Advancements in Dendrite Suppression for Enhanced Energy Storage Technologies

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Abstract. Aqueous zinc batteries have emerged as promising alternatives to conventional lithium-ion batteries, offering an environmentally friendly and cost-effective solution to our growing energy storage needs. However, one of the critical obstacles to realizing their full potential lies in addressing the dendritic structure growth challenges within zinc batteries. These dendrites, unwanted metal protrusions that form during the charging and discharging cycles, can lead to adverse implications, including short circuits, reduced battery performance, and safety concerns. To overcome these challenges, researchers and engineers have been diligently devising strategies. This paper delves into the complexities of dendrite formation in aqueous zinc batteries, outlining their adverse implications for battery performance and safety. Various strategies to address the dendrite challenge are explored, with a focus on their effectiveness and limitations. One promising avenue involves developing innovative three-dimensional (3D) structural designs within the battery architecture to inhibit dendrite formation. Conclusively, harnessing the potential of aqueous zinc batteries hinges on the successful mitigation of dendrite formation through the concerted implementation of ingenious 3D structural designs and other innovative strategies, steering the pathway towards safer and more efficient energy storage solutions.

Keywords: New energy, Battery dendrite, Energy storage technology.

1. Introduction

An aqueous zinc battery is a type of rechargeable battery that utilizes zinc and an aqueous electrolyte as the main components. These batteries have gained significant attention because of their potential for cost-effectiveness, safety, and environmental sustainability compared to traditional lithium-ion batteries. Aqueous zinc batteries typically consist of a zinc anode, a cathode made of materials such as manganese dioxide (MnO_2), and an aqueous electrolyte. During discharge, zinc metal reacts with hydroxyl ions (OH^-) in the electrolyte for the purpose of forming zincate ions ($Zn(OH)4^{2-}$). This reaction generates electrons that flow through an external circuit, which produces electrical energy [1]. One of the primary advantages of aqueous zinc batteries is their rechargeability. When an external electric current is applied, the zincate ions at the cathode undergo a reverse reaction, converting back into zinc metal, and the zinc ions are released into the electrolyte. Unlike some lithium-ion batteries that use flammable and toxic organic electrolytes, aqueous zinc batteries use a water-based electrolyte, which is non-flammable and generally considered safe. Zinc is abundant and relatively inexpensive compared to lithium, cobalt, or other rare metals used in lithium-ion batteries. This abundant availability of zinc contributes to the potential cost-effectiveness of aqueous zinc batteries, making them very useful in large-scale energy storage applications.

The dendrite problem in aqueous zinc batteries is like the dendrite formation seen in lithium-ion batteries. As with dendrites occur in other kinds of batteries. These tiny, finger-like projections grow on the zinc anode's surface during the battery's charge and discharge cycles [2]. The emergence of dendrites can precipitate a series of detrimental outcomes, encompassing short circuits, thermal escalation, compromised efficiency, and potential safety risks. The intrusion of dendrites into the separator, a component segregating the anode and cathode, fosters direct electrical connectivity between these electrodes, culminating in the aforementioned complications. Moreover, the genesis of dendrites depletes the active zinc constituent, undermining the battery's capacity for energy retention, and hampers the uniform migration of ions, thereby diminishing the overall energetic efficacy. The perpetual expansion of dendrites further hastens the attrition of the battery's components, curtailing

its operational lifespan and robustness [3]. Therefore, solving the dendrite dilemma is crucial for unlocking the full potential of aqueous zinc batteries. As a result, it has become a focal point of investigation for scientists and industry experts aiming to advance scalable energy storage systems and incorporate renewable energy sources.

2. An Overview of the Dendrite Problem in Zinc Batteries

When the battery is charged at high rates or subjected to mechanical stresses, zinc ions may not be uniformly deposited on the anode, leading to the dendritic structures growth. Dendrites form in zinc water-based batteries because of the electrochemical reactions occurring at the anode while the battery charges and discharges. During the charging process, the zinc ions in the watery solution get reduced into solid metallic zinc and deposited on the anode's surface. However, non-uniform deposition of zinc can occur due to factors like nucleation sites, overpotential, uneven distribution of zinc ions, and insufficient ion transport to the anode on the anode [4]. These uneven depositions result in the growth of dendritic structures. They can push through the separator and create electrical shortcuts, which can harm the battery's performance and safety (Figure 1).

