

Chinese Chemical Society | Xiamen University

Journal of Electrochemistry

Online First

8-1-2024

Dendrite-Free Strategies for Aqueous Zinc-Ion Batteries: Structure, Electrolyte, and Separator

Gang Wu

Wuhai Yang

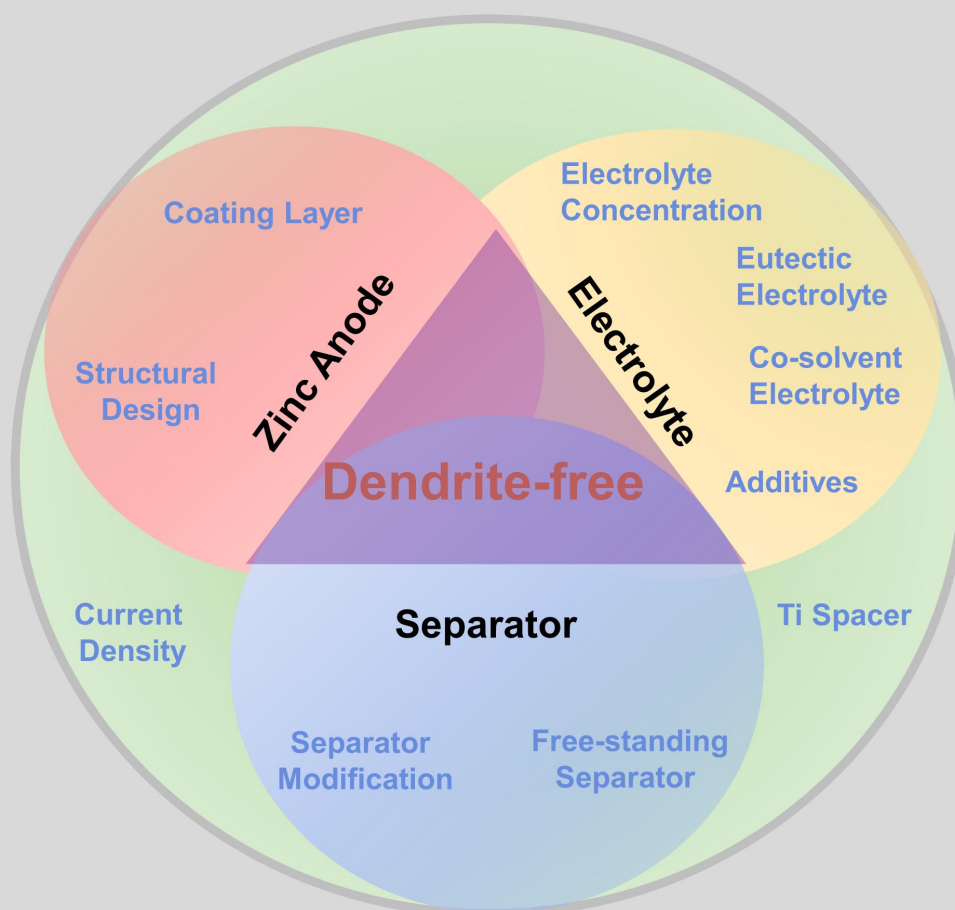
Yang Yang

Huijun Yang

Dendrite-Free Strategies for Aqueous Zinc-Ion Batteries: Structure, Electrolyte, and Separator

Gang Wu, Wuhai Yang, Yang Yang, Huijun Yang*

Graduate School of System and Information Engineering, University of Tsukuba, 1-1-1, Tennoudai, Tsukuba 305-8573, Japan. E-mail: huijun0311@gmail.com



Abstract

Continued growth in energy demand and increased environmental pollution constitute major challenges that need to be addressed urgently. The development and utilization of renewable, sustainable, and clean energy sources, such as wind and solar, are crucial. However, the instability of these intermittent energy sources makes the need for energy storage systems increasingly urgent. Aqueous zinc ion batteries (AZIBs) have received widespread attention due to their unique advantages, such as high energy density, cost-effectiveness, environmental friendliness, and safety. However, AZIBs face significant challenges, mainly the formation of zinc dendrites that seriously affect the stability and lifetime of the batteries, leading to battery failure. Therefore, reducing the formation of zinc dendrites is crucial for improving the performance of AZIBs. This review systematically and comprehensively comprehends the current strategies and advances in inhibiting the formation of zinc dendrites. By comprehensively analyzing the latest developments in zinc anode, electrolyte, separator design and modification, as well as other novel mechanisms, it provides researchers with a thorough understanding to guide future research and advance the development of AZIBs.

Keywords: Aqueous Zinc Ion Batteries • Dendrite-free • Zn Anode • Electrolyte Optimization • Separator Design • HER

1 Introduction

Currently, the continuous growth in energy demand and increasing environmental pollution constitute major challenges that need to be addressed urgently. It is essential to develop and utilize renewable, sustainable and clean energy sources such as wind and solar energy.^[1, 2] However, these intermittent energy sources cannot be directly utilized in the electrical grid, thereby generating a demand for energy storage systems.^[3] In the search for energy storage solutions, electrochemical energy storage systems stand out for their convenience and efficiency. Secondary batteries have become the focus of global research and various battery systems have been investigated in recent decades.^[4-6] In particular, aqueous zinc ion batteries (AZIBs) have attracted much attention by virtue of their unique advantages. Firstly AZIBs use zinc, which is abundant in the earth's reserves, as well as water-based electrolytes that are relatively cheap and have an ionic conductivity at least as high as most organic electrolytes. Secondly, they are environmentally friendly with low toxicity and have a low redox potential (-0.763 V vs. SHE), a high specific volume capacity (5855 mAh cm⁻³), a large theoretical specific volume capacity (820 mAh g⁻¹) and a high hydrogen precipitation overpotential (1.2 V). AZIBs have shown great potential for wide application in portable electronic devices, grid energy storage and electric transport vehicles.^[7-9]

Nevertheless, the development of AZIBs still faces several challenges, notably the formation of dendrites that hinder their practical application, as they can seriously affect the stability and lifetime of the cells and are highly susceptible to cell failure.^[10] Furthermore, the proliferation of zinc dendrites can precipitate a short circuit between the anode and cathode, significantly diminishing the battery's cycle life. In addition, the dendritic structure augments the specific surface area of the zinc electrode, which exacerbates zinc corrosion and impairs zinc utilization efficiency. Moreover, the poor adhesion of zinc dendrites to the electrode surface often results in their detachment, forming "dead" zinc and consequently leading to a reduction in battery capacity.^[11-14] During the charge/discharge cycling of AZIBs, the uneven deposition of zinc ions on the anode surface triggers the formation of zinc dendrites. This not only adversely affects the Coulombic efficiency and cycle stability of the battery, but also increases the risk of short circuit and potential safety hazards.^[15] Therefore, solving the above problems can greatly facilitate the large-scale application of AZIBs in energy storage systems.

The importance of this review is underscored by its systematic and thorough aggregation of the prevailing strategies and advancements in the suppression of zinc dendrite formation,

coupled with its provision of insightful perspectives on prospective research trajectories. This review systematically examines and summarizes the causes of zinc dendrite formation and provides a meticulous and integrated analysis of the latest advancements in the fields of zinc anodes,^[16, 17] electrolytes,^[11, 18, 19] and separator technologies,^[20-22] endeavors to equip researchers with a comprehensive body of knowledge. This endeavor is aimed at guiding future scholarly inquiries and catalyzing the advancement of aqueous zinc-ion battery technology.

2. Mechanisms of Zinc Dendrite Formation and Strategies for Uniform Deposition

2.1 The challenges facing the Zn anode in AZBs

The electrochemical behavior of zinc anodes is significantly influenced by the electrolytic environment, with the electrolyte's composition and pH value playing a crucial role. Zinc metal anodes in alkaline solutions encounter a multitude of challenges,^[23] such as the growth of zinc dendrites, hydrogen evolution reaction (HER), electrolyte depletion, and the formation of by-products like ZnO and Zn(OH)₂.^[24] These phenomena contribute to substantial polarization, diminished capacity, and decreased Coulombic efficiency. Conversely, these adverse impacts are significantly mitigated in environments that are neutral or mildly acidic, where Zn²⁺ ions predominantly remain in their ionic state, thereby enhancing the reversibility of zinc deposition and dissolution processes. Therefore, contemporary research in AZIBs is largely centered around electrolytes with near-neutral pH values. Nevertheless, the problem of dendrite growth remains a significant obstacle in AZIBs. In short, zinc dendrite formation presents a prevalent and formidable challenge in the realm of existing zinc-ion battery technology. Dendrites, characterized by their distinctive branching fractal structures, emerge due to the microscopically uneven surfaces of zinc anodes. The proliferation of such dendrites poses substantial risks, including impaired battery performance, potential short-circuiting, and safety concerns. This irregularity fosters preferential nucleation of Zn²⁺ ions at minute protrusions, a process driven by the minimization of surface energy. This intricate phenomenon was initially explored by J. W. Diggle et al., who proposed that the genesis of zinc dendrites could be comprehensively described by a pyramidal helical growth model on the substrate surface, predominantly governed by diffusion mechanisms.^[25, 26] Crucially, they identified that when the apex of a zinc dendrite precursor attains a critical threshold condition, the growth mechanism transitions from being diffusion-controlled to activation-controlled, thereby altering the growth trajectory and rate. Building upon these foundational insights, Matsushita and colleagues proposed the two-dimensional diffusion-limited

REVIEW

1 aggregation (DLA) model as a new mechanism for
2 understanding zinc dendrite development.^[27] This model has
3 since been acknowledged as a pivotal contribution to the
4 theoretical understanding of dendritic growth patterns in AZIBs.
5 The evolution of computational science has further enriched the
6 field of AZIBs, introducing a variety of phase-field-based
7 models.^[28] Notably, Mashayek et al. made significant strides in
8 elucidating the variations in dendritic morphology attributable to
9 differing current densities within zinc sulfate electrolytes.^[29] In
10 recent years, the advent of advanced in situ microscopy
11 techniques has enabled more nuanced and detailed explorations
12 of zinc dendrite growth mechanisms. These studies have not
13 only augmented our understanding of dendritic structures but
14 have also opened new avenues for potential solutions to
15 mitigate or control this persistent challenge in zinc-ion battery
16 technology. This approach enables better detection of premature
17 cell death caused by dendrite growth.^[30] It is worth noting that
18 some in-situ characterization techniques cannot fully restore the

rapid charge-discharge cycles are particularly prone to inducing dendrite formation. 6) Electrode material and architecture: The choice and architectural design of electrode materials play a vital role in dendrite growth. Electrodes designed with extensive surface areas and porous configurations can promote more homogeneous zinc deposition. A comprehensive understanding and strategic management of these factors are crucial for mitigating dendrite formation in AZIBs, thereby bolstering their operational efficiency and safety.

As shown in Figure 1, among the strategies to slow down the growth of dendrites, researchers are actively investigating a range of strategies including zinc anode design (coatings, structural design), electrolyte optimization (eutectic electrolyte, co-solvent electrolyte, additives, gel electrolyte), and diaphragm design (diaphragm modification, self-supporting diaphragm). In addition to these, there are also methods to retard dendrites by mitigating side reactions such as HER. These methods can significantly slow down or even prevent the formation of dendrites, thus improving the safety and extending the cycle life of AZIBs.

3. Zinc Anode Optimization

The zinc anode, often the site of dendrite formation, is a focal point in battery research and development. The growth of dendrites at the zinc anode is usually accompanied by other issues such as corrosion, passivation, and hydrogen evolution, creating a complex set of interrelated challenges. Therefore, a comprehensive strategy for optimizing the zinc anode is crucial to address the dendrite issue effectively. Current methods to improve the performance of the zinc anode mainly involve advanced coating techniques and innovative structural designs, which are necessary to confront the diverse challenges related to the anode's role in AZIBs.

3.1 Surface Coating

The interaction between the zinc anode and the electrolyte significantly elevates the risks of dendrite formation, corrosion, and HER. To mitigate these challenges, the most straightforward approach is to apply a protective coating on the zinc anode surface. This coating serves as an effective barrier, diminishing the direct contact area between the zinc surface and the electrolyte, thereby attenuating the propensity for dendrite formation, corrosion, and HER during the battery's operational cycles.

