

Anodic protection strategy for zinc ion batteries

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Abstract. With the advent of the national dual-carbon strategy, there is a burgeoning demand for large-scale energy storage systems within the national grid. Nevertheless, lithium-ion batteries have been constrained in large-scale energy storage systems due to their limitations, encompassing scarce raw materials, diminished safety profiles, and environmental concerns. In recent years, zinc-ion batteries have emerged as the most promising option for large-scale energy storage systems, owing to their cost-effectiveness, heightened safety attributes, substantial theoretical capacity, and environmental compatibility. Nonetheless, zinc anodes continue to grapple with significant challenges, including dendrite growth, corrosion passivation, and the hydrogen-evolution reaction (HER), which impede the progressive advancement of zinc-ion battery anodes. This paper provides a comprehensive overview of the principal failure modes and mechanisms inherent to zinc anodes derived from an in-depth analysis of their associated issues. Furthermore, it systematically reviews the primary strategies for modifying zinc-negative electrodes, encompassing diaphragm modifications, electrolyte additives, and anode modifications. This endeavor aims to offer insights and support for enhancing zinc-ion battery anodes.

Keywords: zinc ion battery; zinc anode; diaphragm modification; electrolyte additive; anode modification.

1. Introduction

With the implementation of the national dual-carbon strategy, there has been rapid development in renewable and clean energy sources, notably represented by solar, wind, and hydropower. However, there is an escalating demand for the practical storage of these renewable energy sources within the national grid[1]. Lithium-ion batteries (LIBs), which currently dominate the electric vehicle and mobile electronics markets, encounter significant limitations when applied to large-scale energy storage systems. These limitations stem from various factors, including the mounting costs of raw materials, compromised safety profiles, and environmental concerns. Conversely, rechargeable aqueous zinc-ion batteries (ZIBs) are widely recognized as the most promising contenders for large-scale energy storage systems, given their substantial theoretical capacity (820 mAh g⁻¹), low plating/stripping potential (-0.76 V vs. SHE), cost-effectiveness, heightened safety attributes, and environmentally friendly characteristics[1].

As shown in Figure 1 (a) [2], similar to the charge storage mechanism of LIBs, Zn²⁺ in ZIBs also involves transferring between the anode and cathode materials and reversibly embedding (stripping) zinc ions in the electrode material [3]. In particular, the degree of plating/stripping on the anode surface of ZIB significantly impacts the cell's stability and Coulombic efficiency. It is, therefore, of particular importance to the performance and lifetime of the cell. However, ZIB suffers from zinc dendrites, corrosion, and hydrogen precipitation reaction (HER), which seriously affects the performance of ZIB, and the failure forms are shown in Figure 1 (b) [4]. Specifically, the deposition of Zn ions is accompanied by the formation of Zn dendrites, and the growth of dendrites significantly reduces the capacity and Coulombic efficiency of the Zn anode. Due to the high mechanical strength and Young's modulus of Zn, large dendrites can even puncture the battery diaphragm and lead to short circuits[5]; gases generated by HER may increase the internal pressure of the battery and cause safety hazards[6]; and corrosion depletes the limited amount of zinc anode and electrolyte, thus decreasing the battery capacity and energy density over time. These three problems are interrelated, and the generation of corrosion and HER by-products will hinder the uniformity of ion transport, thus

inducing more dendrites. The falling dendrites will increase the specific area of the Zn anode, thus exacerbating corrosion and HER[1].

Numerous endeavors have been undertaken to address the challenges associated with zinc anodes. These approaches can be briefly categorized into three main strategies: structural design, electrolyte optimization, and interfacial modification[7]. The structural design strategy typically entails the utilization of materials characterized by a high specific surface area as the substrate for zinc deposition. Expanding the working area is believed to reduce the operating current density and the likelihood of dendrite formation and side reactions[8]. Strategies for electrolyte optimization are typically employed to alter the coordination structure of zinc ions within the electrolyte. This is achieved by introducing foreign solvents/additives or reducing water content, leading to modifications in the zinc deposition mechanism[9]. The interfacial modification strategy involves the application of a protective and functionalized layer onto the surface of the zinc anode. Such modification facilitates the uniform deposition of zinc and enhances the reversibility of zinc-related processes[10].

