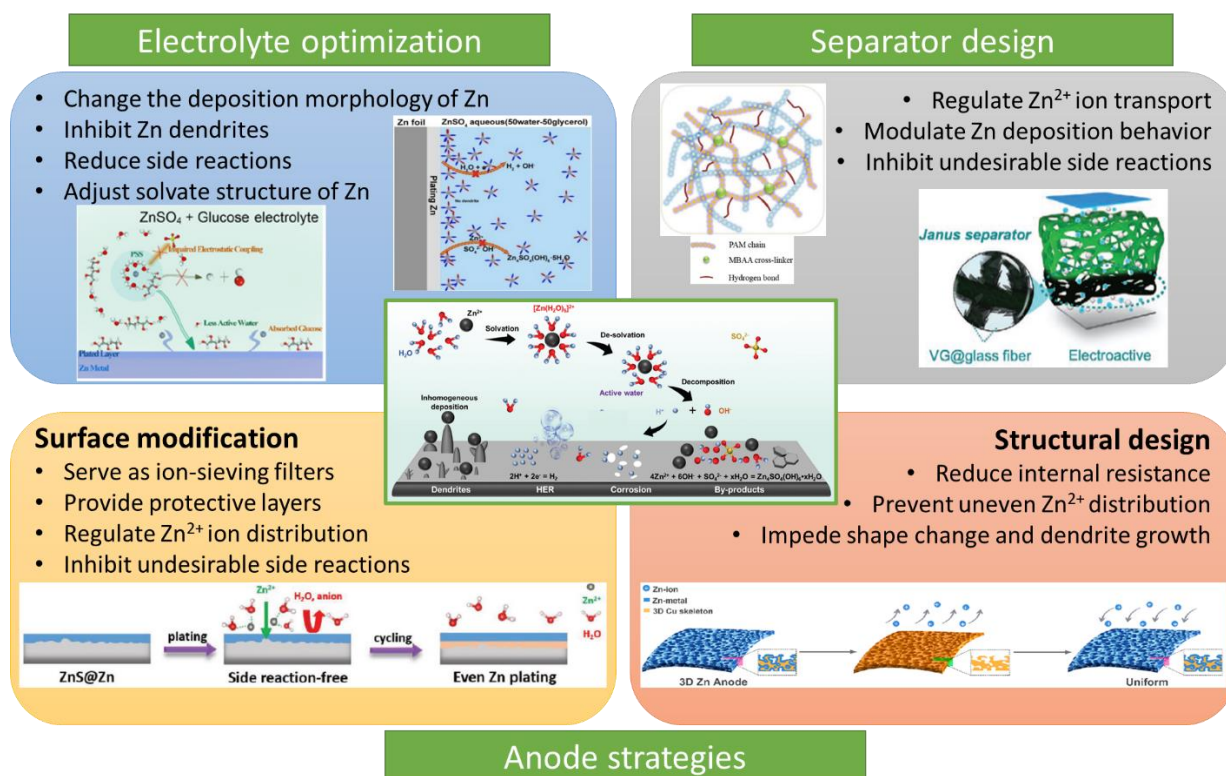


Figure 2. Schematic diagram of issues and strategies related to Zn anodes (Reproduced with permission [24] Copyright 2022, Royal Society of Chemistry [36] Copyright 2021, John Wiley & Son [37] Copyright 2018, John Wiley & Son [38] Copyright 2020, John Wiley & Son [39] Copyright 2020, John Wiley & Son [40] Copyright 2019, American Chemical Society [41] Copyright 2021, Royal Society of Chemistry).

2. Challenges of Zn Anodes

2.1. Dendrite Formation

The formation of Zn dendrites is a critical issue in mild aqueous ZIBs. Zn dendrites are generally caused by an irregular deposition of Zn^{2+} ions during the plating/stripping processes, leading to an uneven surface (Figure 3a,b). The uneven electrode surface may cause an inhomogeneous electric field and intense Zn^{2+} flux at the tips, aggravating dendrite growth and capacity decay [41]. On the other hand, the formation of residual “dead Zn” on the electrode can reduce Coulombic efficiency and battery lifespan. Additionally, the Zn dendrites may continuously grow and even penetrate the separator, leading to a short circuit of the cell. The electrode polarization, especially concentration polarization, affects the Zn deposition. The concentration polarization is caused by the limited migration of Zn^{2+} ions at the electrode/electrolyte interface, leading to a large concentration gradient perpendicular to the anode surface. The concentration polarization results in an increase in overpotential on the Zn anode. The Zn dendrite growth is also related to the current density. Generally, a large current density can aggravate the rampant growth of Zn dendrites [42]. As charge accumulates on Zn tips (also called the “tip effect”), a high electric field is created, further facilitating the growth of Zn dendrites, eventually resulting in capacity fading and short circuits [25]. In contrast, a low current density delays Zn dendrite initiation, decreasing the growth rate. At the low current density, there is less distortion of the surface electric field due to a uniform local current density distribution [43]. A negative relationship between Zn anode lifespan and current density may reflect deteriorating Zn plating/stripping behavior at high current densities that may result in the formation of Zn dendrites, whereas this will be alleviated at low current densities. However, the issue of Zn anodes under low current densities should not be neglected [42]. A short circuit will eventually occur as the dendrites grow cumulatively.

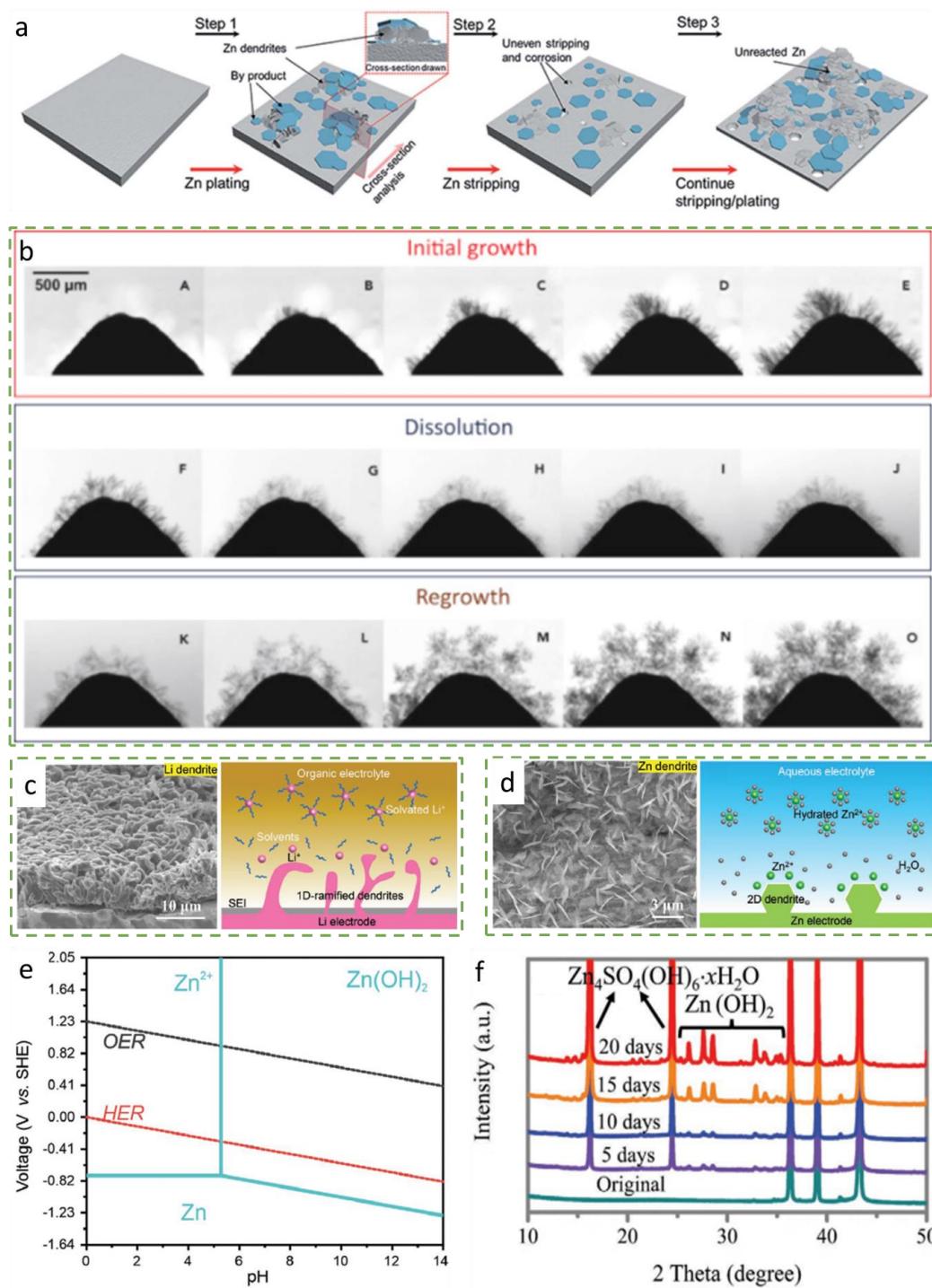


Figure 3. (a) Schematic illustration of the formation of inactive “dead” Zn (Reproduced with permission [41] Copyright 2021, Royal Society of Chemistry). (b) Operando optical microscopic study of Zn dendrite growth, dissolution, and regrowth in aqueous electrolytes (Reproduced with permission [44] Copyright 2019, Elsevier). (c) SEM image of Li dendrites and schematic diagram of dendrite topologies (Reproduced with permission [35] Copyright 2020, John Wiley & Son and Reproduced with permission [45] Copyright 2016, American Chemical Society). (d) SEM image of Zn dendrites and schematic diagram of dendrite topologies (Reproduced with permission [35] Copyright 2020, John Wiley & Son). (e) Pourbaix diagram of Zn in a 2 M ZnSO₄ solution (Reproduced with permission [46] Copyright 2021, John Wiley & Son). (f) XRD patterns of Zn immersed in 2 M ZnSO₄ electrolyte for different periods (Reproduced with permission [47] Copyright 2021, John Wiley & Son).

Additionally, Zn anodes demonstrate less serious dendrite issues compared to Li anodes [25,48]. In terms of its one-dimensional (1D) topology and ramified structure, the Li dendrites derive from the body-centered cubic (BCC) matrix, accounting for the aggressive piercing ability of Li dendrites (Figure 3c) [35]. The surface roughness causes an uneven electric field to develop Li dendrite growth, which stimulates the formation of an inhomogeneous solid electrolyte interface (SEI) during organic electrolyte decomposition [48,49]. The in situ formed Li SEI is not mechanically robust and stable, leading to repeated growth and fracture. Thus, Li dendrites gradually grow until they pierce the separator, causing battery failure [45]. Additionally, Li dendrites can invade the separator from various angles, as the inhomogeneous electric field distribution in the vicinity of the anode/separator interface can result in the uncontrolled ramification texture [50]. Accordingly, it is extremely challenging to eliminate the Li dendrite even using solid-state electrolytes. Unlike Li dendrites, Zn dendrites in near-neutral or mildly acidic media exhibit no invasive topologies or ramifications, reducing the destruction trend of separator piercing. Dendrites of Zn formed in near neutral or mildly acidic electrolytes were found to be two-dimensional (2D) hexagonal platelets, which was a result of a hexagonal close-packed (HCP) crystalline structure of Zn (Figure 3d). The size of 2D hexagonal platelets of plated Zn depends on the cycling conditions, electrode host, and electrolytes [25,51]. Moreover, Zn has a higher critical overpotential for dendrite nucleation than Li [35]. Since Zn dendrites have a unique topology and a high nucleation overpotential, in-depth systematic investigation is of significant scientific importance.

2.2. Hydrogen Evolution Reaction

Hydrogen evolution reaction (HER) is a common side reaction in aqueous ZIBs, determined by thermodynamics. The standard reduction potential of Zn^{2+}/Zn (-0.76 V vs. SHE) is lower than that of HER according to the Pourbaix diagram in the entire pH range of 1–14, suggesting that the HER is more thermodynamically favorable than Zn deposition (Figure 3e) [52,53]. Although a large overpotential for the HER on Zn can suppress its kinetics, the hydrogen gas can still be gradually generated and accumulated in the cells [54]. The HER kinetics is influenced by the composition, surface area, morphology and structure of electrodes, electrolyte species, and pH [55–61]. The cathodic reactions that occur on Zn electrodes during the charging of the cell include:

Zn deposition:



Competing HER:



The hydrogen bubbles accumulated in the cell can increase internal pressure and resistance and inflate the cell [60]. Regardless of the battery's rest (shelf life) or operation state, it is difficult to eliminate the HER [61,62].

2.3. Corrosion

Zn corrosion is another critical problem of ZIBs with mildly acidic electrolytes. The spontaneous Zn corrosion in the low pH can dissolve Zn in the aqueous electrolyte, leading to self-discharge [63]. The corrosion process is shown in Equations (4)–(6)

Anode reaction:



Cathode reaction:



Overall reaction:



The voltage of this overall reaction is calculated as follows:

$$E = E_{\text{Zn}^{2+}/\text{Zn}} - E_{\text{H}^+/\text{H}_2} - \frac{RT}{2F} \ln \left(\frac{c_{\text{Zn}^{2+}}}{(c_{\text{H}^+})^2} \right) \quad (7)$$

where $E_{\text{Zn}^{2+}/\text{Zn}}$, $E_{\text{H}^+/\text{H}_2}$, $c_{\text{Zn}^{2+}}$, c_{H^+} , R , T and F represent the standard potential of Zn/Zn²⁺ (0.763 V vs. SHE) and H⁺/H₂ (0 V vs. SHE), the concentration of Zn²⁺ and H⁺, thermodynamic constant (8.314 J mol^{−1} K^{−1}), temperature (298.15 K) and Faraday constant (96,485 C mol^{−1}), respectively [64]. Taking the ZnSO₄ electrolyte as an example, e.g., 1 M ZnSO₄ with a pH value of 4.6, 2 M ZnSO₄ with a pH value of 3.6 or 2 M ZnSO₄ + 0.5 M MnSO₄ with the pH value of 3.1, the voltage can be calculated, respectively,

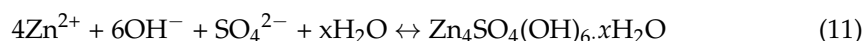
$$E = 0.763 - \frac{298.15 \times 8.314}{2 \times 96485} \ln \left(\frac{1}{(10^{-4.6})^2} \right) = 0.491 \quad (8)$$

$$E = 0.763 - \frac{298.15 \times 8.314}{2 \times 96485} \ln \left(\frac{1}{(10^{-3.6})^2} \right) = 0.541 \quad (9)$$

$$E = 0.763 - \frac{298.15 \times 8.314}{2 \times 96485} \ln \left(\frac{2}{(10^{-3.1})^2} \right) = 0.571 \quad (10)$$

The positive value of E suggests the spontaneous occurrence of this electrochemical reaction shown in Equation (6). 2 M ZnSO₄ (Equation (9)) has a lower pH than 1 M ZnSO₄ (Equation (8)), leading to a more positive voltage value. The addition of other sulfates, e.g., 0.5 M MnSO₄ in 2 M ZnSO₄ further lowers the pH value, thus raising E (Equation (10)) and promoting the corrosion process [64].

The OH[−] ions can be produced when H⁺ ions are consumed by the HER, corrosion reaction, and proton insertion into the battery-positive electrodes. In this case, secondary passive material will be formed. For example, hexagonal Zn(OH)₂ and Zn₄SO₄(OH)₆·*x*H₂O flakes can be formed when Zn metal anodes are soaked in ZnSO₄ electrolyte (Figure 3f). The reaction is as follows:



The reaction (Equation (10)) consumes the same amount of OH[−] produced by the HER. Therefore, the electrolyte pH does not significantly vary [65]. In addition, ZnO and Zn(OH)₂ may also be formed as by-products. Furthermore, these by-products can pose a high barrier to the diffusion of ions and transfer of electrons, leading to increased impedance and cell performance failure [46]. Moreover, the water is consumed in those side reactions, resulting in the drying of lean electrolytes, and increased internal resistance due to the interrupted ion diffusion process [66].

It is noteworthy that these problems can take place concurrently and interplay to accelerate the performance decay of ZIBs. The interactive effect includes but is not limited to (i) the growth of Zn dendrites increases the interfacial area between Zn anode and electrolyte, providing more active reaction sites for both HER and corrosion processes; (b) the coverage of hydrogen bubbles on the anode inhibits the nucleation of zinc, leading to increased overpotentials and uneven zinc deposition; (c) HER accelerates the side reaction (Equation (10)) due to the accumulation of OH[−] in the electrolytes; (d) the preferential oxidation of Zn (Equation (4)) on some active sites increases the roughness of the anode surface, accelerating the formation of zinc dendrites; (e) the curvature and irregularity associated with the formation of by-products induce inhomogeneous electric field distribution. Therefore, the above-mentioned issues in ZIBs must be addressed to achieve the long-term stability of the Zn anode.

3. Improvement Strategies towards High-Performance Zn Anode

3.1. Surface Modification

The charge transfer resistance, ion diffusion behavior, and redox reactions on the surface of the Zn anode are the main problems affecting the stripping and plating of Zn^{2+} ions [32]. The Zn electrodes coated with heterogeneous materials directly operate in the vicinity of Zn electrodeposition and stripping reactions. In addition to regulating Zn ion diffusion in an electrolyte, coating materials serve as ion-sieving filters for ion transfer within the coating. Therefore, an appropriate coating layer can inhibit undesirable reactions such as Zn dendrite formation, HER, corrosion, and other side reactions at the Zn electrode surface, which improves the electrodeposition and extends the lifespan of ZIBs. Recently, many types of materials have been investigated as interfacial layers for Zn anode, such as carbon-based materials [67–76]; metal-based materials such as metal oxides and metal sulfides [77–83], inorganic compounds [84–89], metal nanoparticles [90–97] and MXene [98–101]; metal-organic framework (MOF) materials [102–106]; polymer materials [46,60,61,107–113].

3.1.1. Carbon-Based Materials

The surface electric field is a critical factor in Zn nucleation and growth. Additionally, the random distribution of Zn ions during nucleation can affect the relatively balanced electric field at the surface [114]. According to the “tip effect”, Zn continues to grow because of the roughness of bare Zn, which further aggravates the imbalance of electric field distribution [34]. Therefore, it is necessary to uniformize electric field distribution on the anode surface, preventing Zn dendrites growth during the cycling process to induce a well-defined Zn nucleation. Carbon-based materials have become ideal coating materials for protecting the Zn anode due to their high conductivity, chemical stability, mechanical properties, and material diversity. Consequently, various types of carbon-based materials consisting of graphene, carbon black, activated carbon (AC), and carbon nanotubes (CNTs) are often used as conductive interfacial layers on Zn anodes. This strategy can minimize charge accumulation and balance surface charge distribution, resulting in a smooth Zn deposition process with high stability and reversibility.

For example, Zhou et al. reported a thin and uniform layer of graphene oxide (GO) coated on a Zn mesh ($\sim 15\ \mu\text{m}$) (Zn@GO) using a solution casting method, which effectively alleviates the Zn dissolution into the electrolyte [69]. The GO layer on the Zn surface enables electrons to cross the ZnO insulator (Figure 4a) due to the encapsulation of ZnO by GO, which slows down the dissolution of Zn intermediates into the electrolyte and enhances the rechargeability and utilization of Zn anodes. The results showed that the morphology of Zn@GO remained in its original shape after cycling (Figure 4b), which proved that the GO layer successfully encapsulated ZnO products and reduced the dissolution rate of Zn intermediates. Due to its abundance of O-containing groups, rich functional groups, and flexible matrix, GO benefits homogenous Zn deposition and aids stress release during Zn plating/stripping processes [115].

In addition to GO, carbon black is another ideal coating material for the Zn anode. Wang et al. introduced the coating of carbon black on Zn foil (ZF@CB) with the support of nanofibrillated cellulose (NFC) using a drop coating method [70]. As shown in Figure 4c, spherical carbon black particles can create a continuous conductive network with enough void space to accommodate the plated Zn. Additionally, the coating of carbon black on Zn foil can enlarge the electroactive area. As a result, the modified anode eliminates dendritic growth and side effects. In the meantime, carbon black adheres to Zn foil by an NFC, which an aqueous electrolyte can easily penetrate. The NFC serves as an electrolyte reservoir and guides uniform Zn deposition during charging. Consequently, the symmetric ZF@CB||ZF@CB cells showed a lower overpotential (160 mV) than the ZF||ZF cells (280 mV) at a current density of $0.5\ \text{mA cm}^{-2}$ due to a much larger electroactive area for Zn plating/stripping provided by the carbon black coating layer (Figure 4d). Then, the cycling stability of Zn-MnO₂ batteries was remarkably enhanced by the ZF@CB anode, which exhibited higher capacity retention (87.4%) than that of pure ZF (42.6%) after

1000 cycles at the current density of 3 A g^{-1} . Conclusively, the improvement of cyclability was attributed to a large surface area and high electrical conductivity of the carbon black coating layer.

Carbon nanotubes (CNTs) are another well-known one-dimensional material with high electrical conductivity, low weight, and excellent chemical stability. Li et al. applied a dip-coating method to prepare a Zn-CNTs anode [71]. Zn nuclei with a high overpotential deposit on the surface of the Zn foil due to the anisotropic deposition process of Zn during the charging process, and these dendrites continue to develop with increasing cycles. With the help of charge redistribution effects of CNTs on overpotential, uniform Zn nanosheets can be observed on the Zn foil surface without dendrite formation after 400 h (Figure 4e,f). The Zn-CNTs anode effectively inhibits Zn dendrites and controls the side reaction, thus demonstrating an outstanding cyclability of the Zn-CNTs||Zn-CNTs symmetric cells (33 times longer than the bare Zn foil) without polarization up to 400 h (Figure 4g). Benefitting from the Zn-CNTs anode, the $\text{Mn}^{2+}/\text{Zn}^{2+}$ hybrid batteries performed well over 11,000 cycles with 100% capacity retention (Figure 4h).

Overall, carbon-based material coatings provide conductive protection. Due to their mechanical strength, dendrites cannot penetrate the separator, effectively inhibiting the growth of dendrites. Moreover, high-conductivity carbon-based materials provide strong electric field strength, reduce charge accumulation, and promote uniform electric field distribution. A summary of the coating strategies and electrochemical results for carbon materials can be found in Table 1.

Table 1. Carbon-based coating materials for improving Zn metal anodes.

Anodes	Overpotential	Performance	Cycled Life	Ref
AC-Zn	~20 mV	1 mA cm^{-2} – 1 mAh cm^{-2}	200 h	[67]
CF-Zn	~13 mV	1 mA cm^{-2} – 1 mAh cm^{-2}	2500 h	[68]
CB-Zn	~160 mV	0.5 mA cm^{-2} – 0.5 mAh cm^{-2}	400 h	[70]
PEDOT:PSS/GS-Zn	~25 mV	1 mA cm^{-2} – 1 mAh cm^{-2}	500 h	[72]
rGO-Zn	~20 mV	1 mA cm^{-2} – 1 mAh cm^{-2}	300 h	[73]
rGO-Zn	~80 mV	1 mA cm^{-2} – 2 mAh cm^{-2}	200 h	[74]
NGO-Zn	~32 mV	1 mA cm^{-2} – 1 mAh cm^{-2}	1200 h	[75]
CNTs scaffold-Zn	~36 mV	0.1 mA cm^{-2} – 0.5 mAh cm^{-2}	1800 h	[76]

AC = activated carbon, CF = carbon fiber, CB = carbon black; PEDOT:PSS/GS = Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) decorated graphene sheets; rGO = reduced graphene oxide, NGO = nitrogen-doped graphene oxide, CNT = carbon nanotube.

3.1.2. Metal-Based Materials

Generally, ideal interfacial layers should have the following characteristics: (1) chemical and electrochemical inertness for preventing reactions with the electrolyte; (2) mechanically strong to resist volume change and dendrite growth; and (3) wettability to electrolytes or unique ion channels to facilitate ion diffusion [39,114]. As insulating layers at the Zn-electrolyte interface, various metal-based materials have been reported.

Metal Oxide and Sulfide Materials

Metal oxide and sulfide materials have been recently studied as an effective coating material to form a passivation layer and regulate the distribution of Zn^{2+} ion at the interface, including ZnS [39], Al_2O_3 [77], HfO_2 [78], Sc_2O_3 [79], TiO_2 [80], ZrO_2 [81], MoS_2 [82], ZnO [83]. For instance, Hao et al. introduced a vapor–solid strategy to obtain a robust and homogeneous ZnS artificial layer on the Zn surface at 350°C (ZnS@Zn-350) (Figure 5a), which effectively improved the Zn reversibility [39]. By forming a physical barrier on the surface of Zn, the dense ZnS artificial layer suppressed Zn corrosion by blocking the electrolyte and inhibited dendrite growth by guiding the Zn plating/stripping beneath the artificial layer (Figure 5b). As a result, the ZnS@Zn-350 symmetric cell displayed extended cycling stability over 1100 h at a current density of 2 mA cm^{-2} , while the symmetric cell of bare Zn showed a short circuit after 200 h due to a dynamic dendrite-induced short circuit

(Figure 5c). Moreover, excellent cycling stability of the $\text{MnO}_2/\text{ZnS@Zn}$ -350 full-cell was obtained with 87.6% capacity retention after 2500 cycles (Figure 5d). Due to the mechanical robustness and high ionic conductivity, ZnS is stable in aqueous electrolytes, facilitating dendrite-free Zn during the plating and stripping process.

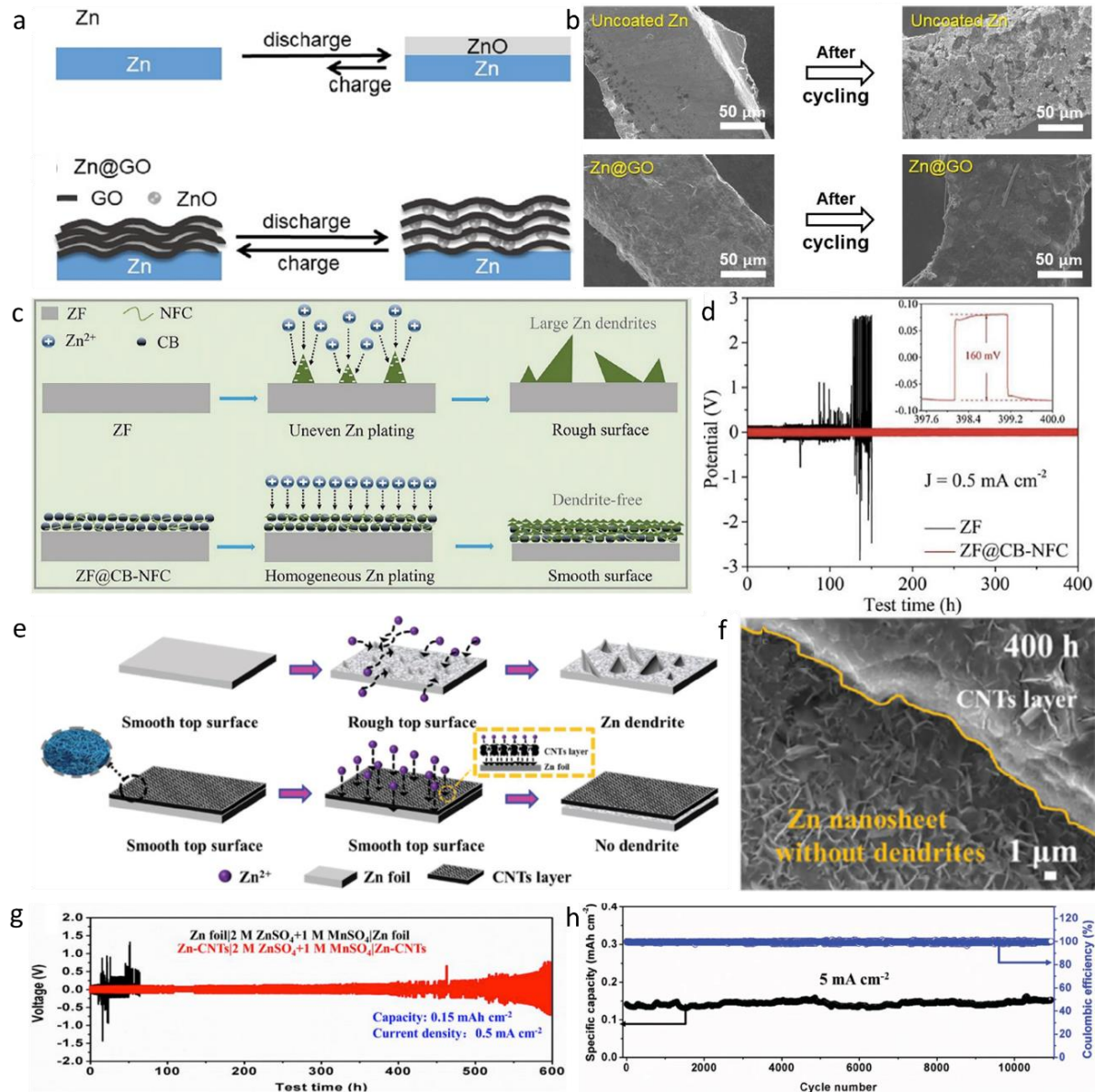


Figure 4. (a) Diagram of morphological changes occurring on zinc electrodes during electrochemical cycling and (b) SEM images of bare Zn anode before and after cycling and SEM images of bare Zn@GO anode before and after cycling (Reproduced with permission [69] Copyright 2019, Elsevier). (c) Schematic illustrations for the evolution of surface morphology of the pure ZF and ZF@CB during Zn plating and (d) Cycling performance of ZF@CB | ZF@CB symmetrical cells at the current density of 0.5 mA cm^{-2} (Reproduced with permission [70] Copyright 2020, Elsevier). (e) Schematic illustrations for morphology evolution of bare Zn anode and anti-dendrite mechanism of Zn-CNTs anode, (f) SEM image of Zn-CNTs surface after 400 h. (g) Typical galvanostatic discharge-charge profiles of symmetric cells with bare Zn foil and Zn-CNTs anode at a current density of 0.5 mA cm^{-2} , and (h) cycling performance at 5 mA cm^{-2} and Coulombic efficiency as a function of cycles (Reproduced with permission [71] Copyright 2019, John Wiley & Son).

