

Review

Strategies to inhibition the dendrites of the anode in zinc ion batteries

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Zinc ion battery has become a significant source of modern energy storage devices due to its high safety, low cost, high theoretical capacity, and environmental friendliness, but there are still some problems hindering the development of the battery. There are three main problems for anodes: zinc dendrite, zinc anode corrosion, and zinc anode passivation. Among them, the zinc dendrite is mainly caused by the uneven deposition of zinc on the anode surface, which will seriously affect the cycle stability and reversibility of the battery, and reduce the Coulombic efficiency. If the dendrite grows through the separator, it may also cause a short circuit, which will make the battery fail. In this paper, methods to solve the problem of the zinc dendrite in recent three years are summarized, including the modification of the anode structure, the modification of the anode surface, and the modification of the electrolyte.

Keyword: New Energy, Zinc Ion Battery, Dendrite, Electrochemistry

1. INTRODUCTION

With the changes of the times, people's demand for energy is increasing. The past energy storage methods have been unable to adapt to the development of the times. As a clean energy source, electrical energy has been widely used in all walks of life[1]. As the main storage device of electrical energy, the battery has gone from primary battery to secondary battery, and then are constantly updated[2, 3]. At present, lithium-ion batteries (LIBs) occupy a dominant position in the market, but we all know that lithium-ion batteries have many shortcomings. For example, flammability of electrolyte, the toxicity of battery, and the relative scarcity and high cost of lithium resources[4-10]. This lead to the emergence of a substitute for it—the zinc ion batteries (ZIBs). Zinc ion battery makes up the shortcomings of the lithium-ion battery. It has many merits. For example, it has good security, low cost, high theoretical capacity, and environmental friendliness. In the research of zinc ion battery, the battery mechanism can

be explained by "Rocking Chair Mechanism"[11], And the research on cathode materials is relatively mature[12], including manganese oxide compounds[13-15], vanadium oxide compounds[16-18], Prussian blue analogs [19-21] and organic materials[22-24]. Which leaves the anode to be a big hinder. Among all kinds of anodes, zinc is the first choice because of its abundant reserves, low price, low redox potential (- 0.76 v vs SHE), and high theoretical capacity^[11, 25-33]. At the same time, however, there are three challenges for the anode, including zinc dendrite, zinc anode corrosion, and zinc anode passivation. The existence of these problems will reduce the capacity and cycle performance of the battery, resulting in a shortened life. Among those three major problems, the dendrite makes a big deal. It could pierce the diaphragm[34] and make the battery fail, so it has become the core problem, which needs to be solved urgently.

In recent years, breakthroughs have been made in solving the dendrite problem. In this paper, the strategies of dendrite treatment in recent years were summarized and divided into three parts, namely, the modification of the anode structure, the modification of the anode surface, and the modification of the electrolyte.

2. CHALLENGES IN ZINC ION BATTERIES

Zinc is an ideal anode for zinc ion batteries because of its large reserves, low cost, stable chemical properties, low reduction potential, and easy production. However, it also has some disadvantages, such as zinc dendrite, zinc corrosion, and zinc passivation, which has become a stumbling block in the development of zinc ion battery.

2.1 zinc dendrite

One of the problems in the charging process is the growth of dendrites. During the charging process, the zinc ions migrate from the electrolyte to the anode surface, and get electrons from the anode, thus depositing metallic zinc. Normally, it would uniformly deposit on the surface of the anode. However, due to the uneven surface morphology and electric field distribution of the anode, it is likely to lead to local current[35], which often leads to the concentrated deposition of zinc, and zinc grows slowly into zinc dendrites. The nucleation of zinc usually occurs where the concentration of zinc ion is high and the zinc crystal already exists (aka "heterogeneous nucleation")[36-38]. And then the zinc nuclei continue to grow and form zinc dendrites. Generally, dendrites are needle-shaped[34, 39], and their tips will become the charge concentration area, which would trigger the tip effect[40] and further accelerating the growth of zinc dendrites. There are studies shown that the formation of dendrites is closely related to the current density[41]. The higher the current density is, the easier the dendrite will be formed. Generally, it is easier to form dendrite while the current density exceeds 10 mA cm⁻²[33]. In addition, Some studies also showed that the formation of zinc dendrites may be related to the high concentration polarization in the electrolyte during charging and discharging[41, 42]. Because liquid phase mass transfer is the main control step in the charging process, coupled with the high concentration

polarization on the electrode surface, zinc ions tend to deposit on the protrusions on the electrode surface and gradually form dendrites. However, the mechanism of dendrite growth is still unclear, and it may be controlled by many factors, which need to be explored. Besides, dendrites could penetrate the separator, causing a short circuit of the battery, which affects the cycle stability and reversibility of the battery[43].