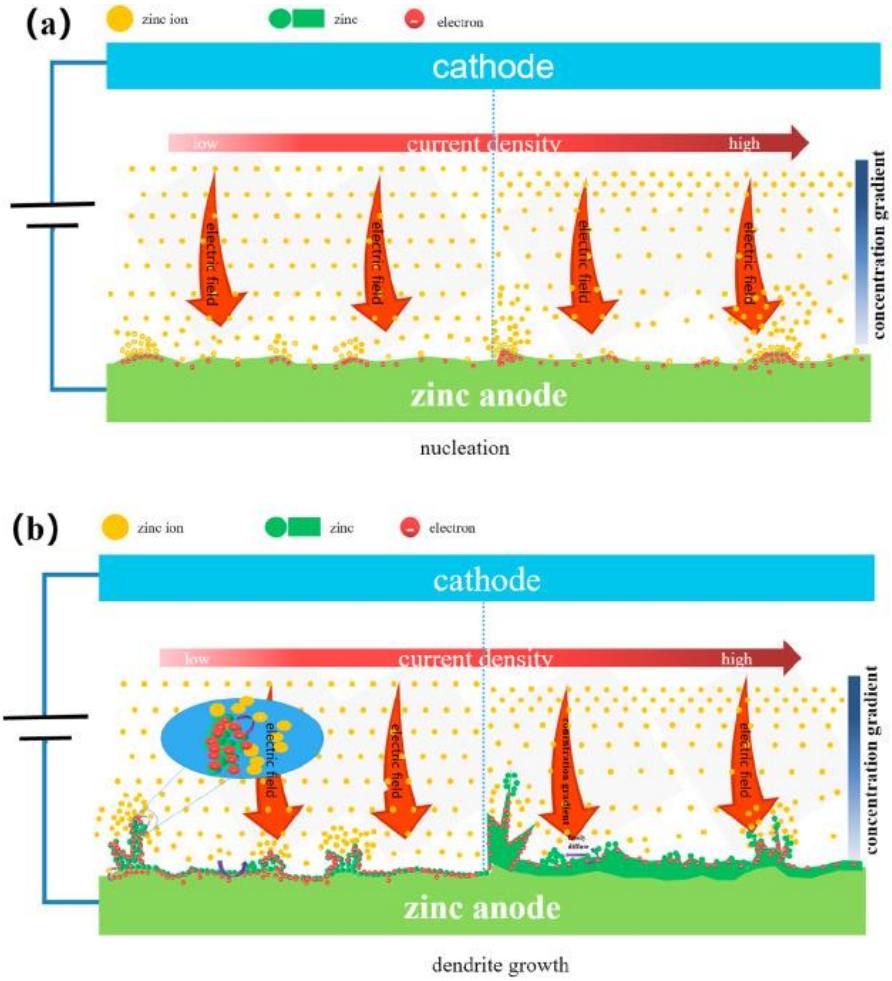

Figure 1. Scheme diagram of dendrites form in aqueous zinc batteries [5]

Dendrite formation in zinc water-based batteries is a complex process with significant implications for battery performance and safety. During charging, zinc ions from the aqueous electrolyte are reduced and deposited onto the anode's surface as solid metallic zinc. However, non-uniform deposition can occur, leading to the growth of dendrites – tiny, finger-like structures. These dendrites can cause numerous problems, including short circuits, reduced performance, and safety hazards.

One critical factor contributing to dendrite formation is the presence of nucleation sites on the anode's surface, where clusters of zinc atoms begin to form [6]. Zinc accumulation continues once

the nucleation process begins, leading to dendrite elongation. Ion transport also plays a role; uniform zinc deposition requires even ion distribution and efficient transport to the anode's surface. Variations in ion distribution can lead to non-uniform deposition and dendrite growth [7]. In addition, the excess voltage needed to drive electrochemical reactions can also influence dendrite formation. High overpotentials in certain regions of the anode can increase zinc deposition rates, contributing to uneven dendrite growth. Additionally, the composition of the aqueous electrolyte, including additives and impurities, can impact dendrite formation, with some additives promoting or inhibiting dendrite growth.

