

# Research progress on electrolyte additives for aqueous zinc-ion batteries

## 1. Introduction

According to a report released by the World Meteorological Organization, key climate change indicators such as rising greenhouse gas concentrations, sea level rise, ocean heat, and ocean acidification have continued to deteriorate in recent years [1]. Excessive anthropogenic carbon dioxide emissions are the primary factors driving global-scale climate changes, which have lasting and harmful impacts on sustainable development and the ecological environment. To further increase the proportion and utilization efficiency of renewable energy, it is necessary to establish corresponding energy storage systems as essential technical support, which is also a critical step in advancing the transformation of the energy structure [2]. Secondary batteries, as electrochemical energy storage devices with grid-scale application potential, have attracted increasing attention and research [3]. An ideal secondary battery should be composed of environmentally friendly and low-cost materials while safely delivering high reversible capacity and excellent performance under various operating conditions. Lithium-ion batteries (LIBs) have been widely used in large-scale energy storage systems, new energy vehicles, portable electronic devices, and other fields due to their high energy density (200–300 Wh/kg) and long cycle life. However, recent incidents such as spontaneous combustion of mobile phones serve as constant reminders that safety is a critical requirement for secondary batteries. Additionally, the scarcity of resources such as lithium, cobalt, and nickel, along with their rising costs, poses challenges for large-scale industrial applications.

Compared to LIBs, environmentally friendly aqueous batteries (ABs) offer high power density and tolerance to improper operations, presenting a potential solution for safe, economical, and scalable energy storage devices [4]. Among various ABs, aqueous zinc-ion batteries (AZIBs) are considered a promising new electrochemical energy storage technology due to their high safety, cost-

effectiveness, and high-power density ( $\sim 12$  kW/kg) [5]. Zinc-ion batteries are rechargeable secondary batteries with a structure similar to LIBs, consisting of a cathode, anode, electrolyte, separator, and current collectors. Among these, cathode, anode, and electrolyte are critical components determining battery performance. Common AZIB electrolytes include hydrogel electrolytes, ionic liquids, water-in-salt electrolytes, and additive-containing electrolytes. The design and selection of AZIB electrolytes must consider fundamental characteristics such as ionic conductivity, electrochemical stability window, and chemical stability. Currently, the most widely used AZIB electrolyte is liquid-based, primarily consisting of neutral or weakly acidic (near-neutral,  $\text{pH} = 4\text{--}6$ ) aqueous solutions containing zinc ions [6]. Zinc sulfate is one of the most commonly used zinc salts, as it dissolves well in water to form aqueous electrolytes with good electrochemical performance and excellent compatibility with zinc anodes [7]. The anode material is typically pure-phase zinc foil or zinc powder. As a naturally abundant, low-cost, non-toxic, and safe metal with high theoretical capacity, zinc is considered an ideal anode material. However, irreversible zinc dendrite growth and side reactions result in poor cycling stability and low Coulombic efficiency (CE) for zinc anodes. To address these challenges, researchers have explored various approaches, such as introducing electrolyte additives or modifying the intrinsic structure of zinc-based anodes. Interface engineering for zinc anodes is considered a viable strategy, including surface modification and electrolyte additives. Among these, electrolyte additives for zinc anodes have gained widespread attention in recent years as an efficient and straightforward optimization method [8]. These additives offer advantages such as simplicity, environmental friendliness, cost-effectiveness, and good compatibility with existing battery technologies (including electrolytes, separators, and zinc anode technologies). Particularly for issues like dendrite formation and hydrogen evolution corrosion during zinc deposition, even trace amounts of electrolyte additives can effectively regulate the anode/electrolyte interface. On one hand, they facilitate uniform  $\text{Zn}^{2+}$  deposition, suppressing dendrite formation; on the other hand, they can adsorb onto the electrode surface, reducing water-electrode contact or altering the solvation structure to lower water activity and mitigate side reactions such as hydrogen evolution. Zinc anode electrolyte additives are mainly categorized into inorganic additives (ionic additives, oxides, and other inorganic compounds such as carbon and graphene oxide) and organic additives (e.g., polyethylene oxide (PEO), polyacrylamide (PAM)) [9].

