

Review

Progress in interface structure and modification of zinc anode for aqueous batteries

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ABSTRACT

Rechargeable aqueous zinc-ion batteries (ZIBs) are an attractive option for large-scale energy storage. However, the zinc anode's poor cycling performance precludes practical implementation, owing to uncontrolled dendrite growth and rampant side reactions. Recently, the strategy of interface modification on the zinc anode has been widely explored, and numerous coating materials are reported to have a positive impact on the electrochemical performance. To facilitate comprehension, we present an overview of this strategy. The challenges of state-of-the-art zinc anodes are first introduced, and the preparation methods of the coating materials are classified. Then, the structures and fundamental functions of various modifications are summarized. Additionally, the optimization mechanisms focusing on dendrite control, coulombic efficiency elevation, and some technical issues are discussed in detail. Finally, various points of contention and confusion are mentioned, and the perspectives are provided. We anticipate this review will inspire the researchers, and serve as a guide for future development on interface modification of zinc anodes and ZIBs.

1. Introduction

Rapid economic and social development bolster the success of large-scale energy storage market and drive up demand for battery technologies. High capacity, high safety, high environmental friendliness, and low cost are the primary requirements for large-scale energy storage devices [1]. Lithium-ion batteries (LIBs), which dominate the electric vehicle and mobile electronics markets, do not meet these standards and are therefore less competitive. Rechargeable aqueous zinc-ion batteries (ZIBs) offer a superior solution due to its non-flammable aqueous electrolytes. In general, ZIBs use an insertion/extraction mechanism in cathodes [2] and a deposition/dissolution mechanism in anodes [3]. Numerous studies have been published on the discovery and development of cathode materials [2], which include manganese oxides [4–6], vanadium oxides [7,8], Prussian blue analogs [9], and organic compounds [10]. On the anode side, zinc metal is always assumed to be the default material in most publications, in order to exploit the benefits of zinc metal, such as low redox potential (-0.762 V vs. standard hydrogen electrode), large volumetric capacity (5585 mAh cm^{-3}), and low cost. Other anode materials capable of insertion/extraction of zinc ions have been reported sporadically [11], but have not entered the academic

mainstream due to capacity loss and cost inefficiency.

Until now, ZIB research has been confined to the laboratory, with no prospect of commercialization. One of the primary impediments is the zinc anodes' poor cycling performance. During the deposition process dendrites are produced on the anodes due to zinc's intrinsic proclivity. The dendrite growth at random would result in penetration of the separator, posing the risk of a cell short circuit. Indeed, the unprotected zinc anode is only capable of surviving very few dozens of cycles under the mild test conditions (for example, 23 cycles at 0.5 mA cm^{-2} and 0.5 mAh cm^{-2} in 3 M ZnSO_4 electrolyte [12]), which is much below the practical standard. Additionally, the zinc metal has an unsatisfactory reversibility in aqueous electrolytes, which continues to be a significant barrier to commercialization of ZIBs.

Numerous attempts have been made to address the zinc anode's difficulties, which can be briefly summarized as structure design, electrolyte tuning [13] and interface modification [14]. Typically, structure design strategies involve the use of materials with a high specific surface area as the deposition substrate [15]. The enlarged working area is thought to lessen the working current density and the potential for dendrites and side reactions [16]. Electrolyte tuning is generally used to alter the coordination structure of zinc ions in the electrolyte by

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introducing foreign solvents/additives or by reducing the water content, resulting in a change in deposition mechanism [12]. The strategy of interface modification is to decorate the zinc anode with a protective and functionalized layer, which can promote even zinc deposition and increase zinc reversibility [17,18]. Specifically, this technique is committed to effectively extending the cycle life of the zinc anode. Additionally, it may utilize the standard and inexpensive zinc foil and common aqueous electrolyte in the battery system, keeping strong economical and practical value. As a result, interface modification appears to be a promising strategy for advancing the practical application of ZIBs.

Recently, numerous interface modification cases have been reported to improve the performance of the zinc anodes. Some review articles introduce the employed materials in detail [19]. There is, however, a dearth of comprehensive understanding on mechanisms and optimizations of this strategy. The purpose of this article is to provide an overview of the interface modifications, especially from the perspective of the action mechanism. The inherent chemical features and the limitations of the zinc anodes are briefly introduced. Then the current progress in variety of modification materials and preparation methods are catalogued. Following that, we present the review on the fundamentals and the significant effects of the interface modification, as well as performance optimization options (Scheme 1). Finally, the existing obstacles and future opportunities associated with interface modifications are discussed.

2. Challenges of interface modification

To achieve the goal of high-performance zinc anodes, interface modifications must address pressing challenges such as morphological control and coulombic efficiency (CE) elevation, both of which are intimately tied to the intrinsic features of zinc metal and the accompanying reactions. The relative background is chiefly summarized in this section in order to better understand the functions of the various interface modifications.

2.1. Uncontrolled deposition morphology

The direct use of metals, such as zinc, as anodes in rechargeable batteries has remained a difficult topic for decades. One particular impediment is the short-circuit problem that is caused by local protuberances (dendrites) formed during the deposition (charging) process. While the zinc anode has been widely employed in alkaline electrolytes for decades, it mainly functions as a primary electrode with nearly no

reversibility due to the rapid growth of dendrites. The change in electrolytes, from alkaline to mild, permits the zinc anode to exhibit a weak dendritic propensity, which makes possible the practical application of rechargeable ZIBs.

The dendrite formation is an intrinsic property of zinc metal. Generally, non-uniform electrochemical reactions would occur as a result of the inevitable heterogeneity of metal electrode and electrolyte, resulting in the even faster growth of certain deposits, namely dendritic seeds. Following that, zinc ions diffuse and accumulate at pre-existing nucleation seeds [20]. Certain protuberances may receive increased electric intensity and higher zinc ion concentration due to the so-called "tip effects", resulting in faster growth. More specifically, zinc ions are typically deposited as hexagonal platelets to reduce the thermodynamic free energy (Fig. 1a). During cycling, these platelets at such protruding sites are not uniformly arranged, but rather grow in an arbitrary manner. They gradually develop into tree-like dendrites of considerable size (Fig. 1b), posing a threat of bridging the cathode [21].

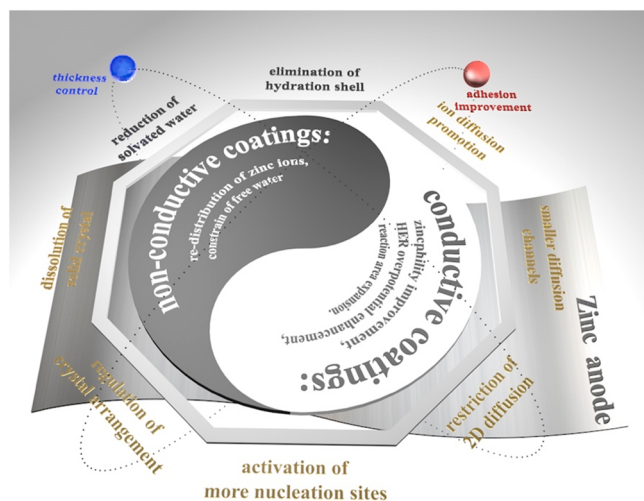
Dendrite formation is a complex process that is influenced by a variety of parameters, including zinc ion concentration, cation type, applied current density, deposition capacity, and even the configuration of the electrode [14]. However, until now, the proposed theories have always been qualitative in nature rather than quantitative. There is no precise description of the evolution of morphology, which complicates the design of interface modifications. For another, severing the chain at any moment throughout the dendritic growth process may result in a more desirable morphology, allowing for a variety of interface modifications. The details will be covered in further detail below.

2.2. Undesirable coulombic efficiency

Another impediment to practical application of zinc anode is its low CE. In typical electrolytes, the zinc electrode has a catastrophic reversibility of 40–81% [18,22] (depends on the electrolytes and test protocols). This means much energy is wasted during the deposition process, and such a low CE value is unacceptable in practice. To facilitate commercialization, Xu et al. established an ambitious goal: the ideal zinc anode should exhibit 100 percent reversibility within 2000 cycles [23]. This is an extremely difficult goal, and additional work should be done on interface modifications to achieve this stringent criterion.

Not only does inefficient efficiency indicate low energy productivity, but it also serves as a warning sign of battery failure. The poor CE is typically caused by unwanted side reactions at the anode, as well as material loss through dendrites. Thermodynamically, the redox potential of H^+/H is always positive than that of Zn^{2+}/Zn across all pH ranges (see the Pourbaix diagram in Fig. 1c), implying that the hydrogen evolution reaction (HER) is unavoidable throughout the charging process in aqueous electrolytes. However, the gaseous hydrogen would diffuse away from the anode surface, preventing it from being oxidized again. The gas escape may also deteriorate the contact between the electrodes and the electrolytes, resulting in impedance increase. Additionally, hydroxide ions are formed as a result of HER, and the alkalinization of the anolyte promotes the formation of a precipitate in the form of $Zn_x(OH)_yA_z \cdot nH_2O$ (where A denotes the zinc salt anion, and x, y, z, and n denote certain stoichiometric quantities) [24]. These byproducts have extremely low K_{sp} (for example, K_{sp} of $Zn_4SO_4(OH)_6 \cdot nH_2O$ is 10^{-51} [25]) and excellent insulation, which may passivate the zinc anode and promote its irreversibility [26] (Fig. 1d). Moreover, uncontrolled side reactions would continuously deplete the electrolyte, increasing the cell impedance [27].

In addition, the sharp tips of the dendrites are brittle, which may easily fall off the framework as the "dead zinc." As with the dead lithium [28], the dead zinc has a strong correlation with the deposition morphology. Dendrite growth theoretically follows fractal geometry, which is self-similar to a fractal tree with a high fractal dimension value (Fig. 1e) [29]. The tree root becomes the configuration's weakest link. Once the root is dissolved during the discharging process, the crown



Scheme 1. mechanism and optimization of interfacial structure and modification for zinc anode.

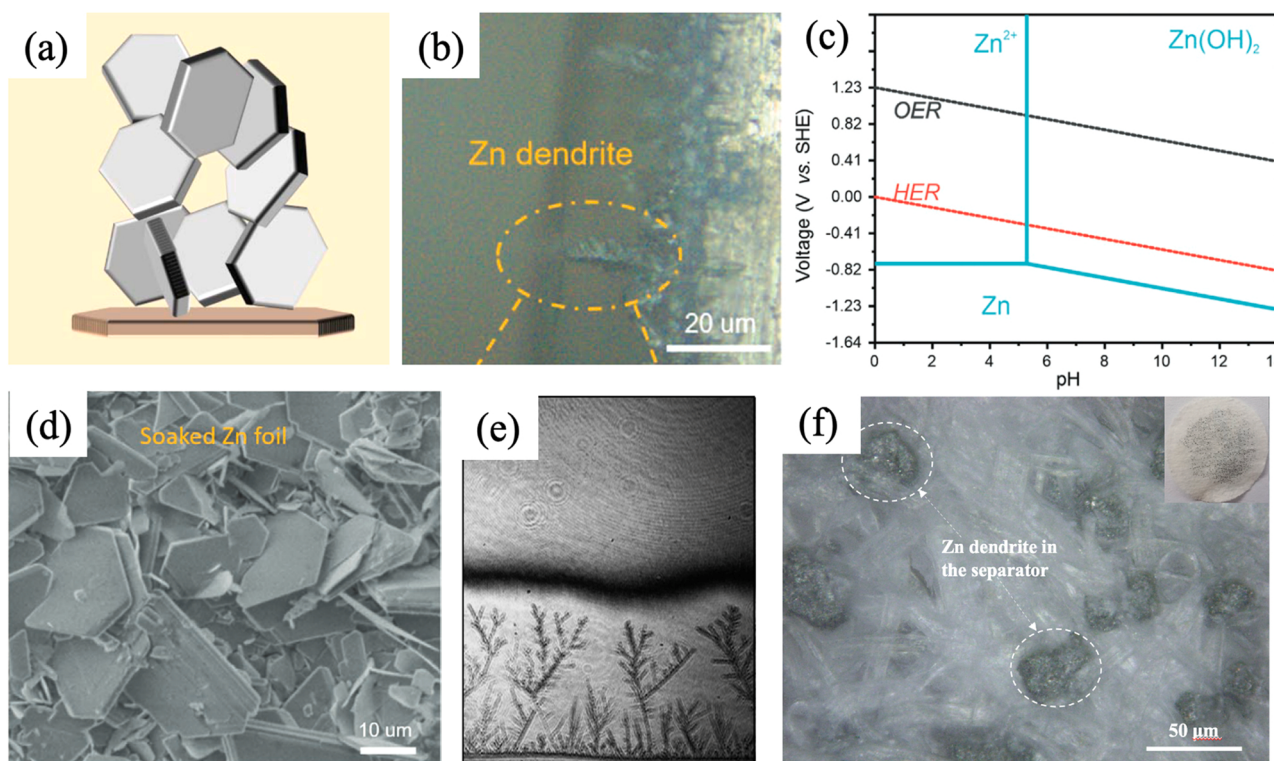


Fig. 1. a) hexagonal platelets of deposited zinc crystals [30]. b) tree-like zinc dendrite [14]. c) Pourbaix diagram of Zn-water system [31]. d) byproducts on the soaked zinc [21]. e) dendrites with fractal geometry [29]. f) dead zinc in separator [12].

separates from the substrate and loses electrical contact, reducing reutilization. This phenomenon has been verified in some literatures, in which large-size dead zinc is captured by the separator (Fig. 1f) [12].

Notably, the increase in CE is a synergistic effect of both side-reaction inhibition and dead zinc suppression. On the one hand, a reduction in the accumulation of passivating byproducts on the anode can improve the uniformity of the electric field, thus slowing dendrite growth. On the other hand, dendrite suppression results in fewer HER active sites. The introduction of functional groups in modification layers can significantly reinforce the reversibility of the anode, as discussed in the following section.