2. Failure Mechanism of Zinc Ion Battery Anodes

2.1 zinc dendrite

At present, it seems that the generation of dendrites with rough tips during ZIB anode zinc deposition/stripping has become a significant problem in ZIB, and this phenomenon poses a severe hazard to the performance of the cell, mainly in the following aspects:

Firstly, the generation of zinc dendrites initiates corrosion and side reactions. The vertical growth of zinc dendrites along the substrate creates a porous and loosely structured anode, thereby increasing its volume. This structural transformation exacerbates not only corrosion but also leads to the emergence of additional sites for side reactions. These side reactions consume both the electrolyte and zinc metal, further deteriorating the battery's overall performance.

Secondly, the exfoliation of zinc dendrites leads to the formation of "dead zinc." A "dead" or "isolated" zinc structure is formed when the dendrites detach from the electrodes. The presence of this structure reduces the Coulombic Efficiency (CE) and reversibility of the cell, thus degrading the overall performance of the cell. In contrast, zinc deposits with a smooth and compact morphology are more favorable for anodes [11]. These "dead zinc" may react with the electrolyte to produce by-products, increasing the impedance of the electrodes, further impairing the battery performance, and significantly reducing the Coulombic efficiency and capacity of the zinc anode [12].

Finally, owing to its exceptionally high mechanical strength, the uninterrupted growth of zinc dendrites may even penetrate the separator and reach the cathode region, ultimately resulting in a short circuit within the battery. This occurrence can significantly impair the system's regular operation, reducing its lifespan and reliability.

Typically, when zinc dendrites are initially formed, the curvature of these protrusions exceeds that of the surrounding area. This phenomenon triggers the "tip effect" as the heightened curvature results in an elevated surface charge density. Consequently, this leads to an uneven distribution of the electric field and ion concentration. The ultimate consequence of this process is the preferential deposition of zinc ions on these tips faster than in other locations. This, in turn, promotes the rapid expansion of minute protrusions and the formation of substantial dendritic structures[4].

As depicted in Figure 2[13], the growth of zinc dendrites can be summarized as follows: (A) At the outset of the battery cycle, zinc ions tend to undergo reduction at sites characterized by more energetically favorable charge transfer kinetics. This results in the formation of minuscule zinc protrusions on the anode surface. (B) Owing to the effect of low surface energy, zinc ions tend to aggregate on these protrusions, thereby initiating the formation of the initial dendritic structure. (C) The "tip effect" associated with the dendrites amplifies the local electric field, further encouraging

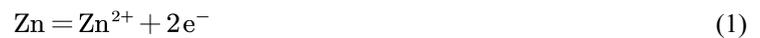
the expansion and surface growth of the dendritic structures. (D) Over time, these zinc dendrites progressively increase in size and ultimately breach the diaphragm layer[12].

In addition to the severe dendritic phenomenon triggered by the uneven distribution of the electric field and zinc ion flux, the concentration polarisation due to the elevated overpotential caused by the formation of a concentration gradient of zinc ions at the anode significantly disturbs the homogeneity of the electric field. This leads to inhomogeneous deposition of zinc, which affects the anode's stability and reversibility [5]. In addition, factors such as current density, cathodic overpotential, carrier concentration, temperature, and residual stress also affect dendrite growth[14].

2.2 Hydrogen precipitation reaction

In addition to zinc deposition occurring at the zinc anode interface, there are side reactions involving other substances, with the most significant being the hydrogen precipitation reaction (HER) induced by water[15]. The reaction mechanism of HER can be briefly summarized as follows: the equilibrium potential of Zn²⁺/Zn consistently remains lower than the equilibrium potential of H₂O/H₂ across the entire pH spectrum, indicating the spontaneous occurrence of HER at the surface of the zinc anode[16]. As depicted in Figure 3 (a) [16], the stable region of Zn metal does not overlap with the electrochemical window of water (the area between the red and blue lines) as pH increases. This suggests that Zn and H₂O do not thermodynamically coexist stably, leading to the spontaneous reduction of water and hydrogen generation. HER is a multifaceted process that can be elucidated as follows[5]:

Anode:



Cathodic hydrogen precipitation:

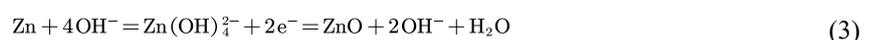


The hydrogen generated through the HER process contributes to increased cell pressure, potentially leading to electrolyte leakage[3]. This, in turn, may result in cell expansion or even explosive events[6], as depicted in Figure 3 (b) [16]. Secondly, the irreversible nature of the HER reaction continuously depletes the zinc anode, significantly diminishing the Coulombic efficiency and capacity of the cell[12]. Lastly, the sustained precipitation of hydrogen leads to the localized alkalization of the electrolyte, resulting in the formation of passivation layers and corrosion by-products. These by-products can interact with Zn²⁺ ions and other electrolyte components, forming insulating substances that hinder uniform galvanic coating[17]. Ultimately, this process leads to the degradation of battery performance or even complete breakdown[18].

2.3 Corrosion and passivation reactions

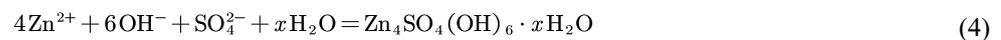
In addition to hydrogen precipitation, the phenomena of corrosion and passivation have garnered significant attention. In the context of electrolytes, the deterioration of zinc anodes can be categorized into two primary modes: chemical corrosion and electrochemical corrosion[19]. In alkaline environments, the zinc anode surface primarily experiences chemical corrosion and exhibits passivation, whereas in neutral or acidic electrolytes, electrochemical corrosion predominantly occurs on the zinc anode surface. The decline and passivation of zinc anodes are visually represented in Figure 4 (a) (b) [10].

In alkaline media, zinc anodes are subjected to severe chemical corrosion. The discharge equation for this corrosion process can be expressed as:



Since the formed is soluble, zinc corrosion can be considered dissolution of the zinc anode. In addition, this corrosion leads to an uneven distribution of zinc dendrites on the electrode surface, which increases the resistance inside the ZIB, as shown in Figure 4 (c) [20]; at the same time, the corrosion-induced by-product is inert, which passivates the surface activity to a large extent, leading to the phenomenon of corrosion-passivation coexistence that is often seen in zinc anodes, as shown in Figure 4 (d) [21], and ultimately leading to capacity decay. In addition, the presence of by-products reduces the active sites on the zinc surface, resulting in an inhomogeneous surface, which aggravates the growth of dendrites [22].

In the electrolyte of neutral or acidic electrolyte, corrosion and passivation are mainly related to the precipitation of H_2 [23]. The decomposition of H_2O and the consumption of H^+ will lead to the increase of OH^- near the Zn anode and the generation of some insoluble by-products to deactivate the anode, taking the commonly used $ZnSO_4$ electrolyte as an example, the results are mainly $ZnSO_4(OH)_6 \cdot xH_2O$ [24], and the formation process can be expressed as follows[24]



This insoluble product forms an interface distinct from the dense Solid Electrolyte Interphase (SEI) film observed in lithium (Li) and sodium (Na) cells, thus inhibiting further interactions between the electrolyte and the anode. However, its porous structure inadequately isolates the electrolyte from fresh zinc, resulting in ongoing corrosion of the anode. Moreover, forming this insoluble product amplifies water and salt consumption, shortening the battery's lifespan.

In addition to theoretical explanations, the corrosion behavior of zinc metal has been confirmed experimentally: Zhao[20] In the experiments of Zhao et al., it was found that after 30 d of standing in a 3 M $ZnSO_4$ electrolyte, the surface of the zinc anode formed flakes $Zn(OH)_6SO_4 \cdot 5H_2O$ of loose material. The severity of the corrosion was visible to the naked eye, as shown in Figure 4 (e) (f) [20] comparison. The white-grey product is unevenly distributed on the surface of the zinc electrode that has been cycled for 30 days, indicating uneven chemical corrosion.