2.2 zinc anode corrosion

The main cause of zinc anode corrosion is the hydrogen evolution reaction (HER). On the one hand, in alkaline electrolytes, HER would occur spontaneously on the surface of zinc anode, which is mainly a chemical reaction process[44]. On the other hand, HER is also related to an electrochemical reaction. Because the potential of zinc reduction (-1.26 V vs. SHE) is obviously more negative than that of HER (-0.83 V vs. SHE), which will make HER thermodynamically inevitable[45]. When the battery is discharged, some high-energy regions would generate H₂, which would leave the OH⁻ to react with Zn²⁺ and generate the passivation layer, as shown in reaction (2-1). This process would not only consume the metal Zn and charging energy, which results in a capacity decay, But also will eventually lead to the self-discharge behavior of the battery and limit the cycle performance[46].



The reasons for this corrosion may also include dendrites, the angle between crystals, defects, impurities, etc. Especially, some impurities may have a low overpotential of hydrogen evolution, which makes hydrogen evolution easier. The unevenness of the surface makes the different areas of the surface have a different activity, which leads to the appearance of positive and negative electrodes respectively, forming micro-batteries, and accelerating hydrogen evolution corrosion.

2.3 zinc anode passivation

Passivation is another challenge in the development of zinc ion batteries. In the process of discharge, zinc is converted into relatively insulating zinc oxide, which leads to an increase of internal resistance of anode[46, 47]. In addition, the passivation layer separates the anode from the electrolyte, which results in the failure of electron transfer from the anode to the Zn²⁺. It can be seen from formula (2-1) that the generation of insoluble Zn(OH)₂ is deposited on the anode surface, which hinders the normal dissolution and deposition of the original anode, and leads to the "passive state" of the surface, which causes the reduction of the Coulomb efficiency, utilization, cycle stability and reversibility of the battery, as well as the shortening of the battery life.

3. SOLUTION OF DENDRITE IN ZINC ANODE

- To maintain the capacity of the battery and improve the cycle stability, the key is to inhibit the growth of dendrite. In recent years, many teams both at home and abroad have put forward effective

methods to solve this problem. There are mainly three parts, including the modification of the anode structure, anode surface, and electrolyte (figure 1a) .Zinc dendrite formation (figure 1b).

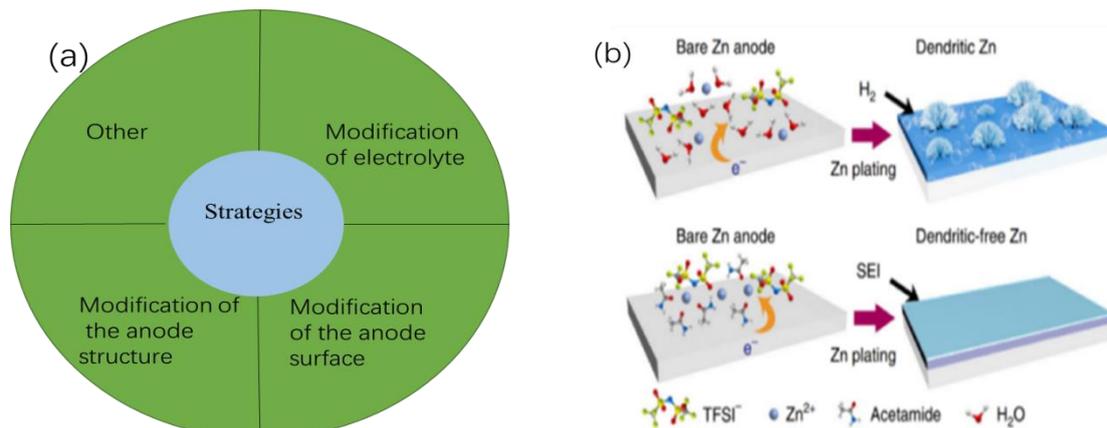


Figure 1. (a) Strategies to inhabit the dendrites of the anode in zinc ion batteries.(b)Zinc dendrite formation