In addition, Dai et al. applied a facile coating method to coat the γ - Al_2O_3 on the surface of Zn foils by using a tetrahedral preparator [77]. The γ - Al_2O_3 artificial layer can guide the uniform deposition of Zn ions and act as a conductive layer to accelerate ion diffusion due to its hydrophilicity. They also emphasized that the thickness of a protective layer should be controlled to achieve superior electrochemical performance. A thick coating can inhibit the contact of Zn foil with the electrolyte and hinder the migration of Zn ions and limit the number of Zn ions transported. A thin coating can promote the migration rate of Zn ions, but the effects of uniformity, anticorrosion, and dendrite suppression may not be optimized. A proper thickness of the γ - Al_2O_3 coating layer lowers the reactivity of Zn anodes with electrolyte and improves the uniformity of Zn plating/stripping, which reduces the development of Zn dendrites and suppresses side reactions. The mechanism of different γ - Al_2O_3 coating thicknesses compared to bare Zn is displayed in Figure 5e. It is observed that the 15 μm thick γ - Al_2O_3 coated Zn foil ($\text{Zn@Al}_2\text{O}_3$ -15) exhibited the best performance and maintained a stable lifetime of 300 h at the lowest overpotential of 21 mV at 1.0 mA cm^{-2} (Figure 5f). The coating layer of γ - Al_2O_3 with a thickness of 15 μm facilitated the rapid migration of Zn^{2+} ions and led to a uniform Zn nucleation and growth process, hindering the formation of dendrites and by-products. Al_2O_3 , TiO_2 , and ZrO_2 have high dielectric constants, enabling them to control electrolyte flux and separate charges over significant distances at the interface [80,81].

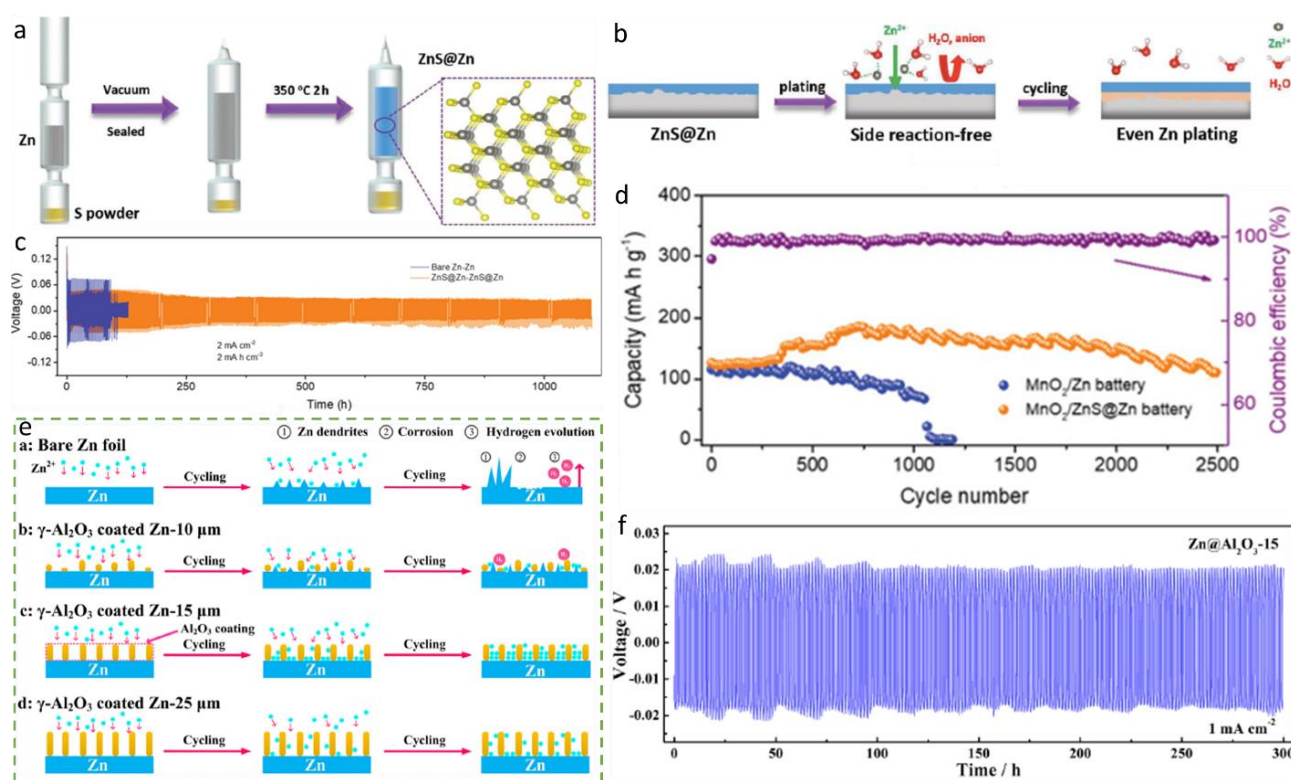


Figure 5. (a) Schematic illustrations for preparing ZnS coated Zn foil. (b) Mechanism of anti-dendrite and blocking site reactions of ZnS during plating process. (c) Cycling performance of symmetric Zn||Zn and ZnS@Zn||ZnS@Zn cells. (d) Specific capacity and Coulombic efficiency of Zn/ZnS@Zn-MnO₂ batteries (Reproduced with permission [39] Copyright 2020, John Wiley & Son). (e) Schematic illustrations for the morphological evolution of bare Zn and γ - Al_2O_3 coated on Zn foils with different coating thicknesses during stripping/plating process. (f) Galvanostatic charge/discharge cycling voltage profiles of Zn@ Al_2O_3 -15 symmetric cell (Reproduced with permission [77] Copyright 2021, Elsevier).

Inorganic Compounds

The porous nature of inorganic compounds allows them to be used as adequate protective layers for inhibiting dendrite growth and buffering volume change during

repeated Zn stripping/plating, redistributing zinc ions, and reducing the ion concentration gradient generated by preferential ion flux [84–89]. For example, a porous nano- CaCO_3 coating material for the protection of Zn anode (nano- CaCO_3 -coated-Zn) was reported by Kang et al. [84]. Due to the high porosity, nano- CaCO_3 -coating can be promptly permeated by an aqueous electrolyte, promoting a relatively uniform electrolyte flux and an even Zn plating rate (Figure 6a). The nanopores of the nano- CaCO_3 coating confine Zn nuclei with small sizes, which explains the lower polarization of these electrodes. As a result, dendrite growth and short-circuit issues were effectively prevented, enabling an extended performance for the Zn anode (Figure 6b).

In addition, Deng et al. proposed kaolin as a coating material owing to its sieve-element function (selective channel of Zn^{2+}) and uniform pore distribution [86]. Because of the uniform pore distribution, the layer structure of kaolin exhibited good mobility and Zn^{2+} transfer in a neutral environment. During the charge/discharge process, Zn ions tend to accumulate on the tips and grow on the surface of the anode to lower the surface energy, which is systematically shown in Figure 6c. The confinement of Zn^{2+} transfer in kaolin is described in Figure 6d. Because of the confined structure of uniform porous kaolin layers, Zn dendrites were prevented. Thus, kaolin was an appropriate interfacial and protective covering on the Zn surface, regulating the transmission of Zn^{2+} and isolating bulk electrolytes from the Zn electrode. Benefiting from these advantages, the kaolin-coated Zn anode (KL-Zn) ensured the growth of dendrite and restrained side reactions (Figure 6e). As a result, the long-time stability of the KL-Zn symmetric cell could be maintained up to 800 h at the current density of 4.4 mA cm^{-2} and 1.1 mAh cm^{-2} areal capacity (Figure 6f).

Hence, the insulating layers, which do not participate in any reactions, not only block zinc dendrites directly but also allow the electrolyte to penetrate and enrich Zn^{2+} within a narrow range near the anode surface, improving the Zn deposition and reversibility of the Zn anode.

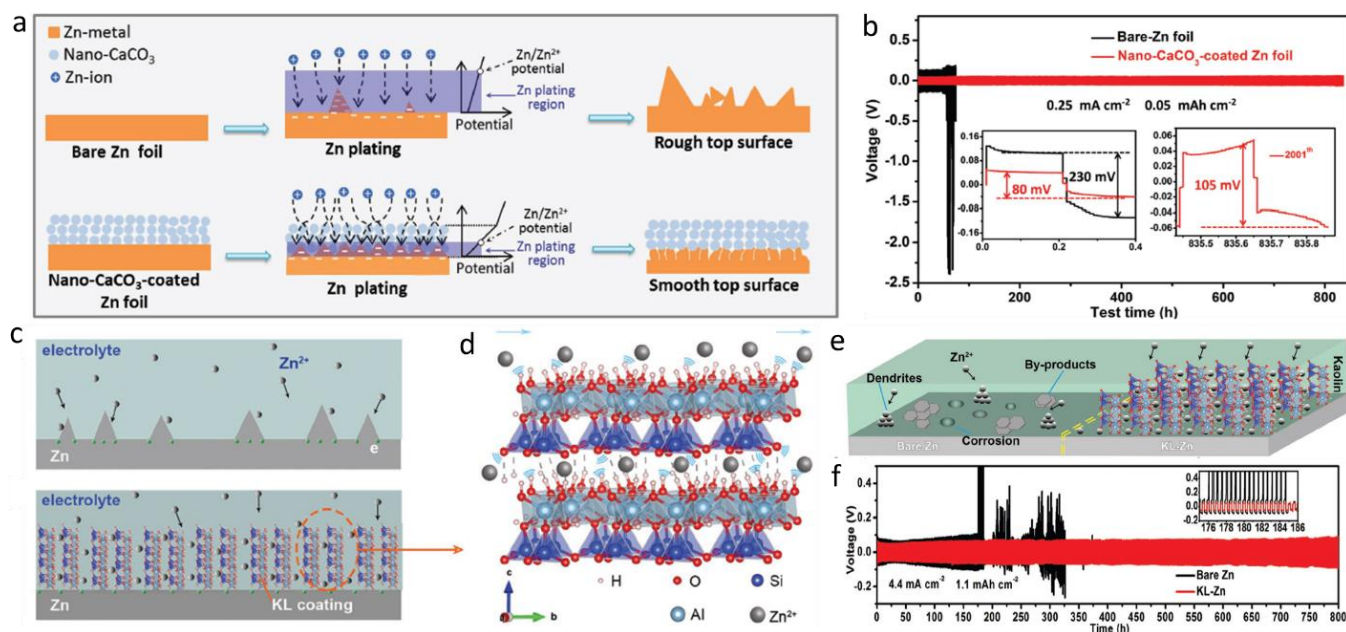


Figure 6. (a) Schematic diagrams of the morphological evolution of bare Zn and nano- CaCO_3 -coated Zn during Zn plating/stripping cycling. (b) Typical GCD profiles of Zn | $\text{ZnSO}_4 + \text{MnSO}_4$ | Zn symmetric cells with bare Zn and nano- CaCO_3 -coated Zn electrodes (Reproduced with permission [84] Copyright 2018, John Wiley & Son). (c) Schematic diagrams of Zn deposition process on bare Zn and KL-Zn. (d) Schematic representation of confined Zn^{2+} transmission in kaolin. (e) Schematic illustrations of morphology transformation of bare Zn and KL-Zn anodes during Zn^{2+} deposition process. (f) Long-term galvanostatic cycling results of symmetrical cells with bare Zn and KL-Zn electrodes (Reproduced with permission [86] Copyright 2020, John Wiley & Son).

Others

Various metal nanoparticles have been investigated for Zn metal anode surface coating, including Au [90], Cu [91], Sn [92], and In [93]. Due to their excellent anticorrosion properties and effectiveness in reducing Zn nucleation energy, metal nanoparticles provide superior electrochemical performance. For instance, a uniform and stable Zn plating/stripping process is enabled by the pre-formed seeds created by sputtering the Au nanoparticles on the Zn anode surface (Figure 7a) [90]. Comparing the NA-Zn-60 electrode with bare ZF, the NA-Zn-60 electrode showed a relatively uniform surface morphology after cycling (Figure 7b). Additionally, Cai et al. successfully coated Zn metal with Cu nanoparticles using 0.1 M CuCl₂ as a precursor solution (Figure 7c) [91]. Improved stability of the Cu/Zn anode was due to the excellent corrosive resistance and positive electrode potential of Cu (Figure 7d), which is electrochemically converted to Cu-Zn alloy/Zn composite during cycling. Table 2 shows different metal nanoparticles coated on Zn anodes. Metal nanoparticles provide homogeneous surface electrical fields due to their superior electric conductivity. The Zn metal may also be inhibited by the anticorrosion properties of some metals in aqueous electrolytes. As seed layers on the surface of the Zn anode, metal nanoparticles could further facilitate easier zinc nucleation. In addition, Zn plating is facilitated by the interaction between metal and Zn atoms, providing several nucleation sites. As a result of the above merits, metal nanoparticle-coated Zn anodes are highly reversible during the stripping/plating process.

Since their superior electrical and mechanical properties, MXene transition metal carbides have been extensively explored as an excellent material in the energy storage field [98–100]. An in situ spontaneously reducing and assembling strategy has been developed to fabricate a highly uniform artificial MXene (Ti₃AlC₂) layer to homogenize the surface electric field and smooth the Zn deposition on the Zn surface (Figure 7e) [98]. Through the charge redistribution effect, the MXene layer confers a lower Zn nucleation energy barrier and uniformly distributed electric field on the Zn anode compared with the pure Zn anode (Figure 7f). Therefore, Zn-ion batteries with MXene-integrated Zn anodes retain the high capacity and have low polarization potential without showing apparent voltage hysteresis (Figure 7g,h). Tian et al. also proved that MXene (Ti₃C₂T_x) effectively regulated Zn deposition behavior (Figure 7i) [100]. In addition to the increased surface area, the enhanced hydrophilicity of MXene can also ensure low current density and high ion mobility, hence obviating the formation of Zn dendrites after long charge–discharge cycles (Figure 7j). Also, the layered structure of MXene introduces zincophilic and chemically inert seed crystals as Zn nucleation sites for more uniform Zn deposition [101]. As a result of its unique layering structure and high conductivity, MXene is an ideal material for anode support.

Table 2. Summary of metal nanoparticles (NP) and MXene as coating materials for improving Zn metal anodes.

Metal NPs	Overpotential	Performance	Cycled Life	Ref
Au	~100 mV	0.25 mA cm ⁻² –0.05 mAh cm ⁻²	2000 h	[90]
Cu	~30 mV	1 mA cm ⁻² –0.5 mAh cm ⁻²	1500 h	[91]
Sn	~25 mV	1 mA cm ⁻² –0.5 mAh cm ⁻²	500 h	[92]
In	~54 mV	0.2 mA cm ⁻² –0.2 mAh cm ⁻²	1500 h	[93]
In	~15 mV	0.25 mA cm ⁻² –0.05 mAh cm ⁻²	1400 h	[94]
Cu	~50 mV	1 mA cm ⁻² –1 mAh cm ⁻²	5000 h	[95]
Ag	~25 mV	0.25 mA cm ⁻² –0.25 mAh cm ⁻²	1500 h	[96]
Ridge-like Zn	~52 mV	1 mA cm ⁻² –0.2 mAh cm ⁻²	400 h	[97]
MXene	47 mV	0.2 mA cm ⁻² –0.2 mAh cm ⁻²	>800 h	[98]
MXene	75 mV	1 mA cm ⁻² –1 mAh cm ⁻²	300 h	[100]

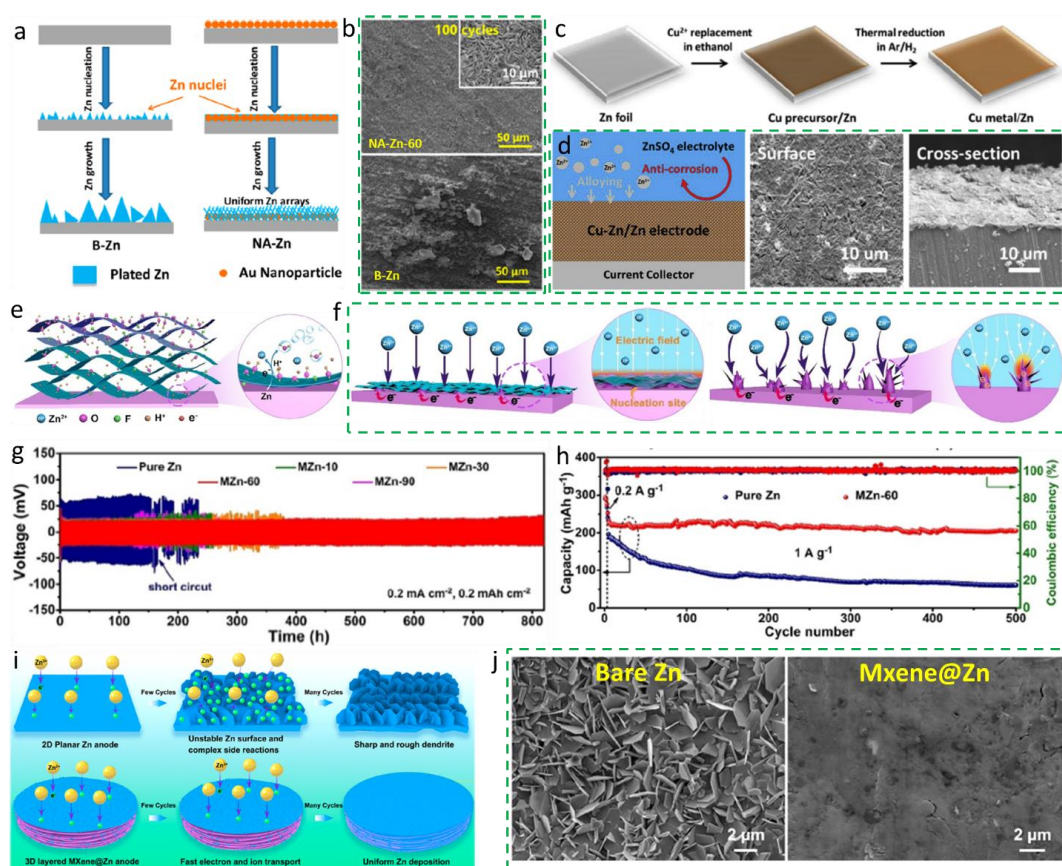


Figure 7. (a) Schematic illustration of the Zn stripping/plating process on B-Zn and NA-Zn anode and (b) SEM images of B-Zn and NA-Zn after 100 cycles at 0.25 mA cm^{-2} – 0.05 mAh cm^{-2} of symmetric Zn cells (Reproduced with permission [90] Copyright 2019, American Chemical Society). (c) Diagram illustrating the fabrication process of the Cu/Zn electrode and (d) Schematic illustration of the function, and the top-view and cross-section SEM images of Cu/Zn electrode (Reproduced with permission [91] Copyright 2020, Elsevier). (e) Schematic illustration of synchronous reduction and assembly of MXene layers on Zn foils, (f) illustration of Zn plating behavior of MXene-coated Zn and pure Zn, (g) long-term cycling performance at 0.2 mA cm^{-2} – 0.2 mAh cm^{-2} , and (h) long-term cycling performance at 1 A g^{-1} after 500 cycles. (Reproduced with permission [98] Copyright 2021, John Wiley & Son). (i) The evolution of the morphology of the bare Zn and Ti₃C₂T_x MXene@Zn anodes during stripping and plating and (j) SEM image bare Zn and Ti₃C₂T_x MXene@Zn anode after being cycled (Reproduced with permission [100] Copyright 2019, American Chemical Society).

3.1.3. Metal-Organic Framework (MOF)

MOF materials have drawn much attention recently because of their large surface area, high microporosity, uniform pore dispersion, and multifunctionality [116,117]. Several MOFs have been utilized as coating protectors for the Zn anode, such as zeolite imidazolate framework-7 (ZIF-7) [102], zeolite imidazolate framework-8 (ZIF-8) [103–105], and Universitetet I Oslo-66 (UIO-66) MOFs [106]. For example, Liu et al. prepared ZIF-8 as a coating layer deposited on Zn foil (ZIF@Zn) by a one-step solvent thermal method [103]. Because of well-organized porous channels and rich N species, ZIF-8 can easily coordinate Zn²⁺ ions and modulate the plating rate at the Zn anode interface. The porous structure of the ZIF-8 layer allows orderly nanosized channels to separate the space above the Zn anode into small confinements, enhancing Zn²⁺ flux within each confinement and guiding a uniform Zn nucleation and plating rate (Figure 8a). Additionally, a certain amount of Zn²⁺ will be held by N species because of the strong interaction between Zn²⁺ ions and N atoms in ZIF-8 (Figure 8b). Since Zn²⁺ ions near Zn surfaces are consumed during plating,

the supplementary Zn^{2+} ions will be more effective on Zn@ZIF-8 , ensuring homogeneous Zn deposition (Figure 8c). Therefore, the symmetric $\text{ZIF@Zn}||\text{ZIF@Zn}$ cell demonstrated a stable overpotential at a low voltage of 58 mV with ultralong cycling for over 1200 h (Figure 8d).

On the other hand, Liu et al. proposed an artificial composite protective layer of UIO-66 to reconstruct the Zn/electrolyte interface [106]. Thus, a good interface contact is formed between UIO-66 particles and the electrolyte (Figure 8e). Due to the hydrophilic property of the UIO-66 coating layer, the UIO-66 particles immersed with electrolyte enabled a well-contacted interface and modulated even Zn plating, leading to the suppression of Zn dendrite. At the same time, insufficient wetting of the electrolyte on the bare Zn anode resulted in localized current flow, which led to dendrite formation. A zincophilic interface formed by the microporous UIO-66 significantly reduced the interface charge transfer resistance and improved the wettability of the Zn anode (Figure 8f). The UIO-66 coating also decreases the overpotential of the battery (Figure 8g), reduces the nucleation energy, and promotes zincophilicity on the interface. As a result, Zn plating and stripping cycles can be maintained for over 500 cycles without short circuits (Figure 8h). According to previous research, a porous structure is observed in the metal-organic framework (MOF), and a unique organic–inorganic structure is discovered in the organic–inorganic composite coating. Further, these coating materials can effectively suppress side reactions caused by water due to the desolvation effect. Table 3 showed the comparison of some MOF materials-coated on Zn anode in previous literature.

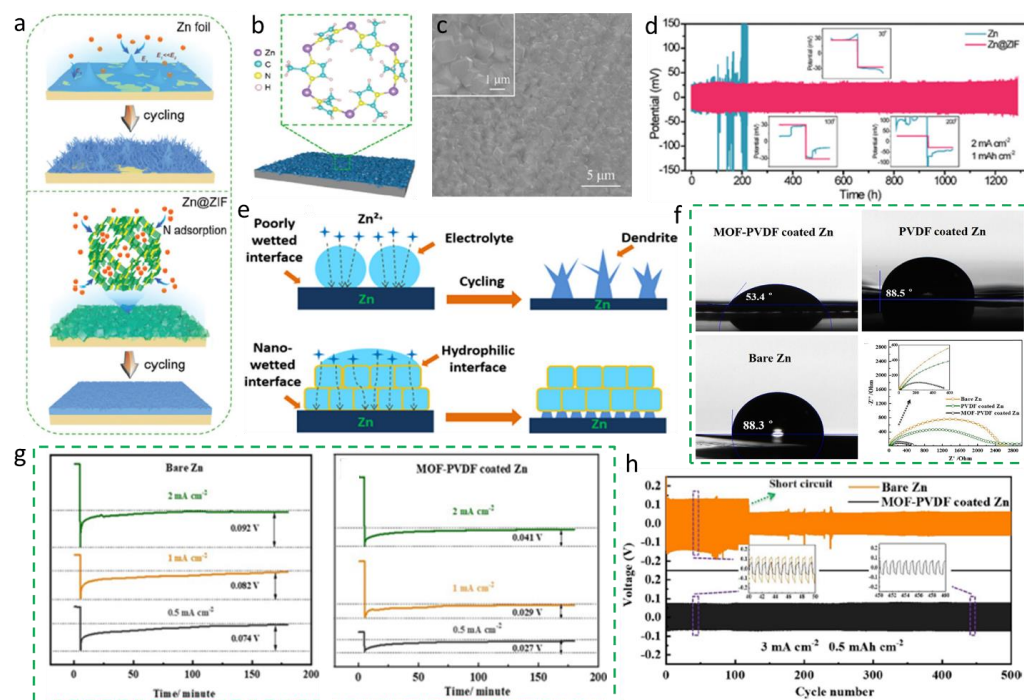


Figure 8. (a) Schematic diagram of the morphology evolution of bare Zn and ZIF@Zn anodes during cycling, (b) schematic illustration of the interaction between Zn and ZIF-8, (c) SEM image of the ZIF@Zn , and (d) voltage profile of symmetric bare Zn and Zn@ZIF cells at 2 mA cm^{-2} with a capacity of 1 mAh cm^{-2} . (Reproduced with permission [103] Copyright 2020, John Wiley & Son). (e) Schematic propose of Zn plating mechanism on bare Zn and UIO-66-coated Zn, (f) the contact angles between the electrolyte and different anodes as well as the electrochemical impedance spectra of Zn-symmetric cells, (g) Zn plating voltage curves for bare and coated Zn at various current densities, and (h) voltage profile of galvanostatic Zn plating/stripping at 3 mA cm^{-2} for different Zn electrodes. (Reproduced with permission [106] Copyright 2019, American Chemical Society).

Table 3. Summary of metal oxides, metal sulfides, metal-organic frameworks (MOFs) and inorganic compounds coated on Zn surface.

Material	Overpotential	Performance	Cycled Life	Ref
ZnS	98 mV	2 mA cm ⁻² –2 mAh cm ⁻²	1100 h	[39]
Al ₂ O ₃	~200 mV	1 mA cm ⁻² –0.5 mAh cm ⁻²	300 h	[77]
HfO ₂	~40 mV	0.4 mA cm ⁻² –0.1 mAh cm ⁻²	150 h	[78]
Sc ₂ O ₃	~40 mV	0.5 mA cm ⁻² –0.5 mAh cm ⁻²	280 h	[79]
TiO ₂	50 mV	0.4 mA cm ⁻² –0.2 mAh cm ⁻²	160 h	[80]
ZrO ₂	24 mV	0.25 mA cm ⁻² –0.125 mAh cm ⁻²	3700 h	[81]
MoS ₂	120 mV	2.5 mA cm ⁻² –0.416 mAh cm ⁻²	160 h	[82]
CaCO ₃	~100 mV	0.25 mA cm ⁻² –0.05 mAh cm ⁻²	836 h	[84]
NaTi ₂ (PO ₄) ₃	17.4 mV	0.4 mA cm ⁻² –0.2 mAh cm ⁻²	200 h	[85]
Kaolin	~100 mV	4.4 mA cm ⁻² –1.1 mAh cm ⁻²	800 h	[86]
ZnP	31 mV	2 mA cm ⁻² –1 mAh cm ⁻²	1100 h	[87]
Zeolite	60 mV	1 mA cm ⁻² –0.5 mAh cm ⁻²	1200 h	[88]
Zn ₃ (PO ₄) ₂	~30 mV	1 mA cm ⁻² –0.5 mAh cm ⁻²	3000 h	[89]
MOF	~60 mV	0.5 mA cm ⁻² –0.5 mAh cm ⁻²	3000 h	[102]
ZIF-8	~25 mV	2 mA cm ⁻² –1 mAh cm ⁻²	1300 h	[103]
ZIF-8	105 mV	0.25 mA cm ⁻² –0.05 mAh cm ⁻²	170 h	[105]
UIO-66	~50 mV	1 mA cm ⁻² –0.5 mAh cm ⁻²	500 h	[106]

3.1.4. Polymer

Polymers have abundant functional groups such as C=O and N–H that can provide absorption/coordination sites and transport the Zn²⁺ to the reaction interface along the polymer chains, modulating the uniform distribution of Zn²⁺ and improving the cycling stability. Some common polymers materials, consisting of polyimide [46], poly(vinyl butyral) [60], polyamide [61], poly(vinylidene difluoride) (PVDF) [107], polyacrylonitrile (PAN) [108], and cyanoacrylate [109] have been studied as coating materials for Zn anode due to their rich functional groups. As shown in Table 4, various polymer coating materials for Zn surface engineering were summarized.