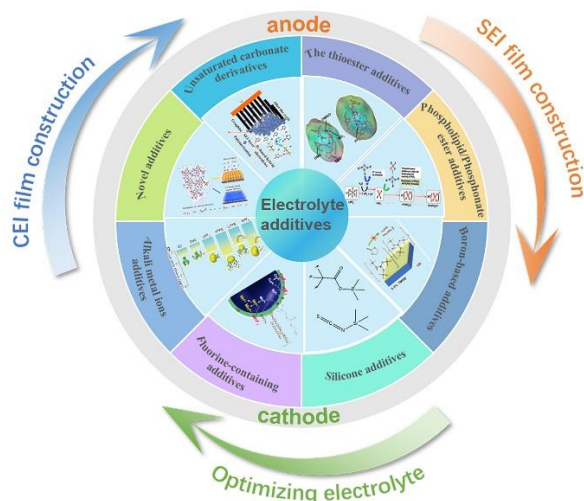


Fig. 1 Effects of additive strategies on the electrolyte, cathode and anode[10]

## 2. Challenges Associated with Zinc Anodes

Metallic zinc is widely used as the anode material in AZIBs due to its low redox potential ( $-0.76$  V vs. SHE), high theoretical capacity ( $820 \text{ mAh} \cdot \text{g}^{-1}$ ), and good stability in aqueous environments [11], where SHE (standard hydrogen electrode) represents the standard hydrogen electrode. However, the highly electrochemically active zinc anode inevitably forms dendrites during cycling. These protruding dendrites lead to uneven local electric fields and electrolyte distribution, exacerbating the "tip effect" and ultimately piercing the separator, causing battery short-circuit failure[12]. Simultaneously, the electrode-electrolyte interface in AZIBs undergoes a hydrogen evolution reaction (HER), transitioning from the liquid phase to the gas phase. This reaction increases internal battery pressure, leading to continuous expansion. Additionally, HER on the zinc metal surface elevates the concentration of  $\text{OH}^-$  in the solution, causing local pH fluctuations. The generated  $\text{OH}^-$  further participates in inside reactions on the anode surface, resulting in metal corrosion [13]. These issues inevitably degrade battery performance, including capacity, Coulombic efficiency (CE), and cycle life, significantly hindering the transition of AZIBs from the experimental stage to commercialization.

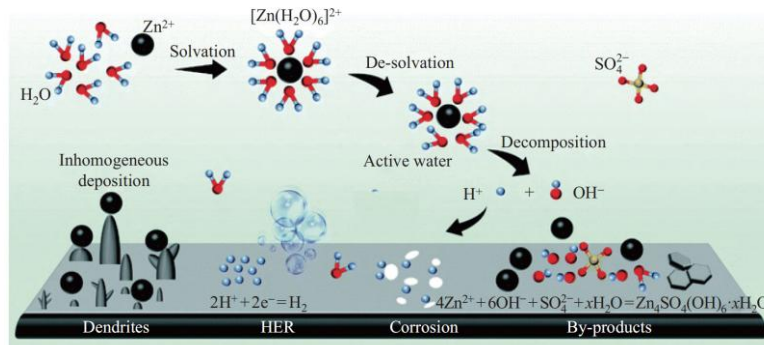
### 2.1 Growth of Zinc Dendrites

The formation of zinc dendrites is one of the critical challenges that must be addressed for zinc anodes in AZIBs [14]. The impact of zinc dendrites on anode performance cannot be overlooked—

their loose structure makes them prone to detaching from the electrode surface, forming "dead zinc," which reduces the utilization efficiency of the zinc anode. Moreover, dendrites growing on the zinc anode may pierce the separator, leading to short circuits, battery failure, and safety hazards[10]. The growth cycle of zinc dendrites can be divided into three stages: initial formation, dissolution, and regeneration. Zinc deposition begins with nucleation, where the migration of zinc ions to nucleation sites at the interface is primarily driven by the electric field. The free energy of the zinc reduction reaction indicates that forming a new phase requires overcoming a certain nucleation barrier. After nucleation, zinc continues to deposit on the initial layer [15]. zinc growth is a diffusion-controlled process influenced by both the electric field and concentration gradients. The nucleation process also plays a crucial role in zinc deposition. Non-uniform nucleation and random zinc distribution strongly affect the electric field and ion distribution, thereby disrupting the relatively balanced electric field at the interface. Since zinc growth depends on electric field strength and ion concentration, electrons and ions tend to accumulate at the tips of zinc nuclei, accelerating dendrite growth—a phenomenon known as the "tip effect" [16].