The functionality of coatings extends beyond mere physical isolation. They play a crucial role in modulating the electric field, facilitating controlled ion transport, directing zinc deposition, and enhancing the kinetics of zinc deposition to ensure uniform nucleation. Additionally, they are instrumental in preventing excessive dissolution of zinc ions, enhancing the compatibility between electrolyte and zinc, reinforcing the mechanical strength of zinc, and reducing zinc corrosion and oxidation. The efficacy of these coatings largely depends on their inherent properties, including thickness, porosity, wettability, insulation characteristics, mechanical strength, and film-forming ability. Hence, the selection of coating materials necessitates careful consideration of their synthesis methods and processing parameters to optimize their protective capabilities. The most common method of film formation for coatings is through the application of a binder-mixed slurry, a process that is simple but often results in poor mechanical strength. To address this,

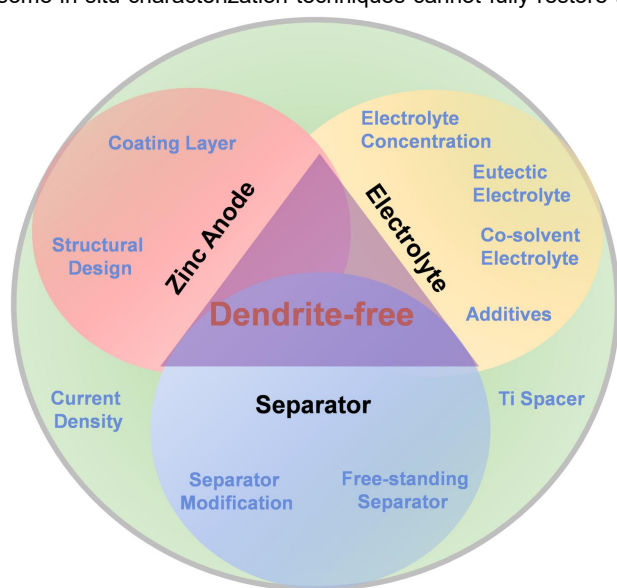


Figure 1 Strategy of dendrite-free in AZIBs.

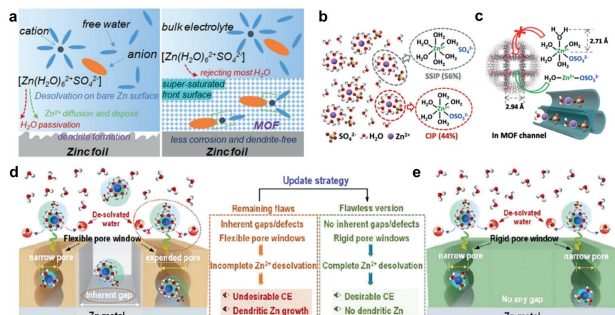
19 actual working state of the battery. The mechanism of dendrite
20 growth in AZIBs represents a complex interplay of various
21 factors and stages.

2.2 The strategies of dendrite-free

23 The key factors influencing the growth of dendrites in AZIBs
24 are summarized as follows: 1) non-uniform deposition: zinc ions,
25 during charging, undergo reduction to metallic zinc on the
26 electrode surface. Surface anomalies, such as roughness and
27 defects, create preferential zones for zinc ion deposition,
28 catalyzing dendrite initiation.^[31] 2) Ion concentration gradient:
29 Disparities in zinc ion concentration within the electrolyte can
30 accelerate dendrite formation. The consumption of zinc ions
31 proximal to the electrode generates a concentration gradient,
32 thereby dictating the pattern of zinc deposition.^[32] 3) Electric field
33 distribution: Inhomogeneous electric field distribution on the
34 electrode surface can lead to areas where zinc ions are more
35 readily reduced, thus fostering dendritic growth.^[33] 4) Electrolyte
36 characteristics: The electrolyte's composition, concentration, and
37 temperature significantly influence the migration and deposition
38 of zinc ions, consequently impacting dendrite formation.^[34] 5)
39 Charge-discharge dynamics: The rate of charge-discharge,
40 current density, and cycle frequency are pivotal in influencing
41 dendrite growth.^[35] Conditions such as high current density and

REVIEW

1 techniques such as chemical vapor deposition (CVD) [36], atomic-
2 layer deposition (ALD) [37] have been developed for in situ film
3 formation, enhancing strength but adding complexity. But these
4 two methods are too complicated. Table 1 compares the
5 performance of different coatings. Even with the same material
6 there is a huge difference in the stability of the electrolyte cycle
7 with different coating methods and different electrolytes. Current
8 research in coating materials encompasses conductive materials



9 like carbon and metals, as well as non-conductive metal
10 compounds, polymers, inorganic non-metals, and various
11 innovative composite materials. Each material presents its
12 unique advantages and challenges in optimizing zinc anodes.

13 It is generally accepted that zinc deposition is triggered by
14 heterogeneous nucleation and that the nucleation energy barrier
15 needs to be overcome to form the solid phase. The introduction
16 of a conductive coating acts as a seed for crystal nucleation, in
17 addition to homogenizing the electric field. Archer's group
18 achieved the directional deposition of Zn based on the low lattice
19 mismatch between graphene and Zn.[38] However, in recent
20 years it has been found that this substrate effect fails with depth
21 of discharge. Therefore, the use of non-conductive coatings has
22 become the main direction of current research. Non-conductive
23 coatings need to have the ability to conduct zinc ions. In their
24 seminal work, Kang et al. advocated for the utilization of porous

Figure 2 (a-c) Schematic illustration of the surface evolution of Zn/ZIF-7-Zn. and schematic illustration of highly coordinated ion complexes of $\text{H}_2\text{O}-\text{Zn}^{2+}-\text{OSO}_3^{2-}$ migrating through MOF channels. Reproduced with the authors' permission of ref. [43]. Copyright 2020, Wiley-VCH. (d, e) The importance of constructing ultrathin crack-free with rigid. Reproduced with the authors' permission of ref. [57] Copyright 2023, Wiley-VCH. (color on line)

25 nano- CaCO_3 as a protective layer, a strategy designed to
26 facilitate uniform and site-selective zinc metal plating/stripping
27 behaviors. [39] The significance of the coating's porous structure
28 cannot be overstated, as it plays a crucial role in the
29 suppression of zinc dendrite formation. The employment of this
30 nano-porous inorganic coating has notably improved the
31 plating/stripping stability of the zinc metal anode.

32 Some other inorganic coatings layer such as TiO_2 and ZrO_2
33 have also been demonstrated to effectively inhibit the growth of
34 zinc dendrites. [40-42] The efficacy of these coatings can be
35 attributed to their dense interfacial structure, characterized by
36 uniformly dispersed nanochannels. These nanochannels play a
37 pivotal role in curtailing the two-dimensional diffusion of zinc ions
38 across the electrode surface. The ion concentration gradient is
39 greatly reduced, resulting in a more uniform distribution of zinc
40 ions near the electrode. Nevertheless, these non-adjustable
41 porous, non-conducting materials always present a large
42 impediment to ion migration, so the search for more suitable
43 porous materials is more in line with the need to improve the
44 stability of AZBs.

Recent developments in battery technology have highlighted metal-organic frameworks (MOFs) as a novel coating material. Zhou's research group pioneered a ZIF-7 based MOF coating to augment the performance of aqueous zinc batteries. [43] Illustrated in Figure 2a, this innovative coating effectively curtails zinc dendrite growth and water decomposition by forming a supersaturated electrolyte precursor layer on the zinc anode surface. The effectiveness of this approach is primarily attributed to the MOF channels' selective exclusion of large solvated ion complexes and their ability to sustain a supersaturated electrolyte under electrical influence. In a symmetric zinc half-cell setup, the MOF-coated zinc demonstrated remarkable endurance, maintaining stability for up to 3000 h at a current density of 0.5 mA cm^{-2} . Building upon this foundation, further theoretical investigations based on ZIF-7 explored the nanoscale dynamics and mechanisms influencing Zn^{2+} ion flux, solvation structure alterations, and the continuous dehydration process of Zn^{2+} ions moving from the electrolyte to the MOF channels. This study revealed that a 2.0 M zinc sulfate electrolyte concentration optimizes conductivity and ensures a uniform distribution of water-mediated ion pairing, effectively balancing the counter-ion effects and spatial constraints during Zn^{2+} dehydration.

Table 1 Comparison of the performance of different coatings

Coating layer	Method	Electrolyte	Current density/Capacity (mA cm^{-2}) / (mAh cm^{-2})	Cycle life(h)	Ref.
CaCO_3	Doctor blading	3M $\text{ZnSO}_4+0.1\text{M MnSO}_4$	0.25/0.05	840	[39]
TiO_2	ALD	3M Zn (OTf) ₂	1/1	150	[44]
TiO_2	Doctor blading	1M ZnSO_4	1/1	460	[45]
TiO_2 -PVDF	Drop cast	2M ZnSO_4	0.885/0.885	2000	[46]
PDMS/ TiO_2 -x	Spin coating	3M ZnSO_4	1/1	900	[47]
ZnO	Chemical deposition	2M $\text{ZnSO}_4+0.1\text{M MnSO}_4$	5/1.25	500	[48]
Al_2O_3	ALD	3M Zn (CF_3SO_3) ₂	1/1	500	[49]
Oxyhydroxide	Chemical decoration	2M ZnSO_4	1/1	4000	[50]
BaTiO_3	Doctor blading	2M ZnSO_4	1/1	2000	[51]
BaTiO_3	Doctor blading	1M $\text{ZnSO}_4+0.1\text{M MnSO}_4$	1/1	4100	[52]
PVDF	Spin coating	2M ZnSO_4	0.25/0.05	2000	[53]
P(VDF-TrFE)	Spin coating	2M ZnSO_4	0.2/0.2	2000	[54]
ZrO_2	Casted	2M ZnSO_4	0.25/0.125	3800	[55]
ZIF-7	Doctor blading	2M ZnSO_4	0.5/1	3000	[43]

This novel coating effectively inhibits the growth of zinc dendrites and water decomposition by forming a supersaturated electrolyte layer on the zinc anode surface. This is primarily attributed to the selective exclusion of large dissolved ion complexes by the ZIF-7 channels and the ability to maintain a supersaturated electrolyte at the zinc anode's frontal interface under an electric field. As shown schematically in Figure 2b, the solvated shell layer of Zn^{2+} in aqueous electrolyte presents six surrounding water ligands. Zn^{2+} must shed these water molecules to complete the deposition and these water molecules will lead to the instability of the zinc negative electrode. Figure 2c shows that the presence of ZIF-7 changes the coordination of Zn^{2+} from solvated ion-pairs mainly a solvent-separated ion-pairs (SSIP) to contact ion-pairs (CIP), thanks to its appropriately sized pores. Leveraging this advantage, symmetric zinc half-cells exhibited remarkable durability, maintaining stability for up to 3000 h at a current density of 0.5 mA cm^{-2} . Further theoretical

studies based on ZIF-7 explored nanoscale dynamics and mechanisms affecting Zn^{2+} ion flux, dissolution structure changes, and the continuous dehydration process of Zn^{2+} ions moving from the electrolyte to ZIF-7 channels. This research confirmed the Zhou's group claim that an electrolyte concentration of 2.0 M zinc sulfate could optimize conductivity.^[56] This concentration ensures uniform water-mediated ion pairing distribution, effectively balancing the counterion effects and spatial constraints during the Zn^{2+} dehydration process. Nevertheless, the coating still faces the risk of cracking during cycling. Following this research direction, Zhou's group developed an ultra-thin, crack-free ZIF-7 \times -8 MOF layer with robust sub-nanometer pores (0.3 nm), facilitating the desolvation of zinc ions before reaching the zinc metal surface. The layer was prepared by the fast current driven synthesis (FCDS) method to grow in situ on the zinc metal surface.^[57] As illustrated in Figure 2d, the flexible pore window will lead an incomplete Zn^{2+} desolvation, resulting a unstable CE and dendrite growth. In contrast, the rigid sub-nanometer structured channels in the coating contribute to highly ordered deposition of zinc ions on the Zn metal (Figure 2e). This protective approach endowed the battery with exceptional cyclic stability (over 2200 h) and achieved an extremely high Coulombic efficiency (99.96%) over 6000 cycles. Additionally, practical soft-pack batteries have surpassed over 120 working cycles. The use of MOF-type coatings effectively regulates Zn^{2+} ion diffusion on zinc metal anodes, ensuring a uniform zinc ion flux and preventing dendrite formation.