For example, polyimide was used as a covering material for Zn anodes to improve Zn deposition and suppress side reactions. Zhu et al. proposed that a polyimide coating layer could act as an insulating layer to provide ohmic resistance control for suppressing corrosion [46]. Figure 9a shows how the polyimide layer acts as an anticorrosion mechanism. By separating Zn and the electrolyte, the polyimide layer prevents the formation of anodic and cathodic sites at the interface between Zn and the electrolyte. Additionally, the strong polar and electron-donating sites in carbonyl oxygen atoms of the polyimide chain (Figure 9b) form stable bonds with the electron-accepting sites on the Zn surface to create coordination ions during cycling. Hence, coordination ions built a Zn blanket at the electrode/electrolyte interface during cycling, which minimized concentration gradients and allowed fast kinetics and low overpotentials during the plating and stripping processes. Consequently, the polyimide-Zn anode had a lower overpotential and longer cycle lifespan than the pure Zn foil counterpart (25 mV vs. 100 mV and 300 h vs. 105 h, respectively), at a current density of 4 mA cm⁻² with a total capacity of 2 mAh cm⁻² (Figure 9c).

In another work, a ternary polymer poly(vinyl butyral, vinyl alcohol, and vinyl acetate), PVB, coating with rich polar functional groups was fabricated by Hao et al. [60]. It was found that PVB coating effectively removed solvated water during Zn plating/stripping and significantly inhibited the occurrence of side reactions, as shown in Figure 9d. The

PVB coating also assisted in dissolving and depositing Zn^{2+} ions evenly on the Zn surface, guiding electrolyte distribution. Hence, PVB coatings prevent Zn dendrites from growing and undergoing side reactions (Figure 9e,f).

On the other hand, Cao et al. utilized a solvent-free cyanoacrylate adhesive (502-glue) as a coating layer on the Zn surface using the spin-coating method (Figure 9g) [109]. As shown in Figure 9h, due to the adsorption function between Zn^{2+} ions and polar cyano groups present in 502-glue backbones, lateral diffusion, and aggregation of Zn^{2+} along the surface can be adjusted during the nucleation process with the 502-glue coating, resulting in fine nuclei of varying sizes. Additionally, absorbed Zn^{2+} could not transfer laterally because of the additional energy barrier and therefore lands close to the initial nucleation sites rather than moving elsewhere. Moreover, the covering layer plays a vital role as an artificial solid/electrolyte interphase, effectively inhibiting the corrosion of the Zn anode from water molecules and O_2 evolution, preventing the formation of dendrite and other side reactions. Furthermore, the Zn nucleation sites are distributed evenly and orderly in the 502-glue backbone due to the adsorption effect between Zn^{2+} and the polar cyano groups. As a result, a constant voltage profile after 400 h at 2 mA cm^{-2} and 1 mAh cm^{-2} was achieved with a smooth surface Zn electrode (Figure 9i,j).

To sum up, an artificial SEI between the electrode and the electrolyte was created by using a polymer coating. Polymers with large functional groups contribute great sites for Zn ions adsorption and coordination, regulating Zn^{2+} migration to the reaction interface along polymer chains. Additionally, polymers also act as an electrostatic shield to avoid Zn^{2+} /electrons accumulation. The superior adhesion of polymers on the Zn surface hinders the corrosion caused by water, O_2 , and other side reactions, leading to the high performance of the Zn anode.

Table 4. Summary of polymers used as coating layers on Zn anodes.

Material	Overpotential	Performance	Cycled Life	Ref
Polyimide	~25 mV	4 mA cm^{-2} – 2 mAh cm^{-2}	300 h	[46]
PVB	~80 mV	0.5 mA cm^{-2} – 0.5 mAh cm^{-2}	2200 h	[60]
Polyamide	~100 mV	0.5 mA cm^{-2} – 0.25 mAh cm^{-2}	8000 h	[61]
PVDF	~60 mV	0.25 mA cm^{-2} – 0.05 mAh cm^{-2}	2000 h	[107]
PAN	~75 mV	1 mA cm^{-2} – 1 mAh cm^{-2}	1150 h	[108]
502-glue	~50 mV	2 mA cm^{-2} – 1 mAh cm^{-2}	400 h	[109]
PVA	~125 mV	0.25 mA cm^{-2} – 0.25 mAh cm^{-2}	5000 h	[110]
PFPE	~40 mV	1 mA cm^{-2} – 1 mAh cm^{-2}	800 h	[111]
PPy	~25 mV	2 mA cm^{-2} – 1 mAh cm^{-2}	600 h	[112]
SPEEK	~40 mV	1 mA cm^{-2} – 1 mAh cm^{-2}	500 h	[113]

PVB = poly(vinyl butyral), PVDF = poly(vinylidene difluoride), PAN = polyacrylonitrile, PVA = polyvinyl alcohol, PFPE = perfluoropolyether, PPy = polypyrrole, SPEEK = sulfonated poly(ether ether ketone) (SPEEK).

3.2. Structural Design Optimization

Reduced dendrite growth can be effectively achieved by modifying the Zn anode structure. The structural design is aimed to reduce the internal resistance and inhibit the uneven distribution of Zn^{2+} ion on the anode surface, which effectively impedes the shape change and dendrite formation [22]. Numerous forms of Zn anodes can be classified based on their internal bulk structure, such as 3D framework-hosted Zn anodes [40,118–120] and Zn alloy anodes [121–128].

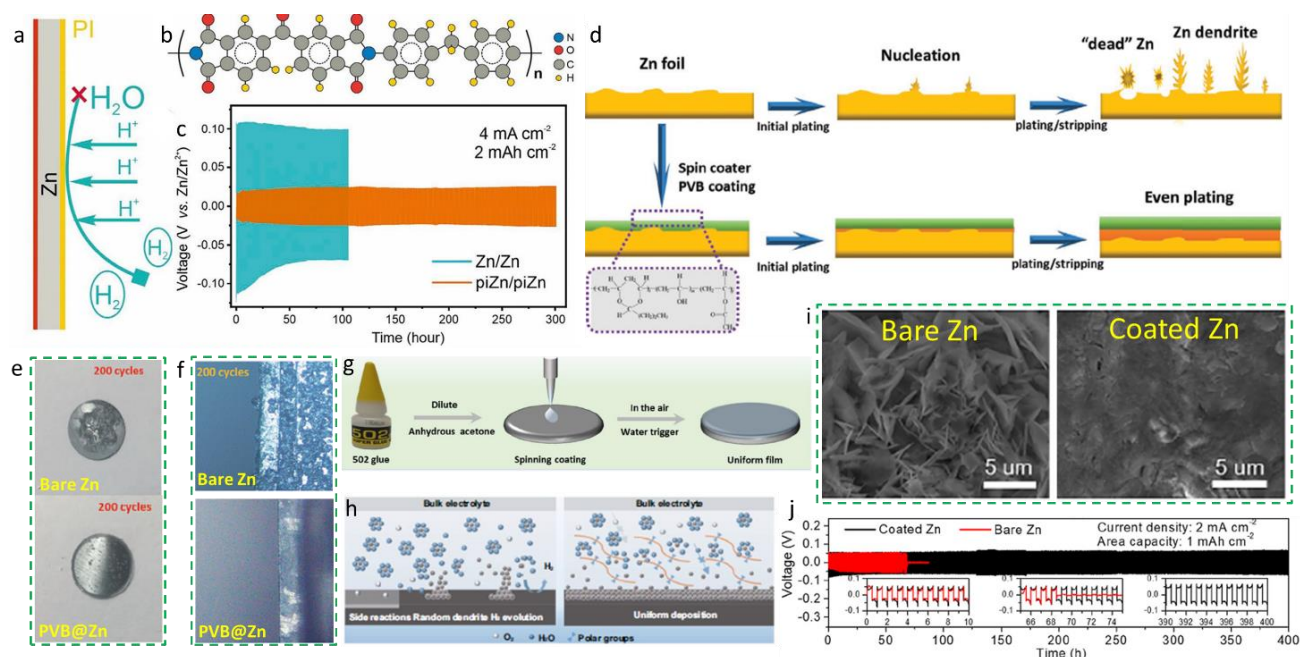


Figure 9. (a) Mechanism of anti-corrosion providing by polyimide layer, (b) structure of polyimide, (c) long-term galvanostatic cycling of symmetrical cells with bare Zn and polyimide-Zn anode at a current density of 4 mA cm^{-2} and capacity of 2 mAh cm^{-2} (Reproduced with permission [46] Copyright 2021, John Wiley & Son). (d) Schematic illustration of the morphological evolution of a bare Zn and PVB@Zn symmetrical cell during stripping/plating cycles, (e) images of electrodes stripped out of cells after 100 cycles of Zn and PVB@Zn, and (f) in situ optical microscope images of Zn electrodes and PVB@Zn electrodes in symmetric transparent cells, along with the specified plating/stripping cycles. (Reproduced with permission [60] Copyright 2020, John Wiley & Son). (g) Schematic diagram of a preparation of cyanoacrylate adhesive (502-glue) coating on Zn foil, (h) schematic diagram of the mechanism of 502-glue for suppressing Zn dendrite, (i) cycling stability for symmetrical cells of bare Zn and 502-Zn at 2 mA cm^{-2} for 1 mAh cm^{-2} , and (j) morphology of bare zinc foil (left) and 502-decorated Zn foil (right) obtained from symmetric Zn cells after zinc stripping/plating for 100 cycles at 0.5 mA cm^{-2} for 0.25 mAh cm^{-2} . (Reproduced with permission [109] Copyright 2021, Elsevier).

3.2.1. Three-Dimensional (3D) Network Hosted Zn Anodes

Increasing the surface area of Zn electrodes is one of the most practical methods for improving the electrochemical performance of Zn anodes, providing a long cyclability of ZIBs. A large surface area of an electrode can form an even electrical field and disperse current density, avoiding the critical current density caused by dendrite growth. Additionally, extensive contact with electrolytes allows the homogeneous dispersion of ions. The 3D structures enable Zn dendrites to grow in confined space, reducing the risk of short circuits puncturing the separator to a certain degree.

For instance, the plating/stripping performances of Zn anodes can be enhanced by supporting 3D porous metal structures. Kang et al. proposed that the 3D porous copper scaffold has good electrical conductivity and a well-defined open structure, facilitating uniform Zn deposition [40]. A highly stable 3D Zn anode was prepared by electrodepositing Zn on a chemically etched porous copper scaffold (3D Zn@Cu) (Figure 10a). As shown in Figure 10b, bare planar Zn foil electrodes exhibit large dendrites and partial oxidation, which suggests that the plating/stripping of Zn has a short lifespan. Due to their dual role as a current collector and an active material, planar Zn foils experience volume and electrical properties variations during the deposition and stripping of Zn from their surface, resulting in unstable electrochemical behavior. As opposed to this, the 3D Zn@Cu electrodes always maintain high electrical conductivity and can effectively accommodate the volume changes that result from Zn deposition/stripping. Thus, the symmetric 3DZn@Cu cell

shows a low voltage hysteresis of only 40 mV, corresponding to cycling stability over 350 h, which is better than that of the bare planar Zn foil with a higher overpotential (100 mV) and a shorter lifespan (110 h) (Figure 10c).

Carbon-based materials have been generally reported as 3D structure electrodes in battery research due to their large surface area, structural stability, and superior electrical conductivity. A simple method for preparing Zn anodes is to electrodeposit dense Zn films onto carbon skeletons. For example, Zeng et al. constructed a 3D carbon nanotubes (CNTs) structure on a carbon cloth substrate (CC) for Zn dendrite-free deposition as a Zn plating/stripping scaffold [118]. It was observed that a higher charge region appears near the isolated Zn nuclei sites compared to other areas on the bare CC surface (Figure 10d). Consequently, more Zn^{2+} flux can adsorb onto nucleation centers, leading to preliminary uneven Zn deposition because of the apparent intensity gradient. According to Figure 10b, Zn dendrite growth occurred from the continuous deposition of Zn^{2+} on protuberance sites during cycling. With the introduction of the 3D CNT scaffold, the electric field streamlines become uniform, and this unique property is attributed to the enlarged specific area due to its 3D architecture and the minimized Zn nuclei size (Figure 10a). The 3D structure ensures more homogeneous Zn^{2+} adsorption to the electrode surface due to the uniformly distributed electric field. Consequently, Zn is evenly distributed onto the CNT surface at the early stage, and further cycling did not result in the development of Zn dendrites (Figure 10e). The Zn/CNT anode showed a remarkable electrochemical performance with a low overpotential and long-time cycling (27 mV and 200 h), while bare Zn deposited on CC (Zn/CC) anode exhibited a larger overpotential and short cyclability (70 mV and 50 h) (Figure 10f), implying that the CNT network plays a vital role in Zn deposition performance. By taking advantage of the low Zn nucleation overpotential and uniformly distributed electric field, the CNT electrode effectively eliminates the negative impacts of Zn dendrites and other byproducts during electrochemical deposition, resulting in highly reversible Zn plating/stripping for a long-life cycle.

In addition to the large surface area, MOFs are another porous material applying battery fields, the same as 3D carbon-based materials. MOFs provide specific chemical compositions and quickly transform into a 3D structure by thermal treatment. For instance, Wang et al. reported that ZIF-8 was an excellent candidate for hosting Zn plating/stripping [120]. Because of its intrinsic porous structure, ZIF-8 can be moderately thermally reduced to create a uniformly distributed elemental Zn that can act as a nucleation site, resulting in an even deposition of Zn. However, high temperatures between 500 and 800 °C could cause Zn volatilization, which seriously diminishes the amount of Zn elemental (Figure 10g). It is observed that the electrochemical performance of the ZIF-8-500 electrode had the highest Coulombic efficiency of 99.8% and cyclic stability over 200 cycles compared to the others (Figure 10h,i), suggesting the best reversibility of Zn deposition using ZIF-8-500 as an anode. As illustrated in Figure 10j, the initial Zn plating occurs mainly on ZIF-8-500 particles because ZIF-8-500 contains trace amounts of Zn^0 , which serve as nuclei for Zn plating. Following initial plating, the ZIF-8-500 particles with Zn can be used as substrates with uniform Zn-nuclei for further plating, resulting in dendrite-free depositing of Zn. Hence, a smooth surface with uniform morphology is consistently produced even at high capacity (Figure 10k). These results proposed that the ZIF-8-500 electrode could be used to develop a high-capacity zinc anode.

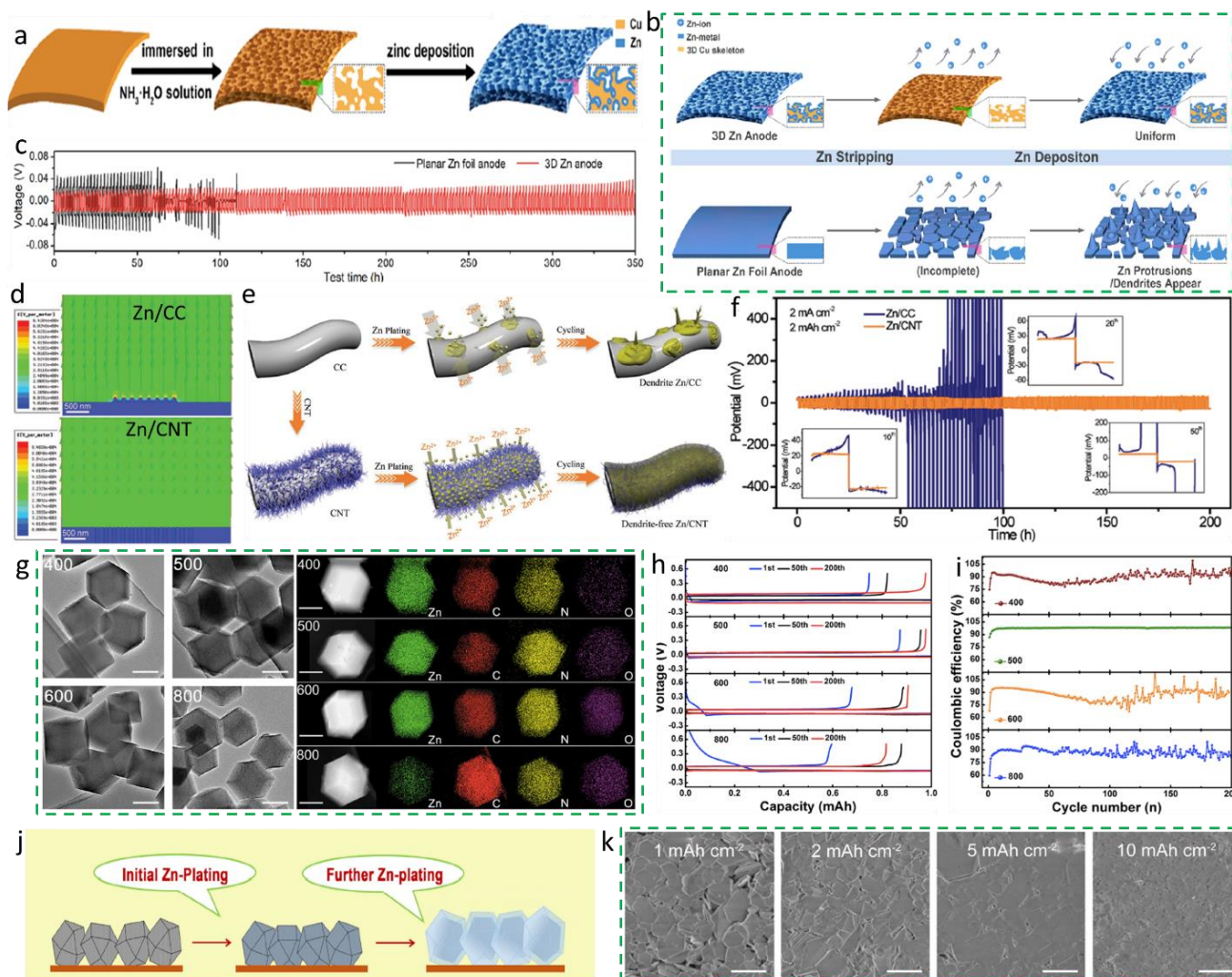


Figure 10. (a) Schematic illustration of the procedures to prepare 3DZn@Cu anode, (b) schematic diagrams of Zn deposition/stripping processes on 3DZn@Cu and planar Zn foil anode, and (c) cycling performance at a constant current of 0.5 mA cm^{-2} of 3DZn@Cu and planar Zn foil anodes. (Reproduced with permission [40] Copyright 2019, American Chemical Society). (d) Simulation of electric field distribution on Zn/CC and Zn/CNT, (e) schematic illustration of Zn deposition on the CC and CNT electrodes, and (f) Electrochemical performance of Zn/CC and Zn/CNT at the current density of 2 mA cm^{-2} and areal capacity of 2 mAh cm^{-2} . (Reproduced with permission [118] Copyright 2019, John Wiley & Son). (g) TEM images and elemental mapping of the ZIF-8 samples prepared at 400, 500, 600, and 800 °C, (h) the polarization of the plating and stripping for the different electrodes at 2 mA cm^{-2} and 1 mAh cm^{-2} , (i) Coulombic efficiency of the plating and stripping for the different electrodes at 2 mA cm^{-2} and 1 mAh cm^{-2} , (j) schematic illustration of Zn plating, and (k) SEM images of Zn plating at a current density of 1 mA cm^{-2} with different capacities. (Reproduced with permission [120] Copyright 2019, Elsevier).

3.2.2. Zn Alloying

In terms of regulating the physiochemical properties of Zn anodes and optimizing their electrochemical performance, the preparation of an alloy is simple and effective [129]. Alloying Zn with other metals to form an anode is another approach for optimizing the Zn bulk structure to address irreversible problems, such as dendrite growth, hydrogen evolution, and corrosion. Most Zn alloys reported on mild aqueous Zn anodes are binary alloys, including Zn–Al [121], Zn–Ni [122], Ga–In–Zn [123], Cu–Zn [124,125], Ag–Zn [126], Zn–Mn [127], and Zn–Sb [128]. In the alloy, a restructuring reaction and a solid solution

reaction are included in the electrochemical alloying of Zn [130]. As an alternative to standard Zn stripping/plating, solid solution reactions should involve dealloying/alloying reactions to indicate the inward transfer of Zn atoms in the alloy and their reversible extraction [131]. Hence, Zn alloy anodes with different alloy phases can significantly increase battery performance due to the stable solution reaction.

Recently, a eutectic-composition alloying of Zn and Al was reported by Wang et al., which effectively tackled irreversible problems due to the lamellar structure of Zn–Al alloy [121]. The Zn lamellae provided the Zn^{2+} charge carriers, whereas the Al lamellae were responsible for accommodating the deposition of Zn (Figure 11a). Also, the presence of Al lamellae reduced the formation of ZnO and $\text{Zn}(\text{OH})_2$ and other byproducts due to the passivation of the Zn anode. In addition, the Al_2O_3 insulating layer can inhibit the electroreduction of Zn^{2+} on Al/ Al_2O_3 cores–shells, decrease the local charge density of the Zn deposition, and lead to Zn deposition at the Zn site, resulting in the continuous inhibition and elimination of Zn dendrites. Because of the layered nanostructure, the plating/stripping time of symmetric cells of $\text{Zn}_{88}\text{Al}_{12}$ alloy maintained a stable overpotential for more than 2000 h (Figure 11b). After more than 1000 cycles of plating and stripping, the surface of the $\text{Zn}_{88}\text{Al}_{12}$ alloy electrode remained smooth compared to that of bare Zn (Figure 11c). Moreover, the cyclic voltammogram of full $\text{Zn}_{88}\text{Al}_{12} \parallel \text{K}_x\text{MnO}_2$ cells exhibited a higher current density and more significant peak displacement than bare $\text{Zn} \parallel \text{K}_x\text{MnO}_2$ cells (Figure 11d). In addition, the $\text{Zn}_{88}\text{Al}_{12} \parallel \text{tK}_x\text{MnO}_2$ battery performs better at a higher rate with a longer cycle life and a higher Coulombic efficiency (Figure 11e).

In addition, a typical Cu–Zn alloy, brass, was thermally and electrochemically transformed into a 3D nanoporous Zn–Cu alloy (3D NP Zn–Cu) by Liu et al. (Figure 11f) [124]. A hallmark of this unique design was the presence of (1) an interconnected electrolyte-filled pore network to facilitate rapid ion transport, (2) a short diffusion length to minimize the effects of sluggish solid-state ion diffusion, (3) a large electrode/electrolyte contact area, and (4) a high electron conductivity (Figure 11g). Hence, an electrode based on 3D NP architecture enables high electron and ion transport paths and increased material loading per unit substrate area, allowing uniform Zn deposition, and enhancing charge storage capability. Due to the architectural features, the 3D NP Zn–Cu anode exhibited a long-life cycle of 300 h at 2 mA cm^{-2} (Figure 11h). Furthermore, preparing a high voltage aqueous Zn– Br_2 battery based on a 3D NP Zn–Cu anode can deliver an excellent areal capacity of approximately 1.56 mAh cm^{-2} , close to typical Li-ion batteries ($1\text{--}3 \text{ mAh cm}^{-2}$).

Additionally, a co-deposition process of various ions has been proposed to design a favorable structure of 3D Zn_3Mn alloy to enhance the performance of the Zn anode [127]. A 3D anode can be formed by H_2 bubbles evaporating at solid–liquid interfaces. Effective migration of Zn^{2+} ions is facilitated by the alloy's porous morphology and large specific surface area. In addition, Zn nucleation and growth are induced and regulated on the alloy surface due to the relatively high binding energy (Figure 11i). During the deposition process, Zn is plated faster in trenches than in protruding areas, minimizing dendrite formation (Figure 11j–l). These advantages make the Zn_3Mn alloy anode a highly reversible anode. Despite interference from several impurity ions in seawater-based electrolytes, it still exhibits high stability and reliability (Figure 11m). By adjusting the solution composition and deposition current or voltage and adjusting the deposition time, this co-electrodeposition strategy can be applied to other alloy systems. Therefore, the alloy structure can be designed by developing the alloy preparation process while introducing more element species to the alloy anode.

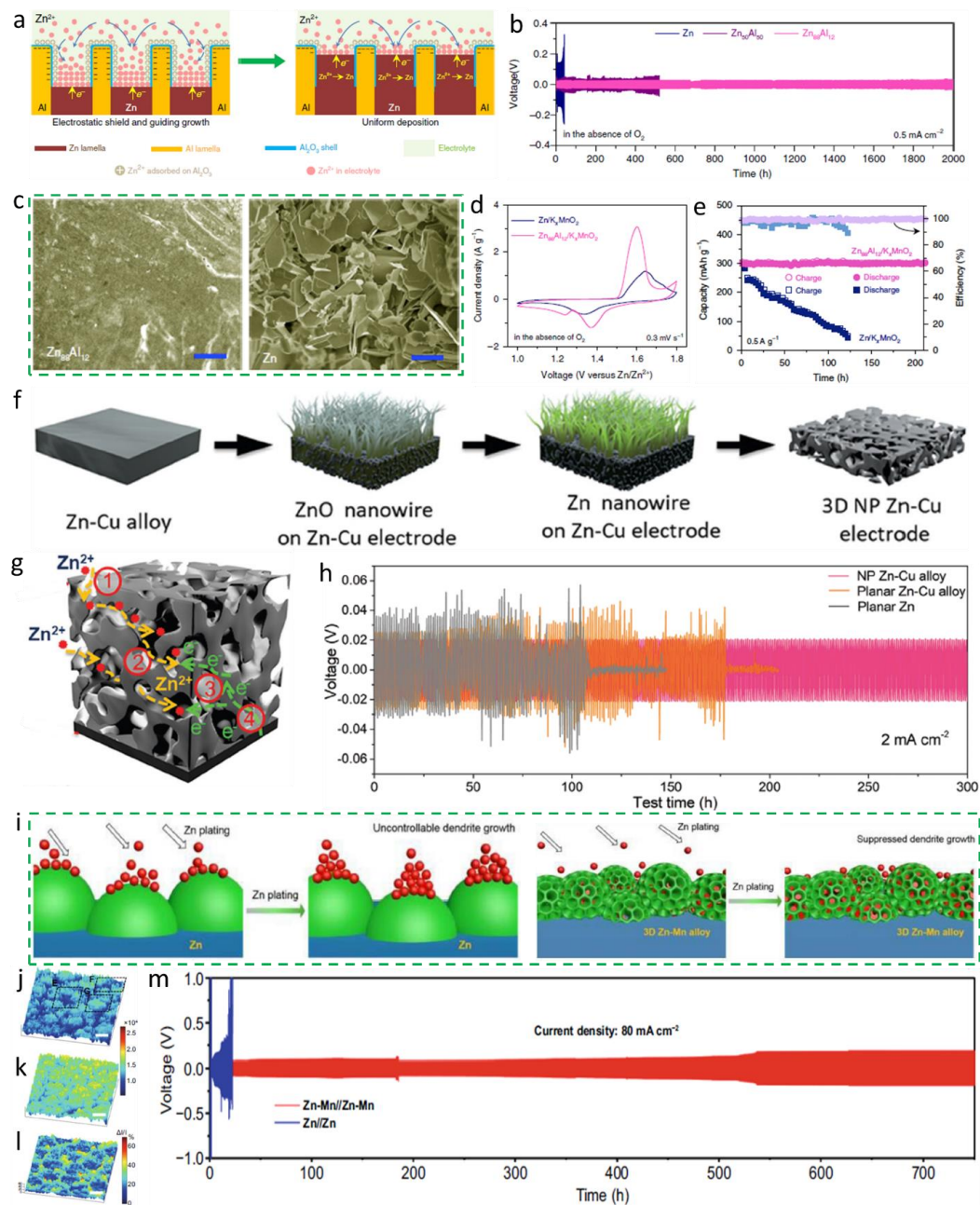


Figure 11. (a) Schematic illustration of eutectic strategy for dendrite and crack suppression, (b) long-term Zn stripping/plating cycling of the symmetric batteries of bare Zn and Zn/Al alloys, (c) SEM images of eutectic $\text{Zn}_{88}\text{Al}_{12}$ and bare Zn after long term Zn stripping/plating, (d) typical CV curves for $\text{Zn}_{88}\text{Al}_{12}||\text{K}_x\text{MnO}_2$ and $\text{Zn}||\text{K}_x\text{MnO}_2$ batteries, and (e) long-term cycling performance of the $\text{Zn}_{88}\text{Al}_{12}/\text{K}_x\text{MnO}_2$ battery at 0.5 A g^{-1} compared to the $\text{Zn}/\text{K}_x\text{MnO}_2$ battery. (Reproduced with permission [121] Copyright 2020, Springer Nature). (f) The fabrication of 3D Zn-Cu alloy electrode, (g) the four primary resistances in 3D NP Zn-Cu alloy electrode, and (h) charge/discharge profiles of 3D NP Zn-Cu alloy and bare Zn anodes at 2 mA cm^{-2} . (Reproduced with permission [124] Copyright 2020, John Wiley & Son). (i) Schematic illustration of Zn plating at the bare Zn anode and Zn-Mn anode, (j,k) is the surface topography images of 3D Zn-Mn alloy before and after Zn plating, (l) the derived image calculated by $(k - j)/k = (\Delta I/I)$. The experiment was performed at a current density of 80 mA cm^{-2} for 320 s, and (m) Long-term galvanostatic cycling performance of symmetric Zn-Mn and pristine Zn cells at a current density of 80 mA cm^{-2} with a capacity of 16 mAh cm^{-2} . (Reproduced with permission [127] Copyright 2021, Springer Nature).