3.1 modification of the anode structure

When a traditional metal zinc plate is directly used as anode material of zinc ion battery, zinc dendrites are easy to form because of the uneven deposition of zinc on the anode surface. To fix that, the design of zinc anode with a new structure that can work against the dendrite and is suitable for zinc ion battery has been gradually studied. Typically, zinc is deposited on a substrate to obtain a composite zinc anode, and the substrate could be a three-dimensional current collector. Generally, by applying the substrate to the zinc anode, the formation of dendrites can be effectively suppressed and the electrochemical performance of the battery can be improved. This is mainly owing to the uniform electric field distribution or uniform surface morphology of the anode, and the crystal orientation which is unfavorable to dendrites.

First, when choosing the current collector, we usually take the copper as our first choice. Because it has many merits, such as great conductivity and good mechanical properties(good elasticity and toughness). And there are quite a number of references for using copper as a current collector. For example, Li⁺ electric field distribution, and zinc can deposit in the porous structure to inhabit the dendrites (figure 2a and b). Also, the good elasticity and toughness of copper itself can tolerate the volume change when charging and discharging to keep the battery from failing. Similarly, Kang .[49] also obtained similar results with a 3D porous copper skeleton obtained by etching copper sheet. In addition, Yu .[50] made some modifications based on the 3D copper skeleton, they electroplated a layer of silver particles on the 3D copper framework to induce zinc deposition (figure 2e), resulting in a more uniform deposition layer (figure 2c and d).

Carbon is also a widely used and effective substrate material. Zeng.[51] used a carbon nanotube (CNT) skeleton as the substrate. In addition to the uniform electric field distribution brought by its porous structure (figure 2f), The CNT itself has many nucleation sites and a low overpotential for Zn²⁺, which are also conducive to the dendrite free growth of zinc. Guan.[52] proposed carbon fiber as the substrate

because of the N and O groups on the surface of carbon fiber have a strong attraction to Zn, which can increase the active sites of Zn^{2+} deposition. And Yin.[53] used magnetron sputtering technology to sputter tin induced layer on 3D porous carbon felt to guide the deposition of zinc. In contrast, Zheng.[54] synthesized graphite which can match the zinc (002) crystal face as the substrate to promote the oriented epitaxial growth of zinc on the graphite to inhibit the generation of the dendrite.