In addition to the desolvation coatings achieved through porous MOFs, the functional groups on the coating surface also serve a similar purpose. For instance, Zhou et al. demonstrated the enhancement of AZIBs performance by designing a polydopamine (PDA) layer on the surface of metallic zinc. The PDA layer, through its dual-effect of rapid desolvation and ion confinement, reduced the number of water molecules and lowered the energy barrier for Zn^{2+} migration, while also modulating the ionic flux through an ion-aggregation effect, thereby improving the deposition kinetics of Zn^{2+} . Furthermore, when paired with a MnO_2 cathode, the $\text{Zn@PDA}/\text{MnO}_2$ full cell exhibited high discharge efficiency and cycling stability over 1000 cycles. Although this coating engineering significantly enhances battery performance, it also adds a layer of complexity to the anode materials, necessitating further improvements in structural design.

3.2 Anode Structural Design

To optimize the deposition behavior of zinc anodes, rational design of the substrate surface or structural optimization can also be employed. Powdered anodes and three-dimensional electrodes, due to their unique structures, expand the surface area.^[58, 59] The increased surface area enhances the contact area between the electrode and the electrolyte, thereby facilitating accelerated ion diffusion within the electrode. This improvement is crucial for enhancing the battery's charge-discharge rate and overall performance. The overpotential of zinc deposition increases with rising current density. Conductive three-dimensional porous anodes, characterized by their large specific surface area, can effectively reduce the surface current density significantly. Additionally, three-dimensional porous anodes provide numerous nucleation and deposition sites for zinc, thereby considerably reducing dendrite formation. For instance, the three-dimensional porous zinc structure developed

by Rolison et al. can be directly used as a zinc anode. This structure effectively accommodates the growth of zinc dendrites and isolates the deposition of zinc oxide. Simpler and more cost-effective approaches involve direct treatment of the zinc foil surface. The protrusions or passivation layers on the original zinc surface are primary contributors to the aggregation of zinc crystals and uneven electro-deposition. In the study conducted by Zhu et al., a novel and efficient electropolishing method was introduced for the first time.^[60] This method, being non-corrosive and superior to the laborious and inconsistently effective mechanical polishing commonly used in laboratories, enables the preparation of a smoother and cleaner zinc metal surface. By removing the original passivation layer on the zinc surface, the newly prepared zinc anodes were able to operate stably at high current densities up to 40 mA cm^{-2} for over 6000 cycles. It provides a reliable foundation for studying the mechanisms of zinc deposition and assessing the effectiveness of protective strategies.

Substrate effects offer a noteworthy strategy for dendrite suppression. In 2019, Archer's group conducted research that highlighted the advantages of the (002) crystal plane.^[38] This finding has since sparked a surge in efforts to engineer substrates featuring an increased prevalence of the (002) crystal plane. However, it is crucial to acknowledge that the efficacy of this substrate effect tends to diminish as cycling progresses. Moreover, the (002) plane is known for its chemical instability, rendering it susceptible to corrosion by the aqueous components present in the electrolyte. This susceptibility results in the formation of disordered zinc dendrites, suboptimal Coulombic efficiency (CE), and limited battery lifespan.

In a recent study, Zhou's group departed from conventional approaches that focused on maximizing the proportion of (002) zinc crystal faces or enhancing strong (002) textures on various zinc substrates.^[61] Instead, they introduced an innovative approach by selectively etching the chemically unstable (002) zinc surface within the original zinc metal. This chemical etching served as an effective means of passivating the zinc. Their research demonstrated that the etched zinc exhibited a unique structure with vertically aligned zinc columns. This structural characteristic proved highly efficient in suppressing the growth of zinc hydroxide sulfate (ZHS) in aqueous electrolytes. Consequently, it facilitated the nucleation and growth of zinc ions along these vertical zinc columns, eliminating zinc dendrites, thereby achieving a high level of average Coulombic efficiency (CE) of 99.94% over 4500 cycles. Additionally, the pouch cell with $\text{NH}_4\text{V}_4\text{O}_{10}$ cathode demonstrated a high specific capacity of 317.3 mA g^{-2} , and maintained 85.2% of its capacity even after 350 cycles. This breakthrough substantially improved the reversibility and longevity of the zinc metal anode.

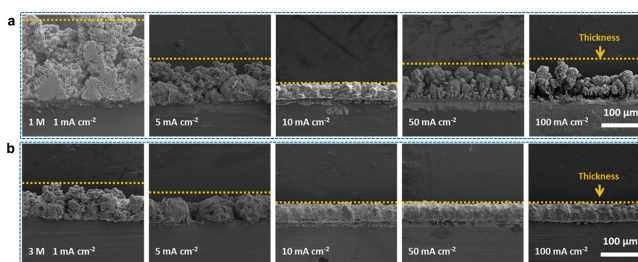


Figure 3 SEM images of zinc metal deposited in (a) 1 M (b) 3 M ZnSO_4 electrolyte at different current densities (1-100 mA cm^{-2}). Reproduced with permission of ref. ^[62]. Copyright 2022, Wiley-VCH. (color on line)

4 Electrolyte Optimizations

The role of the electrolyte in AZIBs is indeed crucial, serving as both the conduit that connects the anode and cathode and the carrier for Zn^{2+} ion migration. Alkaline electrolytes possess the potential to exacerbate undesirable side reactions at the zinc anode, while acidic environments may result in anode corrosion. Consequently, AZIBs predominantly opt for neutral or mildly acidic electrolytes. Electrolytes encompass salts, solvents, and additives, with the solvation structure of different ions significantly impacting the electrolyte's conductivity, electrochemical stability window, and thermal stability. In contemporary research, a range of water-soluble zinc salts finds application, including zinc sulfate (ZnSO_4), zinc perchlorate ($\text{Zn}(\text{ClO}_4)_2$), zinc chloride (ZnCl_2), zinc trifluoromethanesulfonate ($\text{Zn}(\text{CF}_3\text{SO}_3)_2$), and zinc acetate ($\text{Zn}(\text{CH}_3\text{COO})_2$), among others. Among these, ZnSO_4 and $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ aqueous solutions enjoy widespread use due to their expansive electrochemical stability windows and efficiency in zinc deposition/stripping. Present-day electrolyte engineering primarily concentrates on techniques like eutectic electrolytes, cosolvents, additives, and gel electrolytes and other methods to tailor the solvation structure of the electrolyte, broaden the electrochemical window, suppress side reactions, and optimize the deposition characteristics of zinc anodes.

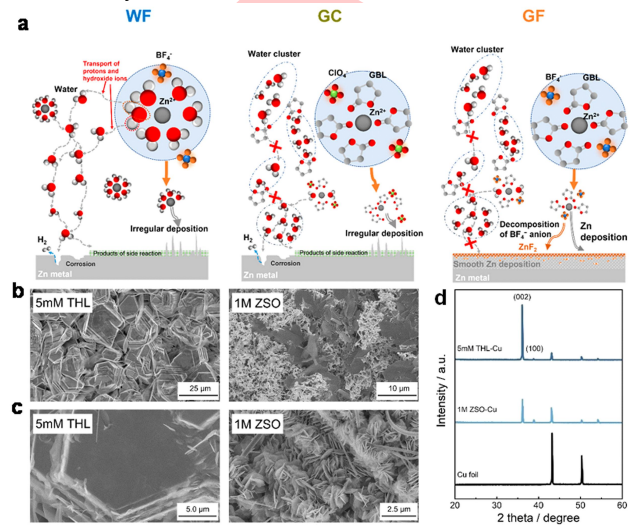
4.1 Electrolyte concentration

Optimizing zinc battery performance can be attained by modifying the concentration of zinc salts. This is mainly related to the presence of hydrated ions (e.g. $\text{Zn}(\text{H}_2\text{O})_x^{2+}$ and $\text{SO}_4^{2-}(\text{H}_2\text{O})_x$), which are highly active species. For example, reducing free water in the bulk electrolyte to diminish the high-energy barriers for Zn^{2+} diffusion can significantly enhance the rate performance of zinc batteries. Wang et al. demonstrated the expansion of the voltage window for aqueous electrolytes by elevating salt concentrations to a high level (approximately 21 mol kg^{-1}). This approach compels excess anions to aggregate around Zn^{2+} , forming an anion-involved solvation structure that suppresses hydrated ions. The "molecularly crowded" electrolyte, introduced at a relatively lower salt concentration (around 2 M), inhibits the activity of water by coordinating with H_2O molecules through the incorporation of high concentrations of crowding agents. Nevertheless, such strategies are deemed unsustainable on a large scale due to their elevated cost, susceptibility to crystallization, and heightened viscosity. In contrast to high concentration electrolyte strategies, a recent study proposed an anomalous ultra-low salt concentration electrolyte strategy. By reducing the concentration of zinc salts, this approach minimizes active hydrated ions, thereby significantly expanding the electrolyte's voltage window and curtailing side reactions induced by water. This strategy diminishes polarization during battery charging and discharging, narrowing the median voltage gap of full-cell operations. Employing this strategy, Zn-polyaniline (PANI) full cells stably function within a voltage range of 0.50-1.50 V, achieving a cathode loading of approximately 11 mg cm^{-2} with minimal sacrifice of rate performance. In stark contrast to the strategies, Sun et al. employed in situ optical imaging and theoretical modeling to confirm the variance in the dynamic electro-deposition behavior of zinc metal under different concentrations of electrolytes and current densities.^[62] As shown is Figure 3a, at

a low-concentration 1 M ZnSO_4 electrolyte, as the working current density increased from 1 to 100 mA cm^{-2} , the zinc deposition morphology transitioned from thermodynamically favorable flake-like shapes to kinetically controlled dense crystals, and finally to diffusion-limited zinc metal columnar morphologies. In contrast, in Figure 3b demonstrated a high-concentration 3 M ZnSO_4 electrolyte promoted ion diffusion and elevated Sand's limiting current density, enabling the formation of dense and highly uniform deposits at high current densities (10-100 mA cm^{-2}), thereby achieving high Coulombic efficiency (>99%).

4.2 Eutectic Electrolyte

As analyzed above, the unfavorable factors for zinc anode



protection in AZBs are mainly due to the large amounts of free water present in the solvent. Besides, electrolytes contain $\text{Zn}[\text{OH}]_6^{2+}$ ions which can also cause severe side reactions such as HER, corrosion and passivation and lead dendrites. To reduce the activity of water molecules, introducing deep eutectic solvents (DES) is an effective strategy. DES is a type of ionic

Figure 4 (a) Schematic illustration of the Zn^{2+} solvation shell and interfacial side reactions in WF, GC, and GF electrolytes. Reproduced with the authors' permission of ref. ^[66]. Copyright 2023, American Chemical Society. SEM images of deposited Zn in 5 mM THL and 1 M ZSO using SEM images of (b) Zn and (c) Cu substrate and (d) XRD after cycling. Reproduced with the authors' permission of ref. ^[60]. Copyright 2023, Wiley-VCH. (color on line)

liquid analogues formed from eutectic mixtures of Lewis or Brønsted acids and bases, or Brønsted acids and bases, which can contain a variety of anions and/or cations. Eutectic electrolytes are typically characterized by low melting-point and freezing-point, high vapor pressure, non-flammable. ^[63] Cui et al. have engineered a eutectic aqueous electrolyte supported by ligand-directed solvation shells. ^[64] This work combined a hydrated zinc salt ($\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$), with a neutral ligand, succinonitrile (SN), to create a new electrolyte. Specifically, SN molecules adeptly supplant the H_2O molecules within the solvation shells of Zn^{2+} ions. This substitution raises the desolvation energy of Zn^{2+} , ensuring a smoother and more controlled zinc deposition process. Recently, Zhang et al. introduced a novel hydrated eutectic electrolyte (HEE) consisting of $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, ethylene glycol (EG), and InCl_3 solution, where the dissociative reduction of the eutectic molecules in-situ forms a zincophobic/zincophilic bilayer interfacial phase. ^[65] The

zincophilic interface lowers the energy barrier for Zn nucleation and promotes the uniform deposition of Zn, while the Zn-phobic interface prevents the active water from contacting the Zn surface, thus suppressing the side reaction. Effectively extends the service life of AZIBs over a wide temperature range of -50 to 50 °C (2500 h (at 50 °C) and 800 h (-50 °C) at 1 mA cm⁻²). While the eutectic electrolyte approach offers significant improvements in protecting zinc anodes and enhancing the performance of AZIBs, its implementation is challenged by material costs, formulation complexity, and potential environmental impacts. Addressing these limitations through continued research and development will be crucial for the practical and widespread application of this technology.