3.3. Electrolyte Optimization

3.3.1. Zinc Salts and Their Concentration

Commonly, the anion can participate in the Zn^{2+} ion solvation process in the electrolyte. Therefore, the compatibility of electrodes with Zn^{2+} ions, which is regulated by their nature of anions, can determine the battery performance. By selecting different zinc salts, these issues can be resolved. Zinc salts soluble in aqueous solutions have become widely used in electrolytes due to the rapid development of ZIBs. Several zinc salts including inorganic zinc salts such as ZnSO_4 , $\text{Zn}(\text{NO}_3)_2$, ZnCl_2 , $\text{Zn}(\text{ClO}_4)_2$, ZnF_2 , and organic zinc salts such as $\text{Zn}(\text{CF}_3\text{SO}_3)_2$, $\text{Zn}(\text{TFSI})_2$, $\text{Zn}(\text{CH}_3\text{COO})_2$, and $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ have been reported [32,132]. As noted, NO_3^- anion is a strong oxidant. Hence, Zn foil can be easily oxidized, causing serious corrosion, local pH changes, and increased acidity in the zinc nitrate electrolyte (Figure 12a) [133]. In comparison with $\text{Zn}(\text{NO}_3)_2$, ZnCl_2 often shows higher compatibility with Zn anodes due to its minor side reaction. However, the narrow anodic potential window limits its practical use since the electrolyte continually decomposes at a higher voltage, as illustrated in Figure 12b [134].

Contrary to $\text{Zn}(\text{NO}_3)_2$ and ZnCl_2 , the ZnSO_4 electrolyte exhibits excellent electrochemical stability in a wider electrochemical window [134]. Furthermore, it possesses the advantages of stable SO_4^{2-} anion structure and compatibility with Zn electrode (Figure 12c), low cost, and sustainability making it one of the most commonly used inorganic salts for aqueous ZIBs [135–137]. However, its practical application is hampered by the HER and byproduct formation (Figure 12d), which can reduce the Zn stripping/plating cycling stability and Coulombic efficiency [138]. Recent studies revealed that the organic zinc salt $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ can enhance electrolyte performance [134,139]. It can reduce the number of water molecules surrounding the Zn^{2+} ions and the solvent effect and release the Zn^{2+} ions from the solvation sheath, boosting the migration of Zn^{2+} ions and charge-transfer rate (Figure 12e). Hence, it can effectively inhibit the formation of Zn dendrites and accelerate Zn deposition/dissolution kinetics. Additionally, suppression of parasitical reactions of O_2 evolution was observed for 1 M $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ and 1 M ZnSO_4 at 2.3 and 2.4 V, respectively (Figure 12f). Above 2.3 and 2.4 V, ZnSO_4 and $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ exhibit anodic processes caused by the oxygen evolution reaction (OER). Overall, $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ exhibits a smaller potential separation between plating and stripping and a higher response current than ZnSO_4 , suggesting significantly improved reversibility and faster kinetics (Figure 12g).

In addition to the types of zinc salt, the salt concentration plays a vital role in the property of electrolytes. As stated in previous publications, Zn^{2+} ions form a solvation sheath structure with water molecules that the formula can be represented by $(\text{Zn}(\text{H}_2\text{O})_6)^{2+}$ ions [140–142]. Since this structure creates a high energy barrier, it is more difficult for solvated Zn^{2+} to desolvate and deposit, thereby increasing the irreversibility issue associated with Zn anodes [140,143]. Further, increasing the electrolyte concentration can decrease the number of solvent molecules around the Zn^{2+} ions, altering solvation structures and cation/anion transport [144,145]. Usually, higher electrolyte concentrations for identical salts will result in improved electrochemical performances, including higher plating/stripping Coulombic efficiencies of active ions and better capacity retention [134]. For example, in a Zn/ V_2O_5 system, an exceptional electrochemical performance was observed as ZnSO_4 electrolyte concentration increased from 0.5 to 3 M (Figure 13a) [146]. Additionally, the Coulombic efficiency of the Zn/ ZnMn_2O_4 system can increase to 100% when the salt concentration ($\text{Zn}(\text{CF}_3\text{SO}_3)_2$) is increased from 1 to 4 M, as reported by Zhang et al. (Figure 13b) [134]. However, an increase in concentration reduces the ionic conductivity of the electrolyte and increases in solution viscosity (Figure 13c). Thus, selecting the appropriate concentration is crucial to obtaining optimum compatibility.

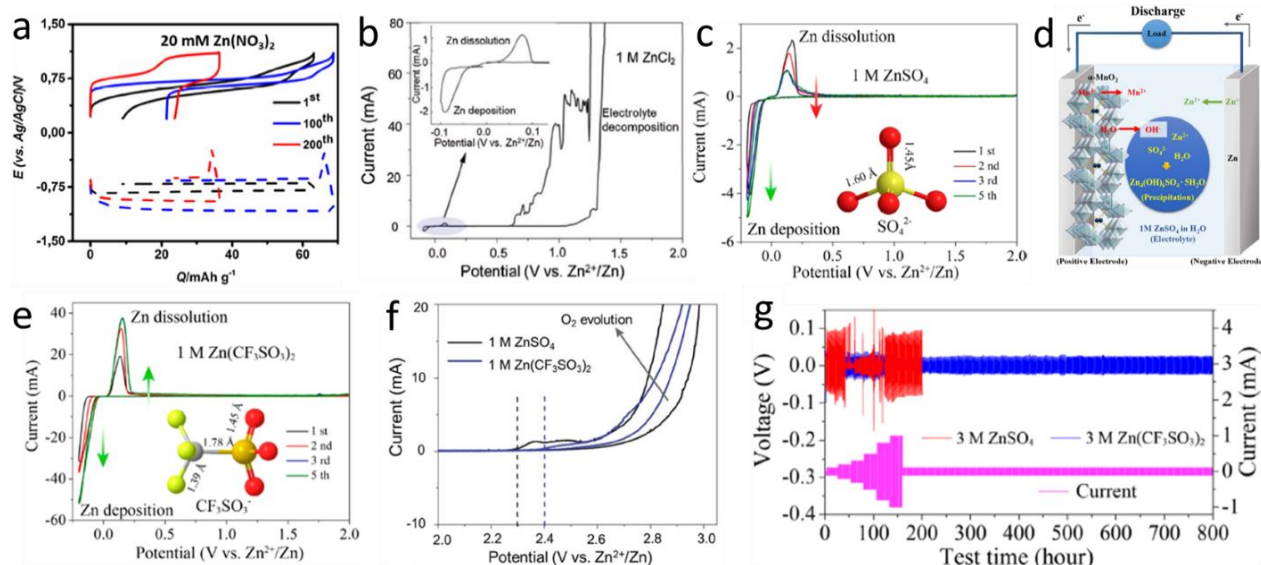


Figure 12. (a) Zn/Zn(NO₃)₂/CuHCF battery potential profile at 1 C current rate. (Reproduced with permission [133] Copyright 2016, Elsevier). Cyclic voltammograms of Zn electrode in aqueous electrolyte of (b) 1 M ZnCl₂ and (c) 1 M ZnSO₄ at the scan rate of 0.5 mV s⁻¹ between −0.2 and 2.0 V (Reproduced with permission [134] Copyright 2016, American Chemical Society). (d) Illustration of reactions that occur in α-MnO₂/Zn cells employing aqueous ZnSO₄ electrolytes during discharge process. (Reproduced with permission [138] Copyright 2016, John Wiley & Son). (e) Cyclic voltammogram of Zn electrode in aqueous electrolyte of 1 M Zn(CF₃SO₃)₂. (f) Electrochemical stability of ZIBs using ZnSO₄ or Zn(CF₃SO₃)₂. (g) Long-term cyclability of Zn/Zn symmetrical cells in ZnSO₄ and Zn(CF₃SO₃)₂ electrolytes (Reproduced with permission [134] Copyright 2016, American Chemical Society).

The effect of concentration could be more apparent in ultrahigh concentration electrolytes or “water in salt” electrolytes. Wang et al. first introduced their concentrated electrolyte of 1 m Zn(TFSI)₂ + 20 m LiTFSI (m represents molality (mol kg⁻¹)), which showed exceptional stability and reversibility of Zn anode without forming byproducts (Figure 13d) [140]. This study also discovered that the pH value increased with electrolyte concentration and reached approximately 7 in 1 m Zn(TFSI)₂ + 20 m LiTFSI (Figure 13e), which indicates an effective suppression of Zn ion interaction with a water molecule. According to FTIR analysis, the intensity of the hydrogen bonding peak at 3414 cm⁻¹ gradually decreased as LiTFSI concentration rose and almost disappeared once LiTFSI concentration reached 10 m (Figure 13f). It indicates that hydrogen bonds between water molecules had been disrupted. In addition to reducing water activity, water-induced side reactions were suppressed. Thus, the cycle stability was remarkably enhanced (Figure 13g). In another study, Zhang et al. developed an extremely concentrated 30 m ZnCl₂ [147]. As shown in Figure 13h and i, the increment of ZnCl₂ concentration raised the plating potential of Zn and declined the onset potential of HER, which contributed to the improved Coulombic efficiency of Zn deposition. Additionally, the Zn²⁺ solvation structures were converted to [ZnCl₄]²⁻, inhibiting the formation of Zn(OH)₂ and ZnO. Consequently, an electrolyte containing concentrated ZnCl₂ could obtain superior cycling stability (compared to 5 m ZnCl₂) and yield a reasonably high Coulombic efficiency of 95.4% (Figure 13j,k).

Developing concentrated electrolytes offers an attractive alternative to a highly reversible Zn anode. Nevertheless, at a low current density (0.2 mA cm⁻²) and low plating or stripping capacity (0.03 mAh cm⁻²), a concentrated electrolyte can cause a relatively large voltage polarization or result in high viscosity and low ionic conductivity, leading to deficient rate performance of Zn anode [23,148]. In addition, concentrated electrolytes cost more than diluted electrolytes, and these factors impede the large-scale application of concentrated electrolytes.

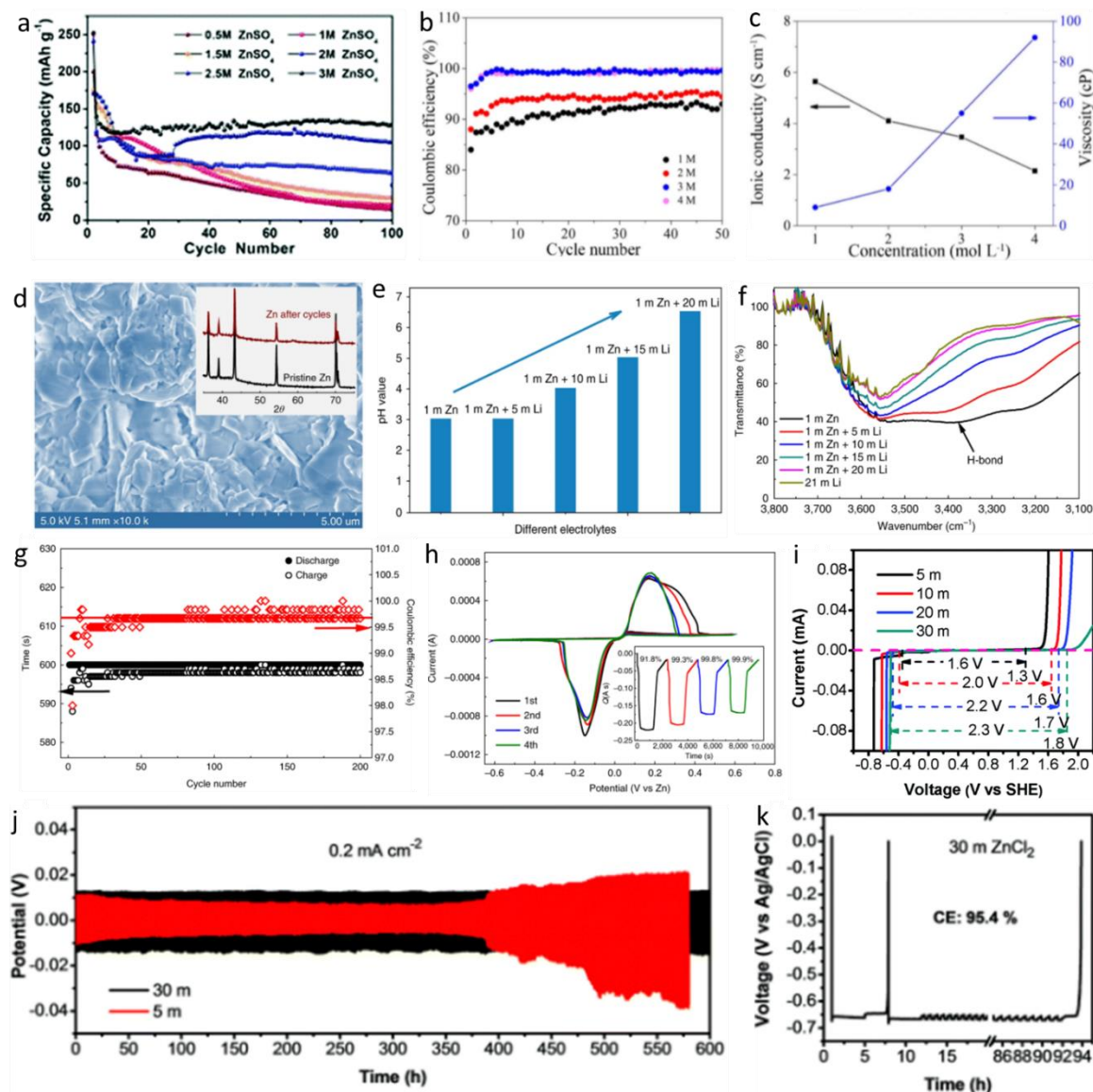


Figure 13. (a) Specific capacity and cycle of Zn/V₂O₅ at different concentrations of ZnSO₄ electrolyte (Reproduced with permission [146] Copyright 2018, Royal Society of Chemistry). (b) Coulombic efficiency as a function of cycle number of Zn/ZnMn₂O₄ and (c) viscosity and ionic conductivity at different Zn(CF₃SO₃)₂ electrolyte concentrations. (Reproduced with permission [134] Copyright 2016, American Chemical Society). (d) SEM image and XRD pattern (inset) of a Zn anode after 500 stripping/plating cycles in 1 m Zn(TFSI)₂ + 20 m LiTFSI, (e) the pH values of the electrolytes with increasing LiTFSI concentrations, (f) FTIR spectra with increasing LiTFSI concentrations, (g) the Zn plating/stripping time and Coulombic efficiency on a Pt working electrode at 1 mA cm⁻², and (h) cyclic voltammogram of Zn plating/stripping at a scan rate of 1 mV s⁻¹. (Reproduced with permission [140] Copyright 2018, Springer Nature). (i) Electrochemical stability window at different ZnCl₂ electrolyte concentrations, (j) the plating/stripping of Zn in 30 m and 5 m ZnCl₂ in a Zn||Zn symmetric cell at 0.2 mA cm⁻², and (k) Coulombic efficiency Zn||Zn symmetric cell in 30 m ZnCl₂ electrolyte. (Reproduced with permission [147] Copyright 2018, Royal Society of Chemistry).

3.3.2. Electrolyte Additives

Instead of changing the Zn salts and concentration, additives have been recently introduced into electrolytes to solve issues related to the anode in ZIBs. Commonly, additives are incorporated into electrolytes to solve non-uniform Zn deposition [149–151].

In addition, the side reactions and the 2D diffusion mechanism are inhibited, and the nucleation rate is enhanced. It is thus possible to significantly improve the electrochemical performance of batteries. Electrolyte additives can be divided into inorganic additives and organic additives.

Inorganic Additives

Ionic additives (inorganic salts or metal cations) are the most used inorganic additives for aqueous ZIBs because of their species diversity and simplicity of control within electrolyte solvents. Adding ionic additives to Zn ions can help improve their deposition location through ion adsorption mechanisms or electrostatic shielding. Hence, the growth of Zn dendrite is hindered, and a uniform deposition layer can be obtained. An overview of inorganic additives used to protect Zn anodes in previous reports was summarized in Table 5. Several research groups reported that adding MnSO_4 to electrolytes suppressed the dissolution of Mn^{2+} ions from the MnO_2 cathode and inhibited the dendrite growth of Zn [152–158]. Cycle performance for $\text{Zn}||\text{MnO}_2$ batteries can be improved by adding Mn^{2+} to the aqueous electrolyte, as shown in Figure 14a,b [154,156]. During cycling, the accessibility of Mn^{2+} ions in the electrolyte stabilized the crystal structure by dealing with limited Mn dissolution, thus limiting the number of vacancies for Zn^{2+} insertion. The cathode was subject to dissolution during the cycling without the Mn^{2+} additive in the electrolyte resulting in instabilities in the crystal structure and poor capacity retention (Figure 14b). Also, other inorganic salts such as MgSO_4 [159], NaSO_4 [160,161], and LiCl [162] have recently been reported as electrolyte additives to prevent Zn dendrites growth and stabilize Zn electrodes. For example, Guo et al. found that the LiCl additive suppressed dendrite growth and stabilized the Zn metal anode [162]. The Li^+ ions preferentially formed Li_2O and Li_2CO_3 on the Zn surface, shielding against the deposition of dendrites. A moderate number of Cl^- anions reduced Zn polarization and enhanced ion transport (Figure 14c). Hence, long-cycled asymmetric cells with LiCl additives demonstrated much higher stability (Figure 14d). Also, the morphology of the Zn anode was smooth after 500 cycles, confirming that the LiCl additive effectively inhibits dendrite growth (Figure 14e). In this research, metal cations and anions synergistically reduced dendrite growth and improved battery performance.

In addition, recent studies have revealed new types of inorganic additives such as MXene [163], polyoxometalate [164], iodine [165,166], GO [167], SeO_2 [168], $\text{Zn}(\text{H}_2\text{PO}_4)_2$ [169], $\text{Zn}(\text{OH})_2$ [170], and $\text{La}(\text{NO}_3)_3$ [171]. For instance, polyoxometalate $(\text{NH}_4)_6[\text{Mo}_7\text{O}_{24}]\cdot 4\text{H}_2\text{O}$ (NMO), was first introduced as a dual-function electrolyte additive by Wu et al. [164]. It is assumed that massive Zn ions would be deposited on the surface of the Zn anode through the $[\text{Mo}_7\text{O}_{24}]^{6-}$ anion clusters to ensure even distribution of Zn ions, while the NH_4^+ cation control a uniform Zn layer deposition during plating due to electrostatic repulsion forces, further impeding the dendrite growth (Figure 14f). Consequently, the cycle life of Zn anodes in symmetric cells has improved substantially in a significantly high current density of 10 mA cm^{-2} (Figure 14g), and full $\text{Zn}||\text{NaV}_3\text{O}_8\cdot 1.5\text{H}_2\text{O}$ cells also demonstrate excellent, rapid charge/discharge and capacity retention (Figure 14h). According to these studies, synergistic effects of anions and cations enhanced the cycle life of aqueous ZIBs, setting the stage for further development.

Organic Additives

The electrochemical performance of ZIBs can also be enhanced using organic additives such as polymers [172–180], surfactants [181–187], and organic compounds [36,188–194]. A summary of previous reports regarding organic additives that preserve Zn anodes was presented in Table 5. Among them, polymers stand out for their wide variety and adjustable molecular weight, suppressing the development of Zn dendrite formation on the anode surface [195]. Zeng et al. applied a polyacrylamide (PAM) electrolyte additive to modify the Zn anode [172]. With large polar amide groups, polymer layers with PAM strongly coordinate with Zn ions to restrict their free movement (Figure 15a), which could

decrease the overpotential of Zn nucleation and increase the stability of zinc deposition. Thus, batteries with PAM additive display 7.5% capacity fading after 24 h, but those without PAM additive display 14.4% capacity fading (Figure 15b), indicating relatively good self-discharge performance. Due to the dendrite-free Zn anode, the symmetric cell could be cycled for more than 180 h at a high current density of 10 mA cm^{-2} with an aerial capacity of 1 mAh cm^{-2} (Figure 15c). Jin et al. recently reported using long-chain polyethylene oxide (PEO) as an electrolyte additive in ZnSO_4 electrolytes to stabilize the Zn metal anode [176]. Through interactions between the ether groups and Zn^{2+} ions, PEO molecules control Zn^{2+} ion transfer kinetics and Zn^{2+} ion concentration adjacent to Zn anodes (Figure 15d), regulating Zn^{2+} ion concentration distribution and electrolyte flux at the electrode/electrolyte interface. Then, Zn^{2+} ion transfer kinetics are suppressed, and Zn^{2+} ions at interfaces are distributed uniformly to facilitate uniform Zn deposition-dissolution processes. Hence, the Cu||Zn cells with PEO additive can enhance the Coulombic efficiency and cycling stability compared to that without PEO (Figure 15e). As shown in Figure 15f, the resulting Zn|| LiMn_2O_4 full cells also significantly improved cycling stability and higher Coulombic efficiency (99%) in electrolytes containing PEO polymer.

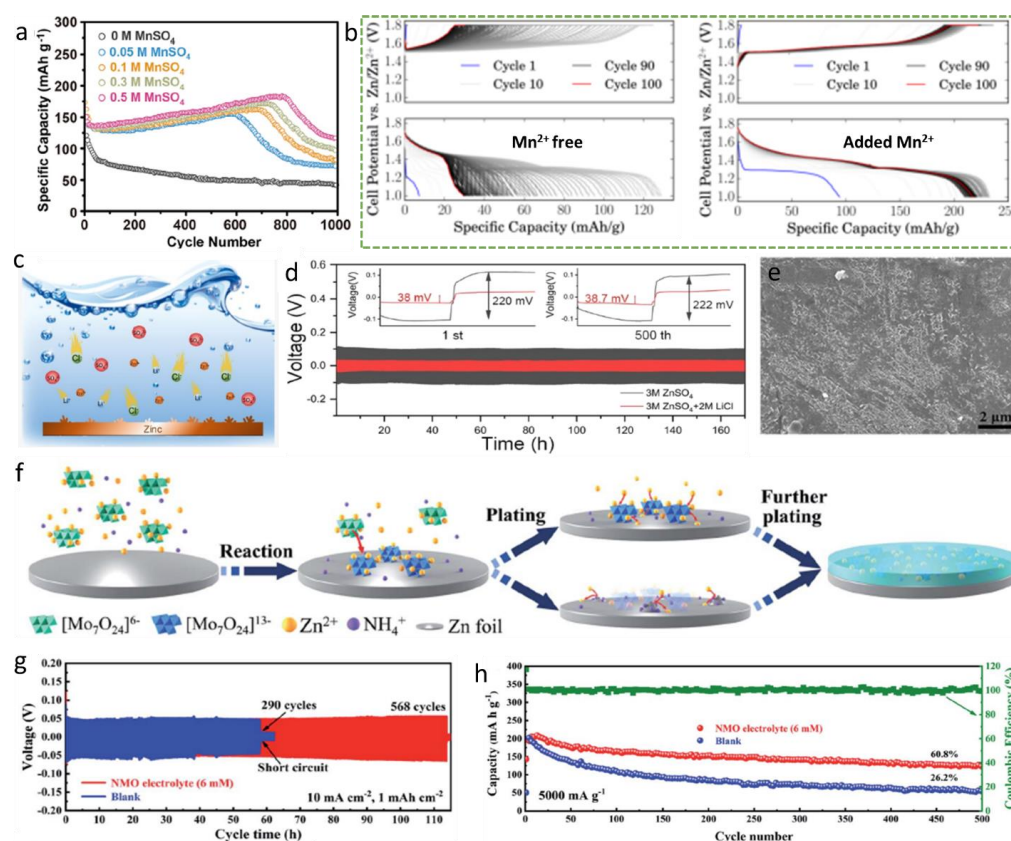


Figure 14. (a). Cycle performances of the Zn|| MnO_2 cells using different electrolytes for 1000 cycles at a current density of 200 mA g^{-1} (Reproduced with permission [154] Copyright 2020, Elsevier). (b) Discharge curves of MnO_2 electrodes in Mn^{2+} free and added Mn^{2+} electrolytes at 60 mA g^{-1} (Reproduced with permission [156] Copyright 2018, Elsevier). (c) Illustration of LiCl additive inhibiting dendrite growth and stabilizing Zn anode, (d) galvanostatic charge–discharge curve under the current density of 0.2 mA cm^{-2} , and (e) SEM of Zn electrode after 500 cycles with 3 M ZnSO_4 + 2 M LiCl (Reproduced with permission [162] Copyright 2021, American Chemical Society). (f) Schematic illustration of Zn deposition with polyoxometalate additive, (g) cycling performance of Zn symmetric cells using electrolytes without or with polyoxometalate additives at 10 mA cm^{-2} and 1 mAh cm^{-2} , and (h) long-term cycling performance of the Zn|| $\text{NaV}_3\text{O}_8 \cdot 1.5\text{H}_2\text{O}$ full cells with or without polyoxometalate additive at 5000 mA g^{-1} (Reproduced with permission [164] Copyright 2021, Royal Society of Chemistry).

Currently, surfactants have drawn much attention due to their protection mechanism on the Zn anode, and their surface tension generally enables easy adsorption at the electrode/electrolyte interface. For example, Bayaguud et al. reported that a cationic surfactant, tetrabutylammonium sulfate (TBA_2SO_4) enabled a uniform Zn deposition by forming a shielding layer via a zincophobic repulsion mechanism, leading to uniform distribution of Zn^{2+} ions (Figure 16a). In contrast, a large amount of Zn dendrites were formed in the absence of TBA_2SO_4 (Figure 16b) [181]. As a result, 3D-Zn||3D-Zn symmetric cells demonstrated remarkable cycle stability for >300 h at a current density of 2 mA cm^{-2} (Figure 16c) and excellent rate performance up to 10 mA cm^{-2} (Figure 16d). In addition to inhibiting corrosion and delaying passivation, surfactant additives also display unique properties as cathode additives for aqueous ZIBs. Hao et al. reported that the sodium dodecylbenzene sulfonate (SDBS) additive could modify the intrinsic deposit pattern of Zn^{2+} ions, making the plating/stripping process highly reversible [182]. On the other hand, the SDBS additive enhanced LiFePO_4 cathode wettability, accelerating Li-ion diffusion at the electrolyte/electrode interface. Thus, Zn|| LiFePO_4 (LFP) batteries provide both coin and pouch cells with high-rate capability and cycling stability (Figure 16e,f).

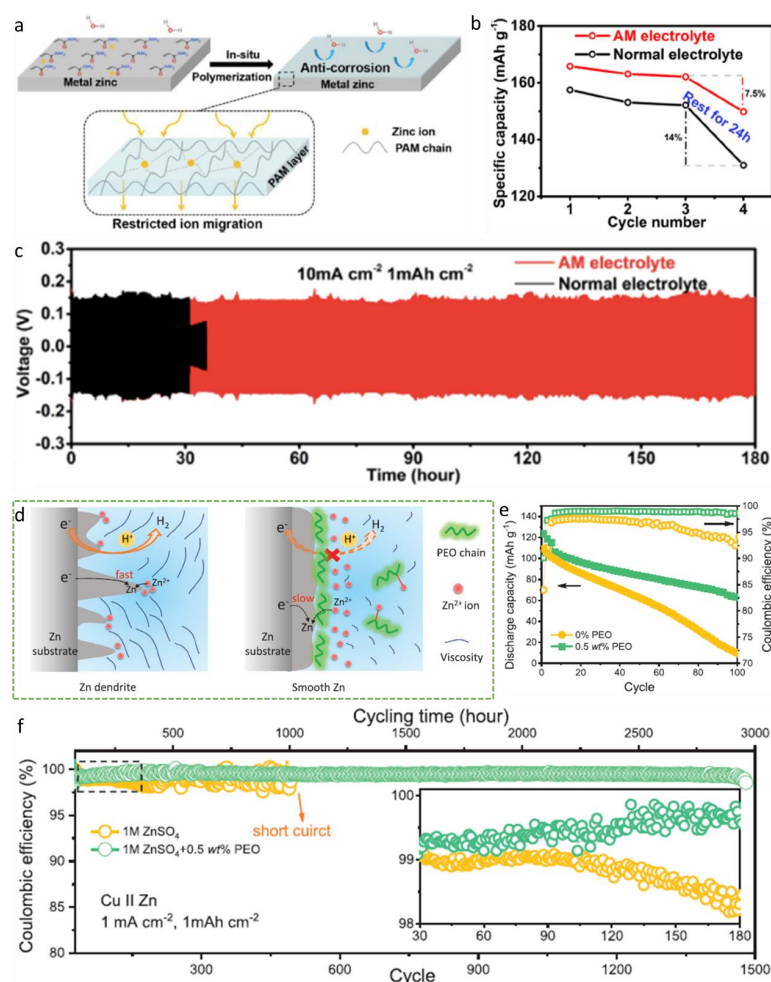


Figure 15. (a) Schematic description of zinc deposition with PAM electrolyte additive, (b) self-discharge tests by standing for 24 h after fully charged, and (c) cycling performance of symmetric cells at 10 mA cm^{-2} for 1 mAh cm^{-2} . (Reproduced with permission [172] Copyright 2021, Elsevier). (d) Schematic illustration of Zn deposition with dendritic surfaces and hydrogen evolution, (e) cycling stability and Coulombic efficiency of Zn|| LiMn_2O_4 cells at 0.5 C with and without PEO additive, and (f) Coulombic efficiency and cycling performance of Zn metals in Cu||Zn cells under a current density of 1 mA cm^{-2} for 1 mAh cm^{-2} . (Reproduced with permission [176] Copyright 2020, John Wiley & Son).