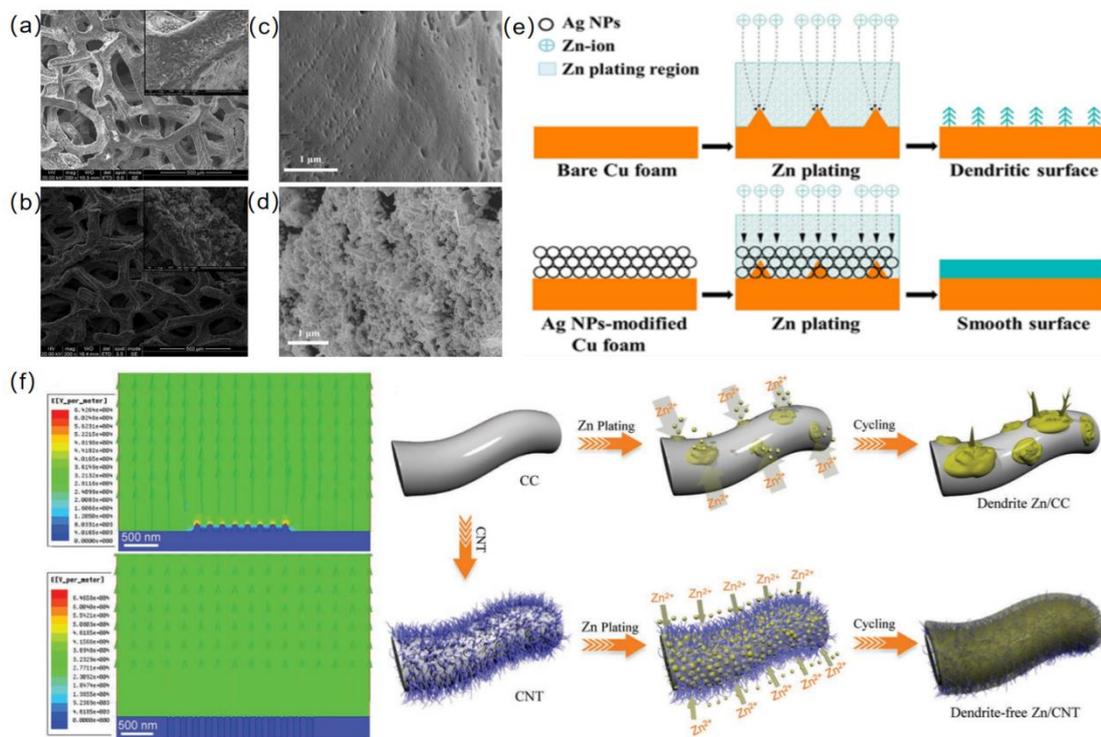


Figure 2. (a)(b) SEM images of Cu foam@Zn in a discharged state and charged state.[48].Copyright 2020 Chemical Engineering Journal. (c)(d).SEM images of bare Cu foam and Ag-modified Cu foam.[50](e) Schematic of Zn deposition in bare Cu foam and Ag-modified Cu foam.[50].Copyright 2019 ACS Applied Nano Materials. (f).Models of the electric field distributions and schematic illustrations of Zn deposition on a Zn/CC electrode and a Zn/CNT electrode.[51].Copyright 2019 Adv Mater.

Recently, the metal-organic framework (MOF) has been used as a substrate to regulate the diffusion, nucleation, and deposition of Zn^{2+} to achieve dendrite-free anode. Wang .[55] used zeolitic imidazole framework-8 (ZIF-8) annealed at 500°C as the substrate. The ZIF-8 itself has a porous structure, but other than that a large amount of metal zinc precipitated uniformly on the surface after annealing, which can be used as a new deposition site. In addition, Lee.[56] used ZIF-8 coated carbon felt as the base and decarburized at a high temperature (1000°C) to generate carbon vacancies on the surface, which have a strong interatomic bonding with Zn atoms, and this bonding can not only guide uniform Zn plating but also prevent surface diffusion at the initial deposition (**figure 3a**).

In addition to different substrate materials, zinc anode can also be modified by the composite method. In recent years, eutectic alloys have been used in the structural design of zinc anode and

achieved excellent performance. Wang.[57] proposed a strategy of Zn/Al-eutectic alloy $Zn_{88}Al_{12}$ with alternating layered nanostructures which was prepared by the casting method. This unique layered structure utilizes the symbiotic aluminum layer to form interlayer nanoparticles with Al/ Al_2O_3 core/shell structure in situ. Among them, Al can resist the irreversible by-products, and the insulating Al_2O_3 shell can prevent the reduction of Zn^{2+} on Al/ Al_2O_3 , thus guiding them to deposit on the precursor Zn sites and eliminating the Zn dendrites (figure 3b and c).

