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Interface Regulation Coupled with Crystal Plane Engineering: Alloy deposition-Modified Zinc Anode Enabling Dual Inhibition of Dendrite Growth and Corrosion

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Abstract

Aqueous zinc-ion batteries (AZIBs) demonstrate irreplaceable application prospects in large-scale energy storage due to their inherent safety, low cost, and high theoretical capacity. However, issues such as dendritic disorderly growth, hydrogen evolution reaction (HER), and corrosion of zinc anodes severely compromise electrode structural integrity, becoming a core bottleneck restricting the commercialization of AZIBs. To achieve efficient protection of zinc anodes, study employed room-temperature immersion deposition using metal nitrate as precursors to construct a Zn@M metallic deposited modification layer on zinc foil surfaces, forming an integrated physical barrier and chemically regulated protective system. The metallic modification layer provides comprehensive protection through multiple synergistic mechanisms: the conductive network co-constructed by homogenizes interfacial electric field distribution and Zn^{2+} ion flux, while their synergistic effect guides zinc deposition preferentially along thermodynamically stable (101) crystal planes, fundamentally suppressing dendritic growth. Additionally, this modification layer restructures Zn^{2+} solvation structures, reduces free water activity, and significantly inhibits side reactions such as HER and corrosion. This study proposes a simple, efficient, and cost-controlled bimetallic co-modification strategy for zinc anodes, elucidating an integrated protective mechanism of "electric field optimization-crystal plane orientation control-interfacial stabilization-side reaction inhibition", laying a critical foundation for the practical application of high-performance aqueous zinc-ion batteries (AZIBs).

Keywords

Aqueous Zinc-Ion Battery, Zinc Anode Protection, Dendrite Inhibition, Corrosion Protection, Interface Regulation.

1. Introduction

As a pivotal force in the global energy transition, high-performance large-scale energy storage technologies have become essential for maintaining grid stability and advancing renewable energy integration. Zinc-ionic batteries (AZIBs) are emerging as the ideal next-generation solution for large-scale energy storage, owing to their zinc anode's exceptional theoretical specific capacity (820 mAh g^{-1}), low redox potential (-0.76 V vs SHE), abundant natural reserves, eco-friendly aqueous electrolytes, and inherent safety. Unlike traditional lithium-ion batteries (LIBs), AZIBs completely eliminate the flammability and explosion risks associated with organic electrolytes while reducing manufacturing costs by over 30%. These advantages make them particularly promising for applications in grid peak shaving and distributed energy storage systems.

Despite their significant technological advantages, the commercial application of zinc anodes remains constrained by a series of severe interface challenges. During repeated chargedischarge cycles, thermodynamic and kinetic inhomogeneities in Zn^{2+} deposition/dissociation induce dendritic disorderly growth, which can penetrate the separator to cause internal short circuits and form irreversible "dead zinc." Concurrently, highly reactive water molecules in aqueous electrolytes trigger hydrogen evolution reactions (HER) and zinc substrate corrosion. Hydrogen evolution elevates internal cell pressure, while the porous interface layer formed by corrosion products further exacerbates impedance increase and performance degradation. These coupled issues severely limit the cycle life and rate performance of AZIBs. Therefore, developing efficient zinc anode protection strategies that simultaneously suppress dendritic growth and side reactions has become the core scientific challenge for overcoming AZIBs' technical bottlenecks.

Current zinc anode protection strategies primarily focus on three key areas: electrolyte optimization, separator modification, and anode surface engineering. Electrolyte optimization involves adjusting components, concentration, or introducing additives to regulate the solvation structure of Zn^{2+}, but it suffers from drawbacks such as complex formulations, high viscosity of high-concentration electrolytes, limited ion transport, and rapid additive consumption, making long-term stable protection challenging. Separator modification employs functional coatings to physically block dendrites, yet this approach often introduces external surface resistance and the coating layer tends to peel off during prolonged cycling, rendering it unsuitable for high-current-density applications. Single-metal or non-metal modification layers have limited functionality, failing to simultaneously address the core issues of dendrite formation and corrosion, which constrains their practical value.