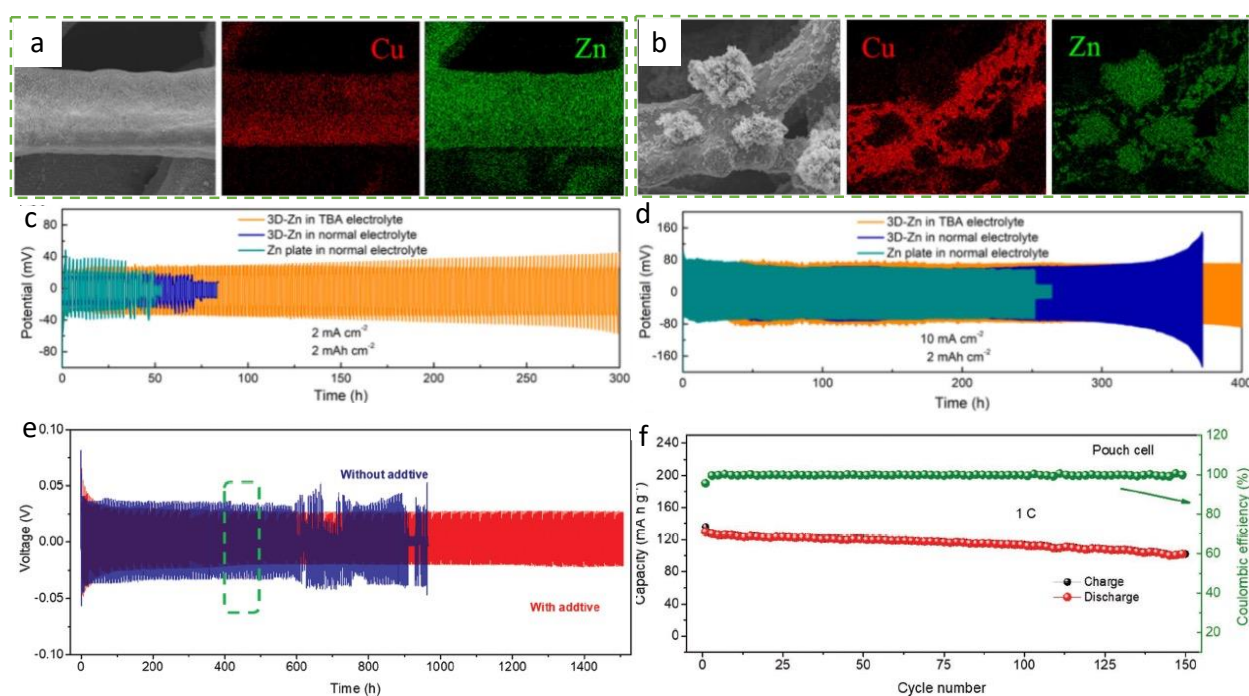


Figure 16. SEM images and EDX mapping of Zn anodes synthesized (a) in 2 M ZnSO_4 electrolyte with 0.05 mM TBA_2SO_4 and (b) in 2 M ZnSO_4 electrolyte. Cycling performance of Zn|Zn and 3D-Zn||3D-Zn symmetric cells in different electrolytes at current densities of (c) 2 mA cm^{-2} and (d) 10 mA cm^{-2} . (Reproduced with permission [181] Copyright 2020, American Chemical Society). (e) Polarization curves of Zn–Zn symmetric cells with/without SBDS additive at a constant current density of 0.5 mA cm^{-2} and (f) cycling stability and Coulombic efficiency of a pouch cell at 1 C. (Reproduced with permission [182] Copyright 2019, John Wiley & Son).

Previous studies have also shown that some organic compounds as additives can have multiple effects by altering the solvated structure of the electrolyte and the morphology of Zn during deposition. Dendrites are inhibited, and side effects are reduced by using these electrolyte additives. These additives make aqueous ZIBs safer and more efficient. Adsorption of macromolecules on the Zn anode surface can modulate the anode surface, leading to simultaneous inhibition of dendrite growth and side reactions. To stabilize reversible plating/stripping on Zn anodes, Sun et al. used glucose as a solvation shell adjustment additive in a typical ZnSO_4 electrolyte [36]. A side reaction caused by the decomposition of active water can be inhibited by adding glucose to the first stage $\text{Zn}^{2+}\cdot 6\text{H}_2\text{O}$ solvation shell (Figure 17a). According to experimental results and theoretical calculations (Figure 17b), glucose has a stronger affinity for Zn ions and has better muscular coordination with them. Simultaneously, glucose molecules also tend to adsorb on Zn anode surfaces at a parallel state (Figure 17c), altering the electric field distribution around Zn layers and inhibiting Zn dendrite growth uncontrollably. Thus, aqueous ZIBs can show long-term stability due to the co-regulation of electrode interfaces and solvation structures. Additionally, Zhou et al. introduced a polyaspartic acid (PASP)-containing electrolyte [193]. This macromolecular compound is composed of carboxyl and amide groups, which absorb readily on metal ions and metal surfaces. As a result of adsorption, a protective layer was formed, providing favorable conditions for the uniform deposition of Zn (Figure 17d). The protective layer transforms irregular flaky particles into homogeneous and dense spheres during the Zn deposition (Figure 17e). By blocking the interaction between active water molecules and Zn^{2+} ions, the protective layer further prevented the release of by-products. Moreover, multifunctional additives can be achieved by regulating the interface between electrodes and electrolytes and the solvation structure.

A hydrolysis strategy was proposed by Wang et al. to promote silk fibroin structural reconfiguration and the formation of more amino/carboxylic groups (NH_2 , COOH) [194]. In combination with spectral characterization, molecular dynamics (MD) and density function theory (DFT) calculations were conducted to investigate the synergistic regulation mechanism of silk peptides' solvation and electrode interfaces (Figure 17f,g). By reducing coordinated active H_2O and SO_4^{2-} , silk peptide regulates the solvation structure of Zn^{2+} and anchors itself on the Zn anode surface for electrostatic shielding as well as the isolation of contact $\text{H}_2\text{O}/\text{SO}_4^{2-}$, showing a synergistic effect on both solvating and controlling interfaces, and effectively alleviating the dendrite formation and by-products (Figure 17h). As a result, silk peptide hydrolyzed from silk fibroin was introduced as an efficient, low-cost, and eco-friendly electrolyte additive to remarkably prolong the cycle life of ZIBs (Figure 17i).

Overall, additive engineering offers a range of opportunities for further innovation to solve critical issues of electrodes. Through additive engineering, dissolution can be reduced, electrostatic interactions can be adjusted, and by-products can be regulated in the cathode [196]. On the anode, the effects consist of inhibiting Zn dendrites and reducing side reactions. Also, appropriate additives can improve the stability of Zn electrodeposition and the reversibility of ZIBs. Moreover, it is crucial to control the level of additives to avoid undesirable effects on Zn deposition. Finally, cost-competitive ZIBs are needed to develop new additives for large-scale applications.

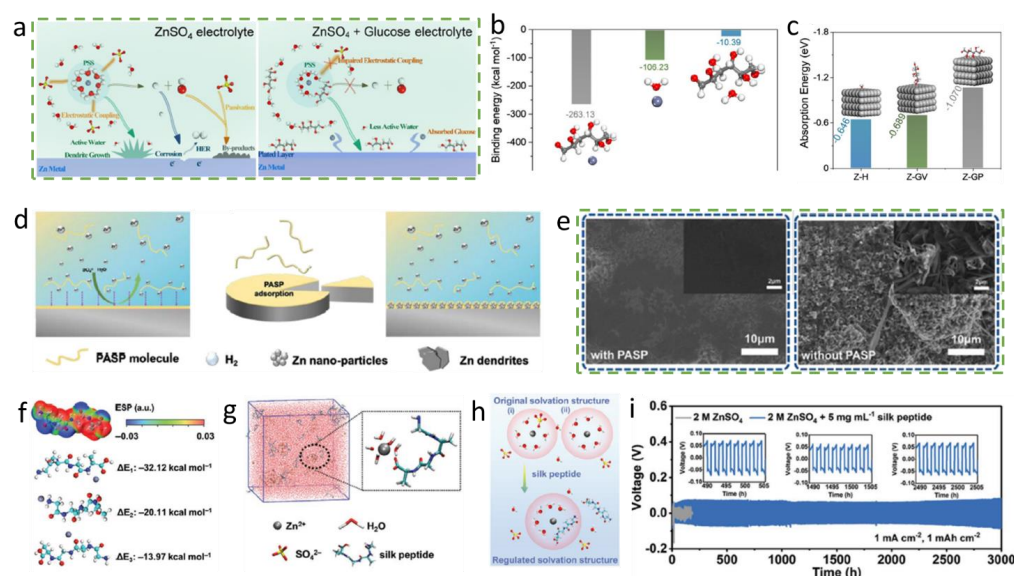


Figure 17. (a) Illustrations of Zn^{2+} solvation structure and interfacial interaction between Zn anode surface and electrolyte under ZnSO_4 and ZnSO_4 -glucose electrolytes, (b) DFT calculation of Zn^{2+} binding energies with glucose and water, and (c) comparison of absorption energies of H_2O and glucose molecules on Zn (002) crystal plane, with insets showing absorbed models for different situations. (Reproduced with permission [36] Copyright 2021, John Wiley & Son). (d) Schematic illustration for the Zn deposition process in the electrolyte with PASP additive and (e) SEM images of the surface of the Zn anode deposited at 1 mA cm^{-2} with a capacity of 1 mAh cm^{-2} with and without PASP additive. (Reproduced with permission [193] Copyright 2022, Elsevier). (f) DFT calculations of binding energies between Zn^{2+} and COOH (ΔE_1), NH_2 (ΔE_2), and CO-NH (ΔE_3) groups, respectively, on the silk peptide chain, (g) MD simulations for Zn^{2+} solvation structure in ZnSO_4 aqueous electrolyte containing silk peptide, (h) schematic illustration of Zn^{2+} solvation structure with/without silk peptide, and (i) cycling performance of Zn-Zn symmetric cells using the ZnSO_4 aqueous electrolytes with/without silk peptide. (Reproduced with permission [194] Copyright 2022, John Wiley & Son).

Table 5. Summary of previously reported electrolyte additives and their effects in ZIBs.

Types	Additives	Effects	Ref
Inorganics	MnSO ₄	Suppress Zn dendrites and dissolution of Mn ²⁺ ions from the MnO ₂ cathode	[152]
	MgSO ₄	Inhibit the HER Enable a uniform nucleation and deposition of Zn Suppress the growth of Zn dendrite	[159]
	Na ₂ SO ₄	Limit the dissolution of cathode Restrict the growth of dendrites on anode	[161]
	LiCl	Inhibit the formation of dendrites Reduce side reactions	[162]
	MXene	Regulate the uniform nucleation of Zn ²⁺ Suppress Zn dendrites growth Relieve the side corrosions	[163]
	NMO	Suppress the formation of protrusions on Zn anodes	[164]
	I ₃ [−]	Passivate the growth hotspots of Zn dendrites Reduce HER and corrosion rate	[166]
	GO	Promote the uniform distribution of electric field Reduce the nucleation overpotential of Zn ²⁺ Eliminate Zn dendrites	[167]
	SeO ₂	Impede dendrite formation Inhibit the parasitic reactions	[168]
	Zn(H ₂ PO ₄) ₂	Provide dendrite-free Zn deposition Restrain the side reactions	[169]
	Zn(OH) ₂	Suppress parasitic reactions and dendrite growth Promote the reaction kinetics	[170]
	La(NO ₃) ₃	Favor dense metallic Zn deposits Regulate the charge distribution at electrode/electrolyte interface	[171]
Organics	Glucose	Restraining side reactions Suppress the growth of Zn dendrite	[36]
	PAM	Inhibit the dendrite growth Induce the uniform Zn deposition Homogeneously distribute Zn on the surface of the electrode	[172]
	PEO	Promote dendrite-free homogeneous Zn deposition Eliminate H ₂ generation	[176]
	PVP	Render less corrosion and more uniform Zn deposition on the anode Modulate the deposition of cathode without aggregations	[179]
	PEG	Inhibit Zn dendrites and side reactions	[180]
	SDS	Suppress the evolution of hydrogen and oxygen Suppress the decomposition of water Inhibit the corrosion of Zn	[183]
	TPAH	Inhibit the Zn dendrite growth	[185]
	TMBA ⁺	Inhibit side reactions Regulate Zn uniform distribution	[187]
	Acetonitrile	Accumulate on the Zn surface to shield water molecules Suppress the HER	[189]
	PASP	Promote dendrite-free Zn deposition Resist the side reactions	[193]
	Silk peptide	Suppress dendrite formation Regulate solvation and interface	[194]
	Vanillin	Promote dendrite-free Zn deposition Suppress HER and by-products	[197]

NMO = polyoxometalate, GO = graphene oxide, PAM = polyacrylamide, PEO = polyethylene oxide, PVP = polyvinyl pyrrolidone, TMBA⁺ = benzyltrimethylammonium, SDS = sodium dodecyl benzene sulfonate, TPAH = tetra propylammonium hydroxide.

3.3.3. Other Electrolytes

In comparison to water, organic solvents form different solvation structures with Zn^{2+} ions that are more thermally stable with Zn anodes and have a larger electrochemical window (up to ~ 3.8 V vs. Zn^{2+}/Zn) [198]. For this reason, there have been numerous attempts to develop an ideal organic electrolyte for ZIBs that would suppress dendrite formation and minimize side reactions [41,199–202]. This strategy can stabilize the electrode and provide high Coulombic efficiency. Recently, triethyl phosphate (TEP) was reported as a cosolvent and a solvent with aqueous electrolytes [202]. The TEP solution leads to the deposition of $\text{Zn}_3(\text{PO}_4)_2$ rather than ZnO on the Zn anode surface. $\text{Zn}_3(\text{PO}_4)_2$ could serve as an in situ formed molecular template to guide Zn nucleation at the interface, resulting in porous morphology instead of dendrites (Figure 18a). The $\text{Zn}||\text{KCuHCF}$ full cells combined with this electrolyte display good cycling stability with average Coulombic efficiency of 97.66% after 1000 cycles (Figure 18b). Nevertheless, the water content must be controlled appropriately because excess water would negatively affect cycling (Figure 18c,d). Hence, this research might aid in developing safer organic electrolytes.

On the other hand, ionic liquids (ILs) offer great promise due to their low vapor pressure, temperature stability, exceptional chemical/physical stability, and extensive electrochemical stability. Thus, recent reports have suggested using ILs in ZIBs to obtain reversible Zn plating/stripping and eliminate HER [149,203–205]. Fan et al. developed a Zn-graphite dual-ion battery (DIB) using an ionic liquid electrolyte (mixture of 0.2 M $\text{Zn}(\text{TfO})_2$ and EMImTfO), in which Zn^{2+} ions were deposited and dissolved on the anode and TfO ions were inserted and removed into/from the cathode (Figure 18e) [203]. It demonstrated a dense and dendritic-free Zn electrodeposition with a cycling performance of 100 cycles and high Coulombic efficiency of 93.5% (Figure 18f). Ma et al. also reported 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF_4) and zinc tetrafluoroborate ($\text{Zn}(\text{BF}_4)_2$) as effective electrolytes for ZIBs [204]. This electrolyte could widen the electrochemical stability window compared with an aqueous solution (Figure 18g). However, ionic-liquid electrolytes pose serious problems for cost-effective ZIBs due to their relatively high cost compared to their aqueous counterparts.

Although aqueous electrolytes have certain benefits, such as high ionic conductivity, low cost, and sustainability, some side reactions initiated by water and unrestricted Zn^{2+} diffusion may appear inevitable and indispensable when the anode is in contact with water [17]. Using a gel electrolyte could effectively reduce the influence of free water on the discharge and charging of batteries. Thus, gel electrolytes have been proven to inhibit the Zn dendrite growth on the anode [47,206,207]. Previously, a gel electrolyte of zinc alginate (Alg-Zn) was reported by Tang et al. [207]. Due to the ion-confinement effect, the diffusion of Zn^{2+} ions was constrained by the carboxyl groups of Alg-Zn, which could firmly bind the ions and guide their migration (Figure 18h left). While in the liquid electrolyte, the Zn tips grow to vast Zn slices with bulk aggregation and non-uniform deposition in the electrolyte and finally crack to form “dead Zn” without electrochemical activity (Figure 18h right). Hence, $\text{Zn}||\text{MnO}_2$ batteries with Alg-Zn gel electrolyte performed well at high rates and cycling stability. In particular, the capacity can rapidly recover and a stable overpotential was maintained after resting over 60 h (Figure 18i). Additionally, flexible batteries are a major development direction in the future, and gel electrolytes will play a major role in this area [208–210].

3.4. Design of Separators

Several studies have been conducted to modify the Zn metal anode and aqueous electrolyte interface to address Zn issues. These methods modify the zinc metal anode-electrolyte interface, which is in the vicinity of the separator. Additionally, Zn ion distribution, ion transfer resistance, and ion migration are significantly influenced by separator properties, including composition, pore size, elastic modulus, and surface functional groups. Therefore, the separator plays a crucial role in the performance of the aqueous ZIBs. The majority of aqueous ZIB research uses glass fiber (GF) separators. However, a drawback

of GF separators is their poor wettability and low elastic modulus with large and uneven pores, which is susceptible to causing Zn dendrites and short-circuit issues [211,212]. Therefore, the mechanical and elastic properties and wettability of ZIB separators should be enhanced to overcome these drawbacks.

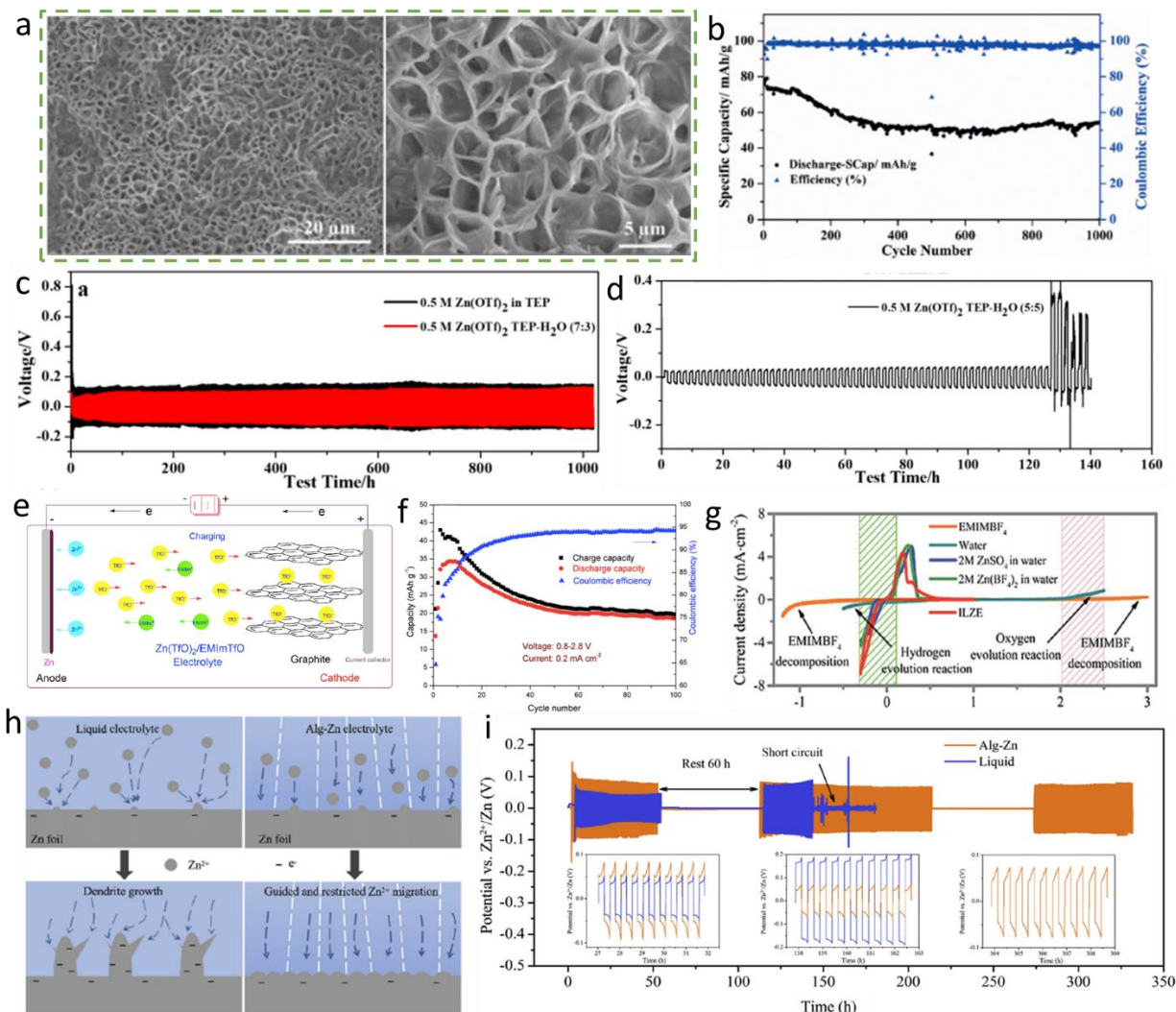


Figure 18. (a) SEM images of the morphologies grown at the Zn anode after plating/stripping 1000 times (2000 h) in a 0.5 M $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ -TEP electrolyte (left) and magnified view (right), (b) cycling performance of a $\text{Zn}||\text{KCuHCf}$ cell at a rate of 1 C in 0.5 M $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ in a TEP: H_2O (7:3) electrolyte, (c,d) influence of water content on the cycling performance of Zn/Zn symmetrical cells. (Reproduced with permission [202] Copyright 2019, John Wiley & Son). (e) Schematic illustration of the working mechanism of the Zn/graphite DIB and (f) Cycling performance of the Zn/graphite DIB. (Reproduced with permission [203] Copyright 2019, Springer Nature). (g) Electrochemical window of water and EMIMBF₄ ionic liquid. (Reproduced with permission [204] Copyright 2020, John Wiley & Son). (h) The mechanism for the deposition behaviors of Zn²⁺ in $\text{ZnSO}_4+\text{MnSO}_4$ aqueous electrolyte and Alg-Zn electrolyte, and (i) Zn plating/stripping performance of the symmetric cell under a current density of 1.77 mA cm⁻² at room temperature after resting for 60 h. (Reproduced with permission [207] Copyright, Elsevier).

A functional group within a separator may strongly interact with electrolyte ions, thus modifying the transport of Zn²⁺ ions and the deposition of Zn. For example, the SO_3^- functional group was utilized to modify Nafion membranes [213,214]. As proposed by Zeng et al., Zn-Nafion separators could be prepared by immersing the Nafion membrane in aqueous solutions of 2 M ZnSO_4 [214]. Based on the finite element simulation, dendrite

seeds have a more significant uniform electric field than GF seeds in Zn-Nafion separators (Figure 19a,b), which is due to the Donnan potential associated with the fixed negative charges in the Nafion material. Compared with that of the GF separator (226 h), the Zn||Zn cell with a Zn-Nafion separator worked better and exhibited lower polarization (553 h at 5 mA cm^{-2}) (Figure 19c). Moreover, the Zn-Nafion promoted the formation of the SEI layer composed of ZHS at the cathode by enhancing the participation of H^+ in $\text{H}^+/\text{Zn}^{2+}$ co-intercalation, preventing cathode from dissolving to the electrolyte. Consequently, the Zn-Nafion separator can significantly increase both cyclability and energy density. However, the cost of Nafion membranes is too high, which makes them unsuitable for the large-scale production of low-cost ZIBs. Thus, low-cost, and environmentally friendly separator materials are highly desirable.

Due to multiple merits including abundance, mechanical strength, hydrophilicity, excellent insulating properties, and biodegradability, cellulose has attracted attention in the membrane technology and rechargeable battery industries [215]. A cellulose film (CF) separator prepared with cotton material was proposed by Zhou et al. [216]. The cellulose obtained after pretreatment with NaOH and H_2O_2 was vacuum filtered to create a CF separator (Figure 19d), which is more hydrophilic than a GF separator (Figure 19e). Therefore, CF separators infiltrated with electrolytes can achieve an ionic conductivity of 56.95 mS cm^{-1} . Additionally, the tensile strength and modulus of a CF separator are 34 and 8.4 times larger than those of a GF separator, respectively. As a result, due to their excellent mechanical properties, Zn dendrites cannot grow vertically in CF separators. On the other hand, CF separators have dense and homogeneous nanopores, whereas GF separators display large, irregular, and non-uniform pores (Figure 19f,g). Thus, the CF separator would produce a more uniform Zn ion flux. As cellulose contains large hydroxy groups, it can attract Zn^{2+} ions and form strong hydrogen bonds with water, which facilitates Zn^{2+} ion transfer, regulates Zn^{2+} ion flux, promotes desolvation, reduces Zn plating barriers, and inhibits parasitic reactions. As shown in Figure 19h, the Zn||Zn cell with a CF separator performs much better than the GF separator and can handle high areal capacity (20 mAh cm^{-2}). This work showed how uniform porosity and functional groups of separators play a role in Zn anodes for aqueous ZIBs.

Additionally, integrated hybrid separators incorporating dielectric materials have been developed. According to Cao et al., cellulose nanofiber- ZrO_2 (CZ) composite separators prepared via the solution casting method (Figure 19i) resulted in a high Zn ion transfer number (0.69) and excellent ionic conductivity (Figure 19j) [217]. Because of the presence of ZrO_2 , the Maxwell–Wagner polarization effect is enabled. In addition to accelerating the diffusion of Zn^{2+} ions and repelling anions, ZrO_2 supports uniform Zn deposition and prevents side reactions during cell cycling by stabilizing the Zn anode. As a result, Zn stripping/plating behavior is stabilized for 2000 h at 0.5 mA cm^{-2} (Figure 19k).

The modification of separators has also attracted interest. As shown in Figure 20a, chemical vapor deposition was used by Li et al. to prepare vertical graphene (VG) on one side of commercial graphite (GF), which was also known as the Janus separator [38]. A 3D-VG scaffold, with a large area and porous structure, is an extension of a planar zinc anode (Figure 20b). The 3D VG separator ensures an even electrical field and prevents localized current concentrations at the anode/electrolyte interface (Figure 20c–e). Hence, zincophilic properties are beneficial in generating a uniform flux of Zn ions. According to Figure 20f, the stable atom configuration of O- and N-doped graphene significantly impacts Zn adsorption. The binding energies in Figure 20g also illustrate the Zn adsorption behavior as a function of the functional groups. Based on FEM modeling simulation, the frontier orbitals surrounding the Fermi level indicate the origin of enhanced Zn-capture ability for the modified separator (Figure 20h). DFT calculation and FEM modeling also proved that the Janus separator of vertical graphene contributes to uniform Zn deposition.

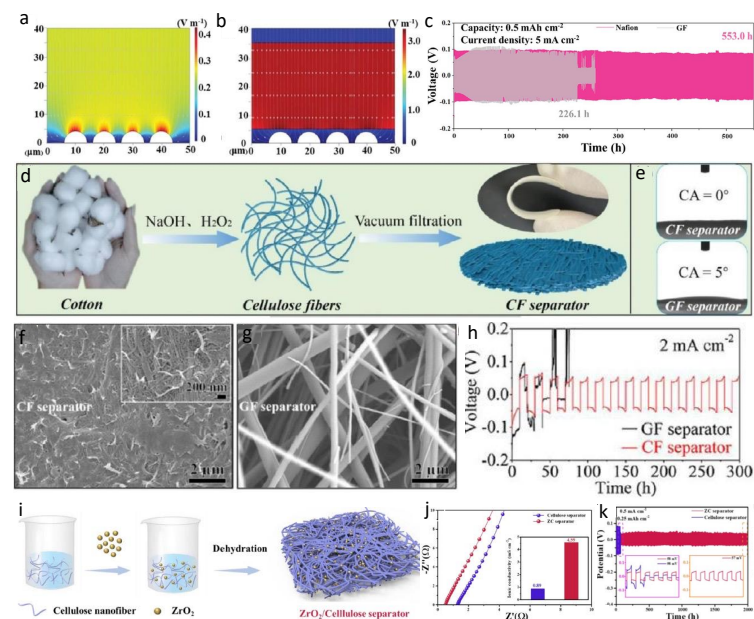


Figure 19. Distribution of electric fields within (a) GF separator and (b) Zn-Nafion separator, and (c) cycle life of the Zn symmetric cell with Nafion and GF separator. (Reproduced with permission [214] Copyright 2021, Royal Society of Chemistry). (d) Diagram illustrating the preparation of CF separators, (e) comparison of contact angles between CF and GF separator, SEM images of (f) CF separator and (g) GF separator, and (h) cycling performance at 2 mA cm^{-2} – 20 mAh cm^{-2} of Zn symmetric cells with CF and GF separators. (Reproduced with permission [216] Copyright 2022, Elsevier). (i) Schematic illustration of fabricating CZ separators, (j) ionic conductivity of cellulose and CZ separator, and (k) voltage–time profiles of Zn symmetrical cells with CZ and cellulose separators. (Reproduced with permission [217] Copyright 2021, Elsevier).