3. Preparation methods of the interface modifications

Numerous materials, such as metals, compound particles, and polymers, can be used to modify the zinc anode's surface. However, the preparation procedure varies according to the material's physical/chemical characters. As a heterogeneous phase, only a slight dosage of modification layer may have a significant effect on the zinc substrate's electrochemical performance. As a result, the preparation procedure is critical for developing a high-quality coating layer. Note that the modification layers in this overview are not related to the SEI induced by electrolyte optimization, thus showing universality to various electrolytes and cathodes. This section summarizes the methodologies and their applicability in order to provide direction and avoid misunderstandings for subsequent researchers.

3.1. ex-situ preparation methods

3.1.1. Doctor blading method

Doctor blading is the most frequently used ex-situ method for coating preparation. The coating material is combined with the binder in an organic solvent in this method. The slurry is then cast onto zinc foils and the thickness is controlled by the blade. After the solvent evaporates, a

thin film is formed on the zinc surface (Fig. 2a). Due to the use of binders that connect the microparticles and provide mechanical strength, this method rarely requires adhesive properties of the coating materials, thereby expanding the selection range. It is applicable to inorganic particles, where PVDF is frequently used as a binder and NMP is frequently the solvent. This method has been reported in the CaCO_3 [20], TiO_2 [32], SiO_2 [33] and Al_2O_3 [34] coatings. Additionally, this method can be used with organic polymers, and no binders are required due to the polymers' self-solidification. Materials such as Nafion [18], SPEEK [17] and PAN [35] have been suggested. Due to its simplicity of operation and established commercialization in other fields (for example, the electrode preparation in LIBs), this method is highly applicable and economically viable.

3.1.2. Spin-coating method

The typical spin-coating also uses coating material's slurry as the mentioned above. A typical spin-coating process consists of four fundamental stages: solution deposition, substrate acceleration, flow dominance, and solvent evaporation (Fig. 2b). Centrifugal force spreads the liquid solution across the wafer, resulting in a uniform film. The layer's thickness is inversely proportional to the cube root of the solvent's viscosity and the square root of the spin speed [36]. Therefore, the critical factor for adequate preparation is to match the spin speed and viscosity of the solvent. This method is appropriate for organic polymers that solidify spontaneously upon solvent evaporation. Various polymers have been used to decorate the zinc anode, including PVB [21], cyanoacrylate [37], and PVDF [38], and the thickness can be adjusted between 200 nm and 5 μm .

3.2. in-situ preparation methods with gaseous deposition

3.2.1. Physical vapor deposition (PVD)

In general, the PVD process forces the coating material to transform from a solid target to a gaseous state, from which it deposits on the zinc

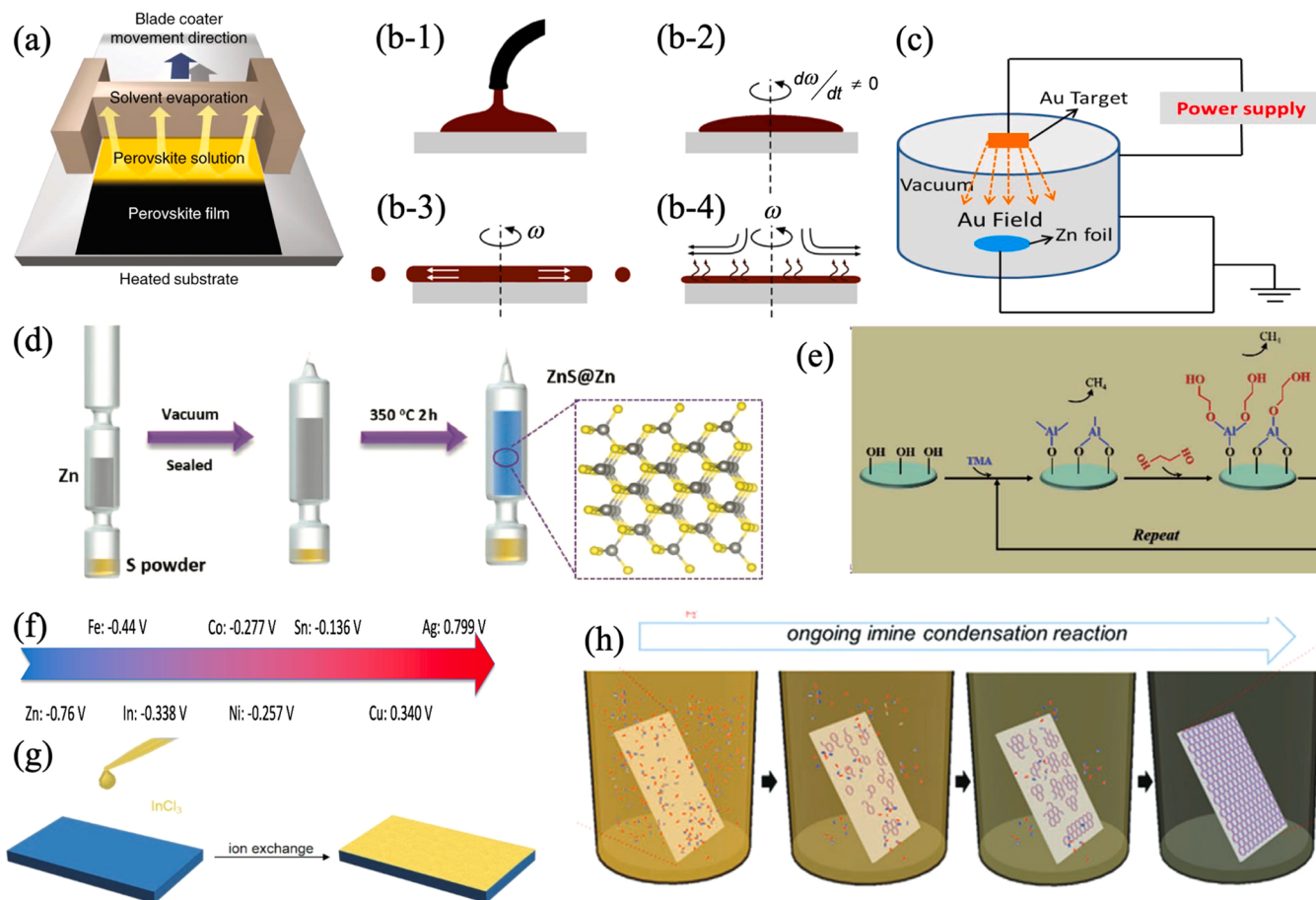


Fig. 2. Preparation method of a) doctor blading [55], b) spin coating [36], c) PVD [39], d) CVD [26], e) MLD [44], g) electrochemical deposition [46], and h) chemical deposition [53]. f) The possible elements and the redox potential for ion-exchange method.

substrate physically. Ion beam sputtering (IBS) is a type of PVD that utilizes an ion source to generate a focused ion beam that impinges on a target material and sputters the atoms (Fig. 2c). The IBS has been used in the membrane manufacturing of metals/alloys, particularly those with a high melting point. Cui et al. use IBS to decorate Au on zinc foil [39]. Due to the extremely short sputtering time (20–60 s), the Au coating is not a continuous membrane but rather a collection of isolated nanoparticles. The particle size increases along with the sputtering time, indicating that Au grows in an island manner on zinc substrate. Continuous film can also be prepared by PVD method. The magnetron sputtering has been proposed to prepare the TiN film on the zinc surface, which utilizes a magnetic field to constrain the electron in the plasma [40]. The atmosphere is studied because it has a significant effect on the growth mode and specific orientation of the deposition. Enrichment of N_2 in the air flux results in increased exposure of the flat (200) facet, whereas dilution of N_2 results in increased exposure of the zigzag (111) facet.

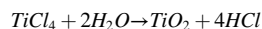
3.2.2. Chemical vapor deposition (CVD)

The interface modification can be constructed using low melting point materials via the chemical vapor deposition (CVD) process, in which the material vapor takes chemical reaction with the zinc substrate. It is a cost-effective technique due to its simplicity and high speed. Guo et al. utilize $SnCl_2$ as the deposition agent [41]. When the $SnCl_2$ is heated to 300 °C in an Ar atmosphere, it vaporizes and reacts with the zinc metal, leaving uniformly distributed Sn nanoparticles as the conductive coating on the zinc surface. High vacuum can also be induced to lowering the vaporization point of the target material. For example in the ZnS coating case, the zinc foil and sulfur are placed in an

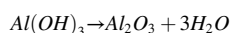
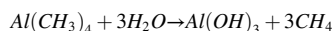
evacuated and sealed tube [26]. When heated, the sulfur vapor reacts with zinc metal, in-situ forming the ZnS layer on the zinc surface (Fig. 2d). Since the vapor is uniformly distributed throughout the tube, the reaction occurs in a well-balanced manner, and the zinc surface is uniformly coated with ZnS. This CVD method enables a novel way to decorate a dense layer with high adhesion while avoiding the crystal anisotropy associated with liquid phase reactions.

3.2.3. Atomic layer deposition & molecular layer deposition

Atomic layer deposition (ALD) is a novel method of thin film deposition in which the coating layer grows atom by atom and layer by layer. As a result, it is capable of achieving superior coverage and conformal deposition on an atomic scale. The film's thickness can be precisely controlled due to the self-limiting nature. The TiO_2 coating has been reported via ALD [42]. The precursors of H_2O and $TiCl_4$ vapor are periodically injected and purged according to the equation [43]:



Besides, the Al_2O_3 layer has been proposed with the trimethylaluminum and H_2O as the precursors. The whole process contains the decomposition of the direct product of $Al(OH)_3$, following the equations [34]:



As with ALD, the molecular layer deposition (MLD) is also a film deposition technique that results in the formation of a metal-based hybrid polymer (Alucone, Mangancones, Zincone, etc.). He et al.

report a novel inorganic–organic hybrid coating of “Alucone” via MLD [44]. By alternatively supplying trimethylaluminum (TMA) and glycol ($\text{HO}-\text{CH}_2-\text{CH}_2-\text{OH}$) into a commercial ALD system at 150°C , a compact ultrathin Alucone film composed of organic and inorganic chains with good adhesion is generated (Fig. 2e).

3.3. *in-situ* preparation methods with liquid-phase reactions

3.3.1. Electrochemical deposition with zinc metal

The most straightforward electrochemical method is the ion-exchange method, which makes use of the redox potential difference between zinc and other elements. Foreign ions in solution with a higher positive potential than zinc ions can be reduced automatically by the zinc metal. The electrochemically inner elements can theoretically be applied via the ion-exchange method, but stability and compatibility must be considered. In Fig. 2f, we listed the possible options of elements and their standard potential vs. standard hydrogen electrode, excluding the toxic ones (for example, Cr and Pb). Certain elements have been reported, including In, Sn, Cu, and Ag, etc. The decoration effect varies according to the solvent, reaction time, and anions used. For example, it has been reported that after prolonged treatment time with InCl_3 solution a porous structure of In coating can be generated [45], whereas a compact structure of microparticles can be observed with shorter treatment time [46] (Fig. 2g). By far, there is a dearth of comprehensive research on reaction parameters. Besides this, it should be noted that the ion-exchange product is not always the final decoration layer, as some additional reaction occurs during the electrochemical process. It is possible to form a Zn-based alloy or even amorphous SEI, as discussed below. Several complex compounds, including GO-based materials [47, 48] and MOF [49], can also be synthesized directly on the zinc foil. The precursors of these materials can be reduced by zinc metal and self-assemble onto the zinc surface to form a dense and flat film.

The electrochemical deposition can also be accelerated by impressed external current. In the case of ZnF_2 [50] and ZnP [51] coatings, anodic polarization is applied which continuously provides zinc ions. Then the zinc ions react with the fluoride ions or hypophosphite ions to form the precipitates from bottom to top. The value of current density and reaction time can be optimized swiftly, thus the electrochemical treatment is a promising method for modification with high efficiency and versatility.

3.3.2. Chemical deposition on the zinc surface

Certain special materials are capable of chemically reacting and aggregating to form a film, and the zinc electrodes act as deposition substrates. For instance, the HsGDY coating is grown *in-situ* via alkynyl-site cross-coupling [52]. When the zinc substrate is immersed in the 1,3,5-Triethynylbenzene (TEB) solution, the TEB monomer undergoes cyclization, resulting in the spontaneous formation of the HsGDY layer on the zinc substrate. The COF layer is also reported using a similar procedure [53]. When adsorbed on zinc, precursors of 1,3,5-triphloroglucinol (TFP) can react with a variety of aromatic amine linkers to form a dense COF layer (Fig. 2h). The straightforward liquid-phase reaction enables the decoration of zinc anodes in a variety of configurations, from large planar to curvilinear. Recently, MXene has been proposed as a coating layer for zinc anodes [54]. The $\text{Ti}_3\text{C}_2\text{Tx}$ MXene is synthesized initially with a high concentration of negatively charged oxygen-containing groups. When the zinc foil comes into contact with the MXene solution, the zinc ions react with the oxygen-containing groups, weakening the electrostatic attraction between the MXene sheets. Then the MXene sheets can be generated uniformly layer by layer on the zinc surface after the static attraction becomes greater than the bonding interaction. Chemical deposition modification layers always have a high adhesion, as discussed below.

4. Structure and basic function of interface modification

According to the conductivity of the coating material and the deposition sites of zinc ions, interface modifications can be classified as conductive layers or non-conductive layers (Fig. 3). Metals/alloys, carbon-based materials, etc. are included in the former. In such cases, the zinc ions tend to be reduced via charge transfer at the interface between conductive layer and electrolyte. The latter category encompasses oxides, sulfides, inorganic salts, and organic polymers, etc. These modification layers act as a non-reactive protective layer on the zinc surface. They provide an additional pathway for zinc ions and may alter the solution composition's distribution. Though many modifications present multifunctional properties, there are some basic and universal mechanisms. This chapter summarizes the fundamental functions of the coating layers, and the advanced ones are discussed in the next chapter.