2. Alloying Modification

2.1. Alloying Elements and Their Functional Mechanisms

The selection of alloying elements is the key to the alloying modification of zinc anodes, and an ideal alloying element should have good compatibility with zinc, no obvious side reactions with aqueous electrolytes, and the ability to improve the interfacial stability of zinc anodes[1]. According to their functional characteristics, alloying elements can be divided into three categories: conductive elements (Ag, Sb, Sn, etc.), inert/barrier elements (Bi, In, etc.), and passivating elements (Al, Mg, etc.), and each type of element plays a unique role in modifying zinc anodes[2].

Conductive elements such as Ag and Sb have high electrical conductivity, which can homogenize the interfacial electric field of the zinc anode, regulate the distribution of Zn^{2+} flux, and guide the uniform deposition of zinc, thereby suppressing dendrite growth[2]. Ag can form a solid solution with zinc, optimize the crystal structure of zinc, and guide zinc to grow along the low-surface-energy crystal plane, further suppressing dendrite growth[1]; Sb can form a conductive network on the zinc anode surface, improve electron transport efficiency, and form intermetallic compounds with zinc to buffer volume expansion[3]. Inert/barrier elements such as Bi and In have good chemical inertness and low solubility in aqueous electrolytes, which can form a dense alloy layer on the zinc anode surface to block the direct contact between the electrolyte and the zinc substrate, thereby inhibiting hydrogen evolution corrosion[4]. Bi can also reduce the adsorption energy of Zn^{2+}, accelerate the deposition/stripping kinetics of zinc, and improve the rate performance of the battery[5]; In can improve the interfacial compatibility between the zinc anode and the electrolyte, further enhancing the cycle stability[2].

Passivating elements such as Al and Mg can form a dense oxide passivation layer on the zinc anode surface, which can effectively prevent the infiltration of electrolyte and water molecules, and improve the corrosion resistance and mechanical strength of the zinc anode[3]. In practical applications, single alloying elements often have limitations, so multi-element alloying is usually adopted to achieve synergistic protection effects by combining the advantages of different elements [2].

2.2. Typical Zinc Alloy Systems

Typical zinc alloy systems include binary, ternary, and quaternary alloys, which have different characteristics and application scenarios. Binary zinc alloy systems are the simplest and most widely studied, mainly including Zn-Bi, Zn-Sb, Zn-Al, Zn-In, etc. Zn-Bi alloy can form a dense protective layer on the zinc surface to inhibit corrosion and dendrite growth, and Zn-Bi alloy anodes prepared by electrodeposition can maintain stable cycling for 1000 cycles at 1 A g^{-1}[3]; Zn-Sb alloy has excellent conductivity and good mechanical stability, and can maintain stable performance under high current density conditions[1]; Zn-Al alloy has excellent corrosion resistance and low cost, showing great potential in large-scale energy storage systems[4].

To further improve the protection effect, ternary and quaternary zinc alloy systems have been developed in recent years. Zn-Bi-Sb alloy combines the corrosion resistance of Bi and the conductivity of Sb, and can maintain stable cycling for 1200 cycles at 3 A g^{-1}[5]; Zn-Ag-Bi alloy combines the high conductivity of Ag and the corrosion resistance of Bi, achieving synergistic suppression of dendrite growth and corrosion[1]; Zn-Al-Mg alloy combines the passivation effect of Al and the mechanical reinforcement effect of Mg, reducing volume expansion during cycling[3]; Zn-Bi-In-Sb quaternary alloy integrates the advantages of multiple elements, achieving comprehensive protection of the zinc anode[5].

2.3. Preparation Methods of Zinc Alloy Anodes

The preparation method of zinc alloy anodes directly affects the component distribution, microstructure, and electrochemical performance of the alloy, and common preparation methods include room-temperature immersion codeposition, electrodeposition, casting, and mechanical alloying[2]. The characteristics of different preparation methods are compared in Table 1, which can provide a reference for the selection of preparation technologies according to actual needs.