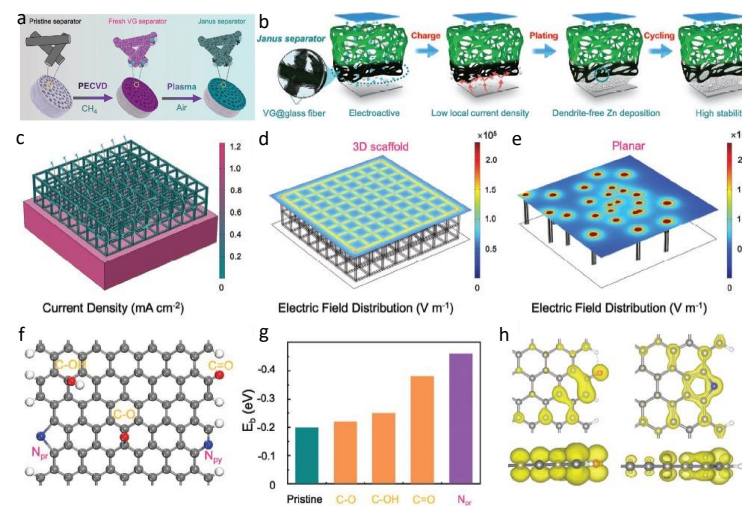


Figure 20. (a) Illustration of the synthetic process of the Janus separator, (b) demonstration of directly grown VG carpet on one side of the Janus separator which lowers local current density and homogenizes ion distribution, (c) current distribution in the 3D scaffold. The distribution of electric fields in (d) 2D planar structures (pristine separator case) and (e) 3D scaffold structures (Janus separator case), (f) N-doped and O-doped graphene configurations. Carbon, oxygen, nitrogen, and hydrogen atoms are indicated by gray, red, blue, and white colors, (g) the binding energy of Zn atoms on the O/N-functionalized graphene, and (h) the yellow contour with the isosurface value of $0.002 \text{ e bohr}^{-3}$ of partial charge density around the fermi level by top view (upper) and side view (lower) in the C=O–G and C–N_{pr}–G configuration from left to right. (Reproduced with permission [38] Copyright 2020, John Wiley & Son).

4. Summary, Challenges, and Perspectives

Since Zn metal anodes possess merits of high theoretical capacity and natural abundance, ZIBs have developed rapidly in recent years and are viewed as a new generation of sustainable energy storage systems. It is essential to address the issues of dendrite growth and parasitic reactions at Zn anodes for large-scale application of ZIBs. Herein, we briefly reviewed the challenges of Zn anodes, including the Zn dendrite formation, HER, side reactions, and corrosion based on the formation mechanisms from a fundamental point of view. To address these issues, several emerging mitigation strategies are systematically summarized, including surface modification, rational design of anode architectures, and electrolyte optimization. Although recent progress has been made in realizing high-performance Zn anodes, some persistent problems still need to be further resolved. Accordingly, some perspectives and future directions are proposed as follows:

- (1) Surface modification with a variety of coating materials that can tune the interaction of Zn with the electrolyte and maintain homogeneous Zn deposition is crucial to optimize the electrode/electrolyte interfacial reactions. However, a high interface impedance may be induced by the surface modification layer, impairing the rate capability. Hence, future efforts should be devoted to developing a surface modification layer with fast ion transport channels and high affinity to Zn anodes. Ideally, the surface modification layer should have the minimum loading and function effectively at both low and high current densities.
- (2) Some conflicting claims were found in the reports about the design principle of the interphase layer of Zn anodes. For example, the roles of surface wettability and zincophilicity in regulating Zn electrochemistry remain elusive and controversial. Some reports claimed that the interphase hydrophilicity is beneficial to the Zn plating/stripping, whereas other reports indicate the interfacial hydrophobicity is favorable. Furthermore, it is still debated whether high or low zincophilicity is beneficial to the plating and stripping of Zn. Therefore, in-depth mechanistic insights into the effects of interphase properties on Zn electrochemistry should be uncovered.
- (3) An in-depth understanding of the zinc ion diffusion through the artificial coating interfaces or in situ formed solid electrolyte interphases on Zn anodes is needed.
- (4) The development of high-performance and inexpensive Zn anodes with excellent structural integrity is highly demanded to promote the widespread application of ZIBs. Alloying with Zn is a promising method for the large-scale preparation of stable anodes. The alkaline Zn batteries have employed the Zn alloyed with some heavy metals. To date, only a few zinc alloy anodes have been investigated for mild ZIBs. A wider range of alloy systems with varied compositions should be considered in the future through the predication based on thermodynamic phase diagrams and theoretical computations coupled with experimental results to optimize functional alloying parameters and phase information.
- (5) A promising way to substantially improve Zn anodes is to optimize the electrolyte formulation composed of solvents, salt concentration, and additives. In the meantime, it is a key challenge how to solve the high corrosion of Zn anodes and suppress other side effects with the appropriate formulation. When an electrolyte formulation is designed, the bond strength between Zn^{2+} ions, various anions, and water molecules should be critically considered. The drying-out of the electrolytes in long-term cycling must be avoided. Moreover, some electrolyte additives may cause sluggish ion or electron transport, and high polarization of the battery system. Especially, the effects of electrolyte formulation and additives on the ionic diffusion into the positive electrodes and the possible electrochemical oxidation of added organic molecules (e.g., glucose) upon high potentials should also be considered.
- (6) A well-balanced combination of multiple strategies and tactics should be explored to improve the comprehensive performance of ZIBs. Since the anode interfacial issues are interconnected, various strategies can be integrated to synergistically address those issues. Some electrolyte additives can destroy the solvation structure by coordinating

with Zn^{2+} ions and adsorb on the metal surface to suppress the H^+ adsorption and HER and regulate Zn nucleation and growth. Structured anodes can be combined with the use of electrolyte additives or gel electrolytes to achieve a stable anode interface. Moreover, by incorporating metal or metal oxide particles into the modified layers or structured anodes, it is possible to design composite anodes to boost Zn deposition.

- (7) A gap usually exists between the anode performance and battery performance, suggesting the observed long-term cycling stability in symmetric Zn cells may not directly translate to the cyclability of full cells and stack systems. Therefore, the effectiveness of developed strategies should also be assessed by validating the performance of the whole battery system.
- (8) It is necessary to consider the costs and high gravimetric energy density of ZIBs in the practical application. A trade-off between economic cost, fabrication process, and electrochemical performance should be established to ensure competitiveness. In this scenario, the mass loading of Zn and utilization are crucial. Most of the reported aqueous ZIBs contain excessive Zn, whereas most Zn does not participate in the electrochemical reaction. This will reduce the Zn utilization and high gravimetric energy density of whole cells. Increasing the Zn plate utilization and employing Zn powder can enhance the gravimetric energy density of ZIBs. However, it is a formidable challenge to address the issues of dendrite growth, HER, and Zn corrosion when the Zn loading is low or high-surface-area Zn powder is used. The use of high-concentration electrolytes can increase the cost and reduce the rate of performance. Note that aqueous ZIBs feature low cost, high safety, and environmental friendliness, making them ideal for long-term usage. However, much research focuses on developing dendrite-free anodes with less consideration of the cost and scalability that are more relevant to practical production and application. Some methods involve the use of expensive and harmful raw materials, require complex procedures and harsh conditions, and have low yields, which significantly limits their viability in industrial applications. Therefore, the cost and benefits should be thoroughly weighed for the future development of viable Zn anodes.
- (9) Most of the reported testing protocols are proper to fundamentally evaluate the Zn anode but inappropriate for assessing the viability of entire batteries for practical application. For example, the long-term cycling performance of full ZIBs are evaluated at high rates, as the cells seemingly show better stability under high rates. However, such good cycling stability is misleading for practical energy storage applications. To bridge the gap between academic research and practical application, rigorous testing protocols towards pouch cells and stack systems should be established beyond lab-scale coin cells, considering the high mass loadings, proper electrolyte dosage (rather than flooded electrolytes), large depth of discharge, and proper negative to positive electrode capacity ratio (N/P ratio) for high utilization of Zn anodes and electrolytes to meet the industrial requirements. Future work may focus on the translation of lab-scale innovation to industrial production and transforming the material-level performance assessment into the device and system-level metrics.
- (10) Rechargeable batteries are an excellent option for smart grids, electric vehicles, and consumer electronics requiring excellent energy storage. Despite their merits, the steady supply of electricity, efficient utilization, operation and safety management, and effective control of these battery systems have always been concerns for many applications. For Zn-ion batteries, their capacity fade, cycling lifetime, possible cell deformation, and release of gases in the practical operation must be rigorously monitored and controlled. Hence, the battery management system (BMS) plays a vital role in evaluating and monitoring battery usage and health. There are several functions performed by a BMS, including (i) estimation of battery condition, (ii) battery cell balance, (iii) pack charging/discharging control, (iv) thermal management, (v) fault prognosis, and (vi) health diagnosis. However, the complexity of internal battery chemistry and difficulty in precisely measuring individual parameters make it

challenging to accurately evaluate the battery's state of health. Additionally, battery modeling can simulate the electrochemical behavior of batteries. In terms of hardware, a sensor can monitor and provide feedback on various battery parameters to establish appropriate models and estimate battery states. To achieve power conversion and information interaction, the controllers will process battery information and issue control instructions. The BMS may also embrace various emerging technologies, such as artificial intelligence (AI), cloud computing (CC), and blockchain technology. Thus, it is desirable to have precise battery models that can be easily computed in an advanced battery management system.

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References

- Schon, T.B.; McAllister, B.T.; Li, P.F.; Seferos, D.S. The Rise of Organic Electrode Materials for Energy Storage. *Chem. Soc. Rev.* **2016**, *45*, 6345–6404. [[CrossRef](#)] [[PubMed](#)]
- Huo, H.; Xing, Y.; Pecht, M.; Züger, B.-J.; Khare, N.; Vezzini, A. Safety Requirements for Transportation of Lithium Batteries. *Energies* **2017**, *10*, 793. [[CrossRef](#)]
- Zeng, Z.; Li, W.; Chen, X.; Liu, X. Bifunctional 3D Hierarchical Hairy Foam toward Ultrastable Lithium/Sulfur Electrochemistry. *Adv. Funct. Mater.* **2020**, *30*, 2004650. [[CrossRef](#)]
- Xing, J.; Bliznakov, S.; Bonville, L.; Oljaca, M.; Maric, R. A Review of Nonaqueous Electrolytes, Binders, and Separators for Lithium-Ion Batteries. *Electrochem. Energy Rev.* **2022**, *5*, 14. [[CrossRef](#)]
- Liu, B.; Jia, Y.; Yuan, C.; Wang, L.; Gao, X.; Yin, S.; Xu, J. Safety Issues and Mechanisms of Lithium-Ion Battery Cell upon Mechanical Abusive Loading: A Review. *Energy Storage Mater.* **2020**, *24*, 85–112. [[CrossRef](#)]
- Li, W.; Yin, Y.X.; Xin, S.; Song, W.G.; Guo, Y.G. Low-Cost and Large-Scale Synthesis of Alkaline Earth Metal Germanate Nanowires as a New Class of Lithium Ion Battery Anode Material. *Energy Environ. Sci.* **2012**, *5*, 8007–8013. [[CrossRef](#)]
- Pang, P.; Wang, Z.; Tan, X.; Deng, Y.; Nan, J.; Xing, Z.; Li, H. LiCoO₂@LiNi_{0.45}Al_{0.05}Mn_{0.5}O₂ as High-Voltage Lithium-Ion Battery Cathode Materials with Improved Cycling Performance and Thermal Stability. *Electrochim. Acta* **2019**, *327*, 135018. [[CrossRef](#)]
- Pang, P.; Pang, P.; Wang, Z.; Deng, Y.; Nan, J.; Xing, Z.; Li, H. Delayed Phase Transition and Improved Cycling/Thermal Stability by Spinel LiNi_{0.5}Mn_{1.5}O₄ Modification for LiCoO₂ Cathode at High Voltages. *ACS Appl. Mater. Interfaces* **2020**, *12*, 27339–27349. [[CrossRef](#)]
- Chombo, P.V.; Laoonual, Y. A Review of Safety Strategies of a Li-Ion Battery. *J. Power Sources* **2020**, *478*, 228649. [[CrossRef](#)]
- Chen, Y.; Kang, Y.; Zhao, Y.; Wang, L.; Liu, J.; Li, Y.; Liang, Z.; He, X.; Li, X.; Tavajohi, N. A Review of Lithium-Ion Battery Safety Concerns: The Issues, Strategies, and Testing Standards. *J. Energy Chem.* **2021**, *59*, 83–99. [[CrossRef](#)]
- Ao, H.; Zhao, Y.; Zhou, J.; Cai, W.; Zhang, X.; Zhu, Y.; Qian, Y. Rechargeable Aqueous Hybrid Ion Batteries: Developments and Prospects. *J. Mater. Chem. A* **2019**, *7*, 18708–18734. [[CrossRef](#)]
- Kim, H.; Hong, J.; Park, K.Y.; Kim, H.; Kim, S.W.; Kang, K. Aqueous Rechargeable Li and Na Ion Batteries. *Chem. Rev.* **2014**, *114*, 11788–11827. [[CrossRef](#)] [[PubMed](#)]
- Monroe, D. Building a Better Battery. *MRS Bull.* **2020**, *45*, 246–247. [[CrossRef](#)]
- Wang, F.; Borodin, O.; Ding, M.S.; Gobet, M.; Vatamanu, J.; Fan, X.; Gao, T.; Edison, N.; Liang, Y.; Sun, W. Hybrid Aqueous/Non-Aqueous Electrolyte for Safe and High-Energy Li-Ion Batteries. *Joule* **2018**, *2*, 927–937. [[CrossRef](#)]

15. Posada, J.O.G.; Rennie, A.J.R.; Villar, S.P.; Martins, V.L.; Marinaccio, J.; Barnes, A.; Glover, C.F.; Worsley, D.A.; Hall, P.J. Aqueous Batteries as Grid Scale Energy Storage Solutions. *Renew. Sustain. Energy Rev.* **2017**, *68*, 1174–1182. [\[CrossRef\]](#)
16. Xing, Z.; Wang, S.; Yu, A.; Chen, Z. Aqueous Intercalation-Type Electrode Materials for Grid-Level Energy Storage: Beyond the Limits of Lithium and Sodium. *Nano Energy* **2018**, *50*, 229–244. [\[CrossRef\]](#)
17. Huang, S.; Zhu, J.; Tian, J.; Niu, Z. Recent Progress in the Electrolytes of Aqueous Zinc-Ion Batteries. *Chem. Eur. J.* **2019**, *25*, 14480–14494. [\[CrossRef\]](#)
18. Liu, Z.; Huang, Y.; Huang, Y.; Yang, Q.; Li, X.; Huang, Z.; Zhi, C. Voltage Issue of Aqueous Rechargeable Metal-Ion Batteries. *Chem. Soc. Rev.* **2020**, *49*, 180–232. [\[CrossRef\]](#)
19. Yu, Y.; Cao, C.; Li, W.; Li, P.; Qu, J.; Song, W. Low-Cost Synthesis of Robust Anatase Polyhedral Structures with a Preponderance of Exposed {001} Facets for Enhanced Photoactivities. *Nano Res.* **2012**, *5*, 434–442. [\[CrossRef\]](#)
20. Chao, D.; Zhou, W.; Xie, F.; Ye, C.; Li, H.; Jaroniec, M.; Qiao, S.Z. Roadmap for Advanced Aqueous Batteries: From Design of Materials to Applications. *Sci. Adv.* **2020**, *6*, eaba4098. [\[CrossRef\]](#)
21. Huang, J.; Guo, Z.; Ma, Y.; Bin, D.; Wang, Y.; Xia, Y. Recent Progress of Rechargeable Batteries Using Mild Aqueous Electrolytes. *Small Methods* **2019**, *3*, 1800272. [\[CrossRef\]](#)
22. Li, H.; Ma, L.; Han, C.; Wang, Z.; Liu, Z.; Tang, Z.; Zhi, C. Advanced Rechargeable Zinc-Based Batteries: Recent Progress and Future Perspectives. *Nano Energy* **2019**, *62*, 550–587. [\[CrossRef\]](#)
23. Blanc, L.E.; Kundu, D.; Nazar, L.F. Scientific Challenges for the Implementation of Zn-Ion Batteries. *Joule* **2020**, *4*, 771–799. [\[CrossRef\]](#)
24. Cao, J.; Zhang, D.; Zhang, X.; Zeng, Z.; Qin, J.; Huang, Y. Strategies of Regulating Zn²⁺ Solvation Structures for Dendrite-Free and Side Reaction-Suppressed Zinc-Ion Batteries. *Energy Environ. Sci.* **2022**, *15*, 499–528. [\[CrossRef\]](#)
25. Yang, Q.; Liang, G.; Guo, Y.; Liu, Z.; Yan, B.; Wang, D.; Huang, Z.; Li, X.; Fan, J.; Zhi, C. Do Zinc Dendrites Exist in Neutral Zinc Batteries: A Developed Electrohealing Strategy to In Situ Rescue In-Service Batteries. *Adv. Mater.* **2019**, *31*, 1903778. [\[CrossRef\]](#)
26. Hao, J.; Li, X.; Zeng, X.; Li, D.; Mao, J.; Guo, Z. Deeply Understanding the Zn Anode Behaviour and Corresponding Improvement Strategies in Different Aqueous Zn-Based Batteries. *Energy Environ. Sci.* **2020**, *13*, 3917–3949. [\[CrossRef\]](#)
27. Jia, X.; Liu, C.; Neale, Z.G.; Yang, J.; Cao, G. Active Materials for Aqueous Zinc Ion Batteries: Synthesis, Crystal Structure, Morphology, and Electrochemistry. *Chem. Rev.* **2020**, *120*, 7795–7866. [\[CrossRef\]](#)
28. Tao, F.; Liu, Y.; Ren, X.; Wang, J.; Zhou, Y.; Miao, Y.; Ren, F.; Wei, S.; Ma, J. Different Surface Modification Methods and Coating Materials of Zinc Metal Anode. *J. Energy Chem.* **2022**, *66*, 397–412. [\[CrossRef\]](#)
29. Zheng, J.; Huang, Z.; Ming, F.; Zeng, Y.; Wei, B.; Jiang, Q.; Qi, Z.; Wang, Z.; Liang, H. Surface and Interface Engineering of Zn Anodes in Aqueous Rechargeable Zn-Ion Batteries. *Small* **2022**, *18*, 2200006. [\[CrossRef\]](#)
30. Qin, R.; Wang, Y.; Yao, L.; Yang, L.; Zhao, Q.; Ding, S.; Liu, L.; Pan, F. Progress in Interface Structure and Modification of Zinc Anode for Aqueous Batteries. *Nano Energy* **2022**, *98*, 107333. [\[CrossRef\]](#)
31. Lu, W.; Zhang, C.; Zhang, H.; Li, X. Anode for Zinc-Based Batteries: Challenges, Strategies, and Prospects. *ACS Energy Lett.* **2021**, *6*, 2765–2785. [\[CrossRef\]](#)
32. Liu, C.; Xie, X.; Lu, B.; Zhou, J.; Liang, S. Electrolyte Strategies toward Better Zinc-Ion Batteries. *ACS Energy Lett.* **2021**, *6*, 1015–1033. [\[CrossRef\]](#)
33. Li, T.C.; Fang, D.; Zhang, J.; Pam, M.E.; Leong, Z.Y.; Yu, J.; Li, X.L.; Yan, D.; Yang, H.Y. Recent Progress in Aqueous Zinc-Ion Batteries: A Deep Insight into Zinc Metal Anodes. *J. Mater. Chem. A* **2021**, *9*, 6013–6028. [\[CrossRef\]](#)
34. Yi, Z.; Chen, G.; Hou, F.; Wang, L.; Liang, J. Strategies for the Stabilization of Zn Metal Anodes for Zn-Ion Batteries. *Adv. Energy Mater.* **2021**, *11*, 2003065. [\[CrossRef\]](#)
35. Yang, Q.; Li, Q.; Liu, Z.; Wang, D.; Guo, Y.; Li, X.; Tang, Y.; Li, H.; Dong, B.; Zhi, C. Dendrites in Zn-Based Batteries. *Adv. Mater.* **2020**, *32*, e2001854. [\[CrossRef\]](#) [\[PubMed\]](#)
36. Sun, P.; Ma, L.; Zhou, W.; Qiu, M.; Wang, Z.; Chao, D.; Mai, W. 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.* **2021**, *60*, 18247–18255. [\[CrossRef\]](#) [\[PubMed\]](#)
37. Wang, D.; Li, H.; Liu, Z.; Tang, Z.; Liang, G.; Mo, F.; Yang, Q.; Ma, L.; Zhi, C. A Nanofibrillated Cellulose/Polyacrylamide Electrolyte-Based Flexible and Sewable High-Performance Zn–MnO₂ Battery with Superior Shear Resistance. *Small* **2018**, *14*, 1803978. [\[CrossRef\]](#)
38. Li, C.; Sun, Z.; Yang, T.; Yu, L.; Wei, N.; Tian, Z.; Cai, J.; Lv, J.; Shao, Y.; Rummeli, M.H. Directly Grown Vertical Graphene Carpets as Janus Separators toward Stabilized Zn Metal Anodes. *Adv. Mater.* **2020**, *32*, 2003425. [\[CrossRef\]](#)
39. Hao, J.; Li, B.; Li, X.; Zeng, X.; Zhang, S.; Yang, F.; Liu, S.; Li, D.; Wu, C.; Guo, Z. An In-Depth Study of Zn Metal Surface Chemistry for Advanced Aqueous Zn-Ion Batteries. *Adv. Mater.* **2020**, *32*, 2003021. [\[CrossRef\]](#)
40. Kang, Z.; Wu, C.; Dong, L.; Liu, W.; Mou, J.; Zhang, J.; Chang, Z.; Jiang, B.; Wang, G.; Kang, F. 3D Porous Copper Skeleton Supported Zinc Anode toward High Capacity and Long Cycle Life Zinc Ion Batteries. *ACS Sustain. Chem. Eng.* **2019**, *7*, 3364–3371. [\[CrossRef\]](#)
41. Zhang, Y.; Zhu, M.; Wu, K.; Yu, F.; Wang, G.; Xu, G.; Wu, M.; Liu, H.-K.; Dou, S.-X.; Wu, C. An In-depth Insight of a Highly Reversibility and Dendrite-free Zn Metal Anode in A Hybrid Electrolyte. *J. Mater. Chem. A* **2021**, *9*, 4253. [\[CrossRef\]](#)
42. Yang, J.; Yin, B.; Sun, Y.; Pan, H.; Sun, W.; Jia, B.; Zhang, S.; Ma, T. Zinc Anode for Mild Aqueous Zinc-Ion Batteries: Challenges, Strategies, and Perspectives. *Nano-Micro Lett.* **2022**, *14*, 42. [\[CrossRef\]](#) [\[PubMed\]](#)

43. Zuo, Y.; Wang, K.; Pei, P.; Wei, M.; Liu, X.; Xiao, Y.; Zhang, P. Zinc Dendrite Growth and Inhibition Strategies. *Mater. Today Energy* **2021**, *20*, 100692. [\[CrossRef\]](#)
44. Yufit, V.; Tariq, F.; Eastwood, D.S.; Biton, M.; Wu, B.; Lee, P.D.; Brandon, N.P. Operando Visualization and Multi-Scale Tomography Studies of Dendrite Formation and Dissolution in Zinc Batteries. *Joule* **2019**, *3*, 485–502. [\[CrossRef\]](#)
45. Zheng, G.; Wang, C.; Pei, A.; Lopez, J.; Shi, F.; Chen, Z.; Sendek, A.D.; Lee, H.W.; Lu, Z.; Schneider, H. High-Performance Lithium Metal Negative Electrode with a Soft and Flowable Polymer Coating. *ACS Energy Lett.* **2016**, *1*, 1247–1255. [\[CrossRef\]](#)
46. Zhu, M.; Hu, J.; Lu, Q.; Dong, H.; Karnaushenko, D.D.; Becker, C.; Karnaushenko, D.; Li, Y.; Tang, H.; Qu, Z. A Patternable and In Situ Formed Polymeric Zinc Blanket for a Reversible Zinc Anode in a Skin-Mountable Microbattery. *Adv. Mater.* **2021**, *33*, 2007497. [\[CrossRef\]](#)
47. Ma, L.; Li, Q.; Ying, Y.; Ma, F.; Chen, S.; Li, Y.; Huang, H.; Zhi, C. Toward Practical High-Areal-Capacity Aqueous Zinc-Metal Batteries: Quantifying Hydrogen Evolution and a Solid-Ion Conductor for Stable Zinc Anodes. *Adv. Mater.* **2021**, *33*, 2007406. [\[CrossRef\]](#)
48. Cao, X.; Ren, X.; Zou, L.; Engelhard, M.H.; Huang, W.; Wang, H.; Matthews, B.E.; Lee, H.; Niu, C.; Arey, B.W. Monolithic Solid-Electrolyte Interphases Formed in Fluorinated Orthoformate-Based Electrolytes Minimize Li Depletion and Pulverization. *Nat. Energy* **2019**, *4*, 796–805. [\[CrossRef\]](#)
49. Gu, Y.; Wang, W.W.; Li, Y.J.; Wu, Q.H.; Tang, S.; Yan, J.W.; Zheng, M.S.; Wu, D.Y.; Fan, C.H.; Hu, W.Q. Designable Ultra-Smooth Ultra-Thin Solid-Electrolyte Interphases of Three Alkali Metal Anodes. *Nat. Commun.* **2018**, *9*, 1339. [\[CrossRef\]](#)
50. Chazalviel, J.-N. Electrochemical Aspects of the Generation of Ramified Metallic Electrodeposits. *Phys. Rev. A* **1990**, *42*, 7355. [\[CrossRef\]](#)
51. Zheng, J.; Zhao, Q.; Tang, T.; Yin, J.; Quilty, C.D.; Renderos, G.D.; Liu, X.; Deng, Y.; Wang, L.; Bock, D.C. Reversible Epitaxial Electrodeposition of Metals in Battery Anodes. *Science* **2019**, *366*, 645–648. [\[CrossRef\]](#) [\[PubMed\]](#)
52. Li, W.; Tian, H.; Ma, L.; Wang, Y.; Liu, X.; Gao, X. Low-Temperature Water Electrolysis: Fundamentals, Progress, and New Strategies. *Mater. Adv.* **2022**, *3*, 5598–5644. [\[CrossRef\]](#)
53. Ali, A.; Long, F.; Shen, P.K. Innovative Strategies for Overall Water Splitting Using Nanostructured Transition Metal Electrocatalysts. *Electrochem. Energy Rev.* **2022**, *5*, 1. [\[CrossRef\]](#)
54. Li, C.; Xie, X.; Liang, S.; Zhou, J. Issues and Future Perspective on Zinc Metal Anode for Rechargeable Aqueous Zinc-Ion Batteries. *Energy Environ. Mater.* **2020**, *3*, 146–159. [\[CrossRef\]](#)
55. Verma, J.; Goel, S. Cost-Effective Electrocatalysts for Hydrogen Evolution Reactions (HER): Challenges and Prospects. *Int. J. Hydrog. Energy* **2022**, *47*, 38964–38982. [\[CrossRef\]](#)
56. Zhao, J.; Bao, K.; Xie, M.; Wei, D.; Yang, K.; Zhang, X.; Zhang, C.; Wang, Z.; Yang, X. Two-Dimensional Ultrathin Networked CoP Derived from Co(OH)₂ as Efficient Electrocatalyst for Hydrogen Evolution. *Adv. Compos. Hybrid Mater.* **2022**, *5*, 2421–2428. [\[CrossRef\]](#)
57. Yu, Z.; Yao, H.; Yang, Y.; Yuan, M.; Li, C.; He, H.; Chan, T.-S.; Yan, D.; Ma, S.; Zapol, P. MoO_xS_y/Ni₃S₂ Microspheres on Ni Foam as Highly Efficient, Durable Electrocatalysts for Hydrogen Evolution Reaction. *Chem. Mater.* **2022**, *34*, 798–808. [\[CrossRef\]](#)
58. Li, W.; Jiang, N.; Hu, B.; Liu, X.; Song, F.; Han, G.; Jordan, T.J.; Hanson, T.B.; Liu, T.L.; Sun, Y. Electrolyzer Design for Flexible Decoupled Water Splitting and Organic Upgrading with Electron Reservoirs. *Chem* **2018**, *4*, 637–649. [\[CrossRef\]](#)
59. Li, W.; Xiong, D.; Gao, X.; Song, W.G.; Xia, F.; Liu, L. Self-Supported Co-Ni-P Ternary Nanowire Electrodes for Highly Efficient and Stable Electrocatalytic Hydrogen Evolution in Acidic Solution. *Catal. Today* **2017**, *287*, 122–129. [\[CrossRef\]](#)
60. Hao, J.; Li, X.; Zhang, S.; Yang, F.; Zeng, X.; Zhang, S.; Bo, G.; Wang, C.; Guo, Z. Designing Dendrite-Free Zinc Anodes for Advanced Aqueous Zinc Batteries. *Adv. Funct. Mater.* **2020**, *30*, 2001263. [\[CrossRef\]](#)
61. Zhao, Z.; Zhao, J.; Hu, Z.; Li, J.; Li, J.; Zhang, Y.; Wang, C.; Cui, G. Long-Life and Deeply Rechargeable Aqueous Zn Anodes Enabled by a Multifunctional Brightener-Inspired Interphase. *Energy Environ. Sci.* **2019**, *12*, 1938–1949. [\[CrossRef\]](#)
62. Zhao, J.; Zhang, J.; Yang, W.; Chen, B.; Zhao, Z.; Qiu, H.; Dong, S.; Zhou, X.; Cui, G.; Chen, L. “Water-in-Deep Eutectic Solvent” Electrolytes Enable Zinc Metal Anodes for Rechargeable Aqueous Batteries. *Nano Energy* **2019**, *57*, 625–634. [\[CrossRef\]](#)
63. Bayaguud, A.; Fu, Y.; Zhu, C. Interfacial Parasitic Reactions of Zinc Anodes in Zinc Ion Batteries: Underestimated Corrosion and Hydrogen Evolution Reactions and Their Suppression Strategies. *J. Energy Chem.* **2022**, *64*, 246–262. [\[CrossRef\]](#)
64. Fitz, O.; Bischoff, C.; Bauer, M.; Gentischer, H.; Birke, K.P.; Henning, H.M.; Biro, D. Electrolyte Study within Operando pH Tracking Providing Insight into the Reaction Mechanism of Aqueous Acidic Zn//MnO₂ Batteries. *ChemElectroChem* **2021**, *8*, 3553–3566. [\[CrossRef\]](#)
65. Sajjadnejad, M.; Mozafari, A.; Omidvar, H.; Javanbakht, M. Preparation and Corrosion Resistance of Pulse Electrodeposited Zn and Zn-SiC Nanocomposite Coatings. *Appl. Surf. Sci.* **2014**, *300*, 1–7. [\[CrossRef\]](#)
66. Xie, C.; Li, Y.; Wang, Q.; Sun, D.; Tang, Y.; Wang, H. Issues and Solutions toward Zinc Anode in Aqueous Zinc-Ion Batteries: A Mini Review. *Carbon Energy* **2020**, *2*, 540–560. [\[CrossRef\]](#)
67. Li, W.; Wang, K.; Zhou, M.; Zhan, H.; Cheng, S.; Jiang, K. Advanced Low-Cost, High-Voltage, Long-Life Aqueous Hybrid Sodium/Zinc Batteries Enabled by a Dendrite-Free Zinc Anode and Concentrated Electrolyte. *ACS Appl. Mater. Interfaces* **2018**, *10*, 22059–22066. [\[CrossRef\]](#)
68. Du, Y.; Liu, C.; Liu, Y.; Han, Q.; Chi, X.; Liu, Y. Carbon Fiber Micron Film Guided Uniform Plating/Stripping of Metals: A Universal Approach for Highly Stable Metal Batteries. *Electrochim. Acta* **2020**, *339*, 135867. [\[CrossRef\]](#)