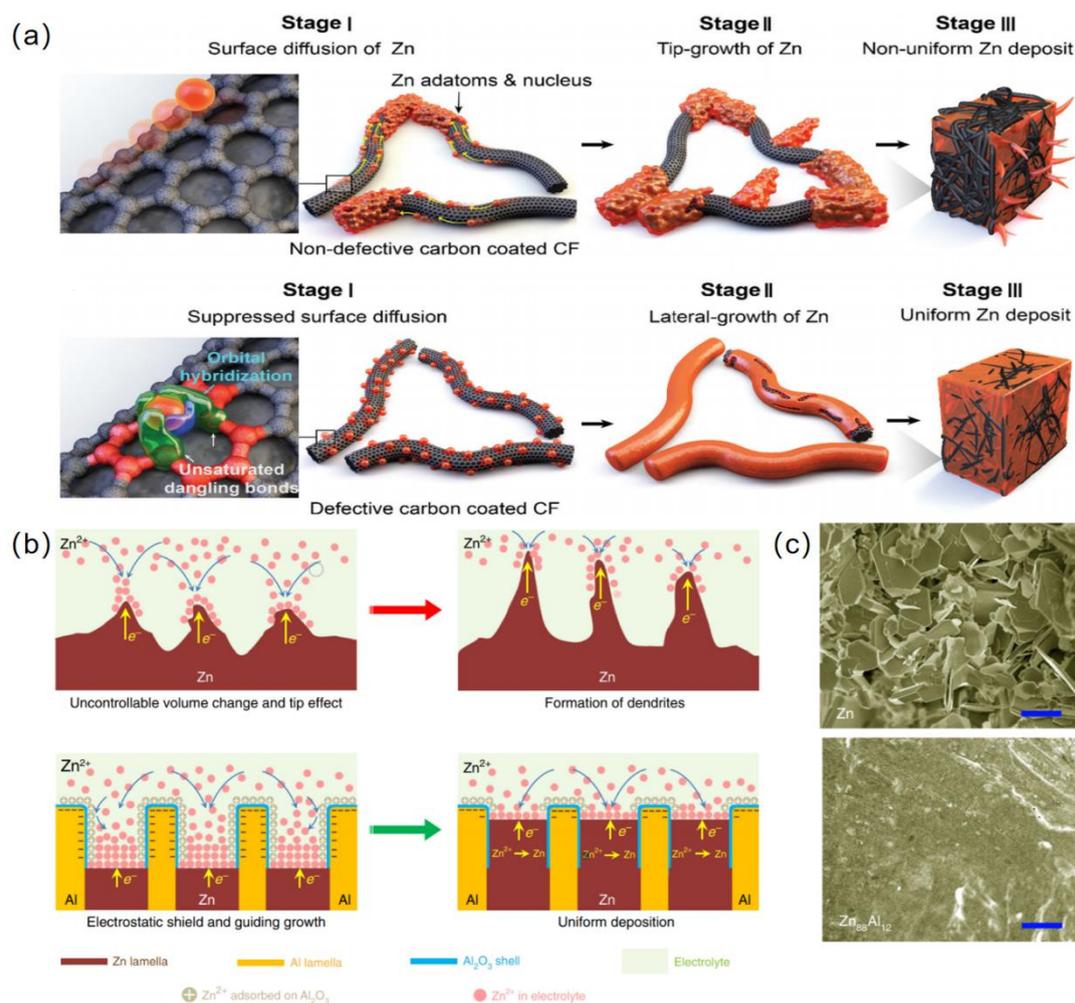


Figure 3. (a) Schematic illustration of Zn aggregation and subsequent non-uniform Zn growth on the non-defective 3D CF, and uniform Zn nucleation and lateral growth on the defective carbon layer-coated 3D CF.[57] .Copyright 2020 Energy & Environmental Science. (b) Schematic illustration of a eutectic strategy for dendrite and crack suppression.[57]. (c) SEM images of eutectic $Zn_{88}Al_{12}$ and monometallic Zn electrodes after long-term Zn stripping/plating cycling measurements.[57].Copyright 2020 Nature Communications.

Although the modification of zinc anode structure has considerable experimental results, there are still some shortcomings that need to be considered. Because most of the modification of the structure of zinc anode is achieved by applying the substrate materials, but the following problems are ignored in

many methods: **1** The applied substrate is likely to increase the internal resistance of the battery, which would reduce the efficiency of the battery and increase its heat production to accelerate battery failure. **2** The structure of the substrate material would be broken in the continuous charge/discharge cycle, and lose its original function. **3** Many substrates are metallic materials, which will dissolve part of them to form an alloy with zinc during the battery cycle. After all, this is possible in thermodynamics, such as copper substrate. And what this brings is the deposition potential of the alloy is different from that of zinc, which will reduce the efficiency and capacity of the battery.

3.2 modification of the anode surface

In addition to the structural modification of zinc anode, the surface modification of the anode is also an important way, which usually refers to surface coating. Most of the coating layers play a role - ion sieving, that is, by physical or chemical means to make useful ions pass through, such as zinc ions, while useless, harmful ions are blocked out of the coating layer, such as water and sulfate ions, so they can inhibit hydrogen evolution, corrosion, and other side reactions. Besides, the most important function of the coating layer is to uniformly disperse the disordered zinc ions on the anode surface, which is an important part of inhibiting dendrite growth.