Table 1. Comparison of Different Preparation Methods for Zinc Alloy Anodes

Preparation Method	Core Principle	Advantages	Disadvantages	Typical Alloy Systems
Room-Temperature Immersion Codeposition	Spontaneous redox reaction between Zn and alloying ions, synchronous codeposition	Mild conditions, low cost, simple operation, large-scale potential; suitable for surface alloying	Alloy layer thickness is limited; uneven deposition may occur	Zn-Bi, Zn-Ag-Bi, Zn-Sb-Bi
Electrodeposition	Regulate potential/current to co-deposit Zn and alloying elements	Precise control of component ratio and thickness; uniform microstructure	High equipment cost, complex process; not suitable for large-scale production	Zn-In, Zn-Sn, Zn-Bi
Casting	High-temperature melting of Zn and alloying elements, cooling solidification	Suitable for bulk alloy, large-scale production, low cost	Coarse grains, uneven component distribution; post-treatment required	Zn-Al, Zn-Mg, Zn-Al-Mg
Mechanical Alloying	High-energy ball milling to realize solid-state alloying of powder	Fine grain size, uniform component; low-temperature preparation	Time-consuming, easy to introduce impurities; high energy consumption	Zn-Sb, Zn-Bi, Zn-Sb-Bi

Room-temperature immersion codeposition utilizes the reducibility of zinc to spontaneously reduce alloying element ions and deposit them on the zinc surface, with the advantages of mild conditions, low cost, and large-scale potential, suitable for surface alloying[3]; electrodeposition can precisely control the component ratio and thickness of the alloy layer, suitable for preparing high-purity and uniform alloy layers, but has high equipment cost[2]; casting is suitable for large-scale production of bulk alloys, but may lead to coarse grains and uneven component distribution[4]; mechanical alloying can prepare nanocrystalline zinc alloys with uniform component distribution, but is time-consuming and has high energy consumption[3].

The performance of typical zinc alloy anodes prepared by different methods is shown in Table 2, which intuitively reflects the advantages of alloying modification compared with pure zinc anodes.

Table 2. Performance Comparison of Typical Zinc Alloy Anodes

Alloy System	Preparation Method	Corrosion Current (mA cm^{-2})	Cycling Performance (Cycles @ Current Density)	Key Advantages
Zn-Bi	Electrodeposition	3.05	1000 @ 1 A g^{-1}	Good corrosion resistance, low cost
Zn-Sb	Mechanical Alloying	3.12	800 @ 5 A g^{-1}	Excellent conductivity, good rate performance
Zn-Al	Casting	2.88	500 @ 2 A g^{-1}	Excellent corrosion resistance, low cost, scalable
Zn-Bi-Sb	Immersion Codeposition	2.75	1200 @ 3 A g^{-1}	Synergistic protection, good cycle stability
Zn-Al-Mg	Casting	2.92	600 @ 2 A g^{-1}	Good mechanical stability, low cost
Pure Zn (Control)	Polishing	3.64	400 @ 1 A g^{-1}	Poor cycle stability, severe dendrite and corrosion

2.4. Synergistic Protection Mechanisms

Alloying modification achieves comprehensive protection of zinc anodes through multiple synergistic mechanisms, mainly including electric field homogenization, physical barrier, crystal plane orientation regulation, and kinetic optimization [4]. The universal synergistic protection mechanisms of alloying-modified zinc anodes are shown in Fig. 1, which clearly reflects the multi-path protection effect of alloying elements.

Alloying modification achieves comprehensive protection of zinc anodes through multiple synergistic mechanisms. Conductive elements homogenize the electric field, inert elements form a physical barrier, passivating elements form a protective layer, and all elements jointly optimize the deposition kinetics, thereby suppressing dendrite growth and corrosion, and improving the cycle stability of the battery.