To address this issue, researchers are investigating various approaches, such as modifying electrolyte composition and anode design and implementing smart battery management systems to minimize dendrite formation and enhance the safety and reliability of zinc water-based batteries for energy storage applications.

3. Existing Solutions to the Dendrite Problem

3.1. Backside-plating configuration

In the conventional frontside plating configuration (Figure. 2a), the Zn metal foil anode serves as both the reference and counter electrodes, facing the copper (Cu) working electrode. While zinc is being plated onto the copper foil, those dendrites might start growing toward the zinc reference electrode. However, the backside metal plating concept (Figure. 2b) offers an ingenious solution to this problem.

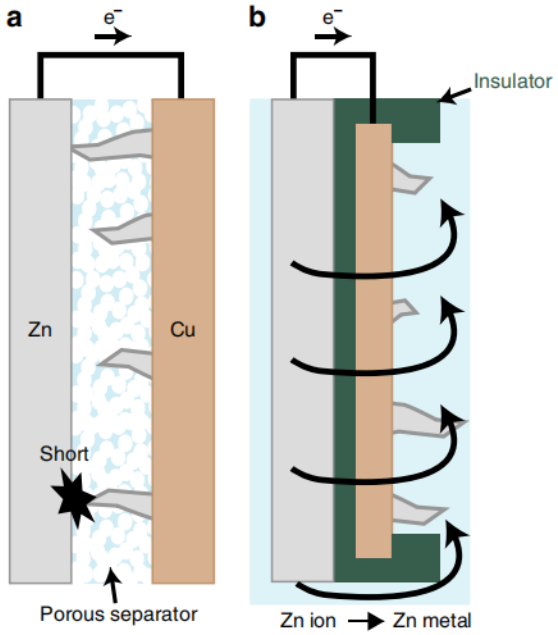

Figure 2. (a) conventional frontside plating configuration; (b) backside metal plating configuration [8]

In the backside metal plating configuration, an insulating layer is applied to both the edges and the front surface of the copper foil that faces the zinc metal counter electrode. When the zinc plating process takes place, zinc ions from the watery electrolyte travel along the edges and get deposited onto the uncovered back surface of the copper foil. This specific design aims to guarantee that, even if zinc dendrites form during the charging process, these dendrites grow in a direction away from the counter electrode. This proactive approach reduces the chances of short circuits and contributes to preserving the battery's overall integrity and performance.

In a research study, a Ni-Zn full-cell battery was tested to operate at a high rate of 20 milliamperes per square centimeter (20 mA cm^{-2}) using the backside-plating configuration. This battery

demonstrated remarkable stability, successfully completing 800 charge-discharge cycles without significant issues. In contrast, when the conventional frontside-plating configuration was used, a noticeable drop in stability occurred after only about 100 cycles due to a short circuit problem. Additionally, the backside-plated cell maintained an impressive 88% capacity retention after 800 cycles, and the backside-plating configuration achieved a Coulombic efficiency of 92% during 160 cycles of plating and stripping processes. When considering the weight of the active materials (Ni $(OH)_2$ and Zn), the estimated specific energy density for the Ni-Zn full cell was approximately 246 watt-hours per kilogram (246 Wh kg^{-1}) for both the conventional and backside-plating configurations. Collectively, the above results illustrate the success of the backside metal plating strategy in preventing dendrite growth and ensuring stable performance of zinc-based batteries over numerous charge-discharge cycles, even under high current densities.

3.2. Polyethylenimine Additive in suppressing dendrite growth

Polyethyleneimines (PEI) [9] additive has emerged as a promising solution to suppress dendritic growth during alkaline zinc (Zn) electrodeposition. As mentioned in the previous text, the mechanism of dendrite suppression involves PEI's adsorption at propagating dendrite tips. Higher concentrations of PEI lead to more pronounced dendrite suppression, offering a concentration-dependent control over dendrite formation [10].