## **2.2 Side Reactions**

In zinc-ion batteries, the hydrogen evolution reaction (HER) occurs primarily for two reasons. On one hand, since the standard reduction potential of  $\text{Zn}^{2+}/\text{Zn}$  ( $-0.76$  V vs. SHE) is lower than that of the standard hydrogen electrode ( $0$  V vs. SHE), HER takes place before zinc deposition [17]. HER is a complex process influenced not only by reaction potential but also by the surface state of the electrode material, the properties of the electrode material, and the reaction temperature. According to the Tafel equation, metallic zinc exhibits a relatively high hydrogen evolution overpotential in aqueous environments, which to some extent suppresses HER[18]. On the other hand, chemical corrosion occurs when metallic zinc comes into contact with electrolyte, also generating hydrogen gas. Even in neutral or weakly acidic electrolytes, metallic zinc inevitably undergoes side reactions with the electrolyte, producing  $\text{H}_2$ . The hydrogen evolution reaction not only reduces the cycling reversibility of the zinc anode and the Coulombic efficiency of the battery, leading to continuous zinc loss, but the released  $\text{H}_2$  also increases internal battery pressure, causing swelling and electrolyte leakage.



**Fig. 2** Formation process of the existing problems on the Zn anode [10]

### 3. Electrolyte Additives for Zinc Anode Optimization

In aqueous electrolytes, zinc anodes inevitably face issues such as dendrite growth and side reactions, the causes of which were discussed in Section 1. Among the modification strategies to address these challenges, electrolyte additives can simultaneously suppress zinc dendrite growth and side reactions, significantly improving the battery's electrochemical performance [19]. Below, we focus on the research progress of electrolyte additives and their improvement mechanisms.

#### 3.1 Suppressing Zinc Dendrites

The growth of zinc dendrites involves the following processes: First,  $\text{Zn}^{2+}$  in the electrolyte undergoes desolvation and adsorbs onto the anode surface, where initial defects such as protrusions and steps exist [20]. To minimize surface energy, these ions diffuse along the interface and aggregate at these defect sites, forming large protrusions. Subsequently,  $\text{Zn}^{2+}$  in the solution tends to reduce and deposit on existing protrusions, causing them to grow and eventually form dendrites[21]. Dendrite growth severely impacts the battery's cycling stability and efficiency. Electrolyte additives, as an effective strategy to inhibit dendrite formation, have been extensively studied. Different types of additives employ distinct mechanisms to suppress dendrite growth: (1) Inorganic electrolyte additives, primarily regulate  $\text{Zn}^{2+}$  deposition sites through ion synergistic effects, crystal orientation induction, or coordination state modulation, thereby achieving uniform Zn deposition layers. (2) Organic electrolyte additives promote homogeneous nucleation sites by chemical adsorption, chelation, or ion flux regulation, enhancing nucleation kinetics to form compact and uniform Zn deposits [22]. Among various regulation strategies, the electrostatic shielding mechanism and surface texture modification of zinc anodes have shown particularly significant effects in suppressing dendrite growth and promoting uniform zinc deposition, making them widely studied and applied

in AZIBs.

### **3.1.1 Electrostatic Shielding**

Na<sub>2</sub>SO<sub>4</sub>, as an ionic additive, can effectively regulate electrostatic shielding in ZnSO<sub>4</sub> electrolytes [23]. During cycling, protrusions on the electrode surface act as charge centers, leading to continuous charge accumulation and eventual dendrite formation. Na<sup>+</sup>, with its lower reduction potential, preferentially adsorbs onto these protrusions, forming a monolayer electrostatic shielding layer[24]. This layer repels Zn<sup>2+</sup>, preventing its aggregation at the protrusions and thereby suppressing dendrite growth.