4.1. Conductive layers

4.1.1. Zincophilicity alteration by foreign metals for dendrite control

Certain partial coverings of foreign metals on the zinc anode have been reported to successfully alter the nucleation process. Cui et al. sputter isolated Au nanoparticles (100 nm) onto the zinc surface [39]. The Au nanoparticles with an increased local electric field act as heterogeneous seeds, and the zinc ions preferentially nucleate at the existing Au particles. The following zinc ions are then deposited on the nucleation sites. After cycling, uniform Zn-flake arrays can be formed (Fig. 4a), effectively extending the cycling lifetime of the zinc anode from 92 to 2000 h (0.25 mA cm^{-2} , 0.05 mAh cm^{-2}). Coating Sn [41,56] and Ag [57,58] nanoparticles have the similar effect on increasing Zn nucleation sites and offers improved cycling performance and decreased polarization as an affordable alternative. The research on In coating reveals this mechanism, that the foreign metal presents a higher adsorption energy than the zinc substrate for zinc ions (-0.525 eV vs. -0.402 eV , see Fig. 4b and c). As a result, the zinc atoms preferentially adsorb and deposit on the In particles [45]. The high zincophilicity of In makes it an excellent nucleating agent for promoting uniform zinc deposition. The symmetric cell with coated electrodes can operate for up to 1500 h (0.2 mA cm^{-2} and 0.2 mAh cm^{-2}), nearly ten times longer than the cell with bare zinc electrodes. Additionally, the decreased polarization confirms the zincophilicity of In particles.

The total coverage of foreign metals can also increase zincophilicity. Cai et al. use the ion-exchange method to decorate a dense Cu layer on the zinc anode [59]. In contrast to the above-mentioned elements, this Cu layer dissolves with zinc during the stripping process and re-deposits with zinc ions at the plating process. Thus, a Cu–Zn alloy can be formed in electrochemical cycling. According to the DFT calculation results [58, 60], the alloy layer is composed of Cu_5Zn_8 and Cu_1Zn_1 , which own higher negative binding energies with zinc ions than zinc metal. Increased zincophilicity leads to in homogeneous adsorption of zinc ions rather than localized aggregation, resulting in significantly improved nucleation. Therefore, the decorated electrode exhibits a significantly increased cycling life of over 500 h in symmetric-cell tests (1 mA cm^{-2} , 0.5 mAh cm^{-2}).

4.1.2. HER overpotential increase for CE elevation

Though HER is thermodynamically feasible during the charging process, it presents sluggish kinetics and needs certain overpotential to take place. Three sources are responsible for HER overpotential, namely activation potential, concentration potential, and resistance potential. For metal/alloy coatings, the differences of the latter two parts are always negligible, and the activation part contributes most. Generally, the HER in mild acid electrolytes obeys Volmer–Heyrovsky or Volmer–Tafel mechanism, of which the Volmer process is the initial and rate-determining step. This process describes the formation of adsorbed H atom at certain reaction site:

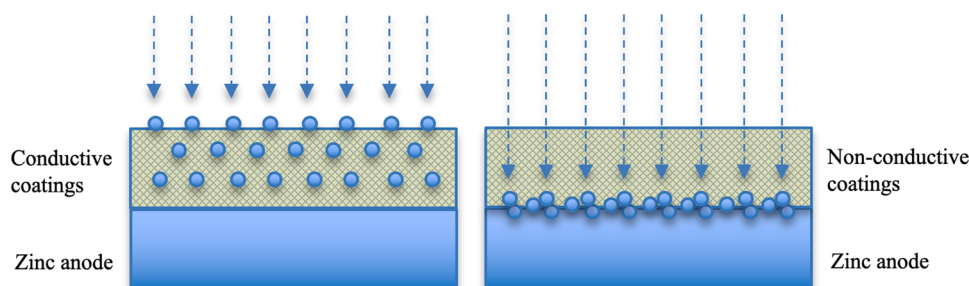


Fig. 3. the comparison of conductive coatings and non-conductive coatings.

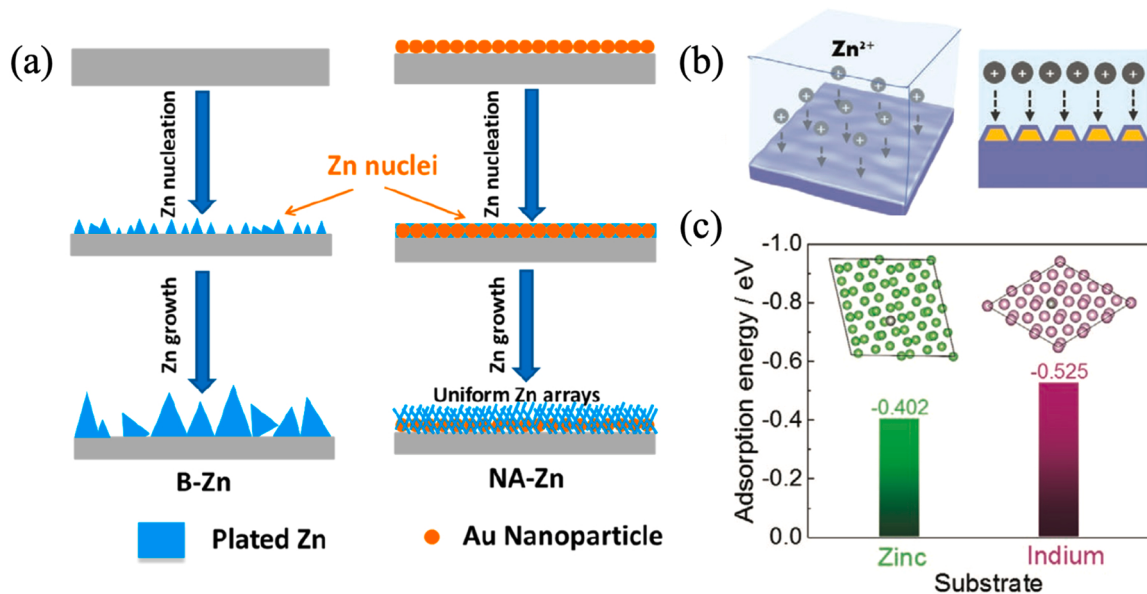
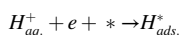


Fig. 4. a) schematic diagram of uniform zinc deposit induced by Au nanoparticles [39]. b) schematic diagram of uniform ion distribution induced by indium particles [45]. c) calculation results of adsorption energy for zinc and indium substrate to zinc ions [45].



which is highly related to the electrochemical adsorption capabilities of the substrate (denoted as *). As illustrated in Fig. 5a, some metal elements, such as Sn, Cu, and In, own lower energy of Metal-H bond than Zn. Therefore, more energy is needed to start the Volmer process on such metals, which leads to higher overpotential [61]. From this point of view, these foreign metal coating can be regarded as the poisoning agent for HER.

Experimentally, due to In's high chemical inactivity and high hydrogen evolution overpotential, doping of the ppm level works [62]. Metallic In significantly reduces the HER activity when coated on the zinc surface [45]. As illustrated in Fig. 5b, the In-coated electrode's onset potential for HER is -1.78 V vs. Ag/AgCl, which is 0.24 V lower than the bare zinc electrode. The effect of the In coating can also be observed in-situ on the electrodes. The coated electrode exhibits a smooth profile during the charging process, whereas the bare zinc suffers HER and large bubbles are released (Fig. 5c and d). Similarly, decoration of Cu [59], Ag [58], and Sn [56] increases the HER over potential, as demonstrated by the increased stability of CE after the long-term cycling test. Due to the chemical stability of such alloying elements, it also provides better anti-corrosion capability than bare zinc.

4.1.3. Reaction area expansion by carbon materials for dendrite control

The improved nucleation sites can be achieved by increasing the active area of the electrode surface, which can be thought of as surface

remodeling. Obviously, the expanded area provides additional reaction sites and reduces the working current density. Theoretically, the lower current density compensates the diffusion of zinc ions and prolongs the Sand's time, slowing down the dendrite growth (Fig. 6a) [64]. Experimentally it is also demonstrated that the dendrite size is proportional to the current density (Fig. 6b), while the cycling lifetime is inversely proportional to the current density (Fig. 6c) [16]. As a consequence, the reaction area expansion could effectively delay zinc ion exhaustion and suppress dendrite growth.

To increase the electrode's active area, carbon-based conductive materials with a high specific surface area and high conductivity can be used as the coating material. Wang et al. reveal the formation of a porous conductive network on zinc anode using carbon black and a nano-fibrillated cellulose binder [65]. The increased electrochemical area of the coating layer greatly facilitates charge transport at the anode, resulting in more uniform zinc stripping/plating and a longer anode life (300 h at 1 mA cm^{-2} , 1 mAh cm^{-2}). Due to graphene's ultra-high specific surface [66], it is reported as an improved coating material. The undulate rGO sheets are layered together to form a stable scaffold with a significantly increased reaction area [69] (Fig. 6d). Zinc ions nucleate in a variety of ways within the layers, and each nucleus grows slowly as the current density decreases (Fig. 6e). As a result, vertical dendrites are severely suppressed, and the cycling lifetime of the anode is prolonged to 300 h. (1 mA cm^{-2} , 1 mAh cm^{-2}). Graphene [67] and carbon hollow spheres [68] all contribute to increasing the surface area and promoting uniform deposition.

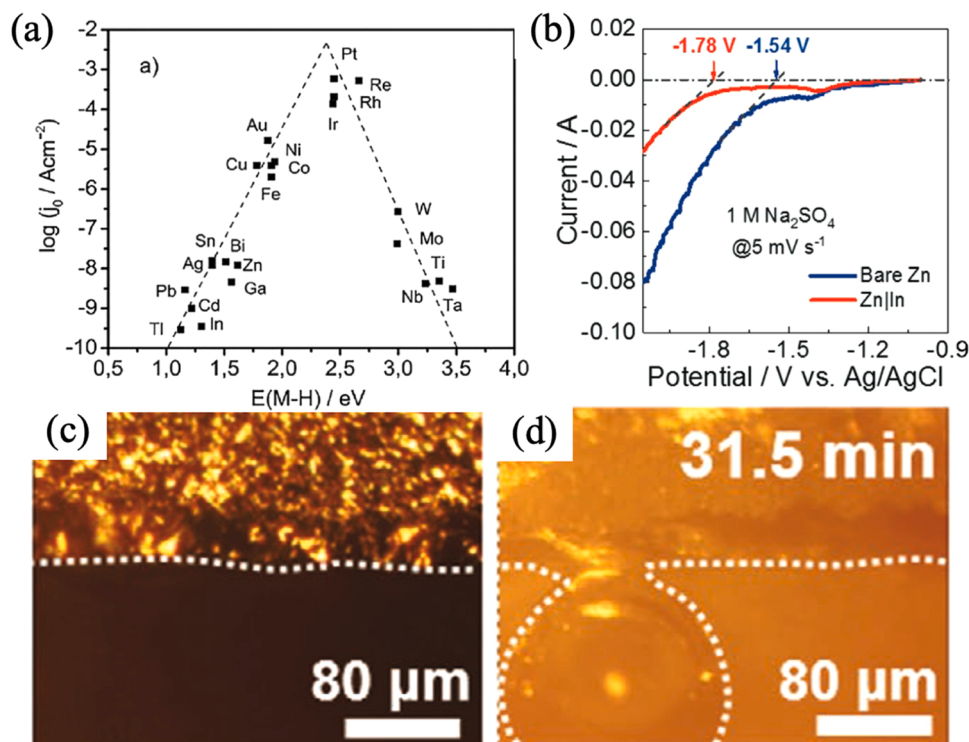


Fig. 5. a) HER “volcano” plot for different metal elements [63]. b) LSV results of bare zinc and In-coated zinc electrode. c) the smooth morphology of coated zinc and d) the released bubbles at bare zinc during the charging process [45].

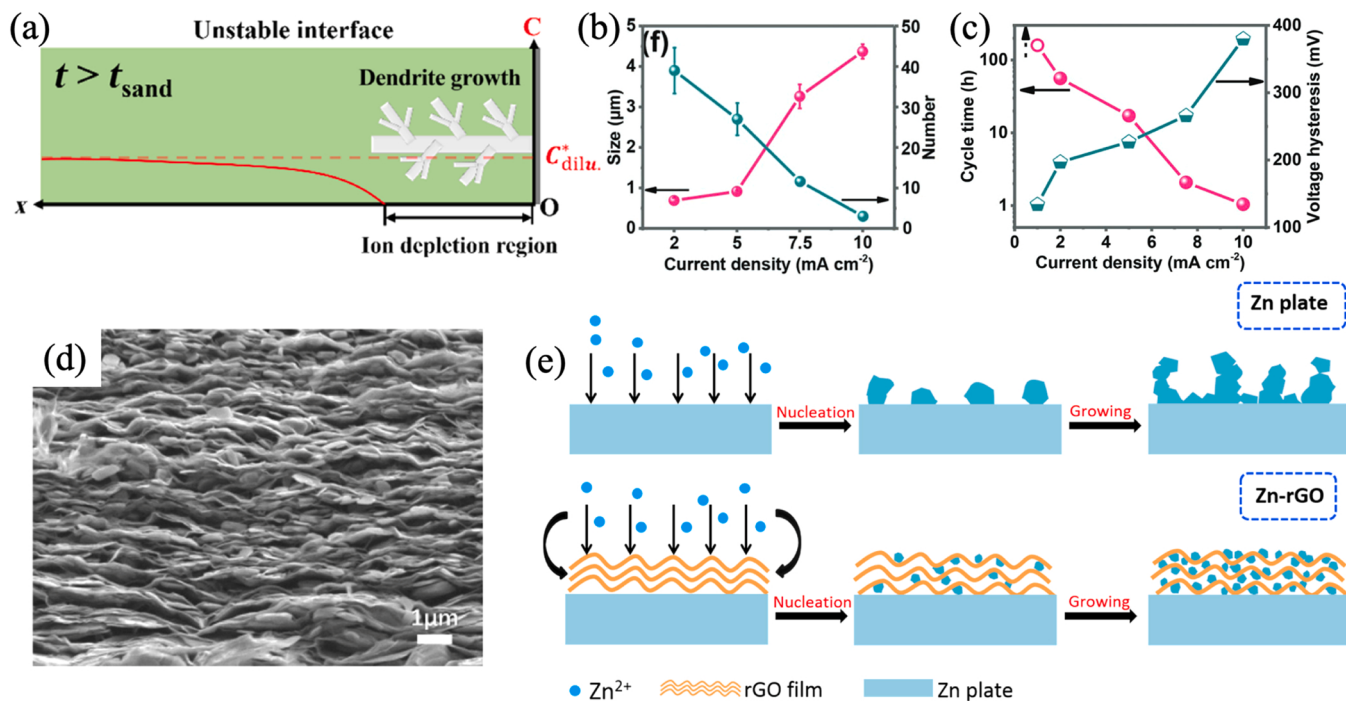


Fig. 6. a) dendrite growth induced by ion depletion [64]. Relationship of b) dendrite size and c) cycle time to charging current density [16]. d) SEM images of graphene scaffold. e) schematic diagram of increased nucleation sites induced by rGO coating [66].