It is essential to highlight the strong correlation between the growth of zinc dendrites, hydrogen precipitation reactions, and corrosion processes. These factors mutually reinforce and exacerbate one another when all three issues coexist. Zinc dendrites' loose and porous nature enhances the contact area between the electrode and the electrolyte, creating more reaction sites and reducing the current density to achieve a lower overpotential. Consequently, this accelerates both the hydrogen precipitation reaction and the corrosion process. Furthermore, the adherence of hydrogen bubbles to the anode surface impedes zinc nucleation, resulting in increased overpotential and uneven zinc deposition. The aggregation of OH^- anions induced by HER further accelerates the corrosion process, resulting in a rougher surface on the produced zinc. This rough surface, in turn, exacerbates the formation of dendrites. Additionally, the by-product layer that forms exhibits a significant curvature and irregular shape, which enhances the contact area and consequently expedites the hydrogen precipitation reaction.

Therefore, anode modification strategies for these three problems must mitigate their effects simultaneously. Specifically, diaphragm modification, electrolyte additives, and anode modification can reduce the overpotential of a hydrogen precipitation reaction, improve the corrosion resistance of electrodes, and improve the growth behavior of zinc dendrites. These modification strategies are expected to enhance the performance and stability of zinc batteries[11].

3. Anode protection strategy

3.1 Separator Modification

One of the crucial components of a battery is the separator, which primarily serves to physically isolate the anode and cathode, preventing direct contact between them. Simultaneously, the wall must maintain sufficient ionic permeability to facilitate continuous battery reactions. Typically, a battery separator consists of multiple layers with distinct characteristics to retain the electrolyte and isolate

dendrites. Conventional walls, such as filter paper and glass fiber, struggle to fulfill all these requirements simultaneously. Therefore, there is an imminent need to develop new partitions [25]. Figure 5 (a) [26] illustrates a schematic comparison of the electric field distribution between unmodified and modified divisions.

Due to dendritic growth and the high internal resistance to mass transfer during the cell cycle, diaphragms with a tall elastic Young's modulus and robust mechanical properties play a crucial role in reducing the resistance encountered by zinc ions during transport and maintaining structural integrity. Diaphragms such as Zn^{2+} -integrated Nafion ionomer membranes[27] and crosslinked polyacrylonitrile-based cation exchange membranes (PAN-S membranes) [25] have been reported to exhibit the capability to inhibit dendrite growth at this stage. For instance, Hu et al. [28] developed an innovative membrane by coating boron nitride nanosheets (BNNSs), known for their high strength and thermal conductivity, onto a porous substrate. This membrane effectively restrained the growth of zinc dendrites, and diaphragms containing BNNSs were employed in alkaline zinc-iron flow batteries, demonstrating stable operation for nearly 500 cycles at a current density of 80 mA cm⁻² (Figure 5(b) (c) [28]).

Additionally, a Zn^{2+} integrated Nafion ionomer membrane has been developed, exhibiting superior electrolyte wettability and mechanical strength compared to conventional diaphragms such as glass fiber and polypropylene, as depicted in Figure 5 (d) [27]. Furthermore, the Nafion membrane's alternating hydrophilic and hydrophobic regions facilitate the uniform transport of zinc ions. These combined characteristics contribute to achieving an even distribution of ions on the electrode surface, resulting in the uniform deposition of Zn^{2+} on the anode surface[29]. Such an ion distribution enhances battery cycle life and stability, reduces dendrite growth on the electrode surface, and improves overall battery performance.

Furthermore, researchers have shown significant interest in ionic pores characterized by a uniform distribution of suitable diameters and porosities, which facilitate efficient ion transport in ZIBs. Liang et al. [30] observed that zinc anodes tended to deposit more readily at locations corresponding to diaphragm pores. They postulated that pore size influences the mode of zinc deposition, with micropores being more likely to guide dendrite formation. Additionally, Wang et al. introduced an innovative diaphragm composed of polyvinyl alcohol (PVA) and Lyocell dual-layer (PLD). This diaphragm exhibits notable electrolyte wettability and features sub-micron-sized pores. These adjustable pores offer a large surface area, significantly enhancing electrochemical performance[31].