The elevated cost of Zn (ClO₄)₂·6H₂O has prompted exploration into cost-effective alternatives. Yang et al. selected cheaper zinc salt Zn (BF₄)₂·xH₂O and introduced a novel eutectic electrolyte featuring γ-butyrolactone (GBL) and Zn (BF₄)₂·xH₂O, which retains the multifunctional attributes of the electrolyte while reducing costs. Zn (BF₄)₂·xH₂O is unstable in a pure water-based electrolyte and stable performance cannot be obtained. Experimental results substantiate the effectiveness of this approach.^[66] By forcibly introducing GBL solvent into the solvation shells of Zn²⁺ ions and promoting the formation of a fluorine-rich interface at the zinc anode surface through anion decomposition as shown in Figure 4a, reactivity between water and the zinc anode is significantly mitigated. The synergistic effect of these factors ensures remarkable zinc reversibility, with an average Coulombic efficiency of 99.74%, high areal capacity (55 mAh/cm²). Consequently, zinc-ion batteries featuring a VO₂ cathode exhibit outstanding stability over 5000 charge-discharge cycles. The main reason for obtaining dendrite-free zinc anodes from eutectic electrolytes is the use of large amounts of organic solvents, which reduces the amount of free water and changes the coordination environment of Zn²⁺, but eutectic electrolytes are usually viscous and expensive.

4.3 Co-solvent electrolyte

In contrast to eutectic electrolytes, an alternative approach known as the co-solvent electrolyte has been developed to address the trade-off between performance and cost in AZIBs. This strategy combines aqueous and non-aqueous components, aiming to harness the inherent non-flammable and non-toxic properties of water-based solutions while effectively modifying the solvation environment of Zn²⁺. The introduction of co-solvents simultaneously reduces the use of organic solvents and water. Specifically, the co-solvent electrolyte involves the replacement of coordinating H₂O molecules in the primary solvation shell of Zn²⁺ with non-aqueous solvents. This alteration in the solvation structure of Zn²⁺ reduces the presence of H₂O and increases the coordination number of co-solvents, thus enhancing the smooth and controlled deposition of zinc. One of the primary advantages of this approach lies in its ability to shield reactive zinc metal from direct contact with water, thus mitigating the detrimental effects of the HER, corrosion, and hasty passivation. The strength of interactions between active sites in co-solvents and Zn²⁺ plays a pivotal role in dictating the interfacial chemistry and the solvation environment, subsequently influencing the kinetics of Zn²⁺ reactions. For instance, organic solvents containing polar groups or lone-pair electrons, including alcohols, ethers, sulfones, nitriles, or amides, have been identified as cosolvent that can effectively modulate the solvation structure of zinc ions or the strength of hydrogen

bonding within the electrolyte.^[67] These co-solvents facilitate stable zinc deposition and stripping processes, consequently enhancing the operational stability and lifespan of AZIBs. It is noteworthy that these mixed electrolytes often exhibit varying physical and electrochemical properties due to the diverse interaction mechanisms between co-solvents and Zn²⁺/H₂O. Co-solvent-based electrolytes typically demonstrate higher viscosity and lower ionic conductivity. Therefore, the selection of appropriate co-solvents becomes imperative, as they must simultaneously improve the stability of the zinc anode, reduce the reactivity of H₂O, and maintain favorable kinetics for Zn²⁺ reactions. Notably, the recent introduction of a highly polar solvent based on urea (TMU) by the Huang research group represents a significant development in co-solvent electrolytes.^[68] TMU, characterized by its dual-hydrophobic -N(CH₃)₂ groups and a hydrophilic -C=O group, exhibits complete miscibility with water. This unique property stems from TMU's ability to replace water molecules in the solvation shell of Zn²⁺ entirely. TMU's influence results in the transformation of the solvation structure of Zn²⁺ from [Zn(H₂O)]²⁺ to [Zn(H₂O)(TMU)]²⁺, accompanied by the disruption of hydrogen bonds through the -C=O group. Simultaneously, the -N(CH₃)₂ groups prevent H₂O from entering the solvation structure of Zn²⁺, thereby isolating H₂O from direct interaction with the zinc anode. A notable feature of urea is its complete miscibility with water in any proportion, rendering it a versatile component that serves both as a co-solvent and an additive at the interface of zinc anode in AZIBs.

4.4 Additives

Common additives in AZIBs include various water-soluble polymers, organic small molecules, metal ions, and other inorganic substances. The addition of small quantities of additives in the electrolyte can play a crucial role at the electrolyte/electrode interface, influencing the behavior of cations and anions, adjusting the electric field strength, forming protective layers, and inhibiting the growth of zinc dendrites. As mentioned in section 4.3, due to the unique properties of TMU, Yang et al. used a 0.25 M TMU-based 4 M Zn (OTF)₂ aqueous electrolyte, which facilitated the formation of an inorganic-organic bilayer solid electrolyte interface (SEI).^[69] This allowed for uniform and rapid transport of Zn²⁺ ions, ultimately achieving dendrite-free zinc deposition in zinc symmetric cells, with over 4000 h of cycling life. However, not all solvents are readily miscible with water in all proportions. Many solvents have limited solubility in water, leading to diverse roles for different solvents as additives in AZIBs.

Table 2 Comparison of cycle life of Zn symmetric cells with different additives.

Electrolyte	Current density/Capacity (mA cm ⁻² /mAh cm ⁻²)	Cycle life(h)	Ref.
2 M ZnSO ₄ + N-Acetyl-ε-caprolactam	0.2/0.2	9800	[70]
1 M ZnSO ₄ + 6 M Acetamide	1/1	3000	[18]
2 M ZnSO ₄ +0.037wt.% fucoidan	1/2	2800	[71]
2 M ZnSO ₄ +0.5 Mm C ₈ TAB	1/1	2000	[15]
0.5 M Zn (CF ₃ SO ₃) ₂ / H ₂ O + TEP (1:1)	1/1	1500	[34]
2 M ZnSO ₄ + 67 wt. % maltose	1/0.5	1200	[72]
1 M ZnSO ₄ + 5 mM TU	1/1	800	[73]

4 M Zn (CF ₃ SO ₃) ₂ + 0.25 m TMU	0.5/0.5	4080	[69]
2 M ZnSO ₄ + 0.9 g β-CD	4/2	1700	[74]
0.5 M ZnCl ₂ + 1 M TC	1/0.5	2145	[75]
2 M ZnSO ₄ + 5 vol % NMP	5/5	200	[76]
2 M ZnSO ₄ + 0.05 M SG	1/1	1000	[77]
3 M Zn (CF ₃ SO ₃) ₂ / H ₂ O + surfoplane	5/5	1100	[78]

Esters are typically immiscible with water, and their role as additives in aqueous electrolytes has received limited attention. As mentioned in section 4.1, γ-butyrolactone (GBL), due to its limited dispersibility in water, was added in small quantities to the electrolyte by Li and co-workers. [79] They observed a significant transformation in the morphology of zinc deposition from loose accumulation to dense deposition. Even under high current density and large areal capacity, the ultra-dense structure remained unchanged, enabling the zinc anode to endure thousands of cycles, with a lifespan exceeding 1250 h (at 5 mA cm⁻² and 5 mAh cm⁻²). Density functional theory (DFT) calculations revealed that GBL preferentially adsorbs at the interface, altering the zinc ion diffusion from 2D to 3D and significantly promoting the abundant generation of nucleation sites on the zinc anode.

In addition to exploring common additives, researchers are also developing novel additives. For instance, recently, the Zhou's group recognized the advantages of trehalose in maintaining biological stability and introduced trehalose into the electrolyte as an additive for the first time. [80] The addition of trehalose facilitated oriented deposition on crystal facets, transforming the electrodeposition from random thin flakes to dense blocks, as shown in Figure 4b and c, exposing the (002) crystal plane (Figure 4d). This resulted in highly reversible zinc anodes, demonstrating an average Coulombic efficiency of up to 99.8% in Zn//Cu cells and stable cycling for over 1500 h with a discharge depth of 9.0% in zinc symmetric cells.

Gel electrolytes, as a novel class of electrolyte materials, combine the advantages of both liquid and solid electrolytes. They effectively mitigate interfacial side reactions caused by the presence of high concentrations of active water molecules in traditional liquid electrolytes, thereby protecting the zinc anode. Gel electrolytes employ a three-dimensional network structure that restricts the mobility of water molecules, significantly reducing the likelihood of undesired chemical reactions occurring at the electrode/electrolyte interface reactions that are prevalent in liquid electrolyte systems. This restriction of water molecules, coupled with the retention of ionic conductivity, provides a promising strategy for enhancing the stability and cyclability of zinc-based batteries. The common gels are sodium alginate (SA)^[81], polyvinyl alcohol (PVA)^[82], polyvinyl pyrrolidone (PVP), polyacrylamide (PAM)^[83], xanthan gum^[84] and guar gum^[85] and so on. In addition to this many new gel electrolytes have been developed in recent years. Yang et al. used cross-linked kappa alginate and chitin (Carra Chi) to prepare a gel electrolyte with many polar functional groups (-OH, -NH₂, -SO₄²⁻) that bind water molecules and inhibit rapid electrolyte evaporation and HER. [86] It was applied to an open symmetric soft-packed battery at 10 mA cm⁻² current density and 35 mAh cm⁻² face capacity, the lifetime reaches about 4000 h. Gel electrolytes not only work wonders in inhibiting HER but have recently been shown to improve zinc deposition orientation as well. Wu et al. designed a multifunctional charged group gel electrolyte using poly(3-(1-vinyl-3-imidazolyl) propane sulfonate) (PVIPS) oligomeric imine gel.^[87] The sulfonate and imidazole charged groups in this gel electrolyte can orient the nucleation and deposition plane of Zn²⁺ to the (002) plane. The (002) plane exhibits higher activation energy, which can resist side reactions and induce uniform growth of Zn metal, resulting in a dendrite-free structure. In order to increase the mechanical properties of gels, Pan et al. developed a highly entangled gel (Acrylamide (AM, AR) and N, N'-Methylenebis (acrylamide) (MBAA)), which balances high mechanical properties (446 kPa tensile

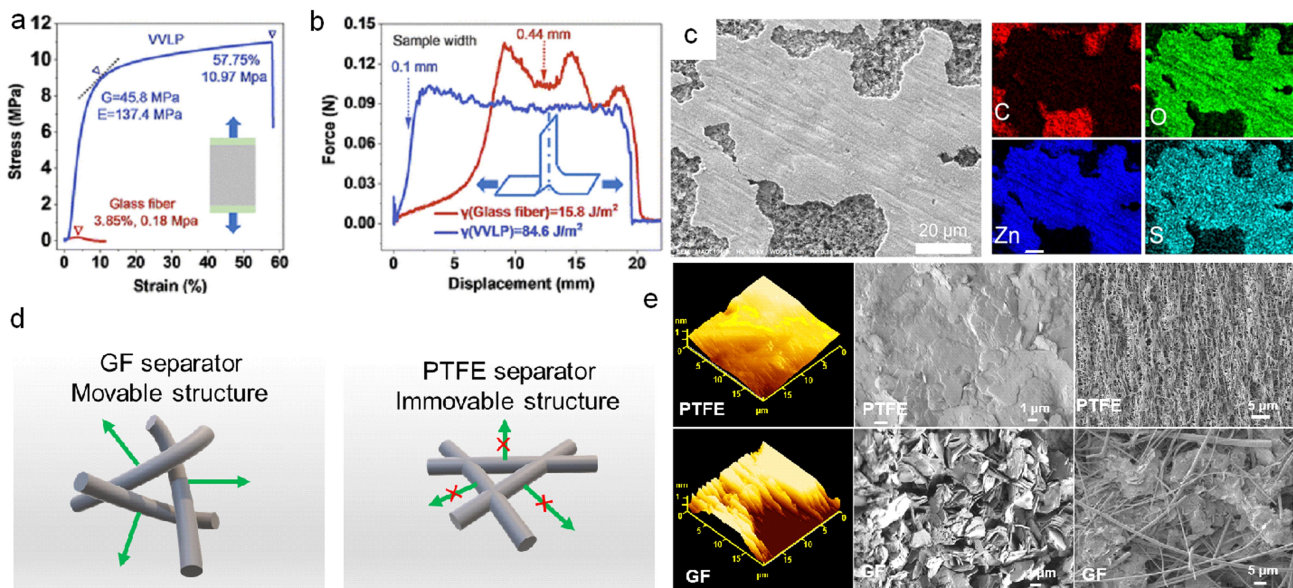


Figure 5 (a) Loading curves of different separators under uniaxial elongation. (b) Tearing toughness of separators. (c) SEM images and EDS mappings of the ZSH-rich composite layer on the VVLP separator. Reproduced with the authors' permission of ref. [96]. Copyright 2023, Royal Society of Chemistry. (d) Schematic construction of the GF and PTFE. (e) PTFE and GF separator after cycle. Reproduced with the authors' permission of ref. [21]. Copyright 2023, Royal Society of Chemistry. (color on line)

stable cycling for 6000 h at a current density of 0.5 mA cm^{-2} .^[88] Nevertheless, the use of gels will increase the weight of AZIBs, which will decrease the energy density.