4.2. Non-conductive layers

4.2.1. Re-distribution of zinc ions for dendrite control

Due to the fact that dendrite formation is a spontaneous process, attempting to prevent dendrite thermodynamically is not feasible. As a result, the focus of dendrite control shifts to the kinetic transformation of

deposition products from large, isolated clusters to multiplied grains with reduced size. Ion flux and electric field have a major impact on the deposition morphology [64]. The ion transfer mechanism alters the crystal orientation and distribution of the deposited products, and the electric field concentration on the dendrite tip accentuates the unevenness of the ion transfer.

The non-conductive layers can act as a sieve, redistributing the zinc ion flux and electric field. The simulation technology of field distribution is proposed as a potent tool for elucidating the sieve mechanism. Once the dendritic seed forms on the bare zinc anode, it is calculated that the sharp ridge receives an uneven localized electric field, which manifests as an increase in intensity and direction distortion (Fig. 7a) [52]. By forming a high charge region, the enhanced electric field at the protuberance site accelerates electrochemical deposition. However, in the case of the coated electrode, the inert coatings prevent distortion of electric field on the top of the dendritic seeds (Fig. 7b), and the zinc ions are re-distributed via the interconnected tunnels. Then a uniform concentration can be obtained across the entire zinc anode.

This function of the coating has been demonstrated experimentally using a variety of materials, both inorganic and organic ones. Notably, the porosity of the coating is dependent on both the substrate and the preparation process. Certain ex-situ preparation techniques enable the usage of dense and stable crystals (for example, the doctor blading method). A class of coatings is composed of inorganic crystal powders that act as a framework and create numerous small gaps between the piled particles, referred to as ion tunnels. For instance, the CaCO_3 coating has an average pore size of 32 nm between the close-packed material [20]. Uniform zinc ion flux can be achieved across the nano-porous coating layer, effectively eliminating the tip effect (Fig. 7c). Under the coating layer, the smooth deposition morphology can be achieved. In comparison, random zinc ion diffusion onto the bare zinc anode results in uncontrolled deposition and the formation of additional detrimental dendrites. The symmetric cell's lifetime is significantly increased from 55 to 836 h (0.25 mA cm^{-2} , 0.05 mAh cm^{-2}). Many such inert crystals such as SiO_2 [33], TiO_2 [32], ZrO_2 [70] as well as organic polymers such as SPEEK [17], PVB [21] and Nafion [18] have also been reported as coating materials due to their sieve effect on dendrite control.

4.2.2. Constraint of free water for CE elevation

Concerning the CE elevation, one possibility for HER inactivation is to reduce the free water content at the anode/electrode interface, which also helps to address the corrosion issue in the open circuit condition

[45,71]. Certain coatings, such as Kaolin [72] and CaCO_3 [20], are claimed to resist the permeation of solution water molecules, though the details are not provided. Besides, the hydrophobic organic binder in the coating layer is hypothesized to contribute to water resistance. Zhao et al. propose a universal concept to account for the increase in CE for inorganic coatings [73]. When PVDF is used as the binder, it can act as an elastic water blocker. The hydrophobic nature of PVDF can be demonstrated through the immersion test, in which the electrolyte corrodes bare zinc while leaving the coated zinc lustrous. The water constraint effect on organic layers is examined in greater detail. Consider the PA coating as an example [74], it contains an abundant hydrogen bonding network that tethers the water molecules together, thereby destroying the solvation-sheath of zinc ions (Fig. 8a and b). As a result, the amount of water components involved in HER is reduced, and the side reaction is weakened. The decorated electrode has a higher CE value than the unadorned electrode (Fig. 8c).

5. Optimization strategies for high-performance interface modification

Since the interface modifications show great potential to address the zinc anode issues such as dendrite formation and side reactions, the researchers are dedicated to developing novel materials and expanding the capabilities of modifications. Numerous optimization strategies for practical application of ZIBs have been proposed. The strategies are summarized and discussed in detail in this section to facilitate comprehension, serving as an inspiration for future development of advanced modification layers.

5.1. Comparison of conductive and non-conductive layers

Conductive coatings have received less attention than non-conductive coatings. The reason is that the range of available conductive materials is limited, and their performance is inferior to that of non-conductive ones. Only those metal elements with a higher positive redox potential can be substituted with zinc metal and applied as an interface layer. After excluding the noxious and precious elements, the options are

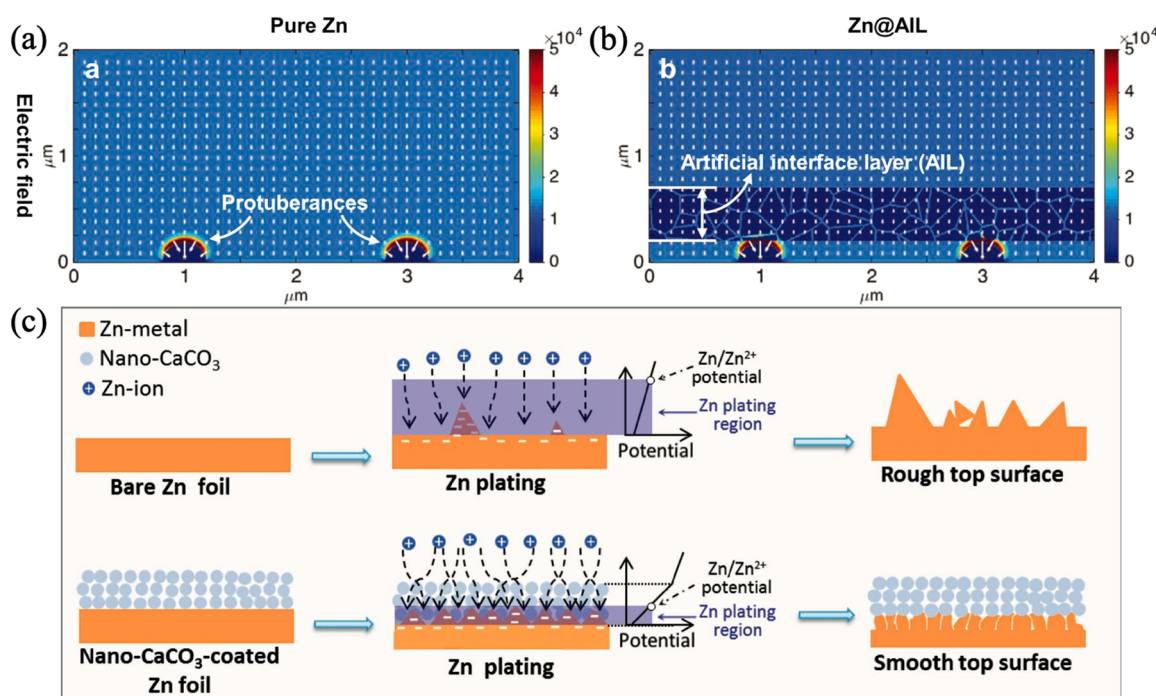


Fig. 7. a) enhanced electric field induced by dendrite seeds [52]. b) uniform electric field induced by coating layer. c) schematic diagram of zinc deposition with/without CaCO_3 coating [20].

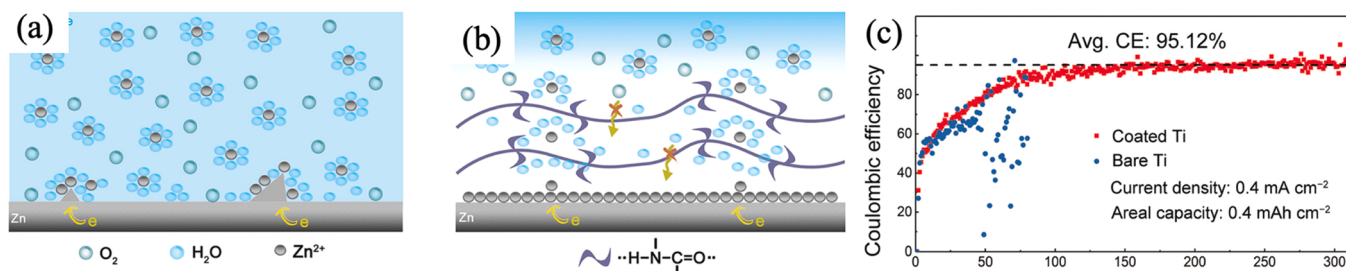


Fig. 8. schematic diagram of a) free water at the zinc surface and the constraint of free water by PA coating. c) the improved CE by PA coating [74].

limited. Additionally, the introduction of heterogeneous elements increases the risk of galvanic corrosion, in which the zinc substrate acts as a sacrificial anode, resulting in accelerated corrosion or zinc "self-discharge." For conductive structure, the effect of dendrite control is not impressive compared to the non-conductive competitors. In fact, the interface structure and zinc metal are somewhat redundant. On the contrary, non-conductive coatings are hotspots. Numerous materials, both porous and non-porous, can be used. Zinc ion re-distribution has a significant effect on dendrite suppression, resulting in excellent electrochemical performance of zinc anodes and full cells. As a result, the non-conductive modification has a great potential of practical application. Nevertheless, the optimizations for both coatings are discussed below.

5.2. Optimization for morphology control

5.2.1. Construction of smaller diffusion channels for zinc ions

The sieve effect is highly dependent on the size of the diffusion channels in the non-conductive coating layers. Though there is no precise value for the pore size threshold, it is widely accepted that large pores (larger than $10\ \mu\text{m}$) in the surface coating or membrane act as electrolyte highways and are incapable of averaging the ion flux and suppressing dendrite formation [20]. A recent study on the separator's

microstructure also confirms the importance of smaller diffusion tunnels [75]. Thus, it is critical to construct smaller dendrite-controlling diffusion channels and improve the cycling performance of zinc anodes.

As mentioned in Section 4.2.1, dense crystal particles can be used as coating materials in conjunction with binders. These particles act as solid barriers, allowing only for ion diffusion at specific intervals. As a result, the lower limits of such channels are determined by the particle size. Typically, the diffusion channels created by dense particles are sub-micrometer in size (Fig. 9a and d) [20]. Certain crystals, such as kaolin [72] and montmorillonite [76], have suitable lattice spaces as diffusion channels (Fig. 9b). Take into account the kaolin silicate [72], it has a narrow interlayer between the lattice planes (001) and (002). As a result, the Kaolin coating has a relatively small pore diameter of 3 nm. Zinc ions can pass through the narrow channels without forming chemical bonds with the material's Si/Al-O bonds (Fig. 9e). Because the layered structure is retained following zinc ion intercalation, the coating layer maintains a high degree of stability during cycling. The coated electrodes in the symmetric cell can operate for 800 h at a high current density of $4.4\ \text{mA cm}^{-2}$ ($1.1\ \text{mAh cm}^{-2}$).

Even smaller channels are possible in some novel artificial molecules that use a special frame structure (Fig. 9c). For instance, the MOF material contains extremely small channels of $2.94\ \text{\AA}$ [77–79]. In hydrogen-substituted graphdiyne (HsGDY) one of the smallest diffusion

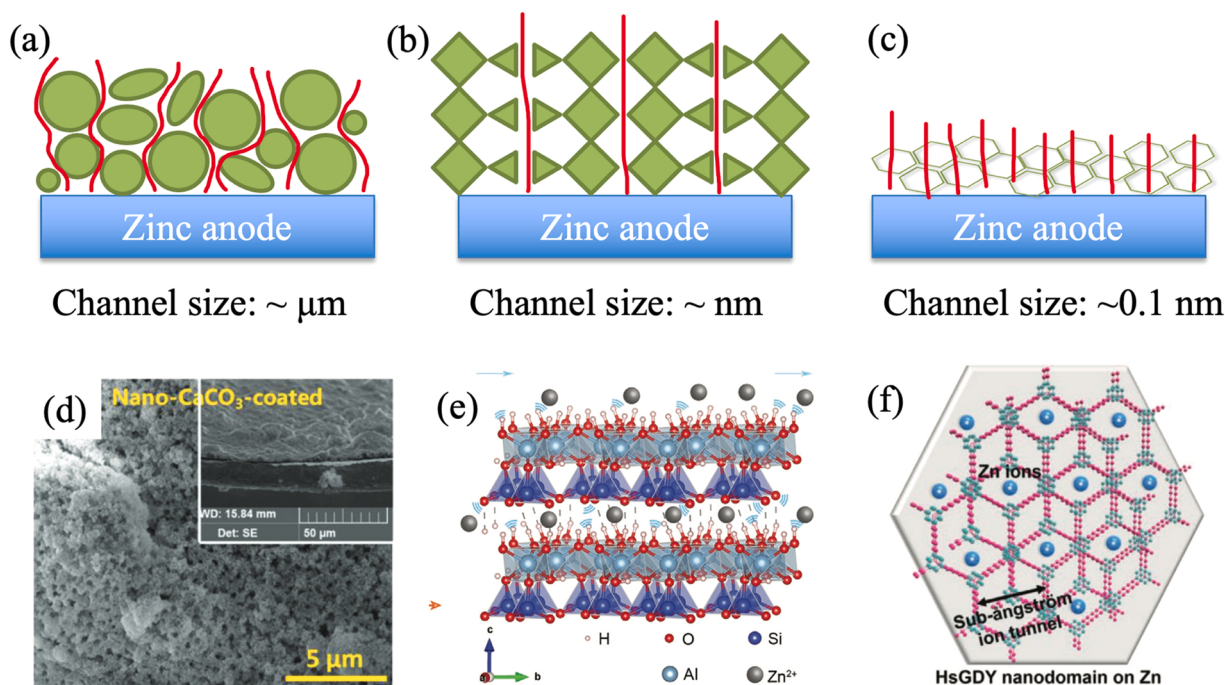


Fig. 9. Relationship of cycle performance and the pore size at coated zinc anode. Schematic diagram of diffusion channels in the coating of a) dense particles, b) mineral crystals, and c) man-made frame structures. d) SEM image of nano- CaCO_3 coating [20]. Schematic diagram of confined zinc ions transmission in e) kaolin [65] and f) HsGDY [48].

tunnels is formed [52]. The hexatomic rings are surrounded by benzene and alkynyl groups, revealing sub-angstrom-scale tunnels (Fig. 9f). The zinc ions can migrate uniformly and longitudinally through the tiny pores, resulting in homogeneous deposition beneath the decoration layer. Due to the sub-angstrom structure, the coated anode can operate without failure for 2400 h at various current densities ranging from 0.5 mA cm^{-2} to 2 mA cm^{-2} . This is one of the best records in all strategies.