3.2 Electrolyte additives

In addition to modified diaphragms, incorporating electrolyte additives represents another common approach to optimize the electric field distribution on the electrode surface. These electrolyte additives are typically classified into two primary categories, organic and inorganic additives, based on their chemical composition [32]. Currently, organic additives that have been reported include organic acids [33], polyvinyl alcohol [34], polyethyleneimine[35], and Triton X-100[36], among others. Commonly employed inorganic additives encompass various metal ions[37] and oxides[38], among other substances.

Common organic additives can guide Zn^{2+} to achieve uniform deposition by an electrostatic screen mechanism on the anode surface. Xu et al.[39] reported minimal ethyl ether (Et₂O) as an electrolyte additive. Et₂O can cover the tip protrusions on the anode surface due to its high polarity and form an electrostatic screen layer that prevents further deposition of Zn^{2+} in the tip region, thus slowing down the growth rate of the dendrites. (Figure 6 (a) [39]), in addition, the polarisation of the cell was significantly reduced from 44mV to 30mV in the initial cycle and remained stable at 30mV for the next 250h (Figure 6 (b) [39]), showing good stability of the

Organic additives can achieve uniform deposition of zinc by electrostatic shielding and prevent the free diffusion of zinc nuclei on the electrode surface by anodic adsorption, thus promoting the consistent testimony of zinc. It has been reported that glycerol[40], polyethylene glycol[41], and other organic molecular additives can prevent the migration of Zn^{2+} on the electrode surface by adsorption

on the anode surface, which both acts as a physical barrier and adsorbs Zn^{2+} ions. Specifically, organic additives such as glycerol allow Zn^{2+} ions to form many tiny nuclei at the initial contact site with the metal (Figure 6 (c) [40]). In contrast, organic additives such as polyethylene glycol allow Zn^{2+} to nucleate preferentially around the additives immobilized on the anode surface[40], thus achieving a homogeneous nucleation process.

In addition, we can also achieve uniform deposition of zinc by inhibiting the zinc deposition kinetics and slowing down the settling rate of zinc ions. Alcohol additives exhibit a strong solvation ability, preferentially solvating with Zn^{2+} , etc., to form strong bonds. This action promotes the achievement of uniform deposition in two ways. On the one hand, water is eliminated from the Zn^{2+} solvated sheath, reducing water activity and inhibiting corrosion passivation; on the other hand, the rate of zinc deposition is slowed down, and uniform deposition is achieved. For example, the introduction of ethylene glycol will lead to the formation of $[Zn(EG)_3]^{2+}$ complexes with a larger radius than, which indicates that the diffusion distance of Zn^{2+} is longer, slowing down the growth of zinc grains on the electrode surface, effectively preventing the local depletion phenomenon of zinc ions, and ensuring the uniformity and densification of zinc deposition[42]

Electrolyte additives serve a dual purpose by facilitating the uniform deposition of zinc and promoting the in-situ formation of a dense and consistent solid electrolyte interface (SEI) layer on the anode surface. This SEI layer effectively suppresses the growth of zinc dendrites and the occurrence of side reactions. Mitigating zinc dendrite growth and side reactions through in-situ SEI formation primarily involves chemical reactions and physical isolation mechanisms. Cao et al. [43] engineered an artificial SEI protective layer by introducing trimethyl ethyl trifluoromethanesulfonate as an additive. This constructed SEI film primarily consisted of ZnF_2 and exhibited a high ZnF_2/Zn interfacial energy, facilitating smooth zinc deposition. Additionally, as depicted in Figure 6 (d) [44], small nodular particles of $ZnCO_3$ and $ZnSO_3$ were embedded in the SEI, enhancing the horizontal diffusion of Zn^{2+} ions instead of vertical migration. This mechanism significantly curtailed the growth of zinc dendrites.

3.3 Anode Modification

Adding some active materials to the zinc anode can change the deposition rule of anode products, Li et al.[45] found that the addition of activated carbon to the anode can make the deposition of Zn dendrites and insoluble anode products occur preferentially in the pores of the activated carbon, thus avoiding that most of the Zn particles will be covered by inactive Zn dendrites and alkaline zinc sulfate, which makes the surface of the Zn particles will remain neat and active, and inhibits the failure of the anode to a certain extent.