5. Separator Optimization

Separators play a crucial role in ensuring the safety and performance of aqueous zinc-ion batteries (AZIBs). To achieve uniform distribution of electric field and ion flux, the separator needs to ensure pore size consistency, distribution, and electrolyte wettability. Commonly employed separators for AZIBs include glass fiber (GF) separators, cellulose-based separators, and polymer-based separators. GF separators are widely used in AZIBs due to their excellent chemical stability, favorable ion conductivity, and compatibility with the electrolyte. However, the low mechanical strength of GF separators has posed challenges, as the highly rigid zinc dendrites with a Young's modulus of 108 GPa can readily penetrate these separators, hindering the superior cycling lifespan of AZIBs. Optimization of separator pore structures and zinc affinity can promote uniform zinc ion flow while suppressing dendrite formation. Recent attention has been directed towards functionalization strategies for separators, primarily achieved through the modification of commercial separators or the design of novel self-supporting separators, to enhance the performance of AZIBs.

5.1 Separator Modification

Methods for the modification of separators primarily involve the incorporation of functional materials on the surface or within the separator matrix, possessing either zinc-affinitive or zinc-repelling properties. These materials serve to regulate the distribution and migration of zinc ions, thereby inhibiting the growth of zinc dendrites and preventing the penetration of harmful species. To address these challenges, researchers have introduced various functional materials into glass fiber separators, such as BaTiO_3 , cellulose, graphene, and molecular sieves. The addition of these functional materials has demonstrated the capacity to enhance the mechanical properties of glass fiber separators, modulate zinc ion flux and crystal orientation, effectively suppress zinc dendrite growth, and consequently improve the stability and efficiency of batteries. For instance, Wang and colleagues introduced supramolecular entities into glass fiber separators (GF@SM).^[89] These entities possess a surface rich in polar functional groups (amino, carbonyl, and triazine), which exhibit favorable adsorption properties towards Zn^{2+} ions. This adsorption behavior prevents the localized accumulation of zinc ions and the formation of zinc dendrites.

Another category of common separators in AZIBs is cellulose-based separators. In comparison to glass fiber, cellulose separators offer multiple advantages, including higher mechanical strength, excellent hydrophilicity, superior insulation properties, and high biodegradability. Wang's group proposed the use of hydrophilic filtration membranes with a uniform pore size distribution as separators for AZIBs.^[90] Research findings indicate that symmetric cells utilizing these filtration membranes exhibited sustained performance for over 2600 h, attributable to the regulatory effect of the uniform porous structure on Zn^{2+} ion flow. Building upon this concept, recent developments have witnessed the emergence of cellulose-based separators utilizing materials such as filter paper and cotton.^[91, 92] These separators hold promise as they leverage the inherent advantages of

cellulose, opening new avenues for enhancing the performance and sustainability of AZIBs.

In addition to glass fiber (GF) and cellulose separator materials, polymer separators have garnered attention for their favorable mechanical properties. However, due to the poor hydrophilicity of most commercial polymer separators, they have not been widely applied in aqueous zinc-ion batteries (AZIBs). Current research is primarily focused on utilizing certain polymers with specific functional groups that can form coordination bonds with zinc ions, thereby facilitating their uniform distribution and mobility within the battery. Therefore, it leads to the development of novel separators that combine hydrophilic substances such as cellulose with these polymers. For example, separators composed of polymer nanofibers, such as polyacrylonitrile (PAN),^[93] polyvinyl alcohol (PVA),^[94] and polyvinylidene fluoride (PVDF),^[95] have been developed. It is worth noting that Zhou's group recently developed a mechanically reinforced separator based on polyvinylidene fluoride (PVDF), named VVLP.^[96] This separator achieves a balance between mechanical toughness, ion conductivity, rapid zinc ion diffusion, and technical feasibility. Notably, the Young's modulus and shear modulus of the VVLP separator are significantly higher than those of the GF separator (Figure 5a and b). VVLP membranes can withstand a high yield stress of 10.9 MPa at 57% strain. As shown in Figure 5c, during the charge-discharge cycling process, the VVLP separator forms an in situ composite layer, which reduces porosity and inhibits the formation of zinc dendrites. The main by-product is zinc sulfate hydroxide hydrate (ZSH , $(\text{Zn}(\text{OH})_2)_3\text{ZnSO}_4 \cdot x\text{H}_2\text{O}$). This means that the PVDF separator is difficult to peel off from the electrode, something that numerous researchers do not want. This shortcoming has been attributed to the lack of ion transport in the ion conducting phase, leading to the occurrence of side reactions. To solve this problem, Wu et al. used PTFE-based commercial filter membranes with better mechanical performance as separators for AZIBs.^[21] Compared to the GF separator, it possesses a more uniform and immobile structure, the structures are shown in Figure 5d. The PTFE separator showed a thin thickness of 50 μm , the ability to be fully infiltrated, and mechanical properties with a Young's modulus of 114 MPa after infiltration. As shown in Figure 5e, the PTFE separator cells are cleaner after cycling of unmodified 2M ZnSO_4 electrolyte, resulting 400h cycling life at high current densities (20 mA cm^{-2}) and high capacities (20 mAh cm^{-2}). This innovative approach utilizes mechanical suppression effects and rapid ion diffusion strategies to address key challenges, including short cycling lifetimes, uncontrolled dendrite growth, and the limited reversibility of zinc metal anodes during high-capacity operation.

Table 3 The comparison of different kinds of separator with various thickness and transference number.

5.2 Free-standing separators

Separator engineering encompasses not only the modification of existing membranes and the implementation of barrier strategies but also the development of novel membrane materials. For example, porous materials such as MOFs and Mexene materials have been used in separators. In a notable contribution, the Zhou's group has introduced a zeolite molecular sieve separator, which effectively lowers the water activity within aqueous electrolytes.^[107] This zeolite-modified electrolyte preserves a highly active solvation layer and significantly mitigates the reactivity of water molecules. As a result, it exhibits reduced hydrogen evolution and enhanced corrosion resistance at the zinc anode. As shown in Figure 6a, the Zn^{2+} ion pairs passing through the molecular sieve are converted from SSIP to CIP. Importantly, due to the reduced water decomposition observed in the zeolite-modified electrolyte, the zinc symmetric cell achieves a substantially extended cycling life, with a remarkable endurance of 4765 h (0.8 mA cm^{-2}). Furthermore, the $\text{Zn-V}_2\text{O}_5$ cell demonstrates exceptional performance, enduring 3000 cycles. As shown in Figure 6b and Figure 6c, space-resolution operando Raman and micro-infrared spectroscopy showed the composition of the etched zinc foil surface. The Zn with zeolite separator showed accumulated lighter by-products. The compact and dense Zn stack deposition pattern also favors the reversibility of the zinc anode.

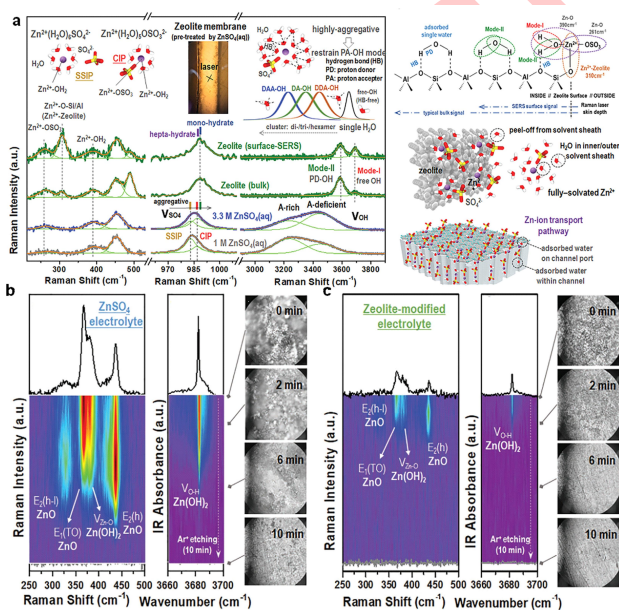


Figure 6 (a) Solvation structure analysis by space-resolution operando component analysis by Raman spectroscopy and micro-infrared spectroscopy and optical microscopy of zinc anodes in (b) pristine ZnSO_4 electrolyte and (c) zeolite-modified electrolyte. Reproduced with the authors' permission of ref. ^[103]. Copyright 2021, Wiley-VCH. (color on line)

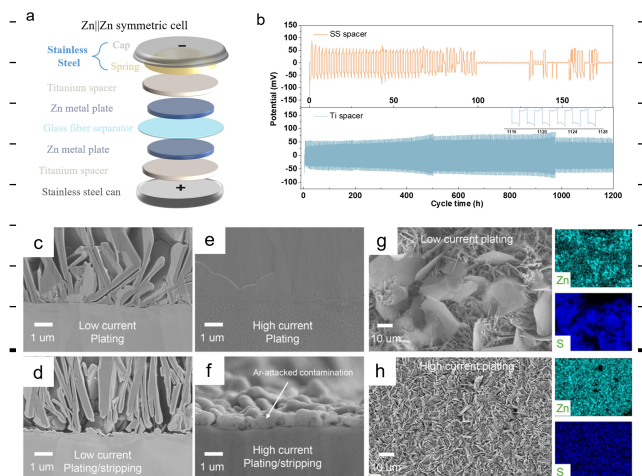
Furthermore, Zhou et al. selected a molecular sieve (4A) with a more suitable pore size for effective application in zinc-iodine batteries,^[108] maintaining an impressive capacity retention rate of 91.0% and achieving a perfect 100% Coulombic efficiency over

an extensive 30,000 cycles, even when operating at a high current density of 4.0 A g^{-1} .