5.2.2. Promotion of the ion diffusion within the coating layer

In the coating layer, the diffusion tunnels for zinc ions are always not aligned, thus the transport route is longer and more tortuous. Though the literatures provide no details on tortuosity, the increased polarization in some cases suggests a possible sluggish kinetics of ion transport [80]. For example, while the gelatin coating may inhibit dendrite growth and improve cycling performance, it results in greater polarization during the plating/stripping process [81]. Some modifications layers, on the other hand, can facilitate ion diffusion within the coating layer and reduce polarization, thereby lowering energy consumption and increasing anode efficiency.

Certain inorganic materials are capable of promoting ion diffusion through the use of a special electric field within the coating. In the compact artificial ZnS layer, the electronegativity of the S atoms can result in strong bonding interactions with the zinc atoms, modifying the charge distribution at the interface [26]. The additional electric field generated by the unbalanced charge distribution then has the potential to accelerate zinc-ion diffusion through the coating (Fig. 10a). As a result, the ZnS has a high ionic conductivity for zinc ions of $\sim 1.3 \times 10^{-5} \text{ S cm}^{-1}$. The transfer of zinc ions is increased from 0.33 to 0.78 when coated with ZnS, indicating accelerated diffusion kinetics. Besides that, the Maxwell–Wagner effect can be used to achieve this enhanced electric field. This effect refers to the phenomenon that charges can be separated over a large distance at the interfaces of two media with different

dielectric constants and conductivities. Given the low dielectric constant of zinc, the non-conductive materials in the coating layer may induce a positive charge at the interface between the coating and the zinc substrate, thereby promoting zinc ion electromigration. ZrO_2 coating was used to investigate this effect [70]. Due to the ZrO_2 coating's high dielectric constant of 25, it can induce favorable Maxwell–Wagner polarization, ensuring a rapid and uniform plating process for zinc ions (Fig. 10b). By contrast, the Al_2O_3 coating with a lower dielectric constant of 9.34 performs poorly. Inspire by this work, the investigation of the similar Maxwell–Wagner polarization in BaTiO_4 [82] and Si_3N_4 [83] are proposed.

In the examples above, the coating materials are considered inert and do not interact with the zinc ions. According to some researchers, certain structures with unique interactions with zinc ions may also aid in diffusion. Using PVDF as an example [38], during the annealing process, the positions of H and F would evolve. The stable all-trans state can be obtained as the β -phase through slow solvent evaporation, whereas the semi-helical state in α -phase can be obtained via rapid annealing (Fig. 10c). The zigzag configuration of β -PVDF results in successive C-F functional groups that attract zinc ions due to the negative charge on the F atoms. After that, the zinc ions diffuse more rapidly along the chains. As a result, high-polarity β -PVDF has a significantly higher zinc ion diffusion coefficient than α -PVDF. In symmetric cells, the well-organized C-F groups in the PVDF coating contribute to the uniform distribution of zinc ions, resulting in a cycling lifetime of over 2000 h (0.25 mA cm^{-2} , 0.05 mAh cm^{-2}) and decreased polarization.

5.2.3. Restriction of 2D diffusion of zinc ions

During deposition, zinc ions absorb from the bulk electrolyte onto the reaction interface, then diffuse laterally along the electrode surface until they reach the most energetic sites for charge transfer. Zinc ions aggregate at protuberances via two-dimensional (2D) diffusion in order to minimize surface energy, resulting in uneven deposition and,

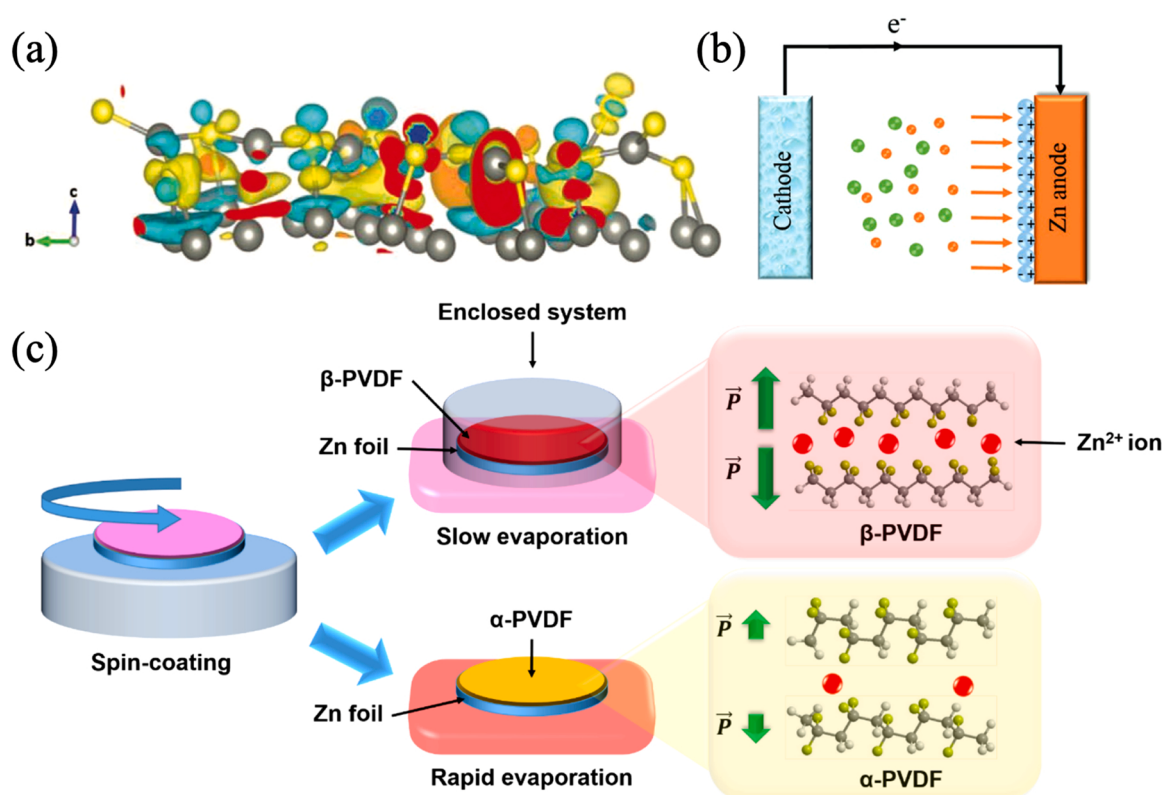


Fig. 10. Schematic diagram of a) electron density difference map at the ZnS/Zn interphase [26], b) plating processes the ZrO_2 -coated zinc anode [70], and c) synthesis processes and structure of β -PVDF and α -PVDF coating [38].

ultimately, the dendrite. As a result, the 2D diffusion of zinc ions is detrimental to morphology control and cycling performance.

The coating materials are able to inhibit dendrite growth by preventing zinc ions from aggregating. The coatings' anchored sites not only provide adhesion to the electrode, but also act as a barrier to 2D diffusion. Due to its sensitivity to the nucleation process and surface change, chronoamperometry is always used to demonstrate this mechanism. Under a -150 mV overpotential, the current density of the bare zinc electrode typically continues to increase for 150 s, indicating a long and rampant 2D diffusion of zinc ions (Fig. 11a) [74]. In comparison, the PA-coated zinc anode has a shorter 2D diffusion time of less than 30 s, indicating that the zinc ions are constrained in close proximity to the initial adsorption sites. As a result, the number of nucleation sites is increased, and each deposition cluster is refined. Dendrite formation occurs infrequently during the plating/stripping process, allowing for an ultra-stable reversibility of the zinc electrode.

In contrast to the anchored physical barrier, Liu et al. propose a novel chemical barrier mechanism for limiting the 2D diffusion of zinc ions [80]. The ZIF-8 coating, which contains a high concentration of nitrogen, has a much stronger interaction with zinc ions than the zinc metal does (Fig. 11b). Zinc ions have a binding energy of only -0.62 eV on the zinc (001) facet, whereas the ZIF-8 has a binding energy of -1.22 eV due to the energy trap of the N element. As a result, the zinc ions become tightly bound to the N atoms in the coating. The energy barrier for the 2D diffusion of zinc ions has been significantly increased from 0.02 to 1.38 eV, imposing severe constraints on random diffusion and inhomogeneous deposition (Fig. 11c). The ZIF-8 coating provides an ultra-long cycling life of over 1200 h (2 mA cm^{-2} , 1 mAh cm^{-2}), nearly ninefold that of the bare zinc electrode.

5.2.4. Activation of more nucleation sites for conductive coatings

Due to the fact that zinc ions are attracted to pre-existing nuclei, one strategy for conductive modifications is to activate additional potential sites for the initial nucleation process. This strategy may result in a dense network of small protrusions rather than isolated, large dendrites, as demonstrated in a study of novel charge/discharge protocols [84]. While the foreign metallic components may act as nucleation seeds, their size (for example, 100 nm for Au particles and 5 μm for In particles) results in a limited nuclei density on the zinc surface.

As an improvement, certain carbon materials can be used as conductive coatings due to their doping capacity for functional groups. Different teams have reported the application of nitrogen-doped graphene oxide (NGO) [47,48]. As a result of N-introduction, the NGO contains a large number of defects in each nanosheet, including N, Nq, Npd, Npr, C=O, C=OH, and others (Fig. 12a). Certain types of defects have higher binding energy for zinc ions, which allows them to capture the zinc ions before other non-defective C atoms or the zinc metal itself. The high density of defects provides extra nucleation sites, resulting in a smooth morphology and enhanced cycling performance. On the

contrary, conventional graphene coatings lack sufficient nucleation sites, resulting in suboptimal dendrite control [66,85]. One particular case demonstrates the critical nature of atom-level dispersed nucleation sites, which also make use of N atoms as nucleus seeds. Jia et al. attack the zinc metal with a N_2 plasma to construct a N-induced surface [86]. A trace amount of nitrogen atoms has been detected on the zinc surface, with a N/Zn atom ratio of only 6.1%. The N element is distributed uniformly across the surface rather than aggregated, primarily as the form of N-Zn/N-Zn-O and N-H. Because the dispersed N atoms have a higher electronegativity than the zinc atoms (-1.699 eV vs. -1.208 eV), they can attract Zn nucleation, resulting in a large number of zinc nuclei during the initial electrodeposition stage (Fig. 12b and c). Then the dendrite is suppressed following the uniform growth of each small nuclei. This groundbreaking study develops a novel technique for non-coating modification of the zinc anode.

5.2.5. Regulation of crystal arrangement

One critical but widely ignored factor for dendrite control is the crystal arrangement of the deposition, which has been extensively studied in the strategy of electrolyte optimization [87–89]. In general, hexagonal zinc platelets exposing the (002) Zn facet are preferable for plating due to their low surface energy [30]. However, under normal circumstances, these platelets are not always well-organized. Rather than that, they are frequently arranged arbitrarily without discipline, resulting in loosely connected building blocks with a porous structure (Fig. 13a and b). Such void-filled structures would result in much faster vertical growth toward the electrolyte, thus are regarded as the origin of dendrites [88]. As a result, an ordered arrangement of crystals with a dense structure and fewer inner interstices is considered an effective strategy for dendrite suppression.

Archer and colleagues reported an epitaxial growth route for zinc crystals in 2019 that takes advantage of the low lattice mismatch between Zn(002) and the prepared graphene. Zinc atoms prefer to be deposited with a locked orientation to the graphene substrate, resulting in a morphology of well-organized platelets parallel to the (002) direction. Inspired by this outstanding work, several literatures on interface modification have been published, with an emphasis on epitaxial deposition. For instance, by acting as a conductive substrate, the NGO can induce a flat deposition morphology with a higher Zn(002) ratio [48]. Li et al. describe the synthesis of several MXene coatings containing identical halogen functional groups ($\text{Ti}_3\text{C}_2\text{F}_2$, $\text{Ti}_3\text{C}_2\text{Cl}_2$, $\text{Ti}_3\text{C}_2\text{F}_2$, $\text{Ti}_3\text{C}_2\text{I}_2$, etc.) [90]. The most extensive (000 l) planes in these MXenes have a high lattice match with Zn(002) facet (81–90%), and thus can guide oriented deposition. Zinc deposition is typically tiled layer by layer on the MXene substrate, resulting in a coherent heterogeneous interface with fewer dendrites (Fig. 13c).