In addition, Zeng et al.[46] developed a flexible three-dimensional (3D) carbon nanotube (CNT) framework as a zinc electrodeposition substrate with the structure shown in Figure 7 (a) [46]. the CNT skeleton has a high specific surface area and good electrical conductivity, which reduces the local current density and the Zn nucleation overpotential, resulting in a more homogeneous electric field distribution on the electrode surface, avoiding the growth of dendrites, thus ensuring uniform zinc plating/peeling with high reversibility. In addition, as shown in Figure 7 (b) [46], the CE of the CC electrode starts to decrease after ten cycles, and it drops to 74% at a current density of 2 mA cm^{-2} , with 30 processes of the cell. In contrast, the CE of the CNT electrode remained about 95-97% after a certain number of cycles. When the current density was increased to 5 mA cm^{-2} , the average CE of CNT was approximately 97.9% after the first two cycles, which was better than that of the CC counterpart (90.3%).

In addition to including non-metallic materials, the incorporation of metallic materials also plays a pivotal role in anode modification. For instance, alternating layered nanostructures of zinc and aluminum can be created by forming eutectic alloys of zinc and aluminum. This structure serves a dual purpose—it facilitates the separation of zinc in the precursor eutectic $Zn_{88}Al_{12}$ alloy. It generates in-situ nanopatterns between the core/shell aluminum/aluminum doubled semi-oxide layers. This

phenomenon further guides the subsequent growth of zinc, as depicted in Figure 7 (c). Consequently, the stripping and plating of dendrite-free zinc can maintain stability for over 2,000 hours in an oxygen-free aqueous electrolyte[47].

This structure facilitates zinc stripping from the precursor eutectic $Zn_{88}Al_{12}$ alloy, generating nanopatterns between the core/shell aluminum/aluminum double semi-oxide layers in situ. This further guides the subsequent growth of zinc (as shown in Figure 7 (c) [47]). As a result, the stripping and plating of zinc without dendritic crystals in an oxygen-free aqueous electrolyte could maintain stability for more than 2,000 hours.

In addition to guiding the uniform deposition of Zn by improving the anode surface structure, anode-coated liquid alloy-diffusion synergistic effects can also be used to modulate Zn deposition. Liu et al [48] proposed to apply gallium-indium alloy coatings on Zn anodes. Liquid gallium-indium alloys have a high affinity and conductivity with Zn and thus rapid electron and mass transfer is achieved at the liquid-liquid alloy-electrolyte interface [49]. At the same time, since Zn atoms prefer to be embedded in the alloy rather than bonded to themselves, newly formed Zn atoms can rapidly diffuse into the alloy interlayer through the binary alloy phase. zinc atoms prefer to be embedded in the alloy rather than bonded to themselves, the newly formed zinc atoms on the liquid gallium-indium surface can diffuse rapidly through the binary alloy phase to the intermediate layer of the alloy, and in addition, the corrosion of the modified zinc anode is improved, with a higher hydrogen precipitation reaction overpotential than that of the reference zinc anode

In addition to better-inducing zinc deposition, anodic alloying also enables the anode to have a higher electrochemical potential during the redox process, which significantly enhances the corrosion resistance of the zinc anode, and it was reported that Zhang et al.[50] For the first time, optical microscopy was used to visualize the process of zinc deposition in crystalline species, and it was recently demonstrated from density functional theory that the zinc stripping process in Zn_xAg_{1-x} alloys has a higher electrochemical potential than the Zn^{2+}/Zn redox.

4. Summary and outlook

Overall, ZIBs have been developing rapidly due to their high specific capacity, safety, environmental friendliness, and low cost, and are expected to dominate the energy storage market in the future. Unfortunately, the problem of anode failure has not been well addressed. Uneven electric field and ion concentration distributions lead to significant forms of anode failure, such as zinc dendrite growth, hydrogen precipitation reaction (HER), and corrosion passivation, affecting zinc ion batteries' stability (ZIBs). At the same time, HER and corrosion passivation are mainly caused by zinc's thermodynamic properties and the water molecules' inherent reactivity.

It is worth noting that zinc dendrite growth, hydrogen precipitation reactions, and corrosion passivation processes are closely related. They interact with each other, making their effects more severe when all three problems are present at the same time. Therefore, anode modification strategies for these three problems must mitigate their impact simultaneously to achieve better performance and stability.