6. Other Strategies

In addition to the common design modification strategies of anode, electrolyte, and separator, there are many other factors that have an impact, such as the collector, cell case, and charging and discharging conditions. Stainless steel (SS) coin cells are widely used to evaluate the electrochemical performance of AZIBs. However, a study by Zhou's group found that HER occurs significantly in SS button cell materials with subsequent accumulation of insulating layered double hydroxide byproducts.^[14] In this study, titanium (Ti) foil was used as a spacer to act as a barrier to prevent direct contact between the electrolyte and the SS material, as shown in Figure 7a. Without modifications to the electrodes, electrolyte, or separator, the Ti foil spacer cells increased the cycle life of the battery by more than 10 times compared to the SS cells, reaching an astonishing 1200 h (Figure 7b). This is mainly attributed to the lower HER activity of Ti relative to SS, which greatly reduces side reactions within the cell. HER and the kinetics of the zinc plating/stripping mechanism are closely related. Recently, Yang et al. found a significant concentration gradient of solvated Zn (H_2O)₆²⁺ species at high current densities, which was identified as the main species triggering HER.^[109] At a low current density (0.3 mA cm^{-2}), zinc electrodeposition exhibits a hexagonal platelet structure, which shows high porosity in cross-sectional view (Figure 7c). Samples subjected to zinc electrodeposition/stripping cycles display numerous irregular residues, characterized by high porosity and difficulty in stripping

Figure 7 (a) Schematic diagram of a Zn symmetric cell with Ti spacer. (b) Comparison of cycle life curves for Zn symmetric cells. Cross-sectional SEM images of zinc electrodeposition on a copper substrate show distinct morphologies under different conditions. Reproduced with the authors' permission of ref. ^[14] Copyright 2023, Royal Society of Chemistry. Zinc plating at (c) low current density and (e) high current density exhibit different structural features. After zinc plating/stripping cycles, the samples reveal (d) the morphology at low current density and (f) the morphology at high current density. Top-sectional SEM images and corresponding elemental mapping further highlight the differences in zinc plating morphology at (g) low current density and (h) high current density. Reproduced with the authors' permission of ref. ^[105]. Copyright 2024, Royal Society of Chemistry. (color on line)



at a high cutoff potential of 0.5 V (Figure 7d). At a high current density (30.0 mA cm^{-2}), zinc electrodeposition forms a densely packed structure without noticeable platelet ZSH species (Figure 7e). The uniform dense pattern observed under repeated high current density electrodeposition facilitates rapid electron/ion

diffusion and high reversibility of stripping (Figure 7f), with negligible byproducts. Surface SEM images (Figure 7g, h) and corresponding EDS mapping clearly illustrate the differences in zinc deposition morphology obtained at high and low current densities. At a low current density, HER near the zinc metal's negative electrode acts as a competitive side reaction, releasing OH^- , which promotes the formation of ZSH. ZSH further precipitates on the zinc metal surface to form a passivation film. High current densities generate high electric fields, resulting in significant $\text{Zn}(\text{H}_2\text{O})_6^{2+}$ concentration gradients, which induce sparse $\text{Zn}(\text{H}_2\text{O})_6^{2+}$ concentrations at the interface, limiting Zn^{2+} mass transport or slowing down the kinetics of zinc electrodeposition. $\text{Zn}(\text{H}_2\text{O})_6^{2+}$ exhibits a relatively low energy barrier in HER, and thus, at high current densities, AZIBs obtained fewer by-products on the zinc-coated/stripped zinc surface.

7. Summary and outlook

The study of inhibiting zinc dendrite formation in AZIBs continues to present several significant challenges. These challenges encompass material design, electrolyte stability, and separator engineering, all of which are directed towards the objective of restraining zinc dendrite formation to enhance the overall performance of AZIBs. Despite notable progress in mitigating zinc dendrite growth at the negative electrode in AZIBs, several unresolved issues persist. Future endeavors will be focused on addressing these challenges with the aim of further enhancing AZIBs performance and its potential applications. Potential research directions include:

1) A theoretical investigation into the mechanisms of zinc dendrites formation at the negative electrode. The major of current research is focused on the development of methods for suppression and elimination zinc dendrite growth, with the aiming of improving the cycling performance of AZIBs. Nevertheless, future research must investigate the fundamental mechanisms regulating zinc nucleation and growth on the negative electrode surface during the initial stages of deposition in greater depth. To achieve this goal, it will be necessary to adopt a multifaceted approach, encompassing experimental, computational, and theoretical calculations.

2) The integration of diverse strategies to jointly suppress or eliminate zinc dendrites. The current research strategies primarily focus on assessment of the impact of individual factors on zinc dendrite growth, including electrode additives, surface modifications, structural optimization, electrolyte adjustments, and separator enhancements. An effective integration of these strategies may facilitate a more comprehensive mitigation of dendrite formation.

3) Using in-situ techniques for tracking zinc ion electrodeposition. The deployment of sophisticated in-situ techniques to monitor the electroplating behavior of zinc ions offer considerable promise for attaining a comprehensive understanding of their deposition dynamics. Direct observation of authentic zinc nucleation and growth within operational batteries can contribute substantially to a deeper comprehension of the mechanisms governing zinc dendrite formation. This insight will guide the development of tailored strategies for dendrite growth inhibition.

These prospective research directions hold considerable potential to advance the field of AZIBs, address its extant challenges, enhance its performance, and facilitate progress toward greater sustainability and efficiency.

Acknowledgements

G. W. acknowledges for the scholarship from the China Scholarship Council (CSC), China, and the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan. Y. Y. and W. Y. acknowledge for scholarships from China Scholarship Council (CSC).

References

- [1] Kang K, Meng YS, Breger J, Grey CP, Ceder G. Electrodes with High Power and High Capacity for Rechargeable Lithium Batteries[J]. *Science*,2006, 311(5763): 977-980.
- [2] Schon TB, McAllister BT, Li P-F, Seferos DS. The Rise of Organic Electrode Materials for Energy Storage[J]. *Chem. Soc. Rev.*,2016, 45(22): 6345-6404.
- [3] Cano ZP, Banham D, Ye S, Hintennach A, Lu J, Fowler M, Chen Z. Batteries and Fuel Cells for Emerging Electric Vehicle Markets[J]. *Nature energy*,2018, 3(4): 279-289.
- [4] Blomgren GE. The Development and Future of Lithium Ion Batteries[J]. *J. Electrochem. Soc.*,2016, 164(1): A5019.
- [5] Lu J, Li L, Park J-B, Sun Y-K, Wu F, Amine K. Aprotic and Aqueous Li-O₂ Batteries[J]. *Chem. Rev.*,2014, 114(11): 5611-5640.
- [6] Wu G, Li X, Zhang Z, Dong P, Xu M, Peng H, Zeng X, Zhang Y, Liao S. Design of Ultralong-Life Li-Co₂ Batteries with Iro₂ Nanoparticles Highly Dispersed on Nitrogen-Doped Carbon Nanotubes[J]. *J. Mater. Chem. A*,2020, 8(7): 3763-3770.
- [7] Deng Y-P, Liang R, Jiang G, Jiang Y, Yu A, Chen Z. The Current State of Aqueous Zn-Based Rechargeable Batteries[J]. *ACS Energy Lett.*,2020, 5(5): 1665-1675.
- [8] Liang Y, Dong H, Aurbach D, Yao Y. Current Status and Future Directions of Multivalent Metal-Ion Batteries[J]. *Nature Energy*,2020, 5(9): 646-656.
- [9] Jia X, Liu C, Neale ZG, Yang J, Cao G. Active Materials for Aqueous Zinc Ion Batteries: Synthesis, Crystal Structure, Morphology, and Electrochemistry[J]. *Chem. Rev.*,2020, 120(15): 7795-7866.
- [10] Wang F, Borodin O, Gao T, Fan X, Sun W, Han F, Faraone A, Dura JA, Xu K, Wang C. Highly Reversible Zinc Metal Anode for Aqueous Batteries[J]. *Nat. Mater.*,2018, 17(6): 543-549.
- [11] Yuan L, Hao J, Kao C-C, Wu C, Liu H-K, Dou S-X, Qiao S-Z. Regulation Methods for the Zn/Electrolyte Interphase and the Effectiveness Evaluation in Aqueous Zn-Ion Batteries[J]. *Energy Environ. Sci.*,2021, 14(11): 5669-5689.
- [12] 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[J]. *Sci. Adv.*,2020, 6(21): eaba4098.
- [13] Li Q, Chen A, Wang D, Zhao Y, Wang X, Jin X, Xiong B, Zhi C. Tailoring the Metal Electrode Morphology Via Electrochemical Protocol Optimization for Long-Lasting Aqueous Zinc Batteries[J]. *Nat. Commun.*,2022, 13(1): 3699.
- [14] Wu G, Yang Y, Zhu R, Yang W, Yang H, Zhou H. The Pitfalls of Using Stainless Steel (Ss) Coin Cells in Aqueous Zinc Battery Research[J]. *Energy Environ. Sci.*,2023, 16(10): 4320-4325.
- [15] Tang D, Zhang X, Han D, Cui C, Han Z, Wang L, Li Z, Zhang B, Liu Y, Weng Z. Switching Hydrophobic Interface with Ionic Valves for Reversible Zinc Batteries[J]. *Adv. Mater.*,2024: 2406071.
- [16] Zhou L-F, Du T, Li J-Y, Wang Y-S, Gong H, Yang Q-R, Chen H, Luo W-B, Wang J-Z. A Strategy for Anode Modification for Future Zinc-Based Battery Application[J]. *Materials Horizons*,2022, 9(11): 2722-2751.
- [17] Sui B-b, Sha L, Wang P-f, Gong Z, Zhang Y-h, Wu Y-h, Zhao L-