Conductive elements such as Ag and Sb form a continuous conductive network to homogenize the interfacial electric field, reduce local current density, and avoid preferential nucleation of dendrites [2]; inert elements such as Bi and In form a dense alloy layer as a physical barrier, blocking electrolyte infiltration and inhibiting corrosion[4]; alloying elements such as Ag and Bi adjust the crystal plane orientation of zinc, guiding zinc to grow along the low-surface-energy

(101) crystal plane to suppress dendrite growth[5]; elements such as Bi and In reduce the desolvation energy barrier of Zn^{2+}, accelerate ion transport, and optimize deposition/stripping kinetics[5]. These mechanisms work together to improve the interfacial stability and electrochemical performance of zinc anodes[1].Alloying modification achieves comprehensive protection of zinc anodes through multiple synergistic mechanisms, as shown in Fig. 2.

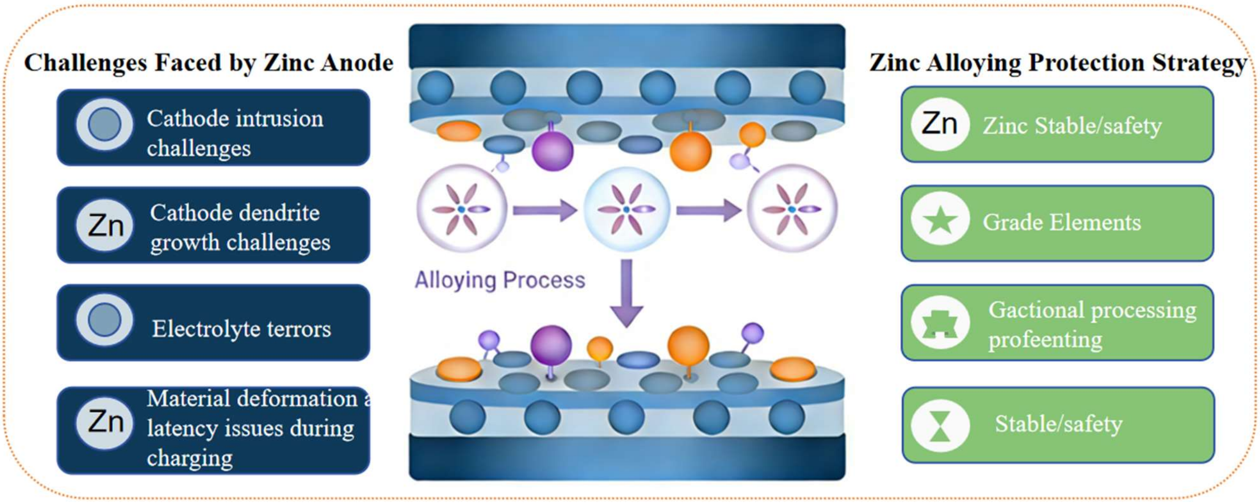

Fig. 1 Schematic Diagram of Universal Synergistic Protection Mechanisms of Alloying-Modified Zinc Anodes

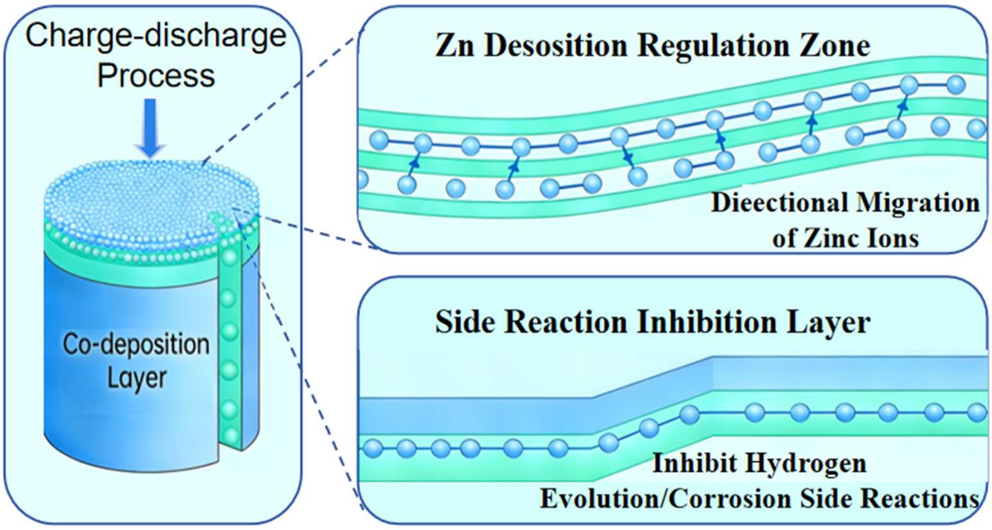

Fig. 2 Schematic Diagram of Synergistic Protection Mechanisms of Codeposition Modification