The central element of this approach involves adding different amounts of branched polyethyleneimine (PEI) to the electrolyte used for zinc electrodeposition. PEI, which is an organic compound, is intentionally included in the electrolyte to modify the process of electrodeposition and hinder the development of dendrites. The specific mechanism of dendrite suppression through PEI's adsorption at the tips of growing dendrites alters the growth dynamics, effectively inhibiting the deposit growth rate at the dendrite tips. As a result, dendrite formation is effectively suppressed, leading to smoother and more uniform Zn electrodeposition. This breakthrough in understanding dendrite suppression through PEI opens up new possibilities for enhancing the cyclability and safety of rechargeable Zn batteries. The investigative efforts encompassed a series of studies and characterization methods geared toward unraveling the influence of PEI on zinc electrodeposition, including rotating disc electrodes (RDE). Among the notable techniques employed in these studies, electrochemical polarization measurements were conducted using a rotating disc electrode (RDE), quartz crystal microbalance (QCM) measurements were taken, and scanning electron microscopy (SEM) was utilized for observation and analysis. It is found that the strategy of introducing branched PEI into the electrolyte has been substantiated as an effective means to curtail dendrite growth during zinc electrodeposition. This conclusion rests on a foundation of diverse experimental methodologies and meticulous data analyses. The overarching aspiration of this research is to elevate the stability and operational prowess of electrochemical systems, most notably rechargeable batteries, by curbing the emergence of detrimental dendritic structures.

3.3. Dendrite Suppression Membranes for Rechargeable Zinc Batteries

Dendrite Suppression Membranes are an innovative class of separators designed to address a significant challenge in rechargeable batteries, particularly in zinc-based aqueous batteries: dendrites. To overcome this issue, Dendrite Suppression Membranes are engineered with specific properties to regulate ion transport and prevent dendrite formation. These membranes serve as selective barriers for positively charged ions, helping to reduce the ion concentration difference that primarily triggers dendrite growth [11]. Furthermore, the solvent channels within these membranes promote a more even distribution of electrical current, leading to a more uniform deposition of zinc on the anode. Traditional separators like Nafion have been investigated for dendrite suppression in nonaqueous batteries but are prohibitively expensive and mechanically challenging for aqueous battery applications. Polyacrylonitrile (PAN)-based cation exchange membrane offers a cost-effective, practical, and scalable solution to enhance the cyclability and safety of zinc-based aqueous batteries. PAN is a low-cost and mechanically robust material [11]. PAN cross-linked with polysulfide

compounds to introduce sulfonate groups. This modification enhances its ability to conduct ions and ensures that it doesn't obstruct the movement of crucial ions necessary for battery function. This leads to improved battery performance. In this context, the PAN-based membrane is engineered to function as a proficient separator. Its role is not only to prevent dendrite formation but also to preserve its structural integrity, ensuring the battery operates effectively. This membrane demonstrates the ability to suppress dendrites effectively while maintaining high energy density and battery performance.

The membrane's synthesis involves cross-linking PAN with a polysulfide compound, resulting in the introduction of sulfonate functional groups. This unique structure combines mechanical robustness with the ability to facilitate ion transport. The membrane's capacity for selective cationic transport and anion immobilization is demonstrated through cross-over tests with various ion solutions. This selectivity is crucial for maintaining stable ion gradients and preventing dendrite growth. Moreover, the PAN-S membrane's morphological characteristics play a pivotal role in dendrite suppression. The nanosized water domains within the membrane facilitate uniform ion transport and hinder dendrite formation on the electrode surface. Furthermore, long-term cycling tests demonstrate the remarkable stability and performance enhancement achieved by the PAN-S membrane. Cells equipped with the PAN-based separator exhibit consistent cycling behavior with minimal voltage hysteresis, confirming the membrane's ability to prevent dendrite-related issues. Overall, the strategy of using a PAN-based cationic exchange membrane represents a promising solution to the challenge of dendrite formation in zinc-based aqueous batteries. It effectively combines mechanical durability, selective ion transport, and dendrite suppression, paving the way for improved battery performance and reliability.