- n, Tang J-j, Shi F-n. In Situ Zinc Citrate on the Surface of Zn Anode Improves the Performance of Aqueous Zinc-Ion Batteries[J]. *Journal of Energy Storage*,2024, 82: 110550.
- [18] Qiu K, Ma G, Wang Y, Liu M, Zhang M, Li X, Qu X, Yuan W, Nie X, Zhang N. Highly Compact Zinc Metal Anode and Wide - Temperature Aqueous Electrolyte Enabled by Acetamide Additives for Deep Cycling Zn Batteries[J]. *Adv. Funct. Mater.*,2024, 34(18): 2313358.
- [19] Xu D, Chen B, Ren X, Han C, Chang Z, Pan A, Zhou H. Selectively Etching-Off the Highly Reactive (002) Zn Facet Enables Highly Efficient Aqueous Zinc-Metal Batteries[J]. *Energy Environ. Sci.*,2024, 17(2): 642-654.
- [20] Zong Y, He H, Wang Y, Wu M, Ren X, Bai Z, Wang N, Ning X, Dou SX. Functionalized Separator Strategies toward Advanced Aqueous Zinc - Ion Batteries[J]. *Adv. Energy Mater.*,2023: 2300403.
- [21] Wu G, Zhu R, Yang W, Yang Y, Okagaki J, Lu Z, Sun J, Yang H, Yoo E. Extension of Aqueous Zinc Battery Life Using a Robust and Hydrophilic Polymer Separator[J]. *Adv. Funct. Mater.*,2024: 2316619.
- [22] Li B, Zeng Y, Zhang W, Lu B, Yang Q, Zhou J, He Z. Separator Designs for Aqueous Zinc-Ion Batteries[J]. *Science Bulletin*,2024.
- [23] Wippermann K, Schultze J, Kessel R, Penninger J. The Inhibition of Zinc Corrosion by Bisaminotriazole and Other Triazole Derivatives[J]. *Corros. Sci.*,1991, 32(2): 205-230.
- [24] He P, Chen Q, Yan M, Xu X, Zhou L, Mai L, Nan C-W. Building Better Zinc-Ion Batteries: A Materials Perspective[J]. *EnergyChem*,2019, 1(3): 100022.
- [25] Diggle J, Despic A, Bockris JM. The Mechanism of the Dendritic Electrocrystallization of Zinc[J]. *J. Electrochem. Soc.*,1969, 116(11): 1503.
- [26] Despic A, Diggle J, Bockris JM. Mechanism of the Formation of Zinc Dendrites[J]. *J. Electrochem. Soc.*,1968, 115(5): 507.
- [27] Matsushita M, Sano M, Hayakawa Y, Honjo H, Sawada Y. Fractal Structures of Zinc Metal Leaves Grown by Electrodeposition[J]. *Phys. Rev. Lett.*,1984, 53(3): 286-289.
- [28] Cogswell DA. Quantitative Phase-Field Modeling of Dendritic Electrodeposition[J]. *Physical Review E*,2015, 92(1): 011301.
- [29] Yurkiv V, Foroozan T, Ramasubramanian A, Ragone M, Shahbazian-Yassar R, Mashayek F. Understanding Zn Electrodeposits Morphology in Secondary Batteries Using Phase-Field Model[J]. *J. Electrochem. Soc.*,2020, 167(6): 060503.
- [30] Yufit V, Tariq F, Eastwood DS, Biton M, Wu B, Lee PD, Brandon NP. Operando Visualization and Multi-Scale Tomography Studies of Dendrite Formation and Dissolution in Zinc Batteries[J]. *Joule*,2019, 3(2): 485-502.
- [31] Yu W, Shang W, He Y, Zhao Z, Ma Y, Tan P. Unraveling the Mechanism of Non-Uniform Zinc Deposition in Rechargeable Zinc-Based Batteries with Vertical Orientation[J]. *Chem. Eng. J.*,2022, 431: 134032.
- [32] Lu X, Zhao C, Chen A, Guo Z, Liu N, Fan L, Sun J, Zhang N. Reducing Zn-Ion Concentration Gradient by SnO_2 -Immobilized Interface Coating for Dendrite-Free Zn Anode[J]. *Chem. Eng. J.*,2023, 451: 138772.
- [33] Zhang Q, Luan J, Huang X, Zhu L, Tang Y, Ji X, Wang H. Simultaneously Regulating the Ion Distribution and Electric Field to Achieve Dendrite - Free Zn Anode[J]. *Small*,2020, 16(35): 2000929.
- [34] Liu S, Mao J, Pang WK, Vongsivut J, Zeng X, Thomsen L, Wang Y, Liu J, Li D, Guo Z. Tuning the Electrolyte Solvation Structure to Suppress Cathode Dissolution, Water Reactivity, and Zn Dendrite Growth in Zinc - Ion Batteries[J]. *Adv. Funct. Mater.*,2021, 31(38): 2104281.
- [35] Yang Y, Yang H, Zhu R, Zhou H. High Reversibility at High Current Density: The Zinc Electrodeposition Principle Behind the "Trick"[J]. *Energy Environ. Sci.*,2023.
- [36] Zhai J, Yan J, Wang G, Chen S, Jin D, Zhang H, Zhao W, Zhang Z, Huang W. Surface Modification of Manganese Monoxide through Chemical Vapor Deposition to Attain High Energy Storage Performance for Aqueous Zinc-Ion Batteries[J]. *J. Colloid Interface Sci.*,2021, 601: 617-625.
- [37] Sun S, Wen Y, Billings A, Rajabi R, Wang B, Zhang K, Huang K. Protecting Zn Anodes by Atomic Layer Deposition of ZrO_2 to Extend the Lifetime of Aqueous Zn-Ion Batteries[J]. *Energy Advances*,2024, 3(1): 299-306.
- [38] Zheng J, Zhao Q, Tang T, Yin J, Quilty CD, Renderos GD, Liu X, Deng Y, Wang L, Bock DC. Reversible Epitaxial Electrodeposition of Metals in Battery Anodes[J]. *Science*,2019, 366(6465): 645-648.
- [39] Kang L, Cui M, Jiang F, Gao Y, Luo H, Liu J, Liang W, Zhi C. Nanoporous CaCO_3 Coatings Enabled Uniform Zn Stripping/Plating for Long - Life Zinc Rechargeable Aqueous Batteries[J]. *Adv. Energy Mater.*,2018, 8(25): 1801090.
- [40] An Y, Tian Y, Xiong S, Feng J, Qian Y. Scalable and Controllable Synthesis of Interface-Engineered Nanoporous Host for Dendrite-Free and High Rate Zinc Metal Batteries[J]. *ACS Nano*,2021, 15(7): 11828-11842.
- [41] 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[J]. *Nano Energy*,2021, 89: 106322.
- [42] Liu Y, Guo T, Liu Q, Xiong F, Huang M, An Y, Wang J, An Q, Liu C, Mai L. Ultrathin ZrO_2 Coating Layer Regulates Zn Deposition and Raises Long-Life Performance of Aqueous Zn Batteries[J]. *Mater. Today Energy*,2022, 28: 101056.
- [43] 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[J]. *Angew. Chem. Int. Ed. Engl.*,2020, 59(24): 9377-9381.
- [44] Zhao K, Wang C, Yu Y, Yan M, Wei Q, He P, Dong Y, Zhang Z, Wang X, Mai L. Ultrathin Surface Coating Enables Stabilized Zinc Metal Anode[J]. *Advanced Materials Interfaces*,2018, 5(16): 1800848.
- [45] Zhang Q, Luan J, Huang X, Wang Q, Sun D, Tang Y, Ji X, Wang H. Revealing the Role of Crystal Orientation of Protective Layers for Stable Zinc Anode[J]. *Nat. Commun.*,2020, 11(1): 3961.
- [46] Zhao R, Yang Y, Liu G, Zhu R, Huang J, Chen Z, Gao Z, Chen X, Qie L. Redirected Zn Electrodeposition by an Anti - Corrosion Elastic Constraint for Highly Reversible Zn Anodes[J]. *Adv. Funct. Mater.*,2021, 31(2): 2001867.
- [47] Guo Z, Fan L, Zhao C, Chen A, Liu N, Zhang Y, Zhang N. A Dynamic and Self - Adapting Interface Coating for Stable Zn-Metal Anodes[J]. *Adv. Mater.*,2022, 34(2): 2105133.
- [48] 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[J]. *Energy Environ. Sci.*,2020, 13(2): 503-510.
- [49] He H, Tong H, Song X, Song X, Liu J. Highly Stable Zn Metal Anodes Enabled by Atomic Layer Deposited Al_2O_3 Coating for Aqueous Zinc-Ion Batteries[J]. *J. Mater. Chem. A*,2020, 8(16): 7836-7846.
- [50] He P, Huang J. Chemical Passivation Stabilizes Zn Anode[J]. *Adv. Mater.*,2022, 34(18): 2109872.
- [51] Wu K, Yi J, Liu X, Sun Y, Cui J. Regulating Zn Deposition Via an Artificial Solid-Electrolyte Interface with Aligned Dipoles for Long Life Zn Anode. *Nano-Micro Lett.* 13, 79 (2021). In.
- [52] Zou P, Zhang R, Yao L, Qin J, Kisslinger K, Zhuang H, Xin HL. Ultrahigh-Rate and Long-Life Zinc-Metal Anodes Enabled by Self - Accelerated Cation Migration[J]. *Adv. Energy Mater.*,2021, 11(31): 2100982.
- [53] Hieu LT, So S, Kim IT, Hur J. Zn Anode with Flexible B-Pvdf Coating for Aqueous Zn-Ion Batteries with Long Cycle Life[J]. *Chem. Eng. J.*,2021, 411: 128584.
- [54] Wang Y, Guo T, Yin J, Tian Z, Ma Y, Liu Z, Zhu Y, Alshareef HN. Controlled Deposition of Zinc - Metal Anodes Via Selectively Polarized Ferroelectric Polymers[J]. *Adv. Mater.*,2022, 34(4): 2106937.

- [55] 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[J]. *Adv. Funct. Mater.*,2020, 30(13): 1908528.
- [56] Jiang Y, Wan Z, He X, Yang J. Fine - Tuning Electrolyte Concentration and Metal - Organic Framework Surface toward Actuating Fast Zn²⁺ Dehydration for Aqueous Zn - Ion Batteries[J]. *Angew. Chem.*,2023, 135(44): e202307274.
- [57] Xu D, Ren X, Xu Y, Wang Y, Zhang S, Chen B, Chang Z, Pan A, Zhou H. Highly Stable Aqueous Zinc Metal Batteries Enabled by an Ultrathin Crack - Free Hydrophobic Layer with Rigid Sub-Nanochannels[J]. *Advanced Science*,2023, 10(27): 2303773.
- [58] Parker JF, Chervin CN, Pala IR, Machler M, Burz MF, Long JW, Rolison DR. Rechargeable Nickel-3d Zinc Batteries: An Energy-Dense, Safer Alternative to Lithium-Ion[J]. *Science*,2017, 356(6336): 415-418.
- [59] Yang Z, Zhang Q, Li W, Xie C, Wu T, Hu C, Tang Y, Wang H. A Semi - Solid Zinc Powder - Based Slurry Anode for Advanced Aqueous Zinc - Ion Batteries[J]. *Angew. Chem. Int. Ed.*,2023, 62(3): e202215306.
- [60] Zhu R, Xiong Z, Yang H, Huang T, Jeong S, Kowalski D, Kitano S, Aoki Y, Habazaki H, Zhu C. A Low-Cost and Non-Corrosive Electropolishing Strategy for Long-Life Zinc Metal Anode in Rechargeable Aqueous Battery[J]. *Energy Storage Mater.*,2022, 46: 223-232.
- [61] Xu D, Chen B, Ren X, Chao H, Chang Z, Pan A, Zhou H. Selectively Etching-Off Highly Reactive (002) Zn Facet Enable Highly Efficient Aqueous Zinc-Metal Batteries[J]. *Energy Environ. Sci.*,2023.
- [62] Cai Z, Wang J, Lu Z, Zhan R, Ou Y, Wang L, Dahbi M, Alami J, Lu J, Amine K, Sun Y. Ultrafast Metal Electrodeposition Revealed by in Situ Optical Imaging and Theoretical Modeling Towards Fast-Charging Zn Battery Chemistry[J]. *Angew. Chem. Int. Ed. Engl.*,2022, 61(14): e202116560.
- [63] Liang Y, Qiu M, Sun P, Mai W. Comprehensive Review of Electrolyte Modification Strategies for Stabilizing Zn Metal Anodes[J]. *Adv. Funct. Mater.*,2023, 33(51): 2304878.
- [64] Yang W, Du X, Zhao J, Chen Z, Li J, Xie J, Zhang Y, Cui Z, Kong Q, Zhao Z. Hydrated Eutectic Electrolytes with Ligand-Oriented Solvation Shells for Long-Cycling Zinc-Organic Batteries[J]. *Joule*,2020, 4(7): 1557-1574.
- [65] Wan J, Wang R, Liu Z, Zhang S, Hao J, Mao J, Li H, Chao D, Zhang L, Zhang C. Hydrated Eutectic Electrolyte Induced Bilayer Interphase for High-Performance Aqueous Zn-Ion Batteries with 100 ° C Wide - Temperature Range[J]. *Adv. Mater.*,2024, 36(11): 2310623.
- [66] Yang W, Wu G, Zhu R, Choe Y-K, Sun J, Yang Y, Yang H, Yoo E. Synergistic Cation Solvation Reorganization and Fluorinated Interphase for High Reversibility and Utilization of Zinc Metal Anode[J]. *ACS nano*,2023.
- [67] Zhuang W, Chen Q, Hou Z, Sun Z, Zhang T, Wan J, Huang L. Examining Concentration - Reliant Zn Deposition/Stripping Behavior in Organic Alcohol/Sulfones - Modified Aqueous Electrolytes[J]. *Small*,2023: 2300274.
- [68] Li Z, Liao Y, Wang Y, Cong J, Ji H, Huang Z, Huang Y. A Co-Solvent in Aqueous Electrolyte Towards Ultralong-Life Rechargeable Zinc-Ion Batteries[J]. *Energy Storage Mater.*,2023, 56: 174-182.
- [69] Yang J, Zhang Y, Li Z, Xu X, Su X, Lai J, Liu Y, Ding K, Chen L, Cai YP. Three Birds with One Stone: Tetramethylurea as Electrolyte Additive for Highly Reversible Zn - Metal Anode[J]. *Adv. Funct. Mater.*,2022, 32(49): 2209642.
- [70] Xu D, Ren X, Li H, Zhou Y, Chai S, Chen Y, Li H, Bai L, Chang Z, Pan A. Chelating Additive Regulating Zn - Ion Solvation Chemistry for Highly Efficient Aqueous Zinc - Metal Battery[J]. *Angew. Chem. Int. Ed.*,2024, 63(21): e202402833.
- [71] Huang J, Zhong Y, Fu H, Zhao Y, Li S, Xie Y, Zhang H, Lu B, Chen L, Liang S. Interfacial Biomacromolecular Engineering toward Stable Ah - Level Aqueous Zinc Batteries[J]. *Adv. Mater.*,2024: 2406257.
- [72] Chen W, Guo S, Qin L, Li L, Cao X, Zhou J, Luo Z, Fang G, Liang S. Hydrogen Bond - Functionalized Massive Solvation Modules Stabilizing Bilateral Interfaces[J]. *Adv. Funct. Mater.*,2022, 32(20): 2112609.
- [73] Qin H, Kuang W, Hu N, Zhong X, Huang D, Shen F, Wei Z, Huang Y, Xu J, He H. Building Metal - Molecule Interface Towards Stable and Reversible Zn Metal Anodes for Aqueous Rechargeable Zinc Batteries[J]. *Adv. Funct. Mater.*,2022, 32(47): 2206695.
- [74] Meng C, He W, Jiang L, Huang Y, Zhang J, Liu H, Wang JJ. Ultra - Stable Aqueous Zinc Batteries Enabled by B - Cyclodextrin: Preferred Zinc Deposition and Suppressed Parasitic Reactions[J]. *Adv. Funct. Mater.*,2022, 32(47): 2207732.
- [75] 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[J]. *Adv. Energy Mater.*,2022, 12(2): 2102780.
- [76] Li TC, Lim Y, Li XL, Luo S, Lin C, Fang D, Xia S, Wang Y, Yang HY. A Universal Additive Strategy to Reshape Electrolyte Solvation Structure toward Reversible Zn Storage[J]. *Adv. Energy Mater.*,2022, 12(15): 2103231.
- [77] Hao J, Yuan L, Zhu Y, Jaroniec M, Qiao SZ. Triple - Function Electrolyte Regulation toward Advanced Aqueous Zn - Ion Batteries[J]. *Adv. Mater.*,2022, 34(44): 2206963.
- [78] Wang Y, Wang T, Bu S, Zhu J, Wang Y, Zhang R, Hong H, Zhang W, Fan J, Zhi C. Sulfolane-Containing Aqueous Electrolyte Solutions for Producing Efficient Ampere-Hour-Level Zinc Metal Battery Pouch Cells[J]. *Nat. Commun.*,2023, 14(1): 1828.
- [79] Xiao P, Wu Y, Fu J, Liang J, Zhao Y, Ma Y, Zhai T, Li H. Enabling High-Rate and High-Areal-Capacity Zn Deposition Via an Interfacial Preferentially Adsorbed Molecular Layer[J]. *ACS Energy Lett.*,2022, 8(1): 31-39.
- [80] Li H, Ren Y, Zhu Y, Tian J, Sun X, Sheng C, He P, Guo S, Zhou H. A Bio - Inspired Trehalose Additive for Reversible Zinc Anodes with Improved Stability and Kinetics[J]. *Angew. Chem.*,2023, 135(41): e202310143.
- [81] Yang Y, Hua H, Lv Z, Zhang M, Liu C, Wen Z, Xie H, He W, Zhao J, Li CC. Reconstruction of Electric Double Layer for Long - Life Aqueous Zinc Metal Batteries[J]. *Adv. Funct. Mater.*,2023, 33(10): 2212446.
- [82] Lin Y, Zhang M, Hu Y, Zhang S, Xu Z, Feng T, Zhou H, Wu M. Nitrogen-Doped Carbon Coated Zinc as Powder-Based Anode with Pva-Gel Electrolyte Enhancing Cycling Performance for Zinc-Ion Batteries[J]. *Chem. Eng. J.*,2023, 472: 145136.
- [83] Wang Q, Liu Y, Zhang Z, Cai P, Li H, Zhou M, Wang W, Wang K, Jiang K. Activating the Intrinsic Zincophilicity of Pam Hydrogel to Stabilize the Metal - Electrolyte Dynamic Interface for Stable and Long - Life Zinc Metal Batteries[J]. *ChemSusChem*,2024: e202400479.
- [84] Deng Y, Wu Y, Wang L, Zhang K, Wang Y, Yan L. Polysaccharide Hydrogel Electrolytes with Robust Interfacial Contact to Electrodes for Quasi-Solid State Flexible Aqueous Zinc Ion Batteries with Efficient Suppressing of Dendrite Growth[J]. *J. Colloid Interface Sci.*,2023, 633: 142-154.
- [85] Huang Y, Zhang J, Liu J, Li Z, Jin S, Li Z, Zhang S, Zhou H. Flexible and Stable Quasi-Solid-State Zinc Ion Battery with Conductive Guar Gum Electrolyte[J]. *Mater. Today Energy*,2019, 14: 100349.
- [86] Wang F, Zhang J, Lu H, Zhu H, Chen Z, Wang L, Yu J, You C, Li W, Song J. Production of Gas-Releasing Electrolyte-Replenishing Ah-Scale Zinc Metal Pouch Cells with Aqueous Gel Electrolyte[J]. *Nat. Commun.*,2023, 14(1): 4211.
- [87] Hao Y, Feng D, Hou L, Li T, Jiao Y, Wu P. Gel Electrolyte