The pure zinc anode has severe dendrite growth and corrosion after cycling, while the alloying-modified zinc anode maintains a dense and smooth surface, which is attributed to the synergistic protection effect of alloying elements. The uniform and dense alloy layer ensures the structural stability of the anode during long-term cycling.

2.5. Application of Alloying-Modified Zinc Anodes

Alloying-modified zinc anodes have been widely applied in various AZIB systems, showing excellent compatibility and performance advantages[4]. In MnO$_2$//Zn batteries, Zn-Bi-Sb alloy anodes can effectively suppress dendrite growth and corrosion, and the battery can maintain a capacity retention rate of 85% after 2000 cycles at 1 A g^{-1}[3]; in V$_2$O$_5$//Zn batteries, Zn-Sb alloy anodes have excellent rate performance, with a specific capacity of 380 mAh g^{-1} at 0.1 A g^{-1} [3]; in Prussian blue analogs//Zn batteries, Zn-Al alloy anodes have good corrosion resistance, maintaining stable cycling for 1500 cycles at 2 A g^{-1} [4]. In addition, alloying-modified zinc anodes also show good application prospects in flexible AZIBs and large-scale energy storage systems[2].

3. Conclusion and Prospects

3.1. Conclusion

Alloying modification is an effective strategy to solve the interfacial instability problem of zinc anodes in AZIBs, which can significantly improve the cycle stability, corrosion resistance, and rate performance of zinc anodes. Through the rational selection of alloying elements (conductive, inert/barrier, passivating elements) and the design of alloy systems (binary, ternary, quaternary alloys), the intrinsic properties and interfacial behavior of zinc anodes can be precisely regulated. Different preparation methods (room-temperature immersion codeposition, electrodeposition, casting, mechanical alloying) have their own advantages and application scenarios, and can be selected according to actual needs.

The synergistic protection mechanisms of alloying modification, including electric field homogenization, physical barrier, crystal plane orientation regulation, and kinetic optimization, jointly suppress dendrite growth and hydrogen evolution corrosion, and alleviate volume expansion, thereby improving the comprehensive performance of zinc anodes. A large number of studies have shown that alloying-modified zinc anodes have excellent electrochemical performance and broad application prospects in various AZIB systems. The literature review shows that the research on alloying modification of zinc anodes has made remarkable progress in recent years, laying a solid foundation for the commercialization of AZIBs.

3.2. Full Battery Performance

Although alloying modification has achieved significant progress in improving the performance of zinc anodes, there are still some challenges to be solved: some alloying elements (such as Ag, In) have high costs, limiting large-scale application; the component ratio and microstructure of zinc alloys are difficult to precisely control; the interfacial compatibility between alloying-modified zinc anodes and electrolytes needs to be further improved; the synergistic protection mechanism of multi-element alloy systems at the atomic level is not yet fully clear.

In view of the above challenges, the future development directions of alloying-modified zinc anodes are as follows: first, develop low-cost alloying elements, replace high-cost elements with low-cost elements such as Al, Mg, Sb, and optimize the component ratio to reduce costs; second, improve preparation technology, develop advanced technologies such as atomic layer deposition and laser cladding to precisely control the component distribution and microstructure of zinc alloys; third, enhance interfacial compatibility, modify the surface of alloying-modified zinc anodes to suppress side reactions; fourth, design composite alloy systems, combine alloying modification with other modification strategies to further improve performance; fifth, deepen mechanism research, use in-situ characterization technologies and theoretical calculation methods to clarify the synergistic protection mechanism at the atomic level; sixth, promote large-scale production, optimize the preparation process and develop continuous production technology to realize the large-scale application of alloying-modified zinc anodes in AZIBs.

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