3.4. Evaluation of the effectiveness and limitations of these strategies

Even though these solutions seem good, there remain some problems. The backside plating configuration might hinder ion conductivity and reduce rate capability. In conventional frontside plating configurations, the Zn anode is in direct contact with the Cu foil, allowing ions to easily travel between the two electrodes. This direct contact facilitates rapid ion conduction, enabling high-rate capabilities for the battery. Nonetheless, in the backside metal plating setup, the presence of the insulating layer disrupts this direct contact and necessitates that zinc-related ions take a detour around the layer to reach the exposed back surface of the copper foil [12]. This added route may elevate the resistance to ion mobility, potentially resulting in reduced efficiency during the charge and discharge processes. This effect can have implications for the overall performance and suitability of this configuration, particularly in high-power applications.

At the same time, it did not prevent the dendrite growth. Since the dendrite growth needs material, it will cause the consumption of active electrode material and reduce the effective surface area available for electrochemical reactions. This leads to reduced battery performance and a decrease in its capacity to store and deliver energy. As a result, the battery may not provide the expected power output and runtime, affecting its overall usability and reliability.

4. Overview of recent research on dendrite suppression

While dendrite-solving inventions, such as the use of additives or specialized membranes, offer promising solutions to address dendrite-related challenges in rechargeable batteries, they may encounter some issues and limitations. Some of the common issues include:

Performance Trade-offs: Some dendrite-suppressing techniques may come with performance trade-offs. For example, certain additives or membrane designs may improve dendrite suppression but could impact other battery performance metrics like energy density, capacity, or cycling stability.

Additive Compatibility: The compatibility of additives with the battery chemistry and electrolyte needs to be carefully considered. Some additives may interact unfavorably with other battery components or degrade over time, affecting battery performance and safety.

Long-Term Stability: The long-term stability of dendrite-suppressing techniques is critical. Additives or membranes should maintain their effectiveness over multiple charge and discharge cycles, ensuring consistent performance throughout the battery's lifetime.

Side Reactions and Impurities: Some additives may introduce side reactions or impurities during battery operation, leading to degradation of the battery components or electrolyte and potentially affecting safety and performance.

5. Conclusion

In conclusion, the pursuit of higher energy storage capabilities has spotlighted aqueous zinc batteries as a promising contender, boasting an approximate specific energy of 2600 Wh kg^-1 due to the substantial capacities of sulfur cathodes and zinc anodes. However, akin to their zinc-ion counterparts, LSBs encounter challenges stemming from the growth of zinc dendrites on the anode, leading to reduced efficiency and safety concerns. To address this issue, a range of strategies have been explored, categorized into separator, anode, and electrolyte modifications.

In the realm of separators, 3D structural designs show potential in hindering dendrite expansion, as they limit the orientation of free zinc crystals. Anodes with 3D architectures similarly curb dendrite growth by impeding crystal orientation. Surface treatment of the zinc anode presents a straightforward yet effective approach, as it enables the controlled electrochemical deposition of metal zinc along the coated structure. Electrolyte modifications, on the other hand, offer avenues to enhance safety. Ionic liquid electrolytes influence zinc deposition through control of the solid electrolyte interphase (SEI) layer, while additives contribute to stable interfaces and catalytic behavior, effectively suppressing dendrite formation.

Despite the progress made, several challenges require attention. Establishing a theoretical model for dendrite growth on zinc metal surfaces within LSBs is crucial for devising targeted suppression methods. Identifying cost-effective and efficient surface treatment strategies for metal zinc is ongoing. Additionally, developing electrolytes with the capability to catalyze zinc dendrite dissolution is pivotal for fundamental suppression. Overcoming these hurdles holds the key to enhancing the security and practicality of LSBs. Through continued research, LSBs have the potential to find broad applications in high-energy devices, moving us closer to realizing their promise in advanced energy storage technology.

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