69. Zhou, Z.; Zhang, Y.; Chen, P.; Wu, Y.; Yang, H.; Ding, H.; Zhang, Y.; Wang, Z.; Du, X.; Liu, N. Graphene Oxide-Modified Zinc Anode for Rechargeable Aqueous Batteries. *Chem. Eng. Sci.* **2019**, *194*, 142–147. [\[CrossRef\]](#)
70. Wang, A.; Zhou, W.; Huang, A.; Chen, M.; Chen, J.; Tian, Q.; Xu, J. Modifying the Zn Anode with Carbon Black Coating and Nanofibrillated Cellulose Binder: A Strategy to Realize Dendrite-Free Zn-MnO₂ Batteries. *J. Colloid Interface Sci.* **2020**, *577*, 256–264. [\[CrossRef\]](#)
71. Li, M.; He, Q.; Li, Z.; Li, Q.; Zhang, Y.; Meng, J.; Liu, X.; Li, S.; Wu, B.; Chen, L. A Novel Dendrite-Free Mn²⁺/Zn²⁺ Hybrid Battery with 2.3 V Voltage Window and 11000-Cycle Lifespan. *Adv. Energy Mater.* **2019**, *9*, 1901469. [\[CrossRef\]](#)
72. Qiu, M.; Wang, D.; Tawiah, B.; Jia, H.; Fei, B.; Fu, S. Constructing PEDOT:PSS/Graphene Sheet Nanofluidic Channels to Achieve Dendrite-Free Zn Anode. *Compos. B Eng.* **2021**, *215*, 108798. [\[CrossRef\]](#)
73. Xia, A.; Pu, X.; Tao, Y.; Liu, H.; Wang, Y. Graphene Oxide Spontaneous Reduction and Self-Assembly on the Zinc Metal Surface Enabling a Dendrite-Free Anode for Long-Life Zinc Rechargeable Aqueous Batteries. *Appl. Surf. Sci.* **2019**, *481*, 852–859. [\[CrossRef\]](#)
74. Shen, C.; Li, X.; Li, N.; Xie, K.; Wang, J.G.; Liu, X.; Wei, B. Graphene-Boosted, High-Performance Aqueous Zn-Ion Battery. *ACS Appl. Mater. Interfaces* **2018**, *10*, 25446–25453. [\[CrossRef\]](#) [\[PubMed\]](#)
75. Zhou, J.; Xie, M.; Wu, F.; Mei, Y.; Hao, Y.; Huang, R.; Wei, G.; Liu, A.; Li, L.; Chen, R. Ultrathin Surface Coating of Nitrogen-Doped Graphene Enables Stable Zinc Anodes for Aqueous Zn-Ion Batteries. *Adv. Mater.* **2021**, *33*, 2101649. [\[CrossRef\]](#) [\[PubMed\]](#)
76. Dong, L.; Yang, W.; Yang, W.; Tian, H.; Huang, Y.; Wang, X.; Xu, C.; Wang, C.; Kang, F.; Wang, G. Flexible and Conductive Scaffold-Stabilized Zinc Metal Anodes for Ultralong-Life Zinc-Ion Batteries and Zinc-Ion Hybrid Capacitors. *Chem. Eng. J.* **2020**, *384*, 123355. [\[CrossRef\]](#)
77. Dai, L.; Wang, T.; Jin, B.; Liu, N.; Niu, Y.; Meng, W.; Gao, Z.; Wu, X.; Wang, L.; He, Z. γ -Al₂O₃ Coating Layer Confining Zinc Dendrite Growth for High Stability Aqueous Rechargeable Zinc-Ion Batteries. *Surf. Coat. Technol.* **2021**, *427*, 127813. [\[CrossRef\]](#)
78. Li, B.; Xue, J.; Han, C.; Liu, N.; Ma, K.; Zhang, R.; Wu, X.; Dai, L.; Wang, L.; He, Z. A Hafnium Oxide-Coated Dendrite-Free Zinc Anode for Rechargeable Aqueous Zinc-Ion Batteries. *J. Colloid Interface Sci.* **2021**, *599*, 467–475. [\[CrossRef\]](#)
79. Zhou, M.; Guo, S.; Fang, G.; Sun, H.; Cao, X.; Zhou, J.; Pan, A.; Liang, S. Suppressing By-Product via Stratified Adsorption Effect to Assist Highly Reversible Zinc Anode in Aqueous Electrolyte. *J. Energy Chem.* **2021**, *55*, 549–556. [\[CrossRef\]](#)
80. Li, B.; Xue, J.; Lv, X.; Zhang, R.; Ma, K.; Wu, X.; Dai, L.; Wang, L.; He, Z. A Facile Coating Strategy for High Stability Aqueous Zinc Ion Batteries: Porous Rutile Nano-TiO₂ Coating on Zinc Anode. *Surf. Coat. Technol.* **2021**, *421*, 127367. [\[CrossRef\]](#)
81. Liang, P.; Yi, J.; Liu, X.; Wu, K.; Wang, Z.; Cui, J.; Liu, Y.; Wang, Y.; Xia, Y.; Zhang, J. Highly Reversible Zn Anode Enabled by Controllable Formation of Nucleation Sites for Zn-Based Batteries. *Adv. Funct. Mater.* **2020**, *30*, 1908528. [\[CrossRef\]](#)
82. Bhoyate, S.; Mhin, S.; Mhin, S.; Jeon, J.E.; Park, K.; Kim, J.; Choi, W.; Choi, W. Stable and High-Energy-Density Zn-Ion Rechargeable Batteries Based on a MoS₂-Coated Zn Anode. *ACS Appl. Mater. Interfaces* **2020**, *12*, 27249–27257. [\[CrossRef\]](#) [\[PubMed\]](#)
83. Xie, X.; Liang, S.; Gao, J.; Guo, S.; Guo, J.; Wang, C.; Xu, G.; Wu, X.; Chen, G.; Zhou, J. Manipulating the Ion-Transfer Kinetics and Interface Stability for High-Performance Zinc Metal Anodes. *Energy Environ. Sci.* **2020**, *13*, 503–510. [\[CrossRef\]](#)
84. Kang, L.; Cui, M.; Jiang, F.; Gao, Y.; Luo, H.; Liu, J.; Liang, W.; Zhi, C. Nanoporous CaCO₃ Coatings Enabled Uniform Zn Stripping/Plating for Long-Life Zinc Rechargeable Aqueous Batteries. *Adv. Energy Mater.* **2018**, *8*, 1801090. [\[CrossRef\]](#)
85. Li, B.; Jin, B.; Zhang, R.; Ma, K.; Wu, X.; Dai, L.; Wang, L.; He, Z. Structural Design and Interfacial Characteristics Endow NaTi₂(PO₄)₃ Coated Zinc Anode with High Capacity and Better Cycling Stability. *Surf. Coat. Technol.* **2021**, *425*, 127699. [\[CrossRef\]](#)
86. Deng, C.; Xie, X.; Han, J.; Tang, Y.; Gao, J.; Liu, C.; Shi, X.; Zhou, J.; Liang, S. A Sieve-Functional and Uniform-Porous Kaolin Layer toward Stable Zinc Metal Anode. *Adv. Funct. Mater.* **2020**, *30*, 2000599. [\[CrossRef\]](#)
87. Wang, T.; Xi, Q.; Li, Y.; Fu, H.; Hua, Y.; Shankar, E.G.; Kakarla, A.K.; Yu, J.S. Regulating Dendrite-Free Zinc Deposition by Red Phosphorous-Derived Artificial Protective Layer for Zinc Metal Batteries. *Adv. Sci.* **2022**, *9*, 2200155. [\[CrossRef\]](#)
88. Xia, Y.; Wang, H.; Shao, G.; Wang, C.A. Realizing Highly Reversible and Deeply Rechargeable Zn Anode by Porous Zeolite Layer. *J. Power Sources* **2022**, *540*, 231659. [\[CrossRef\]](#)
89. Wang, X.; Meng, J.; Lin, X.; Yang, Y.; Zhou, S.; Wang, Y.; Pan, A. Stable Zinc Metal Anodes with Textured Crystal Faces and Functional Zinc Compound Coatings. *Adv. Funct. Mater.* **2021**, *31*, 2106114. [\[CrossRef\]](#)
90. Cui, M.; Xiao, Y.; Kang, L.; Du, W.; Gao, Y.; Sun, X.; Zhou, Y.; Li, X.; Li, H.; Jiang, F. Quasi-Isolated Au Particles as Heterogeneous Seeds to Guide Uniform Zn Deposition for Aqueous Zinc-Ion Batteries. *ACS Appl. Energy Mater.* **2019**, *2*, 6490–6496. [\[CrossRef\]](#)
91. Cai, Z.; Ou, Y.; Wang, J.; Xiao, R.; Fu, L.; Yuan, Z.; Zhan, R.; Sun, Y. Chemically Resistant Cu–Zn/Zn Composite Anode for Long Cycling Aqueous Batteries. *Energy Storage Mater.* **2020**, *27*, 205–211. [\[CrossRef\]](#)
92. Guo, W.; Zhang, Y.; Tong, X.; Wang, X.; Zhang, L.; Xia, X.; Tu, J. Multifunctional Tin Layer Enabled Long-Life and Stable Anode for Aqueous Zinc-Ion Batteries. *Mater. Today Energy* **2021**, *20*, 100675. [\[CrossRef\]](#)
93. Han, D.; Wu, S.; Zhang, S.; Deng, Y.; Cui, C.; Zhang, L.; Long, Y.; Li, H.; Tao, Y.; Weng, Z. A Corrosion-Resistant and Dendrite-Free Zinc Metal Anode in Aqueous Systems. *Small* **2020**, *16*, 2001736. [\[CrossRef\]](#) [\[PubMed\]](#)
94. Hu, K.; Guan, X.; Lv, R.; Li, G.; Hu, Z.; Ren, L.; Wang, A.; Liu, X.; Luo, J. Stabilizing Zinc Metal Anodes by Artificial Solid Electrolyte Interphase through a Surface Ion-Exchanging Strategy. *Chem. Eng. J.* **2020**, *396*, 125363. [\[CrossRef\]](#)
95. Zhang, Y.; Wang, G.; Yu, F.; Xu, G.; Li, Z.; Zhu, M.; Yue, Z.; Wu, M.; Liu, H.K.; Dou, S.X. Highly Reversible and Dendrite-Free Zn Electrodeposition Enabled by a Thin Metallic Interfacial Layer in Aqueous Batteries. *Chem. Eng. J.* **2021**, *416*, 128062. [\[CrossRef\]](#)

96. Wang, Y.; Chen, Y.; Liu, W.; Ni, X.; Qing, P.; Zhao, Q.; Wei, W.; Ji, X.; Ma, J.; Chen, L. Uniform and Dendrite-Free Zinc Deposition Enabled by In Situ Formed AgZn₃ for the Zinc Metal Anode. *J. Mater. Chem. A* **2021**, *9*, 8452–8461. [\[CrossRef\]](#)
97. Wang, J.; Cai, Z.; Xiao, R.; Ou, Y.; Zhan, R.; Yuan, Z.; Sun, Y. A Chemically Polished Zinc Metal Electrode with a Ridge-like Structure for Cycle-Stable Aqueous Batteries. *ACS Appl. Mater. Interfaces* **2020**, *12*, 23028–23034. [\[CrossRef\]](#)
98. Zhang, N.; Huang, S.; Yuan, Z.; Zhu, J.; Zhao, Z.; Niu, Z. Direct Self-Assembly of MXene on Zn Anodes for Dendrite-Free Aqueous Zinc-Ion Batteries. *Angew. Chem. Int. Ed.* **2021**, *60*, 2861–2865. [\[CrossRef\]](#)
99. Etman, A.S.; Halim, J.; Rosen, J. MXene-Based Zn-Ion Hybrid Supercapacitors: Effects of Anion Carriers and MXene Surface Coatings on the Capacities and Life Span. *J. Energy Storage* **2022**, *52*, 104823. [\[CrossRef\]](#)
100. Tian, Y.; An, Y.; Wei, C.; Xi, B.; Xiong, S.; Feng, J.; Qian, Y. Flexible and Free-Standing Ti₃C₂T_x MXene@Zn Paper for Dendrite-Free Aqueous Zinc Metal Batteries and Nonaqueous Lithium Metal Batteries. *ACS Nano* **2019**, *13*, 11676–11685. [\[CrossRef\]](#)
101. Wei, C.; Tao, Y.; An, Y.; Tian, Y.; Zhang, Y.; Feng, J.; Qian, Y. Recent Advances of Emerging 2D MXene for Stable and Dendrite-Free Metal Anodes. *Adv. Funct. Mater.* **2020**, *30*, 2004613. [\[CrossRef\]](#)
102. Yang, H.; Chang, Z.; Qiao, Y.; Deng, H.; Mu, X.; He, P.; Zhou, H. Constructing a Super-Saturated Electrolyte Front Surface for Stable Rechargeable Aqueous Zinc Batteries. *Angew. Chem. Int. Ed.* **2020**, *59*, 9377–9381. [\[CrossRef\]](#) [\[PubMed\]](#)
103. Liu, X.; Yang, F.; Xu, W.; Zeng, Y.; He, J.; Lu, X. Zeolitic Imidazolate Frameworks as Zn²⁺ Modulation Layers to Enable Dendrite-Free Zn Anodes. *Adv. Sci.* **2020**, *7*, 2002173. [\[CrossRef\]](#) [\[PubMed\]](#)
104. Yuksel, R.; Buyukcikir, O.; Seong, W.K.; Ruoff, R.S. Metal-Organic Framework Integrated Anodes for Aqueous Zinc-Ion Batteries. *Adv. Energy Mater.* **2020**, *10*, 1904215. [\[CrossRef\]](#)
105. Pu, X.; Jiang, B.; Wang, X.; Liu, W.; Dong, L. High-Performance Aqueous Zinc-Ion Batteries Realized by MOF Materials. *Nano-Micro Lett.* **2020**, *12*, 152. [\[CrossRef\]](#)
106. Liu, M.; Yang, L.; Liu, H.; Amine, A.; Zhao, Q.; Song, Y.; Yang, J.; Wang, K.; Pan, F. Artificial Solid-Electrolyte Interface Facilitating Dendrite-Free Zinc Metal Anodes via Nanowetting Effect. *ACS Appl. Mater. Interfaces* **2019**, *11*, 32046–32051. [\[CrossRef\]](#)
107. Hieu, L.T.; So, S.; Kim, I.T.; Hur, J. Zn Anode with Flexible β -PVDF Coating for Aqueous Zn-Ion Batteries with Long Cycle Life. *Chem. Eng. J.* **2021**, *411*, 128584. [\[CrossRef\]](#)
108. Chen, P.; Yuan, X.; Xia, Y.; Zhang, Y.; Fu, L.; Liu, L.; Yu, N.; Huang, Q.; Wang, B.; Hu, X. An Artificial Polyacrylonitrile Coating Layer Confining Zinc Dendrite Growth for Highly Reversible Aqueous Zinc-Based Batteries. *Adv. Sci.* **2021**, *8*, 2100319. [\[CrossRef\]](#)
109. Cao, Z.; Zhu, X.; Xu, D.; Dong, P.; Chee, M.O.L.; Li, X.; Zhu, K.; Ye, M.; Shen, J. Eliminating Zn Dendrites by Commercial Cyanoacrylate Adhesive for Zinc Ion Battery. *Energy Storage Mater.* **2021**, *36*, 132–138. [\[CrossRef\]](#)
110. Chen, X.; Li, W.; Hu, S.; Akhmedov, N.G.; Reed, D.; Li, X.; Liu, X. Polyvinyl Alcohol Coating Induced Preferred Crystallographic Orientation in Aqueous Zinc Battery Anodes. *Nano Energy* **2022**, *98*, 107269. [\[CrossRef\]](#)
111. Tao, S.; Zhang, C.; Zhang, J.; Jiao, Y.; Li, M.; Lin, W.; Ran, L.; Clement, B.; Lyu, M.; Gentle, I. A Hydrophobic and Fluorophilic Coating Layer for Stable and Reversible Aqueous Zinc Metal Anodes. *Chem. Eng. J.* **2022**, *446*, 136607. [\[CrossRef\]](#)
112. Zhang, F.; Wang, C.; Pan, J.; Tian, F.; Zeng, S.; Yang, J.; Qian, Y. Polypyrrole-Controlled Plating/Stripping for Advanced Zinc Metal Anodes. *Mater. Today Energy* **2020**, *17*, 100443. [\[CrossRef\]](#)
113. Jian, Q.; Wan, Y.; Lin, Y.; Ni, M.; Wu, M.; Zhao, T. A Highly Reversible Zinc Anode for Rechargeable Aqueous Batteries. *ACS Appl. Mater. Interfaces* **2021**, *13*, 52659–52669. [\[CrossRef\]](#) [\[PubMed\]](#)
114. Zhang, Q.; Luan, J.; Tang, Y.; Ji, X.; Wang, H. Interfacial Design of Dendrite-Free Zinc Anodes for Aqueous Zinc-Ion Batteries. *Angew. Chem. Int. Ed.* **2020**, *59*, 13180–13191. [\[CrossRef\]](#) [\[PubMed\]](#)
115. Kucinskis, G.; Bajars, G.; Kleperis, J. Graphene in Lithium Ion Battery Cathode Materials: A Review. *J. Power Sources* **2013**, *240*, 66–79. [\[CrossRef\]](#)
116. Xiao, X.; Zhang, G.; Xu, Y.; Zhang, H.; Guo, X.; Liu, Y.; Pang, H. A New Strategy for the Controllable Growth of MOF@PBA Architectures. *J. Mater. Chem. A* **2019**, *7*, 17266–17271. [\[CrossRef\]](#)
117. Li, Y.; Xu, Y.; Liu, Y.; Pang, H. Exposing {001} Crystal Plane on Hexagonal Ni-MOF with Surface-Grown Cross-Linked Mesh-Structures for Electrochemical Energy Storage. *Small* **2019**, *15*, 1902463. [\[CrossRef\]](#) [\[PubMed\]](#)
118. Zeng, Y.; Zhang, X.; Qin, R.; Liu, X.; Fang, P.; Zheng, D.; Tong, Y.; Lu, X. Dendrite-Free Zinc Deposition Induced by Multifunctional CNT Frameworks for Stable Flexible Zn-Ion Batteries. *Adv. Mater.* **2019**, *31*, 1903675. [\[CrossRef\]](#)
119. Dong, W.; Shi, J.L.; Wang, T.S.; Yin, Y.X.; Wang, C.R.; Guo, Y.G. 3D Zinc@carbon Fiber Composite Framework Anode for Aqueous Zn-MnO₂ Batteries. *RSC Adv.* **2018**, *8*, 19157–19163. [\[CrossRef\]](#)
120. Wang, Z.; Huang, J.; Guo, Z.; Dong, X.; Liu, Y.; Wang, Y.; Xia, Y. A Metal-Organic Framework Host for Highly Reversible Dendrite-Free Zinc Metal Anodes. *Joule* **2019**, *3*, 1289–1300. [\[CrossRef\]](#)
121. Wang, S.B.; Ran, Q.; Yao, R.Q.; Shi, H.; Wen, Z.; Zhao, M.; Lang, X.Y.; Jiang, Q. Lamella-Nanostructured Eutectic Zinc–Aluminum Alloys as Reversible and Dendrite-Free Anodes for Aqueous Rechargeable Batteries. *Nat. Commun.* **2020**, *11*, 1634. [\[CrossRef\]](#) [\[PubMed\]](#)
122. Liu, Z.; Cui, T.; Pulletikurthi, G.; Lahiri, A.; Carstens, T.; Olschewski, M.; Endres, F. Dendrite-Free Nanocrystalline Zinc Electrodeposition from an Ionic Liquid Containing Nickel Triflate for Rechargeable Zn-Based Batteries. *Angew. Chem. Int. Ed.* **2016**, *55*, 2889–2893. [\[CrossRef\]](#) [\[PubMed\]](#)
123. Liu, C.; Luo, Z.; Deng, W.; Wei, W.; Chen, L.; Pan, A.; Ma, J.; Wang, C.; Zhu, L.; Xie, L. Liquid Alloy Interlayer for Aqueous Zinc-Ion Battery. *ACS Energy Lett.* **2021**, *6*, 675–683. [\[CrossRef\]](#)

124. Liu, B.; Wang, S.; Wang, Z.; Lei, H.; Chen, Z.; Mai, W. Novel 3D Nanoporous Zn–Cu Alloy as Long-Life Anode toward High-Voltage Double Electrolyte Aqueous Zinc-Ion Batteries. *Small* **2020**, *16*, 2001323. [\[CrossRef\]](#) [\[PubMed\]](#)
125. Kwon, M.; Lee, J.; Ko, S.; Lim, G.; Yu, S.-H.; Hong, J.; Lee, M. Stimulating Cu–Zn Alloying for Compact Zn Metal Growth Towards High Energy Aqueous Batteries and Hybrid Supercapacitors. *Energy Environ. Sci.* **2022**, *15*, 2889–2899. [\[CrossRef\]](#)
126. Zhang, Y.; Howe, J.D.; Ben-Yoseph, S.; Wu, Y.; Liu, N. Unveiling the Origin of Alloy-Seeded and Nondendritic Growth of Zn for Rechargeable Aqueous Zn Batteries. *ACS Energy Lett.* **2021**, *6*, 404–412. [\[CrossRef\]](#)
127. Tian, H.; Li, Z.; Feng, G.; Yang, Z.; Fox, D.; Wang, M.; Zhou, H.; Zhai, L.; Kushima, A.; Du, Y. Stable, High-Performance, Dendrite-Free, Seawater-Based Aqueous Batteries. *Nat. Commun.* **2021**, *12*, 237. [\[CrossRef\]](#) [\[PubMed\]](#)
128. Tian, Y.; An, Y.; Liu, C.; Xiong, S.; Feng, J.; Qian, Y. Reversible Zinc-Based Anodes Enabled by Zincophilic Antimony Engineered MXene for Stable and Dendrite-Free Aqueous Zinc Batteries. *Energy Storage Mater.* **2021**, *41*, 343–353. [\[CrossRef\]](#)
129. Fu, J.; Cano, Z.P.; Park, M.G.; Yu, A.; Fowler, M.; Chen, Z. Electrically Rechargeable Zinc–Air Batteries: Progress, Challenges, and Perspectives. *Adv. Mater.* **2017**, *29*, 1604685. [\[CrossRef\]](#)
130. Zhang, W.J. Lithium Insertion/Extraction Mechanism in Alloy Anodes for Lithium-Ion Batteries. *J. Power Sources* **2011**, *196*, 877–885. [\[CrossRef\]](#)
131. Jin, S.; Ye, Y.; Niu, Y.; Xu, Y.; Jin, H.; Wang, J.; Sun, Z.; Cao, A.; Wu, X.; Luo, Y. Solid-Solution-Based Metal Alloy Phase for Highly Reversible Lithium Metal Anode. *J. Am. Chem. Soc.* **2020**, *142*, 8818–8826. [\[CrossRef\]](#) [\[PubMed\]](#)
132. Du, Y.; Li, Y.; Xu, B.-B.; Liu, T.-X.; Liu, X.; Ma, F.; Gu, X.; Lai, C. Electrolyte Salts and Additives Regulation Enables High Performance Aqueous Zinc Ion Batteries: A Mini Review. *Small* **2021**, *18*, 2104640. [\[CrossRef\]](#) [\[PubMed\]](#)
133. Kasiri, G.; Trócoli, R.; Bani Hashemi, A.; La Mantia, F. An Electrochemical Investigation of the Aging of Copper Hexacyanoferrate during the Operation in Zinc-Ion Batteries. *Electrochim. Acta* **2016**, *222*, 74–83. [\[CrossRef\]](#)
134. Zhang, N.; Cheng, F.; Liu, Y.; Zhao, Q.; Lei, K.; Chen, C.; Liu, X.; Chen, J. Cation-Deficient Spinel ZnMn_2O_4 Cathode in $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ Electrolyte for Rechargeable Aqueous Zn-Ion Battery. *J. Am. Chem. Soc.* **2016**, *138*, 12894–12901. [\[CrossRef\]](#) [\[PubMed\]](#)
135. Lu, K.; Song, B.; Zhang, Y.; Ma, H.; Zhang, J. Encapsulation of Zinc Hexacyanoferrate Nanocubes with Manganese Oxide Nanosheets for High-Performance Rechargeable Zinc Ion Batteries. *J. Mater. Chem. A* **2017**, *5*, 23628–23633. [\[CrossRef\]](#)
136. Hao, J.; Mou, J.; Zhang, J.; Dong, L.; Liu, W.; Xu, C.; Kang, F. Electrochemically Induced Spinel-Layered Phase Transition of Mn_3O_4 in High Performance Neutral Aqueous Rechargeable Zinc Battery. *Electrochim. Acta* **2018**, *259*, 170–178. [\[CrossRef\]](#)
137. Zhang, H.; Liu, Q.; Fang, Y.; Teng, C.; Liu, X.; Fang, P.; Tong, Y.; Lu, X. Boosting Zn-Ion Energy Storage Capability of Hierarchically Porous Carbon by Promoting Chemical Adsorption. *Adv. Mater.* **2019**, *31*, 1904948. [\[CrossRef\]](#)
138. Lee, B.; Seo, H.R.; Lee, H.R.; Yoon, C.S.; Kim, J.H.; Chung, K.Y.; Cho, B.W.; Oh, S.H. Critical Role of pH Evolution of Electrolyte in the Reaction Mechanism for Rechargeable Zinc Batteries. *ChemSusChem* **2016**, *9*, 2948–2956. [\[CrossRef\]](#)
139. Zhang, N.; Cheng, F.; Liu, J.; Wang, L.; Long, X.; Liu, X.; Li, F.; Chen, J. Rechargeable Aqueous Zinc-Manganese Dioxide Batteries with High Energy and Power Densities. *Nat. Commun.* **2017**, *8*, 405. [\[CrossRef\]](#)
140. Wang, F.; Borodin, O.; Gao, T.; Fan, X.; Sun, W.; Han, F.; Faraone, A.; Dura, J.A.; Xu, K.; Wang, C. Highly Reversible Zinc Metal Anode for Aqueous Batteries. *Nat. Mater.* **2018**, *17*, 543–549. [\[CrossRef\]](#)
141. Nagy, T.; Nagy, L.; Erdélyi, Z.; Baradács, E.; Deák, G.; Zsuga, M.; Kéki, S. “In Situ” Formation of Zn Anode from Bimetallic Cu–Zn Alloy (Brass) for Dendrite-Free Operation of Zn–Air Rechargeable Battery. *Batteries* **2022**, *8*, 212. [\[CrossRef\]](#)
142. Xu, M.; Ivey, D.G.; Xie, Z.; Qu, W.; Dy, E. The State of Water in 1-Butyl-1-Methyl-Pyrrolidinium Bis(Trifluoromethanesulfonyl)Imide and Its Effect on Zn/Zn(II) Redox Behavior. *Electrochim. Acta* **2013**, *97*, 289–295. [\[CrossRef\]](#)
143. Kundu, D.; Adams, B.D.; Duffort, V.; Vajargah, S.H.; Nazar, L.F. A High-Capacity and Long-Life Aqueous Rechargeable Zinc Battery Using a Metal Oxide Intercalation Cathode. *Nat. Energy* **2016**, *1*, 11619. [\[CrossRef\]](#)
144. Suo, L.; Borodin, O.; Gao, T.; Olguin, M.; Ho, J.; Fan, X.; Luo, C.; Wang, C.; Xu, K. “Water-in-Salt” Electrolyte Enables High-Voltage Aqueous Lithium-Ion Chemistries. *Science* **2015**, *350*, 938–943. [\[CrossRef\]](#)
145. Yamada, Y.; Furukawa, K.; Sodeyama, K.; Kikuchi, K.; Yaegashi, M.; Tateyama, Y.; Yamada, A. Unusual Stability of Acetonitrile-Based Superconcentrated Electrolytes for Fast-Charging Lithium-Ion Batteries. *J. Am. Chem. Soc.* **2014**, *136*, 5039–5046. [\[CrossRef\]](#)
146. Zhou, J.; Shan, L.; Wu, Z.; Guo, X.; Fang, G.; Liang, S. Investigation of V_2O_5 as a Low-Cost Rechargeable Aqueous Zinc Ion Battery Cathode. *Chem. Commun.* **2018**, *54*, 4457–4460. [\[CrossRef\]](#)
147. Zhang, C.; Holoubek, J.; Wu, X.; Daniyar, A.; Zhu, L.; Chen, C.; Leonard, D.P.; Rodríguez-Pérez, I.A.; Jiang, J.X.; Fang, C. A ZnCl_2 Water-in-Salt Electrolyte for a Reversible Zn Metal Anode. *Chem. Commun.* **2018**, *54*, 14097–14099. [\[CrossRef\]](#)
148. Ye, Z.; Cao, Z.; Lam Chee, M.O.; Dong, P.; Ajayan, P.M.; Shen, J.; Ye, M. Advances in Zn-Ion Batteries via Regulating Liquid Electrolyte. *Energy Storage Mater.* **2020**, *32*, 290–305. [\[CrossRef\]](#)
149. Liu, Z.; Cui, T.; Lu, T.; Shapouri Ghazvini, M.; Endres, F. Anion Effects on the Solid/Ionic Liquid Interface and the Electrodeposition of Zinc. *J. Phys. Chem. C* **2016**, *120*, 20224–20231. [\[CrossRef\]](#)
150. Geng, M.; Northwood, D.O. Development of Advanced Rechargeable Ni/MH and Ni/Zn Batteries. *Int. J. Hydrogen Energy* **2003**, *28*, 633–636. [\[CrossRef\]](#)
151. Kan, J.; Xue, H.; Mu, S. Effect of Inhibitors on Zn-Dendrite Formation for Zinc-Polyaniline Secondary Battery. *J. Power Sources* **1998**, *74*, 113–116. [\[CrossRef\]](#)