### **3.2 Suppressing Side Reactions**

The addition of organic electrolyte additives with anti-solvation properties can effectively inhibit side reactions. These additives typically regulate the electrolyte's solvation structure at the molecular level and exhibit strong coordination ability with Zn<sup>2+</sup>, significantly enhancing the reversibility of the zinc anode[25]. The structure and composition of the additives—such as carbon chain length, spatial configuration, and molecular polarity—play a crucial role in modulating the solvation structure. These parameters influence the hydrogen bond network in the solution by forming hydrogen bonds with H<sub>2</sub>O molecules, thereby improving the deposition environment on the anode surface and reducing H<sub>2</sub>O content[26]. Moreover, additives with strong coordination ability to Zn<sup>2+</sup> can modify or even replace the H<sub>2</sub>O coordination in the [Zn(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> complex, optimizing the solvation structure.

### **3.3 Constructing a Stable Solid Electrolyte Interface**

The in-situ formation of a solid electrolyte interface (SEI) on the anode surface through electrolyte additives can effectively mitigate side reactions such as corrosion[27]. The formation of an in-situ SEI layer is closely related to the decomposition of solvents and additives in the electrolyte. The SEI structure primarily consists of a compact inner layer and a porous outer layer: The inner SEI layer mainly contains elements such as Zn, F, and O, exhibiting dense structure and excellent mechanical properties. This layer reduces direct contact between the Zn electrode and the electrolyte, alleviating corrosion caused by side reactions like hydrogen evolution while also suppressing Zn dendrite formation to some extent[28]. The outer SEI layer is predominantly composed of organic compounds, characterized by porosity and good flexibility. It demonstrates strong compatibility with both the inner SEI layer and the surrounding electrolyte, playing a crucial role in adhering to

the inner SEI to prevent cracking and facilitating  $\text{Zn}^{2+}$  transport [29]. Optimizing the electrolyte with additives enables the construction of a stable SEI, modifies the solvation structure of  $\text{Zn}^{2+}$  in the electrolyte, increases the availability of free Zn ions, and widens the electrochemical stability window of the electrolyte, thereby suppressing various side reactions.

#### **4. Conclusion and Outlook**

Zinc is abundant, low-cost, and environmentally friendly, making zinc-ion batteries (ZIBs) a highly promising candidate for next-generation energy storage devices. However, several challenges remain before their commercialization can be realized. Future research should focus on the following aspects:

(1) Mechanism of Dendrite Formation: The understanding of zinc dendrite growth mechanisms on the anode surface remains incomplete, and there are still disagreements regarding the factors influencing ZIB performance. Advanced modeling and simulation techniques should be employed to deepen the study of dendrite formation and develop solutions to suppress its growth.

(2) Comprehensive Optimization of ZIBs: Optimization strategies should not only focus on enabling long-term  $\text{Zn}^{2+}$  deposition/stripping but also address key issues such as providing efficient ion migration pathways and inducing uniform zinc deposition. A holistic approach is needed to ensure compatibility and coordination among all battery components. Combining anode modifications with electrolyte optimization could significantly enhance ZIB performance.

(3) Environmental and Economic Considerations: Future research must prioritize environmentally friendly, highly recyclable, and low-cost materials to ensure sustainable development and large-scale deployment of ZIBs.

By addressing these challenges, ZIBs can move closer to practical applications, offering a viable and sustainable alternative for energy storage.