Apart from conductive coatings that act as the deposition substrate, non-conductive coatings can also be used to guide the placement of zinc deposition. Yang et al. proposed a ZnSe coating with a specific (111)

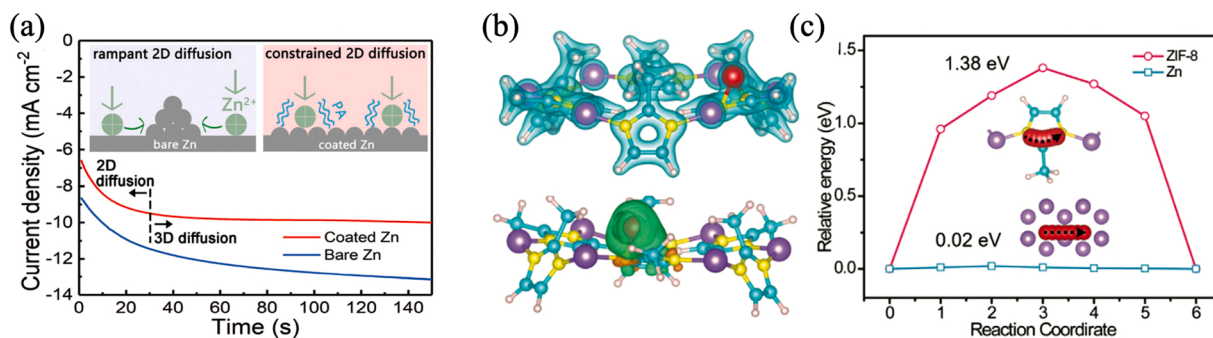


Fig. 11. a) Chronoamperograms of bare zinc and PA-coated zinc. Insets: Schematics of the diffusion of zinc ions in reduction processes on bare and coated Zn electrodes [74]. b) Charge density diagram and charge density differences of the ZIF with zinc ion adsorption [80]. c) The activation energy for zinc ion to migrate from one energy minima to the other nearby minima on Zn (001) and ZIF [80].

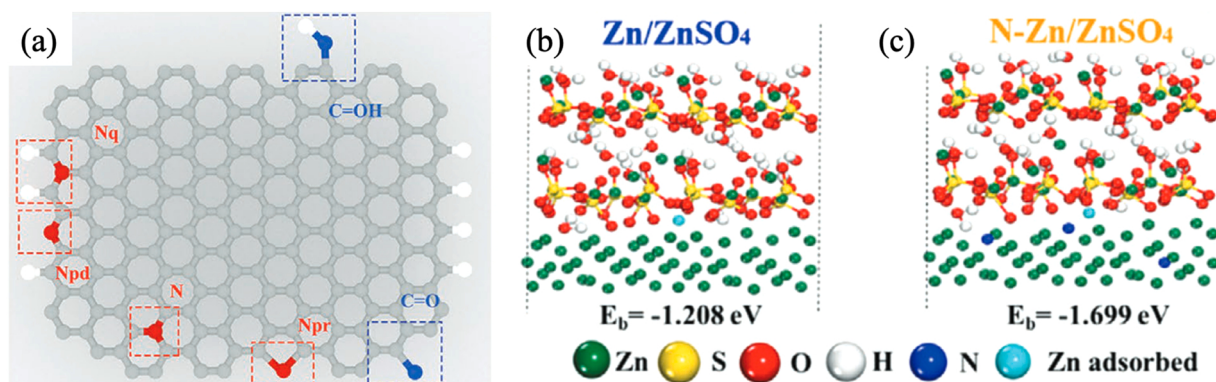


Fig. 12. a) The configuration of N- and O-doped graphene. The gray, red, blue, and white colors indicate carbon, nitrogen, oxygen, and hydrogen atom, respectively [48]. Calculated binding energy of zinc ion on b) Zn and c) N-Zn electrodes [86].

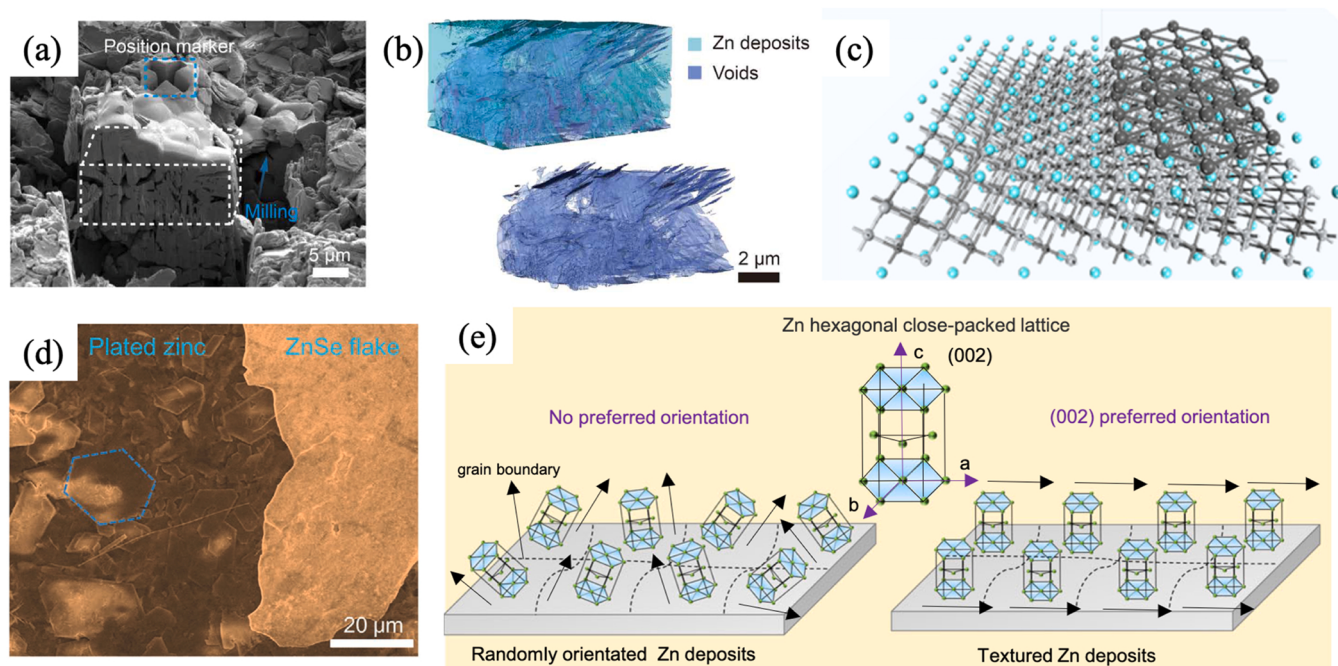


Fig. 13. a) Cross-sectional images produced by FIB and b) the corresponding three-dimensional morphology reconstructions of zinc deposits [88]. c) Schematic diagram of the zinc deposition process on the MXene matrix concerning the coherent heterogeneous interface construction [90]. d) SEM image of ZnSe coating and the plated zinc [27]. e) Schematic diagram of the preferred orientations of zinc crystal plane [91].

direction orientation [27]. The (111) plane has a hexagonal lattice structure similar to that of the Zn (002) plane, with a low lattice mismatch of interplanar spacing (2.31 Å compared to 2.66 Å). When zinc ions diffuse through the pyramidal ZnSe_4 stacks and deposit beneath the coating layer, they also prefer epitaxial growth of the (002) plane. The peak intensity ratio of the Zn(002)/(101) plane increases 12 folds after cycling, and the SEM image of deposition confirms the hexagonal platelets' highly ordered morphology (Fig. 13d). The zinc anode with ZnSe coating has a significantly enhanced cycling lifetime of 1530 h at 1 mA cm^{-2} and 1 mAh cm^{-2} due to the suppressed dendrite tendency. Zhao et al. describe an additional mechanism for the preferential growth of zinc deposition [91]. The F-induced COF layer serves as the interface coating, while the zinc ions pass through the framework's nanochannels. Due to the strong interaction between F atoms and Zn (002) plane, the surface energy of the F-terminated (002) plane is greater than that of the F-(101) plane, indicating that reduced zinc atoms are more likely to aggregate along the (002) direction to lower the surface energy (Fig. 13e). Thus, the abundant F atoms in the COF

structure may aid in crystal orientation regulation, resulting in a highly ordered morphology and enhanced cycling performance.

5.2.6. Dissolution of the solid zinc by liquid alloys

Generally, due to the solid nature of the zinc crystal, the deposited zinc will become anchored at the location of the initial nucleus, and the asymmetric plating/stripping process will result in the dendrite's annoying net growth. The abovementioned strategies are less concerned with the dendrite's intrinsic growth pattern than with external influence factors. Recently, some researchers have used liquid alloys to modify the interface, which has the potential to fundamentally alter the deposition of zinc ions. Two Ga-In-Zn systems are chosen as the classical liquid alloys at room temperature (Fig. 14a). They contain 75–25–3.22 wt% [92] and 80–10–10 wt% [93] of Ga-In-Zn, respectively. When zinc ions in the electrolyte are reduced to zinc atoms, the atoms do not form crystalline aggregates. Rather than that, they are dissolved by the liquid alloy that serves as the zinc solution (Fig. 14b). The surface tension of the liquid alloy ensures the clean and dendrite-free morphology. When

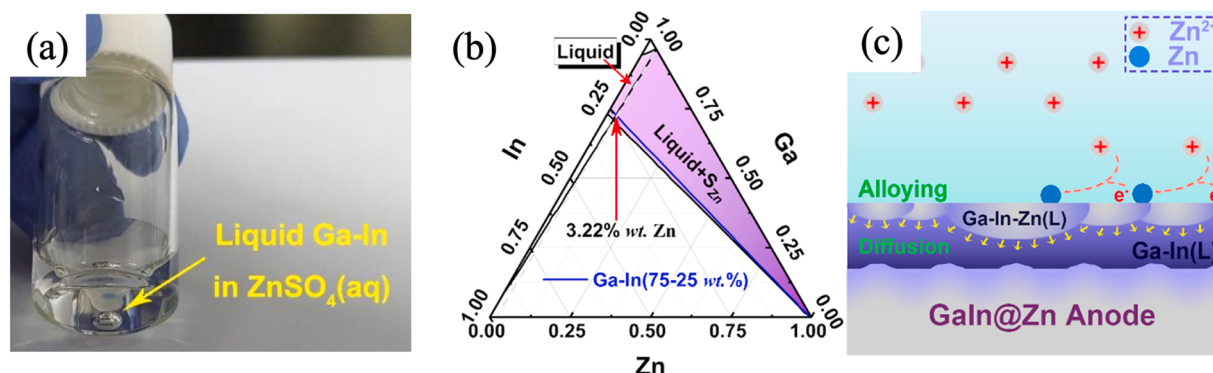


Fig. 14. a) The liquid Ga-In alloy in 3 M ZnSO_4 aqueous electrolyte. b) Ga–In–Zn ternary isothermal section phase diagram at 25 °C. c) Schematic diagram of dendrite-free GaIn@Zn anode by alloying–diffusion synergistic strategy [92].

the zinc element in the alloy becomes saturated, the excess zinc atoms get crystallized and deposited beneath the alloy, ensuring a soft contact between the electrode and the electrolyte (Fig. 14c). Notably, because the diffusion of zinc atoms in the alloy is driven by the concentration gradient, the heterogeneity of electric intensity that exists in an aqueous electrolyte is eliminated. As a result, the zinc deposition beneath the alloy would be homogeneous as well. The liquid alloy acts as a buffer layer, allowing the zinc ions to be re-distributed. In symmetric cells, the dendrite is effectively suppressed, extending the cycling lifetime to over 2100 h at 0.25 mA cm^{-2} and 0.05 mAh cm^{-2} . This strategy converts the zinc deposition from a solid crystal to a soft liquid, introducing a novel and universal concept of morphology control for metal anodes.

5.3. Optimization for CE improvement

Numerous publications assert that the coating layers act as a physical barrier between the water and the zinc metal electrode. Nevertheless, the mechanism and supporting evidence are not always provided. This ambiguous explanation is unconvincing because the ordinary channels in the coating layer are insufficiently small to resist solution permeation. Additionally, the zinc ions in aqueous electrolytes always bring water molecules as the hydration shell [12], which can act as an abundant reactant for HER. The research of electrolyte- or separator-related strategy has verified the concept that stripping the coordinated water in the hydration shell of zinc ion can effectively suppress the side reactions [24,94,95]. Therefore, the functionalized interfacial modification should follow the same manner to promote CE [96,97]. The mechanisms of novel coating layers are discussed in full detail below.

5.3.1. Reduction of the solvated water in the hydration shell

Yang et al. report a MOF layer capable of reducing solvated water molecules via the steric effect, which is consistent with our thesis [77]. Each diffusion channel in the MOF structure is 2.94 Å wide, which

prevents the migration of large solvated zinc ion complexes (in the form of $[\text{Zn}^{2+}(\text{H}_2\text{O})_6\text{SO}_4^{2-}]$ or $[\text{Zn}^{2+}(\text{H}_2\text{O})_5\text{OSO}_3^{2-}]$). When an electric field is applied, the hydrated zinc ions are forced to abandon some water molecules and partially de-solvate as $[\text{H}_2\text{O}-\text{Zn}^{2+}\text{SO}_4^{2-}]$ to pass through the MOF channels (Fig. 15a). Free water is kept away from the coating surface, and coordination water is reduced to a minimum on the anode surface. Thus, a supersaturated electrolyte environment is created within the MOF, which benefits the reversibility of the zinc anode significantly.

Apart from the steric effect, chemical interactions can also result in the decomposition of the hydration shell. Cui et al. describe a composite coating of Nafion and zeolite that effectively resists water and cation permeation [18]. The Zn-X zeolite is embedded in the Nafion layer, blocking the hydrophilic channels, and an interfacial bridge is formed between the zeolite and the sulfonic groups in the Nafion. When zinc ions hop across the organic-inorganic interfaces, the sulfonic groups with negative charge in the Nafion chains can absorb them, while other anions and water are obstructed. As a result, the hydrated zinc ions become de-solvated as they pass through the coating layer, forming the more stable $\text{R-SO}_3^-[\text{Zn}(\text{H}_2\text{O})_6-x]\text{SO}_3\text{-R}$ structures (Fig. 15b). The composite coating enables the anode to achieve a CE of 97%. In another instance of F-COF coating, the zinc ions can diffuse only through the COF's 1D channels [91]. The addition of the F element to the channel walls confers a strong hydrophobic property, which repels coordinated water molecules, leaving only de-solvated zinc ions for transport (Fig. 15c).