152. Olbasa, B.W.; Fenta, F.W.; Chiu, S.F.; Tsai, M.C.; Huang, C.J.; Jote, B.A.; Beyene, T.T.; Liao, Y.F.; Wang, C.H.; Su, W.N. High-Rate and Long-Cycle Stability with a Dendrite-Free Zinc Anode in an Aqueous Zn-Ion Battery Using Concentrated Electrolytes. *ACS Appl. Energy Mater.* **2020**, *3*, 4499–4508. [\[CrossRef\]](#)
153. Zhang, Y.; Li, H.; Huang, S.; Fan, S.; Sun, L.; Tian, B.; Chen, F.; Wang, Y.; Shi, Y.; Yang, H.Y. Rechargeable Aqueous Zinc-Ion Batteries in $\text{MgSO}_4/\text{ZnSO}_4$ Hybrid Electrolytes. *Nano-Micro Lett.* **2020**, *12*, 60. [\[CrossRef\]](#) [\[PubMed\]](#)
154. Qiu, C.; Zhu, X.; Xue, L.; Ni, M.; Zhao, Y.; Liu, B.; Xia, H. The Function of Mn^{2+} Additive in Aqueous Electrolyte for Zn/ δ - MnO_2 Battery. *Electrochim. Acta* **2020**, *351*, 136445. [\[CrossRef\]](#)
155. Huang, Y.; Mou, J.; Liu, W.; Wang, X.; Dong, L.; Kang, F.; Xu, C. Novel Insights into Energy Storage Mechanism of Aqueous Rechargeable Zn/ MnO_2 Batteries with Participation of Mn^{2+} . *Nano-Micro Lett.* **2019**, *11*, 49. [\[CrossRef\]](#) [\[PubMed\]](#)
156. Chamoun, M.; Brant, W.R.; Tai, C.W.; Karlsson, G.; Noréus, D. Rechargeability of Aqueous Sulfate Zn/ MnO_2 Batteries Enhanced by Accessible Mn^{2+} Ions. *Energy Storage Mater.* **2018**, *15*, 351–360. [\[CrossRef\]](#)
157. Chen, X.; Li, W.; Zeng, Z.; Reed, D.; Li, X.; Liu, X. Engineering Stable Zn- MnO_2 Batteries by Synergistic Stabilization between the Carbon Nanofiber Core and Birnessite- MnO_2 Nanosheets Shell. *Chem. Eng. J.* **2021**, *405*, 126969. [\[CrossRef\]](#)
158. Chen, X.; Li, W.; Xu, Y.; Zeng, Z.; Tian, H.; Velayutham, M.; Shi, W.; Li, W.; Wang, C.; Reed, D. Charging Activation and Desulfurization of MnS Unlock the Active Sites and Electrochemical Reactivity for Zn-Ion Batteries. *Nano Energy* **2020**, *75*, 104869. [\[CrossRef\]](#)
159. Wang, P.; Xie, X.; Xing, Z.; Chen, X.; Fang, G.; Lu, B.; Zhou, J.; Liang, S.; Fan, H.J. Mechanistic Insights of Mg^{2+} -Electrolyte Additive for High-Energy and Long-Life Zinc-Ion Hybrid Capacitors. *Adv. Energy Mater.* **2021**, *11*, 2101158. [\[CrossRef\]](#)
160. Xu, Y.; Zhu, J.; Feng, J.; Wang, Y.; Wu, X.; Ma, P.; Zhang, X.; Wang, G.; Yan, X. A Rechargeable Aqueous Zinc/Sodium Manganese Oxides Battery with Robust Performance Enabled by Na_2SO_4 Electrolyte Additive. *Energy Storage Mater.* **2021**, *38*, 299–308. [\[CrossRef\]](#)
161. Wan, F.; Zhang, L.; Dai, X.; Wang, X.; Niu, Z.; Chen, J. Aqueous Rechargeable Zinc/Sodium Vanadate Batteries with Enhanced Performance from Simultaneous Insertion of Dual Carriers. *Nat. Commun.* **2018**, *9*, 1656. [\[CrossRef\]](#) [\[PubMed\]](#)
162. Guo, X.; Zhang, Z.; Li, J.; Luo, N.; Chai, G.L.; Miller, T.S.; Lai, F.; Shearing, P.; Brett, D.J.L.; Han, D. Alleviation of Dendrite Formation on Zinc Anodes via Electrolyte Additives. *ACS Energy Lett.* **2021**, *6*, 395–403. [\[CrossRef\]](#)
163. Sun, C.; Wu, C.; Gu, X.; Wang, C.; Wang, Q. Interface Engineering via $\text{Ti}_3\text{C}_2\text{T}_x$ MXene Electrolyte Additive toward Dendrite-Free Zinc Deposition. *Nano-Micro Lett.* **2021**, *13*, 89. [\[CrossRef\]](#)
164. Wu, H.Y.; Gu, X.; Huang, P.; Sun, C.; Hu, H.; Zhong, Y.; Lai, C. Polyoxometalate Driven Dendrite-Free Zinc Electrodes with Synergistic Effects of Cation and Anion Cluster Regulation. *J. Mater. Chem. A* **2021**, *9*, 7025–7033. [\[CrossRef\]](#)
165. Weng, G.M.; Li, Z.; Cong, G.; Zhou, Y.; Lu, Y.C. Unlocking the Capacity of Iodide for High-Energy-Density Zinc/Polyiodide and Lithium/Polyiodide Redox Flow Batteries. *Energy Environ. Sci.* **2017**, *10*, 735–741. [\[CrossRef\]](#)
166. Liu, S.; Shang, W.; Yang, Y.; Kang, D.; Li, C.; Sun, B.; Kang, L.; Yun, S.; Jiang, F. Effects of I_3^- Electrolyte Additive on the Electrochemical Performance of Zn Anodes and Zn/ MnO_2 Batteries. *Batter. Supercaps* **2022**, *5*, e202100221. [\[CrossRef\]](#)
167. Abdulla, J.; Cao, J.; Zhang, D.; Zhang, X.; Sriprachubwong, C.; Kheawhom, S.; Wangyao, P.; Qin, J. Elimination of Zinc Dendrites by Graphene Oxide Electrolyte Additive for Zinc-Ion Batteries. *ACS Appl. Energy Mater.* **2021**, *4*, 4602–4609. [\[CrossRef\]](#)
168. Huang, C.; Zhao, X.; Hao, Y.; Yang, Y.; Qian, Y.; Chang, G.; Zhang, Y.; Tang, Q.; Hu, A.; Chen, X. Self-Healing SeO_2 Additives Enable Zinc Metal Reversibility in Aqueous ZnSO_4 Electrolytes. *Adv. Funct. Mater.* **2022**, *32*, 2112091. [\[CrossRef\]](#)
169. Zeng, X.; Mao, J.; Hao, J.; Liu, J.; Liu, S.; Wang, Z.; Wang, Y.; Zhang, S.; Zheng, T.; Liu, J. Electrolyte Design for In Situ Construction of Highly Zn^{2+} -Conductive Solid Electrolyte Interphase to Enable High-Performance Aqueous Zn-Ion Batteries under Practical Conditions. *Adv. Mater.* **2021**, *33*, 2007416. [\[CrossRef\]](#)
170. Xin, W.; Miao, L.; Zhang, L.; Peng, H.; Yan, Z.; Zhu, Z. Turning the Byproduct $\text{Zn}_4(\text{OH})_6\text{SO}_4 \cdot x\text{H}_2\text{O}$ into a Uniform Solid Electrolyte Interphase to Stabilize Aqueous Zn Anode. *ACS Mater. Lett.* **2021**, *3*, 1819–1825. [\[CrossRef\]](#)
171. Zhao, R.; Wang, H.; Du, H.; Yang, Y.; Gao, Z.; Qie, L.; Huang, Y. Lanthanum Nitrate as Aqueous Electrolyte Additive for Favourable Zinc Metal Electrodeposition. *Nat. Commun.* **2022**, *13*, 3252. [\[CrossRef\]](#) [\[PubMed\]](#)
172. Zeng, X.; Meng, X.; Jiang, W.; Ling, M.; Yan, L.; Liang, C. In-Situ Constructing Polyacrylamide Interphase Enables Dendrite-Free Zinc Anode in Aqueous Batteries. *Electrochim. Acta* **2021**, *378*, 138106. [\[CrossRef\]](#)
173. Zhang, Q.; Luan, J.; Fu, L.; Wu, S.; Tang, Y.; Ji, X.; Wang, H. The Three-Dimensional Dendrite-Free Zinc Anode on a Copper Mesh with a Zinc-Oriented Polyacrylamide Electrolyte Additive. *Angew. Chem. Int. Ed.* **2019**, *58*, 15841–15847. [\[CrossRef\]](#) [\[PubMed\]](#)
174. Zhao, Z.; Wang, J.; Lv, Z.; Wang, Q.; Zhang, Y.; Lu, G.; Zhao, J.; Cui, G. In-Situ Formed All-Amorphous Poly (Ethylene Oxide)-Based Electrolytes Enabling Solid-State Zn Electrochemistry. *Chem. Eng. J.* **2021**, *417*, 128096. [\[CrossRef\]](#)
175. Yan, M.; Xu, C.; Sun, Y.; Pan, H.; Li, H. Manipulating Zn Anode Reactions through Salt Anion Involving Hydrogen Bonding Network in Aqueous Electrolytes with PEO Additive. *Nano Energy* **2021**, *82*, 105379. [\[CrossRef\]](#)
176. Jin, Y.; Han, K.S.; Shao, Y.; Sushko, M.L.; Xiao, J.; Pan, H.; Liu, J. Stabilizing Zinc Anode Reactions by Polyethylene Oxide Polymer in Mild Aqueous Electrolytes. *Adv. Funct. Mater.* **2020**, *30*, 20203932. [\[CrossRef\]](#)
177. Lin, C.; Liu, Y.; Zhang, X.; Miao, X.; Chen, Y.; Chen, S.; Zhang, Y. Regulating the Plating Process of Zinc with Highly Efficient Additive for Long-life Zinc Anode. *J. Power Sources* **2022**, *549*, 232078. [\[CrossRef\]](#)
178. Bani Hashemi, A.; Kasiri, G.; La Mantia, F. The Effect of Polyethyleneimine as an Electrolyte Additive on Zinc Electrodeposition Mechanism in Aqueous Zinc-Ion Batteries. *Electrochim. Acta* **2017**, *258*, 703–708. [\[CrossRef\]](#)

179. Gao, S.; Han, J.; Liu, Z.; Wang, K.; Jiang, K.; Guo, C.; Tan, Y.; Zhou, D.; Shi, W. Polyvinyl Pyrrolidone as Electrolyte Additive for Aqueous Zinc Batteries with MnO_2 Cathode. *J. Electrochem. Soc.* **2021**, *168*, 080514. [\[CrossRef\]](#)
180. Cao, Z.; Zhu, X.; Gao, S.; Xu, D.; Wang, Z.; Ye, Z.; Wang, L.; Chen, B.; Li, L.; Ye, M. Ultrastable Zinc Anode by Simultaneously Manipulating Solvation Sheath and Inducing Oriented Deposition with PEG Stability Promoter. *Small* **2022**, *18*, 2103345. [\[CrossRef\]](#)
181. Bayaguud, A.; Luo, X.; Fu, Y.; Zhu, C. Cationic Surfactant-Type Electrolyte Additive Enables Three-Dimensional Dendrite-Free Zinc Anode for Stable Zinc-Ion Batteries. *ACS Energy Lett.* **2020**, *5*, 3012–3020. [\[CrossRef\]](#)
182. Hao, J.; Long, J.; Li, B.; Li, X.; Zhang, S.; Yang, F.; Zeng, X.; Yang, Z.; Pang, W.K.; Guo, Z. Toward High-Performance Hybrid Zn-Based Batteries via Deeply Understanding Their Mechanism and Using Electrolyte Additive. *Adv. Funct. Mater.* **2019**, *29*, 1903605. [\[CrossRef\]](#)
183. Hou, Z.; Zhang, X.; Li, X.; Zhu, Y.; Liang, J.; Qian, Y. Surfactant Widens the Electrochemical Window of an Aqueous Electrolyte for Better Rechargeable Aqueous Sodium/Zinc Battery. *J. Mater. Chem. A* **2017**, *5*, 730–738. [\[CrossRef\]](#)
184. Hosseini, S.; Lao-atiman, W.; Han, S.J.; Arpornwicheanop, A.; Yonezawa, T.; Kheawhom, S. Discharge Performance of Zinc-Air Flow Batteries Under the Effects of Sodium Dodecyl Sulfate and Pluronic F-127. *Sci. Rep.* **2018**, *8*, 14909. [\[CrossRef\]](#)
185. Kurmanbayeva, I.; Rakhymbay, L.; Korzhynbayeva, K.; Adi, A.; Batyrbekuly, D.; Mentbayeva, A.; Bakenov, Z. Tetrapropylammonium Hydroxide as a Zinc Dendrite Growth Suppressor for Rechargeable Aqueous Battery. *Front. Energy Res.* **2020**, *8*, 599009. [\[CrossRef\]](#)
186. Yao, R.; Qian, L.; Sui, Y.; Zhao, G.; Guo, R.; Hu, S.; Liu, P.; Zhu, H.; Wang, F.; Zhi, C. A Versatile Cation Additive Enabled Highly Reversible Zinc Metal Anode. *Adv. Energy Mater.* **2022**, *12*, 2102780. [\[CrossRef\]](#)
187. Guan, K.; Tao, L.; Yang, R.; Zhang, H.; Wang, N.; Wan, H.; Cui, J.; Zhang, J.; Wang, H.; Wang, H. Anti-Corrosion for Reversible Zinc Anode via a Hydrophobic Interface in Aqueous Zinc Batteries. *Adv. Energy Mater.* **2022**, *12*, 2103557. [\[CrossRef\]](#)
188. Xu, W.; Zhao, K.; Huo, W.; Wang, Y.; Yao, G.; Gu, X.; Cheng, H.; Mai, L.; Hu, C.; Wang, X. Diethyl Ether as Self-Healing Electrolyte Additive Enabled Long-Life Rechargeable Aqueous Zinc Ion Batteries. *Nano Energy* **2019**, *62*, 275–281. [\[CrossRef\]](#)
189. Shi, J.; Xia, K.; Liu, L.; Liu, C.; Zhang, Q.; Li, L.; Zhou, X.; Liang, J.; Tao, Z. Ultrahigh Coulombic Efficiency and Long-Life Aqueous Zn Anodes Enabled by Electrolyte Additive of Acetonitrile. *Electrochim. Acta* **2020**, *358*, 136937. [\[CrossRef\]](#)
190. Wu, Z.; Li, M.; Tian, Y.; Chen, H.; Zhang, S.J.; Sun, C.; Li, C.; Kiefel, M.; Lai, C.; Lin, Z. Cyclohexanodecyl-Assisted Interfacial Engineering for Robust and High-Performance Zinc Metal Anode. *Nano-Micro Lett.* **2022**, *14*, 110. [\[CrossRef\]](#)
191. Zhu, J.; Deng, W.; Yang, N.; Xu, X.; Huang, C.; Zhou, Y.; Zhang, M.; Yuan, X.; Hu, J.; Li, C. Biomolecular Regulation of Zinc Deposition to Achieve Ultra-Long Life and High-Rate Zn Metal Anodes. *Small* **2022**, *18*, 2202509. [\[CrossRef\]](#) [\[PubMed\]](#)
192. Li, M.; Xie, K.; Peng, R.; Yuan, B.; Wang, Q.; Wang, C. Surface Protection and Interface Regulation for Zn Anode via 1-Hydroxy Ethylidene-1,1-Diphosphonic Acid Electrolyte Additive toward High-Performance Aqueous Batteries. *Small* **2022**, *18*, 2107398. [\[CrossRef\]](#) [\[PubMed\]](#)
193. Zhou, T.; Mu, Y.; Chen, L.; Li, D.; Liu, W.; Yang, C.; Zhang, S.; Wang, Q.; Jiang, P.; Ge, G. Toward Stable Zinc Aqueous Rechargeable Batteries by Anode Morphology Modulation via Polyaspartic Acid Additive. *Energy Storage Mater.* **2022**, *45*, 777–785. [\[CrossRef\]](#)
194. Wang, B.; Zheng, R.; Yang, W.; Han, X.; Hou, C.; Zhang, Q.; Li, Y.; Li, K.; Wang, H. Synergistic Solvation and Interface Regulations of Eco-Friendly Silk Peptide Additive Enabling Stable Aqueous Zinc-Ion Batteries. *Adv. Funct. Mater.* **2022**, *32*, 2112693. [\[CrossRef\]](#)
195. Wilcox, G.D.; Mitchell, P.J. Electrolyte Additives for Zinc-Anoded Secondary Cells I. Brighteners, Levellers and Complexants. *J. Power Sources* **1989**, *28*, 345–359. [\[CrossRef\]](#)
196. Geng, Y.; Pan, L.; Peng, Z.; Sun, Z.; Lin, H.; Mao, C.; Wang, L.; Dai, L.; Liu, H.; Pan, K. Electrolyte Additive Engineering for Aqueous Zn Ion Batteries. *Energy Storage Mater.* **2022**, *51*, 733–755. [\[CrossRef\]](#)
197. Zhao, K.; Liu, F.; Fan, G.; Liu, J.; Yu, M.; Yan, Z.; Zhang, N.; Cheng, F. Stabilizing Zinc Electrodes with a Vanillin Additive in Mild Aqueous Electrolytes. *ACS Appl. Mater. Interfaces* **2021**, *13*, 47650–47658. [\[CrossRef\]](#)
198. Han, S.D.; Rajput, N.N.; Qu, X.; Pan, B.; He, M.; Ferrandon, M.S.; Liao, C.; Persson, K.A.; Burrell, A.K. Origin of Electrochemical, Structural, and Transport Properties in Nonaqueous Zinc Electrolytes. *ACS Appl. Mater. Interfaces* **2016**, *8*, 3021–3031. [\[CrossRef\]](#)
199. Chae, M.S.; Heo, J.W.; Kwak, H.H.; Lee, H.; Hong, S.T. Organic Electrolyte-Based Rechargeable Zinc-Ion Batteries Using Potassium Nickel Hexacyanoferrate as a Cathode Material. *J. Power Sources* **2017**, *337*, 204–211. [\[CrossRef\]](#)
200. Kundu, D.; Hosseini Vajargah, S.; Wan, L.; Adams, B.; Prendergast, D.; Nazar, L.F. Aqueous: Vs. Nonaqueous Zn-Ion Batteries: Consequences of the Desolvation Penalty at the Interface. *Energy Environ. Sci.* **2018**, *11*, 881–892. [\[CrossRef\]](#)
201. Wang, F.; Sun, W.; Shadike, Z.; Hu, E.; Ji, X.; Gao, T.; Yang, X.Q.; Xu, K.; Wang, C. How Water Accelerates Bivalent Ion Diffusion at the Electrolyte/Electrode Interface. *Angew. Chem. Int. Ed.* **2018**, *57*, 11978–11981. [\[CrossRef\]](#) [\[PubMed\]](#)
202. Naveed, A.; Yang, H.; Yang, J.; Nuli, Y.; Wang, J. Highly Reversible and Rechargeable Safe Zn Batteries Based on a Triethyl Phosphate Electrolyte. *Angew. Chem. Int. Ed.* **2019**, *58*, 2760–2764. [\[CrossRef\]](#) [\[PubMed\]](#)
203. Fan, J.; Xiao, Q.; Fang, Y.; Li, L.; Yuan, W. A Rechargeable Zn/Graphite Dual-Ion Battery with an Ionic Liquid-Based Electrolyte. *Ionics* **2019**, *25*, 1303–1313. [\[CrossRef\]](#)
204. Ma, L.; Chen, S.; Li, N.; Liu, Z.; Tang, Z.; Zapfen, J.A.; Chen, S.; Fan, J.; Zhi, C. Hydrogen-Free and Dendrite-Free All-Solid-State Zn-Ion Batteries. *Adv. Mater.* **2020**, *32*, 1908121. [\[CrossRef\]](#) [\[PubMed\]](#)
205. Liu, Z.; Pulletikurthi, G.; Lahiri, A.; Cui, T.; Endres, F. Suppressing the Dendritic Growth of Zinc in an Ionic Liquid Containing Cationic and Anionic Zinc Complexes for Battery Applications. *Dalton Trans.* **2016**, *45*, 8089–8098. [\[CrossRef\]](#)

206. Han, Q.; Chi, X.; Liu, Y.; Wang, L.; Du, Y.; Ren, Y.; Liu, Y. An Inorganic Salt Reinforced Zn²⁺-Conducting Solid-State Electrolyte for Ultra-Stable Zn Metal Batteries. *J. Mater. Chem. A* **2019**, *7*, 22287–22295. [[CrossRef](#)]
207. Tang, Y.; Liu, C.; Zhu, H.; Xie, X.; Gao, J.; Deng, C.; Han, M.; Liang, S.; Zhou, J. Ion-Confinement Effect Enabled by Gel Electrolyte for Highly Reversible Dendrite-Free Zinc Metal Anode. *Energy Storage Mater.* **2020**, *27*, 109–116. [[CrossRef](#)]
208. Zeng, Y.; Zhang, X.; Meng, Y.; Yu, M.; Yi, J.; Wu, Y.; Lu, X.; Tong, Y. Achieving Ultrahigh Energy Density and Long Durability in a Flexible Rechargeable Quasi-Solid-State Zn–MnO₂ Battery. *Adv. Mater.* **2017**, *29*, 1700274. [[CrossRef](#)]
209. Qiu, W.; Li, Y.; You, A.; Zhang, Z.; Li, G.; Lu, X.; Tong, Y. High-Performance Flexible Quasi-Solid-State Zn–MnO₂ Battery Based on MnO₂ Nanorod Arrays Coated 3D Porous Nitrogen-Doped Carbon Cloth. *J. Mater. Chem. A* **2017**, *5*, 14838–14846. [[CrossRef](#)]
210. Chao, D.; Zhu, C.; Song, M.; Liang, P.; Zhang, X.; Tiep, N.H.; Zhao, H.; Wang, J.; Wang, R.; Zhang, H. A High-Rate and Stable Quasi-Solid-State Zinc-Ion Battery with Novel 2D Layered Zinc Orthovanadate Array. *Adv. Mater.* **2018**, *30*, 1803181. [[CrossRef](#)]
211. Ho, V.C.; Lim, H.; Kim, M.J.; Mun, J. Improving the Performance of Aqueous Zinc-Ion Batteries by Inhibiting Zinc Dendrite Growth: Recent Progress. *Chem. Asian J.* **2022**, *17*, e202200289. [[CrossRef](#)] [[PubMed](#)]
212. Chen, J.; Chen, M.; Ma, H.; Zhou, W.; Xu, X. Advances and Perspectives on Separators of Aqueous Zinc Ion Batteries. *Energy Rev.* **2022**, *1*, 100005. [[CrossRef](#)]
213. Yuan, D.; Manalastas, W.; Zhang, L.; Chan, J.J.; Meng, S.; Chen, Y.; Srinivasan, M. Lignin@Nafion Membranes Forming Zn Solid–Electrolyte Interfaces Enhance the Cycle Life for Rechargeable Zinc-Ion Batteries. *ChemSusChem* **2019**, *12*, 4889–4900. [[CrossRef](#)] [[PubMed](#)]
214. Wu, B.; Wu, Y.; Lu, Z.; Zhang, J.; Han, N.; Wang, Y.; Li, X.M.; Lin, M.; Zeng, L. A Cation Selective Separator Induced Cathode Protective Layer and Regulated Zinc Deposition for Zinc Ion Batteries. *J. Mater. Chem. A* **2021**, *9*, 4734–4743. [[CrossRef](#)]
215. Wang, Z.; Lee, Y.H.; Kim, S.W.; Seo, J.Y.; Lee, S.Y.; Nyholm, L. Why Cellulose-Based Electrochemical Energy Storage Devices? *Adv. Mater.* **2021**, *33*, 2000892. [[CrossRef](#)] [[PubMed](#)]
216. Zhou, W.; Chen, M.; Tian, Q.; Chen, J.; Xu, X.; Wong, C.P. Cotton-Derived Cellulose Film as a Dendrite-Inhibiting Separator to Stabilize the Zinc Metal Anode of Aqueous Zinc Ion Batteries. *Energy Storage Mater.* **2022**, *44*, 57–65. [[CrossRef](#)]
217. Cao, J.; Zhang, D.; Gu, C.; Zhang, X.; Okhawilai, M.; Wang, S.; Han, J.; Qin, J.; Huang, Y. Modulating Zn Deposition via Ceramic-Cellulose Separator with Interfacial Polarization Effect for Durable Zinc Anode. *Nano Energy* **2021**, *89*, 106322. [[CrossRef](#)]

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