- Constructing Zn (002) Deposition Crystal Plane toward Highly Stable Zn Anode[J]. *Advanced Science*,2022, 9(7): 2104832.
- [88] He Q, Chang Z, Zhong Y, Chai S, Fu C, Liang S, Fang G, Pan A. Highly Entangled Hydrogel Enables Stable Zinc Metal Batteries Via Interfacial Confinement Effect[J]. *ACS Energy Lett.*,2023, 8(12): 5253-5263.
- [89] Liu T, Hong J, Wang J, Xu Y, Wang Y. Uniform Distribution of Zinc Ions Achieved by Functional Supramolecules for Stable Zinc Metal Anode with Long Cycling Lifespan[J]. *Energy Storage Mater.*,2022, 45: 1074-1083.
- [90] Qin Y, Liu P, Zhang Q, Wang Q, Sun D, Tang Y, Ren Y, Wang H. Advanced Filter Membrane Separator for Aqueous Zinc-Ion Batteries[J]. *Small*,2020, 16(39): e2003106.
- [91] Li L, Peng J, Jia X, Zhu X, Meng B, Yang K, Chu D, Yang N, Yu J. Pbc@ Cellulose-Filter Paper Separator Design with Efficient Ion Transport Properties toward Stabilized Zinc-Ion Battery[J]. *Electrochim. Acta*,2022, 430: 141129.
- [92] 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[J]. *Energy Storage Mater.*,2022, 44: 57-65.
- [93] Lee B-S, Cui S, Xing X, Liu H, Yue X, Petrova V, Lim H-D, Chen R, Liu P. Dendrite Suppression Membranes for Rechargeable Zinc Batteries[J]. *ACS Appl. Mater. Inter.*,2018, 10(45): 38928-38935.
- [94] Wang Y, Long J, Hu J, Sun Z, Meng L. Polyvinyl Alcohol/Lyocell Dual-Layer Paper-Based Separator for Primary Zinc-Air Batteries[J]. *J. Power Sources*,2020, 453: 227853.
- [95] Liu Y, Liu S, Xie X, Li Z, Wang P, Lu B, Liang S, Tang Y, Zhou J. A Functionalized Separator Enables Dendrite - Free Zn Anode Via Metal-Polydopamine Coordination Chemistry[J]. *InfoMat*,2023, 5(3): e12374.
- [96] Yang H, Zhu R, Yang Y, Lu Z, Chang Z, He P, Zhu C, Kitano S, Aoki Y, Habazaki H. Sustainable High-Energy Aqueous Zinc-Manganese Dioxide Batteries Enabled by Stress-Governed Metal Electrodeposition and Fast Zinc Diffusivity[J]. *Energy Environ. Sci.*,2023, 16(5): 2133-2141.
- [97] Song Y, Ruan P, Mao C, Chang Y, Wang L, Dai L, Zhou P, Lu B, Zhou J, He Z. Metal-Organic Frameworks Functionalized Separators for Robust Aqueous Zinc-Ion Batteries[J]. *Nano-Micro Lett.*,2022, 14(1): 218.
- [98] Su Y, Liu B, Zhang Q, Peng J, Wei C, Li S, Li W, Xue Z, Yang X, Sun J. Printing - Scalable Ti3c2tx Mxene - Decorated Janus Separator with Expedited Zn2+ Flux toward Stabilized Zn Anodes[J]. *Adv. Funct. Mater.*,2022, 32(32): 2204306.
- [99] Yang Z, Li W, Zhang Q, Xie C, Ji H, Tang Y, Li Y, Wang H. A Piece of Common Cellulose Paper but with Outstanding Functions for Advanced Aqueous Zinc-Ion Batteries[J]. *Mater. Today Energy*,2022, 28.
- [100] Yang S, Zhang Y, Zhang Y, Deng J, Chen N, Xie S, Ma Y, Wang Z. Designing Anti - Swelling Nanocellulose Separators with Stable and Fast Ion Transport Channels for Efficient Aqueous Zinc - Ion Batteries[J]. *Adv. Funct. Mater.*,2023: 2304280.
- [101] 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[J]. *Nano Energy*,2021, 89.
- [102] Sun Y-Y, Yan L, Zhang Q, Wang T-B, Zha Y-C, Fan L, Jiang H-F. Mixed Cellulose Ester Membrane as an Ion Redistributor to Stabilize Zinc Anode in Aqueous Zinc Ion Batteries[J]. *J. Colloid Interface Sci.*,2023, 641: 610-618.
- [103] Yang Y, Chen T, Zhu M, Gao G, Wang Y, Nie Q, Jiang Y, Xiong T, Lee WSV, Xue J. Regulating Dendrite-Free Zn Deposition by a Self-Assembled Oh-Terminated Sio2 Nanosphere Layer toward a Zn Metal Anode[J]. *ACS Appl. Mater. Inter.*,2022, 14(33): 37759-37770.
- [104] Xu L, Meng T, Zheng X, Li T, Brozena AH, Mao Y, Zhang Q, Clifford BC, Rao J, Hu L. Nanocellulose - Carboxymethylcellulose Electrolyte for Stable, High - Rate Zinc-Ion Batteries[J]. *Adv. Funct. Mater.*,2023: 2302098.
- [105] Zhang Y, Liu Z, Li X, Fan L, Shuai Y, Zhang N. Loosening Zinc Ions from Separator Boosts Stable Zn Plating/Stripping Behavior for Aqueous Zinc Ion Batteries[J]. *Adv. Energy Mater.*,2023, 13(42): 2302126.
- [106] Yang X, Wu W, Liu Y, Lin Z, Sun X. Chitosan Modified Filter Paper Separators with Specific Ion Adsorption to Inhibit Side Reactions and Induce Uniform Zn Deposition for Aqueous Zn Batteries[J]. *Chem. Eng. J.*,2022, 450.
- [107] Yang H, Qiao Y, Chang Z, Deng H, Zhu X, Zhu R, Xiong Z, He P, Zhou H. Reducing Water Activity by Zeolite Molecular Sieve Membrane for Long-Life Rechargeable Zinc Battery[J]. *Adv. Mater.*,2021, 33(38): e2102415.
- [108] Li Z, Wu X, Yu X, Zhou S, Qiao Y, Zhou H, Sun SG. Long-Life Aqueous Zn-I2 Battery Enabled by a Low-Cost Multifunctional Zeolite Membrane Separator[J]. *Nano Lett.*,2022, 22(6): 2538-2546.
- [109] Yang H, Yang Y, Yang W, Wu G, Zhu R. Correlating Hydrogen Evolution and Zinc Deposition/Dissolution Kinetics to the Cyclability of Metallic Zinc Electrodes[J]. *Energy Environ. Sci.*,2024.

水性锌离子电池的无枝晶策略：结构、电解质和隔膜

吴刚，杨武海，杨洋，杨慧军*

（筑波大学系统与信息工程研究生院，日本筑波市天王台 1-1-1， 305-8573）

摘要：能源需求的持续增长和环境污染的加剧构成了亟待解决的主要挑战。开发和利用风能和太阳能等可再生、可持续的清洁能源至关重要。然而，这些间歇性能源的不稳定性使得对储能系统的需求日益迫切。水系锌离子电池（AZIBs）因其独特优势，如高能量密度、成本效益、环保性和安全性，受到广泛关注。然而，AZIBs 面临着重大挑战，主要是锌枝晶的形成严重影响了电池的稳定性和寿命，导致电池失效。因此，减少锌枝晶的形成对于提高 AZIBs 的性能至关重要。本综述系统而全面地梳理了当前抑制锌枝晶形成的策略和进展。通过综合分析锌阳极、电解质、隔膜设计和改性以及其他新机制的最新发展，为研究人员提供一个透彻的理解，以指导未来的研究，推动水性锌离子电池技术的发展。

关键词：水系锌离子电池 无枝晶 锌阳极 电解质优化 隔膜设计 析氢反应