This paper synthesizes three aspects of research on diaphragm modification, electrolyte modification, and anode modification to summarize the strategies against anode failure. The diaphragm modification gives the diaphragm high electrolyte wettability and high mechanical strength, which can effectively inhibit the growth of zinc dendrites by homogenizing the surface electric field. The electrolyte modification can effectively regulate the local current density at the electrode tip, uniformly distributing the electric field and promoting uniform zinc deposition. In contrast, the alloying and surface coating of the anode modification enables zinc to be uniformly deposited on the anode by optimizing the electric field distribution on the electrode surface. In summary, it can be concluded that the key to anode modification is to achieve homogenization of the electric field on the surface, directly affecting the homogeneous deposition of zinc.

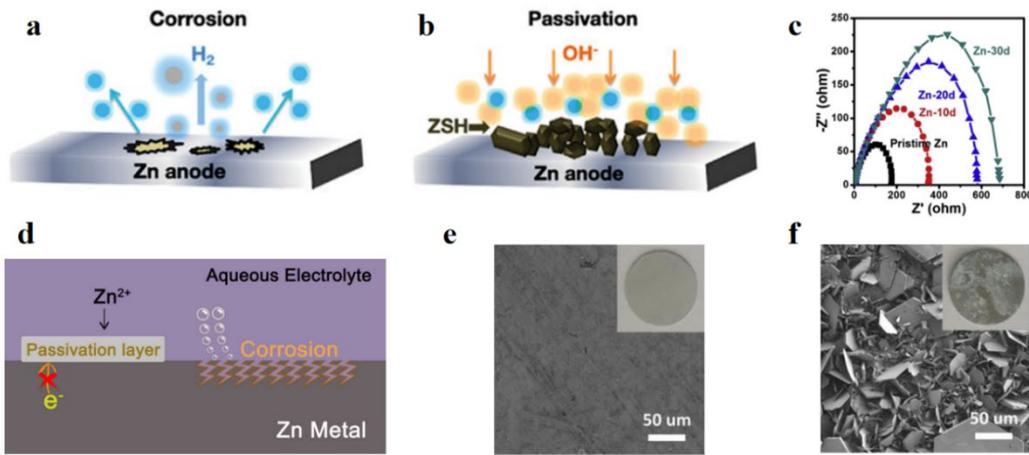


Figure 4. (a) Schematic diagram of zinc anodic corrosion phenomenon.[10] . (b) Schematic diagram of zinc anodic passivation phenomenon[10]. (c) The dendrites that by-products can initiate increase the impedance of the cell[20]. (d) Passivation and corrosion occurring on the surface of zinc anode[21].(e) Top view SEM image of an uncirculated zinc electrode[20]. (f) Full view SEM image of a zinc electrode that cycled for 30 days[20].

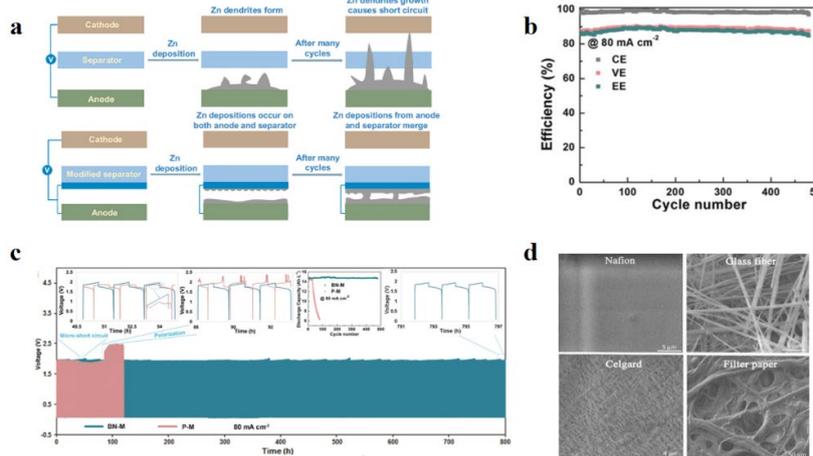


Figure 5. (a) Schematic diagram of the original and modified diaphragm's electric field distribution[26]. (b) Discharge capacity graph of alkaline zinc-iron flow entire cell with BNNs membrane in nearly 500 cycles[28]. (c) Stable voltage profile of alkaline zinc-iron flow whole cell with BNNs membrane[28]. (d) SEM images of different diaphragms[27].