5.3.2. Elimination of the hydration shell by non-aqueous interlayer

One of the most efficient methods for CE enhancement is to completely dehydrate the zinc ions and remove the water molecules. For instance, the use of organic solvents demonstrates an extraordinarily high CE (99.4% for EG [89] and 99.7% for liquified gas [98]). However, such a high value is extremely difficult to achieve in traditional aqueous

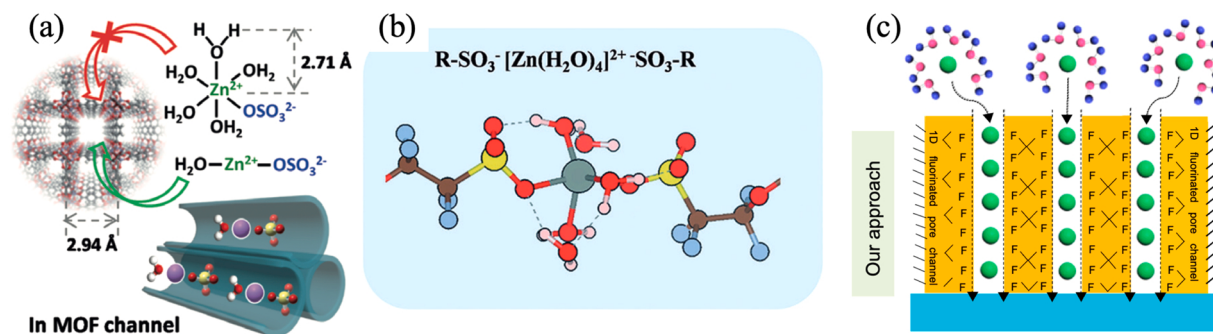


Fig. 15. a) Schematic diagram of a) highly coordinated ion complexes of zinc ions migrating through MOF channels [77]. b) coordination environment of zinc ion in Nafion with 4 H_2O [18]. and c) the physicochemical structure of the F-COF film, which repelling the solvated water [91].

electrolytes. As a result, the design of a non-aqueous thin layer on the anode is recommended in order to mitigate the influence of water molecules. Cai et al. develop a solid-state electrolyte (SSE) as the modification coating [22]. Unlike the previous reported SSE which replaces the whole electrolyte [99], this new SSE is actually a decoration layer, which is activated in-situ in the sulfate solution from the metallic In coating. The coating layer contains amorphous indium hydroxide sulfate (IHS, see Fig. 16a), and the unstable water molecules are repelled in the IHS layer due to their extremely high bonding energy. As a result, the zinc ions in the IHS coating are completely dehydrated. Additionally, because the hydrogen-bonded sulfate anion channels in the coating aid the passage of positive zinc ions, the bare zinc ions are deemed to be deposited onto the substrate without further de-solvation, resulting in an increased CE of 99.6%. This research will expand the use of solid-state electrolytes in ZIBs.

Cao et al. utilize phase separation of the water/organic solvent to build an organic thin layer on the zinc surface, while the bulk electrolyte remains the inexpensive, environmentally friendly, and highly conductive aqueous solution [100] (Fig. 16b). The authors design a porous MOF layer on the zinc substrate and fill it with tris(2,2,2-trifluoroethyl)phosphate (TEEP). When the as-prepared electrode works in a standard aqueous electrolyte, the zinc ions diffuse from the aqueous phase into the organic phase, displacing the water molecules in the solvation shell due to TEEP's strong hydrophobic characteristic. Indeed, TEEP acts as the anolyte, whereas aqueous solution acts as the catholyte. As a result, HER rarely occurs on the anode side. Additionally, some TEEP molecules may be degraded to create an SEI layer, hence increasing the resistance to water permeability (Fig. 16c). The cell is capable of achieving an extremely high average CE of 99.1%. The inventive design of dual electrolytes based on phase separation would serve as a catalyst for further research on ZIBs.

5.4. Some technical issues

5.4.1. Adhesion improvement

The electrochemical performance of the anode is heavily dependent on the non-conductive coatings' re-distribution property. To prevent the permeation of stray zinc ions, the coating layer must be tightly adhered to the zinc surface. Taking into account the volume change of the zinc during the plating/stripping process, the coating layer's adherence is critical to maintaining the optimal connection [81]. Insufficient adherence, on the other hand, would result in exfoliation of the decorated layer, further impairing the electrochemical performance.

Though it is the most commonly used approach, doctor blading is insufficient to maintain adequate adhesion. The van der Waals force by which the PVDF form a connection between the coating material and the electrode is not strong enough to guarantee a secure adherence. Zhang et al. provide an excellent example, demonstrating that a zinc electrode coated with ex-situ manufactured MXene with PVDF as binders performs

worse than one ornamented with in-situ synthesized MXene [50]. The former operates for 315 h before experiencing a short circuit and an unstable voltage profile in the symmetric cell, whereas the latter can safely operate for over 800 h with stable polarization. The twisting and folding experiment also demonstrates the outstanding adherence of in-situ produced MXene, as the coating remains conglutinated on the zinc surface when the force is removed (Fig. 17a).

The satisfactory adhesion can be achieved by other in-situ coating preparing methods, where strong chemical bonds are constructed between the coating materials and zinc electrodes. For example, the ZnS coating is created via the CVD method, in which the zinc (002) facet is converted directly into ZnS (002) [26]. Additionally, the altered charge distribution at the ZnS/Zn interface enhances the adhesion effect. As a result, the ZnS coating maintains excellent integrity during the twisting experiment (Fig. 17b), and the coated electrodes can cycle for more than 1100 h in a symmetric cell (2 mA cm^{-2} , 2 mAh cm^{-2}), about 11 times longer than the bare electrodes. Similarly, ZnF_2 is electrodeposited in-situ on the zinc surface, which retains its integrity following bending test [50]. Certain organic polar groups have a high degree of electronegativity and can thus be employed to enhance adhesion. Li et al. develop a composite organic coating consisting of PAM and PVP for zinc interface modification [101]. PAM's numerous polar groups in the form of C=O and N-H bonds can form strong connections with active surfaces, anchoring the polymer to the zinc electrode. In another scenario, the researchers directly treat the substrate with dilute commercial cyanoacrylate adhesives (502 glue) [37]. The very rich polar groups of $\text{C}\equiv\text{N}$ guarantee the strong conglutination. Several other coating materials, including SPEEK [17], F-COF [91] (Fig. 17c) and ZCO ($\text{Zn}_4\text{SO}_4(\text{OH})_6 \cdot 5 \text{ H}_2\text{O} + \text{Cu}_2\text{O}$) [102], have been reported to survive in the bending test, indicating their significant potential for a variety of applications, such as flexible cells.

5.4.2. Thickness control

The interface modification layer, as an attached component, is unable to supply energy capacity. Rather than that, it decreases the energy density of the full cell. Additionally, the coating layer adds to the economic cost of the material and production process. Some researchers claim that the coating should not be too thick to avoid impairing conductivity for carbon-based materials [66] or zinc ion mobility for non-conductive coatings [71]. Controlling the thickness of the coating layer is therefore a practical concern. However, blindly thinning the coating is irrational. On the one hand, coating thickness is constrained by the preparation procedure, which is dependent on the coating material employed. For example, the doctor blading process can seldom reduce the thickness below $1 \mu\text{m}$ because to the scraper size restriction and the particle size of the material (typically 100 nm for inorganic minerals). On the other hand, even if the thin film is successfully created, its protective efficacy may be diminished. A balance between price & weight and electrochemical performance must be established.

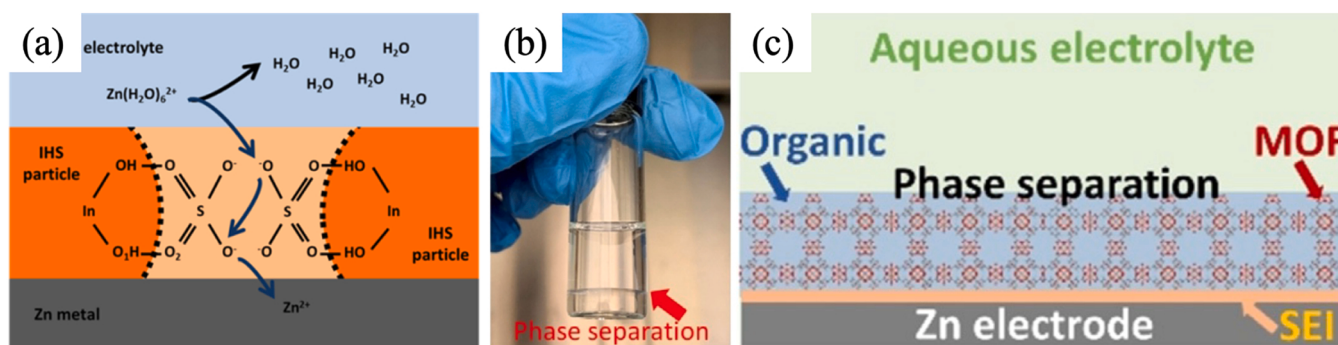


Fig. 16. a) Schematic illustration of the zinc ion diffusion in IHS solid electrolyte on Zn metal [22]. b) Phase separation of 1.0 m $\text{Zn}(\text{TFSI})_2\text{-H}_2\text{O}$ (on the top) from 1.0 m $\text{Zn}(\text{TFSI})_2\text{-TFEP}$ (on the bottom) [100]. c) Schematic illustration of the MOF layer on the zinc surface and the phase separation of electrolytes [100].



Fig. 17. a) MXene-coated zinc foil at twisting and bending tests [54]. b) ZnS-coated zinc foil at twisting test [26]. c) F-COF-coated zinc foil at twining, bending, and twisting tests [91].

Several literatures have been published concerning the thickness optimization. He et al. evaluate the thickness of an Al_2O_3 layer produced by ALD [34]. Due to the self-limiting nature of ALD, the coating thickness can be easily regulated with certain ALD cycles. The zinc electrode decorated with 100 ALD cycles (10 nm) has the lowest R_{ct} , while the thinner and thicker coatings increase the charge transfer resistance. As a result, the Al_2O_3 coating with a thickness of 10 nm is chosen as the optimal sample. Likewise, the ALD-deposited TiO_2 coating is tuned to be 8 nm thick in 100 ALD cycles (Fig. 18a) [48]. Additionally, the investigation of Kaolin [72] (Fig. 18b) and MXene [54] (Fig. 18c) coatings reveals that the layer with a medium thickness provides the optimum protection, while the optimization impact is dependent on the coating material qualities. The ideal coating thickness for Kaolin is 21 μm , however for MXene it is only 200 nm.

Currently, the thinnest coating layers recorded on zinc anodes are Al_2O_3 with a thickness of 10 nm and TiO_2 with a thickness of 8 nm, both of which are created by ALD. Such ultrathin surface alteration would have little effect on the anode's specific capacity. It should be noted, however, that the electrochemical performance of the zinc anode decorated with the ultrathin coating is not optimal, indicating a rather ineffective suppression of dendrites. Certain options (for example, MXene and NGO) provide a significantly longer cycling lifetime with a moderate thickness (200 nm and 120 nm, respectively). Setting a standard for the coating layer is challenging, given the large variety of application scenarios for ZIB systems and the associated varied requirements for specific capacity and cost. However, one thing is certain: the lofty goal of creating a thin but effective modification layer should be pursued further.

6. Discussions on some controversies and confusions

Though the technique of interface modification has been widely explored, there are still some disagreements on the performance and mechanism of the decoration layer, which naturally creates uncertainty for researchers. Conflicts are fairly prevalent, given the ZIB is in its

infancy. Additionally, we believe that the clear disclosure can elicit discussions that are beneficial to the continued development of ZIBs. A few brief examples are discussed below.

6.1. Non-uniform baseline of zinc anode

Due to the fact that ZIBs are worldwide hotspots, hundreds of publications are produced each year. Surprisingly, we discover that in the majority of literatures focusing on the cathode side, full cells are built utilizing the unprotected zinc plates as anodes without modification. The full cells, always in the coin cell form (CR2032 or CR2016), exhibit excellent electrochemical performances over a wide range of charge/discharge cycles and current densities. For instance, it is reported that the full cell can operate for thousands [103], or even tens of thousands [104] of cycles. These results imply that the bare zinc plates are sufficiently robust in the absence of dendrites or side-reactions. However, according to the literature focusing on the anode side, bare zinc could never survive for such a long period of time. This type of contradicting information may significantly mislead readers, resulting in an over-estimation of anode development. There is no intention of accusation, for we are well aware that the anode is not a controlled variable in cathodic literatures. Nonetheless, it is hoped that the following publications would clarify the (possible) alteration of the zinc anode.