## References

- [1] O. Hoegh-Guldberg *et al.*, "The human imperative of stabilizing global climate change at 1.5°C," *Science*, vol. 365, no. 6459, p. eaaw6974, 2019/09/20 2019.
- [2] S. VijayaVenkataRaman, S. Iniyar, and R. Goic, "A review of climate change, mitigation and adaptation," *Renewable and Sustainable Energy Reviews*, vol. 16, no. 1, pp. 878-897, 2012/01/01/ 2012.
- [3] C. S. Lai and M. D. McCulloch, "Levelized cost of electricity for solar photovoltaic and electrical energy storage," *Applied Energy*, vol. 190, pp. 191-203, 2017/03/15/ 2017.
- [4] D. Chao *et al.*, "Roadmap for advanced aqueous batteries: From design of materials to applications," *Science Advances*, vol. 6, no. 21, p. eaba4098.
- [5] D. Chao *et al.*, "An Electrolytic Zn–MnO<sub>2</sub> Battery for High-Voltage and Scalable Energy Storage," *Angewandte Chemie International Edition*, vol. 58, no. 23, pp. 7823-7828, 2019/06/03 2019.
- [6] N. Zhang *et al.*, "Cation-Deficient Spinel ZnMn<sub>2</sub>O<sub>4</sub> Cathode in Zn(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> Electrolyte for Rechargeable Aqueous Zn-Ion Battery," *Journal of the American Chemical Society*, vol. 138, no. 39, pp. 12894-12901, 2016/10/05 2016.
- [7] C. Liu, X. Xie, B. Lu, J. Zhou, and S. Liang, "Electrolyte Strategies toward Better Zinc-Ion Batteries," *ACS Energy Letters*, vol. 6, no. 3, pp. 1015-1033, 2021/03/12 2021.
- [8] Y. Geng *et al.*, "Electrolyte additive engineering for aqueous Zn ion batteries," *Energy Storage Materials*, vol. 51, pp. 733-755, 2022/10/01/ 2022.
- [9] L. Yuan *et al.*, "Regulation methods for the Zn/electrolyte interphase and the effectiveness evaluation in aqueous Zn-ion batteries," *Energy & Environmental Science*, 10.1039/D1EE02021H vol. 14, no. 11, pp. 5669-5689, 2021.
- [10] J. Cao, D. Zhang, X. Zhang, Z. Zeng, J. Qin, and Y. Huang, "Strategies of regulating Zn<sup>2+</sup> solvation structures for dendrite-free and side reaction-suppressed zinc-ion batteries," *Energy & Environmental Science*, 10.1039/D1EE03377H vol. 15, no. 2, pp. 499-528, 2022.
- [11] Q. Li *et al.*, "Dendrites issues and advances in Zn anode for aqueous rechargeable Zn-based batteries," *EcoMat*, vol. 2, no. 3, p. e12035, 2020/09/01 2020.
- [12] H. Lu *et al.*, "Amino Acid-Induced Interface Charge Engineering Enables Highly Reversible Zn Anode," *Advanced Functional Materials*, vol. 31, no. 45, p. 2103514,



2021/11/01 2021.

- [13] L. E. Blanc, D. Kundu, and L. F. Nazar, "Scientific Challenges for the Implementation of Zn-Ion Batteries," *Joule*, vol. 4, no. 4, pp. 771-799, 2020/04/15/ 2020.
- [14] Q. Zhao, S. Stalin, and L. A. Archer, "Stabilizing metal battery anodes through the design of solid electrolyte interphases," *Joule*, vol. 5, no. 5, pp. 1119-1142, 2021/05/19/ 2021.
- [15] A. Pei, G. Zheng, F. Shi, Y. Li, and Y. Cui, "Nanoscale Nucleation and Growth of Electrodeposited Lithium Metal," *Nano Letters*, vol. 17, no. 2, pp. 1132-1139, 2017/02/08 2017.
- [16] M. Song, H. Tan, D. Chao, and H. J. Fan, "Recent Advances in Zn-Ion Batteries," *Advanced Functional Materials*, vol. 28, no. 41, p. 1802564, 2018/10/01 2018.
- [17] V. Verma, S. Kumar, W. Manalastas, Jr., and M. Srinivasan, "Undesired Reactions in Aqueous Rechargeable Zinc Ion Batteries," *ACS Energy Letters*, vol. 6, no. 5, pp. 1773-1785, 2021/05/14 2021.
- [18] S. J. Banik and R. Akolkar, "Suppressing Dendrite Growth during Zinc Electrodeposition by PEG-200 Additive," *Journal of The Electrochemical Society*, vol. 160, no. 11, p. D519, 2013/09/21 2013.
- [19] S. Guo *et al.*, "Fundamentals and perspectives of electrolyte additives for aqueous zinc-ion batteries," *Energy Storage Materials*, vol. 34, pp. 545-562, 2021/01/01/ 2021.
- [20] Z. Yang *et al.*, "Revealing the Two-Dimensional Surface Diffusion Mechanism for Zinc Dendrite Formation on Zinc Anode," *Small*, vol. 18, no. 43, p. 2104148, 2022/10/01 2022.
- [21] A. Mitha, A. Z. Yazdi, M. Ahmed, and P. Chen, "Surface Adsorption of Polyethylene Glycol to Suppress Dendrite Formation on Zinc Anodes in Rechargeable Aqueous Batteries," *ChemElectroChem*, vol. 5, no. 17, pp. 2409-2418, 2018/09/03 2018.
- [22] D. Wang *et al.*, "Insight on Organic Molecules in Aqueous Zn-Ion Batteries with an Emphasis on the Zn Anode Regulation," *Advanced Energy Materials*, vol. 12, no. 9, p. 2102707, 2022/03/01 2022.
- [23] F. Wan, L. Zhang, X. Dai, X. Wang, Z. Niu, and J. Chen, "Aqueous rechargeable zinc/sodium vanadate batteries with enhanced performance from simultaneous insertion of dual carriers," *Nature Communications*, vol. 9, no. 1, p. 1656, 2018/04/25 2018.
- [24] J. Zheng and L. A. Archer, "Controlling electrochemical growth of metallic zinc electrodes:

- Toward affordable rechargeable energy storage systems," *Science Advances*, vol. 7, no. 2, p. eabe0219.
- [25] W. Xu *et al.*, "Diethyl ether as self-healing electrolyte additive enabled long-life rechargeable aqueous zinc ion batteries," *Nano Energy*, vol. 62, pp. 275-281, 2019/08/01/ 2019.
- [26] S.-B. Wang *et al.*, "Lamella-nanostructured eutectic zinc–aluminum alloys as reversible and dendrite-free anodes for aqueous rechargeable batteries," *Nature Communications*, vol. 11, no. 1, p. 1634, 2020/04/02 2020.
- [27] Z. Chen *et al.*, "Texture Control of Commercial Zn Foils Prolongs Their Reversibility as Aqueous Battery Anodes," *ACS Energy Letters*, vol. 7, no. 10, pp. 3564-3571, 2022/10/14 2022.
- [28] S. Li *et al.*, "Toward Planar and Dendrite-Free Zn Electrodepositions by Regulating Sn-Crystal Textured Surface," *Advanced Materials*, vol. 33, no. 21, p. 2008424, 2021/05/01 2021.
- [29] H. Zhang *et al.*, "Inducing the Preferential Growth of Zn (002) Plane for Long Cycle Aqueous Zn-Ion Batteries," *Advanced Energy Materials*, vol. 13, no. 1, p. 2203254, 2023/01/01 2023.

#### **Statement on the Use of Artificial Intelligence:**

In the preparation of this manuscript, artificial intelligence (AI) technology was employed to assist in language refinement, grammatical corrections, and ensuring consistency in technical terminology. Specifically, AI-powered tools were used for the following purposes:

**Language Enhancement:** To improve the clarity, coherence, and fluency of the English text while maintaining the original scientific intent.

**Terminology Standardization:** To ensure the accurate and consistent use of technical terms related to aqueous zinc-ion batteries (AZIBs), electrochemistry, and materials science.

**Structural Optimization:** To assist in organizing sections and transitions to enhance readability without altering the core technical content.

All AI-generated suggestions were rigorously reviewed, cross-checked against authoritative sources,

and manually revised by the authors to guarantee scientific accuracy and compliance with academic standards. The final content reflects the original research insights and interpretations of the authors.

**Areas Requiring Modification:**

- 1. Technical Content:** Section 3.1.1: The electrostatic shielding mechanism description should clarify the concentration threshold of  $\text{Na}_2\text{SO}_4$  (typically 0.5-2M) for effective operation  
References [22] & [26]: Update to include 2023 studies on organic additive design.
- 2. Methodological Transparency:** In Section 3.3, specify the characterization techniques (XPS, TEM, etc.) used for SEI analysis  
Table: Add a comparative matrix of additive performance metrics (CE improvement %, dendrite suppression efficiency).