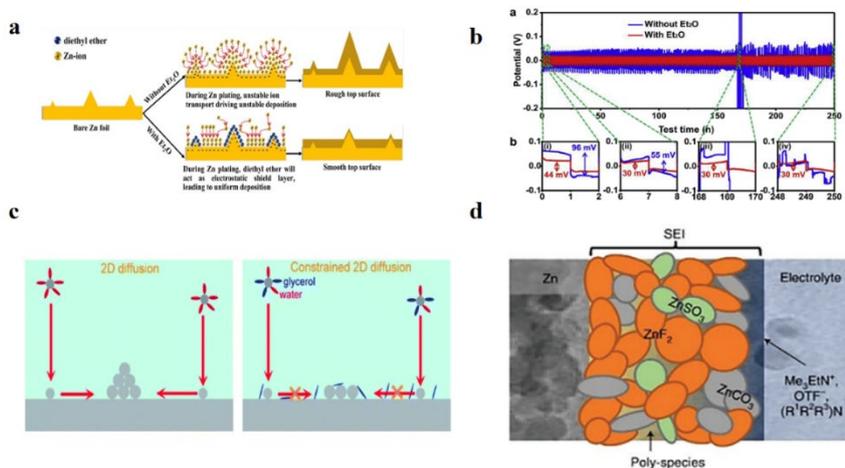


Figure 6. (a) Schematic representation of the morphological evolution of the Zn anode in the electrolyte with and without EtO₂ additive during the Zn stripping/plating cycle[39]. (b) Plots of cyclic electroplating/stripping process and voltage magnification for different cycles of Zn-Zn

symmetric cells with (red curves) and without (blue curves) EtO₂[39]. (c) Schematic diagrams of Zn²⁺ diffusion and reduction processes at the Zn electrode in aqueous and mixed electrolytes[40].(d) Schematic diagram of ZnCO₃ and ZnSO₃ nodular particles embedded in SEIs[44].

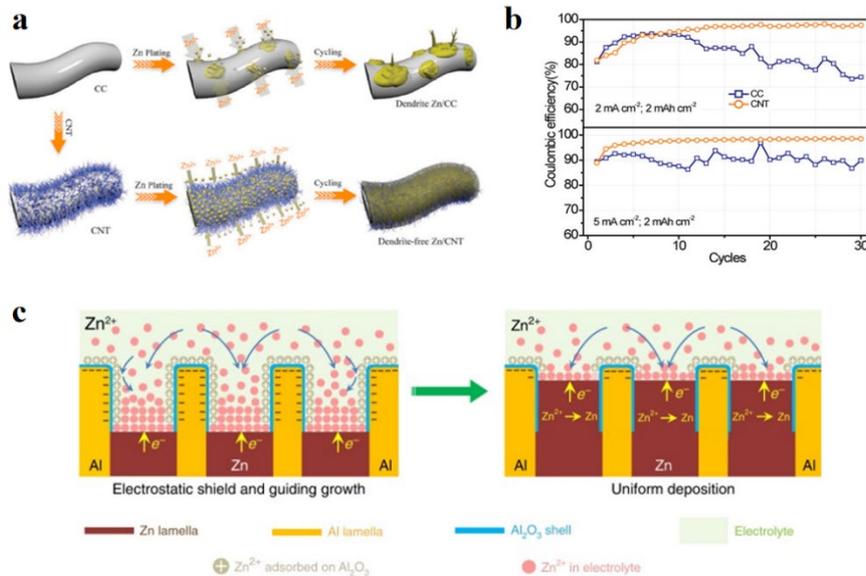


Figure 7. (a) Schematic representation of Zn deposition on carbon cloth (CC) and CNT electrodes[46]. (b) Comparison of Coulombic efficiency of carbon cloth (CC) and CNT electrodes[46]. (c) Al/Al₂O₃ interlayer pattern contributes to the uniform deposition of Zn[47].

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