We ran into another issue while conducting this literature review on zinc anodes. That is the disunity of the bare zinc anode's baseline. Zinc metal, which is frequently used as a control sample, should theoretically exhibit comparable physical and electrochemical properties under the same test conditions. Unfortunately, the results are always inconsistent in different literatures, including contact angle, exchange current density, charge/discharge profiles, EIS data, cycling lifetime, and dendritic morphology, etc. For example, it is reported that bare zinc operates for only 32 h in the galvanostatic charge/discharge test [18] (symmetrical cells at 1 mA cm^{-2} and 0.5 mAh cm^{-2} , in 2 M ZnSO_4 electrolyte), but another publication indicates that bare zinc operates for 110 h [105], more than three times the previous value. Due to the rarity with which

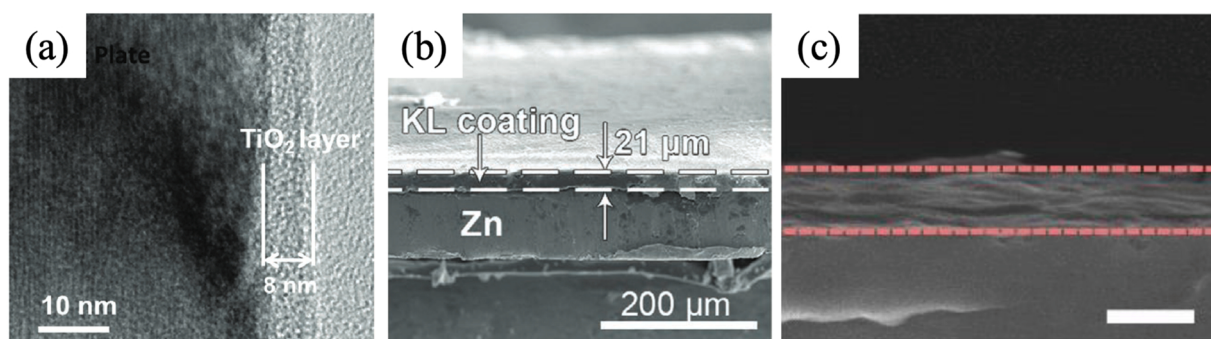


Fig. 18. Cross-sectional STEM image of a) TiO_2 -coated zinc electrode [48], b) kaolin-coated zinc electrode [72], and c) MXene-coated zinc electrode (Scale bars: 200 nm) [54].

error bars are provided, such a large discrepancy casts doubt on the strategies' universality. Indeed, the variability of each study may be a result of the modest variation in raw materials and/or operating processes. Moreover, the soft short caused by localized connection through small dendrites is a potential hazard for normal operation of the cell, especially in high current and capacity conditions (Fig. 19a and b) [106]. However, it has been seldom reported in the coating-related literatures. We suggest more standardized roles for material selection and measurement methodologies be proposed, which is delightedly supported by other researchers [1].

6.2. Design principle for the modification layer: hydro-/zincophilic or phobic?

According to recent literature, non-conductive coatings act as a barrier between the zinc metal and the electrolytes, preventing direct invasion of the bulk electrolytes through the comparatively narrow diffusion pathways. The interplay between the coating material and the electrolyte is intriguing. Many researchers assert that the coating should be hydrophilic, resulting in increased electrode wettability and decreased interfacial resistance [34]. Specifically, Kim et al. emphasize the coating layer's water affinity and demonstrate that the deposition morphology is highly dependent on the layer's hydrophilicity [107]. The hydrophilic APTES coating presents a contact angle of 13.9° , which is significantly less than that of bare zinc (81.5°) or the hydrophobic TOS coating (134.2°). It is hypothesized that the hydrophilic coating benefits the uniform flux of zinc ions and nuclei formation, hence facilitating the subsequent smooth deposition. On the contrary, the hydrophobic coating promotes zinc ion aggregation, resulting in local deposition at energetically advantageous locations and finally in the formation of water-droplet-shaped zinc dendrites. When it comes to this subject, other researchers take a contrary position. Lee decorates zinc metal with an ionic liquid gel that is highly water repellent and has a larger contact angle than bare zinc [97]. With fewer dendrites and a higher CE, the coated zinc anode shows improved cycling performance. Therefore, the researchers believe such a hydrophobic layer can decrease interfacial side reactions produced by water, which is also rather realistic.

The zinc-affinity of the coating substance is also a point of contention. Wang et al. investigated the protective layer's crystal orientation

[32]. According to the researchers, the coating layer with a high zincophilicity, in this example (100) faceted TiO_2 , has a greater binding energy with the zinc atoms. The high zinc affinity results in preferential adsorption of zinc atoms and even unexpected deposition on the coating layer, impairing the dendrite control function. On the other hand, as-prepared (001) faceted TiO_2 exhibits low zincophilicity, allowing for uniform deposition of zinc atoms on the substrate and an extended cycle lifespan. Several other publications emphasize the significance of low zincophilicity, i.e. the zincophobicity of the coating material [108,109]. Nonetheless, other papers praise the coating materials' zincophilicity. It is claimed that the coating layer's high zincophilicity enables it to easily grab zinc atoms and guide subsequent deposition locally on the zinc substrate, resulting in a smooth shape and improved cycle performance [27]. Certain coating materials, including ZnSe [27] and BaTiO_3 [82], have been proposed to be well-suited for this mechanism. Although it is impossible to determine the relevance of the two claims, their conflict may generate additional discussion and debate about the underlying mechanism of interface modification.

6.3. Requirement of mechanical strength for the interface modifications

Zinc metal that serves as the anode is unavoidably subjected to volume change. When the full battery is charged, the thickness of the anode increases by $1.8 \mu\text{m}$ at per unit capacity of 1 mAh cm^{-2} , assuming that all the zinc atoms are tightly packed. However, in practice, dendrites always appear, which may also be viewed as a local volume growth. Zinc dendrites have long been believed to be capable of piercing the separator due to their high Young's modulus of 108 GPa. It is well claimed that the interface modification layer should be strong enough and possess sufficient mechanical strength to withstand dendrite invasion [67,76]. Some inorganic minerals, such as layered double hydroxides (LDH) [110] and SiO_2 [33], are used as coating materials due to their high strength. In one instance, it is observed that a coating without robust LDH exhibits greater dendrites and a lower cycling lifetime, emphasizing the importance of the interface modification's mechanical strength.

However, when we expand the horizons, this does not make sense for organic coatings. Although the majority of the organic layers are soft or elastic, significantly weaker than the zinc dendrites, they may also guide

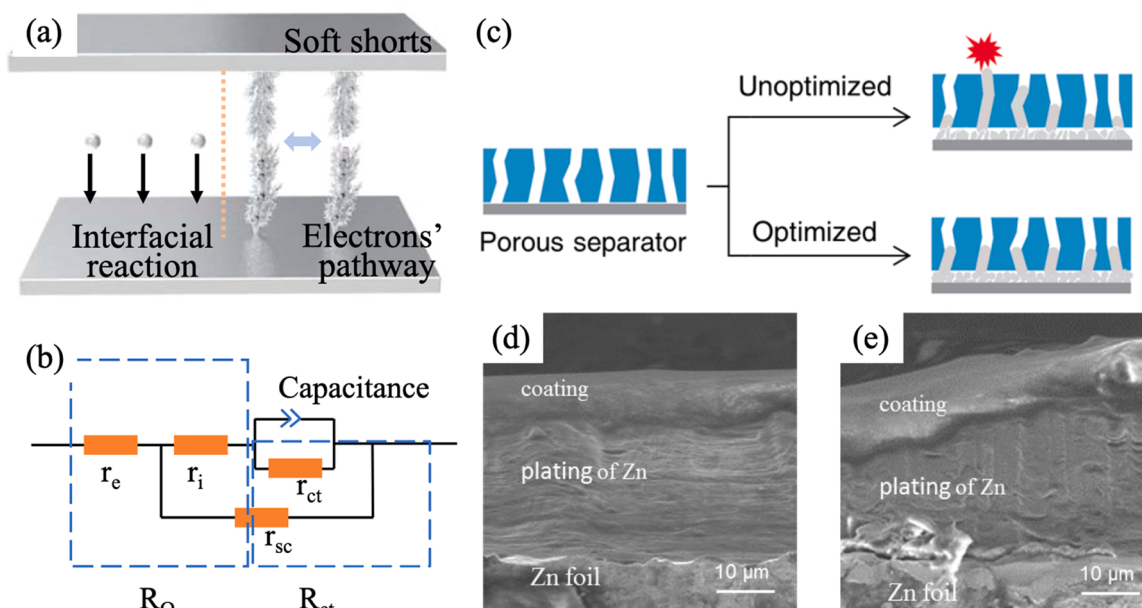


Fig. 19. a) Schematic illustration and b) corresponding equivalent circuit of the soft shorts [106]. c) Schematic illustration of the pore-filling zinc deposition behavior under practical conditions [75]. SEM images show slow dendrite growth beneath the coating after d) the first cycle and e) the 200th cycles [111].

the smooth morphology, resulting in improved cycling performance. These findings cast doubt on the requirement of mechanical strength for interface modifications. Recently, research of the separator found that certain zinc dendrites can grow along the separator's channels toward the counter electrode, posing real threat to the cell's operation (Fig. 19c) [75]. If zinc is deposited beneath the coating layer in this manner, the hazardous dendrites are not forced to compete with the coating material. Rather than that, they circumvent these impediments. Then it may be deduced that the most critical requirement for the coating layer is its chemical properties, not its mechanical strength. Additionally, in terms of bulk volume change, an elastic [111] or self-healing [112] coating layer may be a superior option.

6.4. Failure of the interface modifications

The topic of interface modification has been extensively investigated and proposed as a scientific strategy. Numerous publications assert their superior performance; yet, symmetric cells or full cells do fail after a specific period of time, suggesting the anode's ultimate failure. Additionally, some experimental results clearly demonstrate dendritic development beneath the protective coating layer, indicating a slow but certain failure (Fig. 19d and e) [111]. Regrettably, the mechanism of failure of the modification layers has been rarely discussed.

The anode system composed of zinc metal and modification layer may fail in two ways: the coating material itself deteriorates and/or the coating decouples from the substrate. The coating material may disintegrate gradually, either chemically in the electrolyte or electrochemically in the repeated electric field. Non-conductive coatings might lose their efficiency due to clogged or expanded diffusion channels, while conductive coatings get de-functionalized when newly deposited zinc completely covers the outer surface. Additionally, the accumulation of stress may lead to the detachment of the decoration layer [17], which can occur as a result of zinc volume change, coating material phase transition, or even gas and byproducts evolution. As with the negative concept of cathodic protection in the corrosion field, simply a little exposed domain can initiate a rampant dendrite and a quick short-circuit locally. After all, we advocate for a thorough examination of coating materials, covering not only their merits but also their disadvantages. This might help to clarify the strategy and aid in its continued development.

7. Summary and perspective

In summary, the bare zinc anode suffers low cycling performance and poor CE, which hinders the practical application of ZIBs. Interface modification is a viable method for addressing these difficulties and optimizing the electrochemical performance of zinc anode. The material category and associated preparation processes are summarized to ensure that the reader has a firm grasp on the subject of interface modification. The emphasis is then placed on the analysis of the structures and mechanisms of the interface modifications, including the increased active sites for zinc deposition in the conductive coating layer, as well as the non-conductive layer's re-distribution effect on zinc ions and water/anions. Additionally, performance enhancement options are discussed in detail to highlight inspiration to design principles. Following that, several conflicts and misunderstandings are listed in order to provide a thorough comprehension of this strategy.

As concluded, improved stability and reversibility of zinc anode can be accomplished through interface modification, indicating a wide range of possible applications. However, the ideal zinc anode must possess the following characteristics: a long cycle lifetime, a high degree of reversibility, and low energy consumption, none of which could be achieved in the current research. Additional development is required to solve these research issues, and the following perspectives are proposed:

- (1) Though the interface modifications have a significant effect on dendritic suppression, in the majority of the literatures the improved cycling performance is achieved with a low current density and a small capacity in the galvanostatic plating/stripping test. At high current density and capacity conditions, the decorated zinc anode's cycling life was significantly reduced. For example, a zinc anode coated with TiO_2 can safely run for 2000 h at 0.885 mA cm^{-2} and $0.885 \text{ mAh cm}^{-2}$, but fails after just 250 h at 8.85 mA cm^{-2} and 8.85 mAh cm^{-2} . To meet the emerging demand, the fast-charge feature must be realized through future interface modifications, which must address the more violent dendritic difficulties associated with high depth of charge [16].
- (2) As previously stated, the zinc anode's low CE is deemed to be an obstacle to practical implementation of ZIBs [23]. The final solution for CE enhancement is to create a water-free interface for zinc deposition. NTP and Nafion-zeolite coatings are excellent examples of a solid-state or quasi-solid-state electrolyte that enables only zinc ion diffusion. This objective is accomplished by the use of functional structures or organic groups. Though the notion is still in its infancy, continued research into enhanced solid-state electrolytes as protective coatings is vital.
- (3) While we have highlighted the benefits and functions of interface modification, there are still certain challenges that this technique cannot easily resolve. For example, the freezing nature of the aqueous electrolytes severely inhibits the use of ZIBs in cold climates, and the narrow electrochemical window limits cathode selection and capacity enhancement. As a result, additional methods, such as electrolyte tuning, could be used in conjunction with interface modification to address the difficulties associated with ZIBs. We expect that a well-balanced combination of several tactics can improve ZIBs' electrochemical performance, as each strategy can focus on a certain area. Additional research should be undertaken on cooperation.
- (4) In the context of actual application, the cost of the coating material and fabrication process should be considered to ensure the competitiveness. Certain coatings, such as Nafion-zeolite and hydrogen-substituted graphdiyne, are prohibitively expensive for large-scale use, despite their great performance. Additionally, some preparation procedures, such as ALD, MLD, and others, are expensive and time-consuming, making them inappropriate. Therefore, affordable minerals and organic polymers with induced functional groups may serve as the foundation for future interface modification research.
- (5) In our opinion, the most applicable interfacial modification would present multifunction of controlling dendrites and side reactions. On one hand, the zinc ions should be allocated by the even diffusion channels, which reduce the possible deposition accumulation. On the other hand, water molecules and anions should not pass through these channels to reduce the side reactions, which calls for special physical/chemical interaction between these molecules and the function groups of the channels. With the current technology, we prefer the proper combination of two or more basic materials as coating. Several literatures have discussed the combination, for example, TiO_2/PVDF [73], Cu/ZnF_2 [113], Nafion/ $\text{Zn}_3(\text{PO}_4)_2$ [114], and MXene/poly-pyrrole [115]. The synergy of different mechanisms should get more attention.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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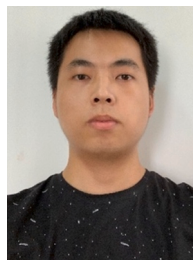
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