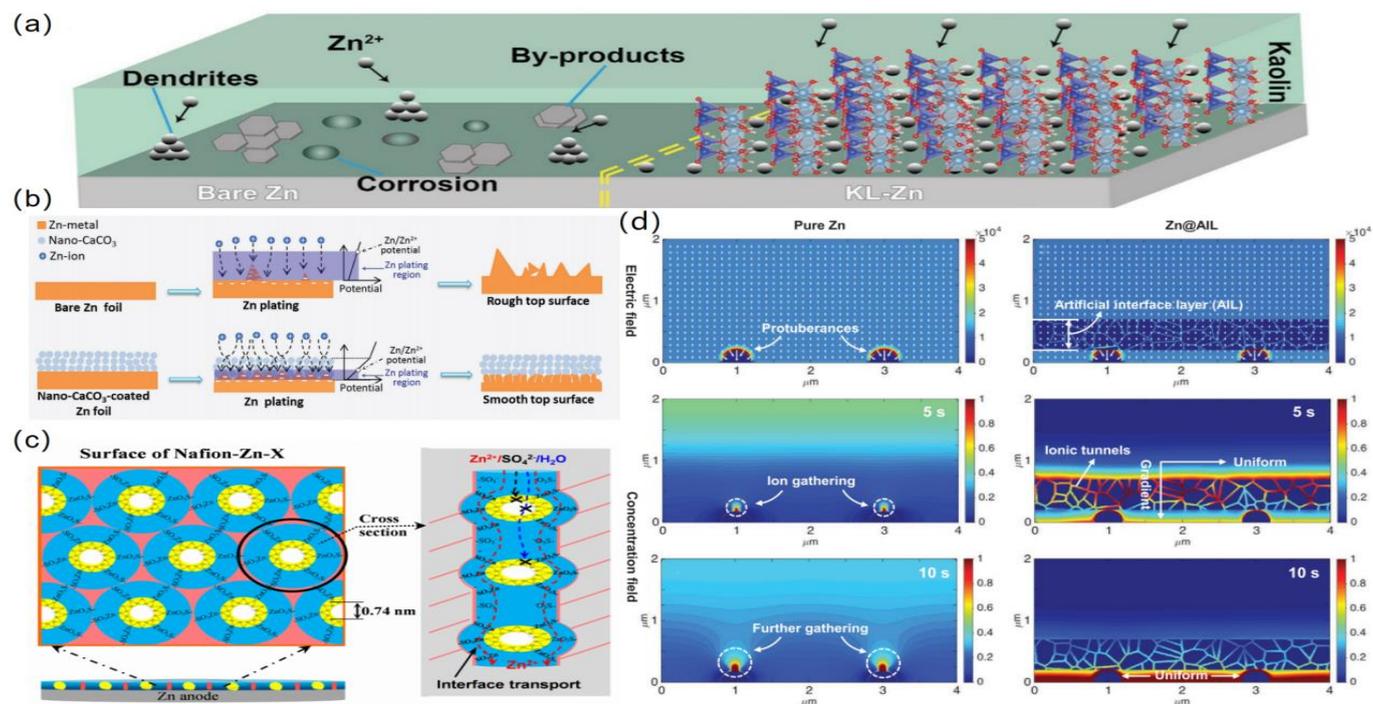


Figure 4. (a) Schematic illustrations of the morphology of Zn and KL-Zn anodes during the Zn^{2+} deposition process.[59].Copyright 2020 Advanced Functional Materials. (b) Schematic illustrations of morphology evolution for bare and nano- $CaCO_3$ -coated Zn foils during Zn stripping/plating cycling.[59].Copyright 2018 Advanced Energy Materials. (c) Ion transport mechanisms in Nafion-Zn-X protective layers.[63]Copyright 2020 Angew Chem Int Ed Engl. (d) Electric field simulation and Concentration field simulation on pure Zn anode and HsGDY coating anode.[64].Copyright 2020 Advanced Materials.

Nowadays, a variety of coatings have been proposed and applied to the zinc anode. Their anti dendritic effect is nothing more than the ion sieving which mentioned above. But each coating has its own different sieving mechanism. Most of the physical sieving is achieved by adjusting the pore size and its confinement effect (figure 4a and b), such as CaCO₃ coating[58], kaolin coating[59], ZrO₂ nano coating[60], ZnO coating[61], and ZnS coating[62], etc. There are also a few using the zinc affinity to construct ion tunnel and achieve chemical sieving, such as Nafion-Zn-X coating[63] (figure 4c) which is developed by complexing inorganic Zn-X zeolite nanoparticles with Nafion, hydrogen-substituted graphdiyne (HsGDY) coating[64] (figure 4d) and so on. In addition to the ion sieving mentioned above, some coatings have their own special features.

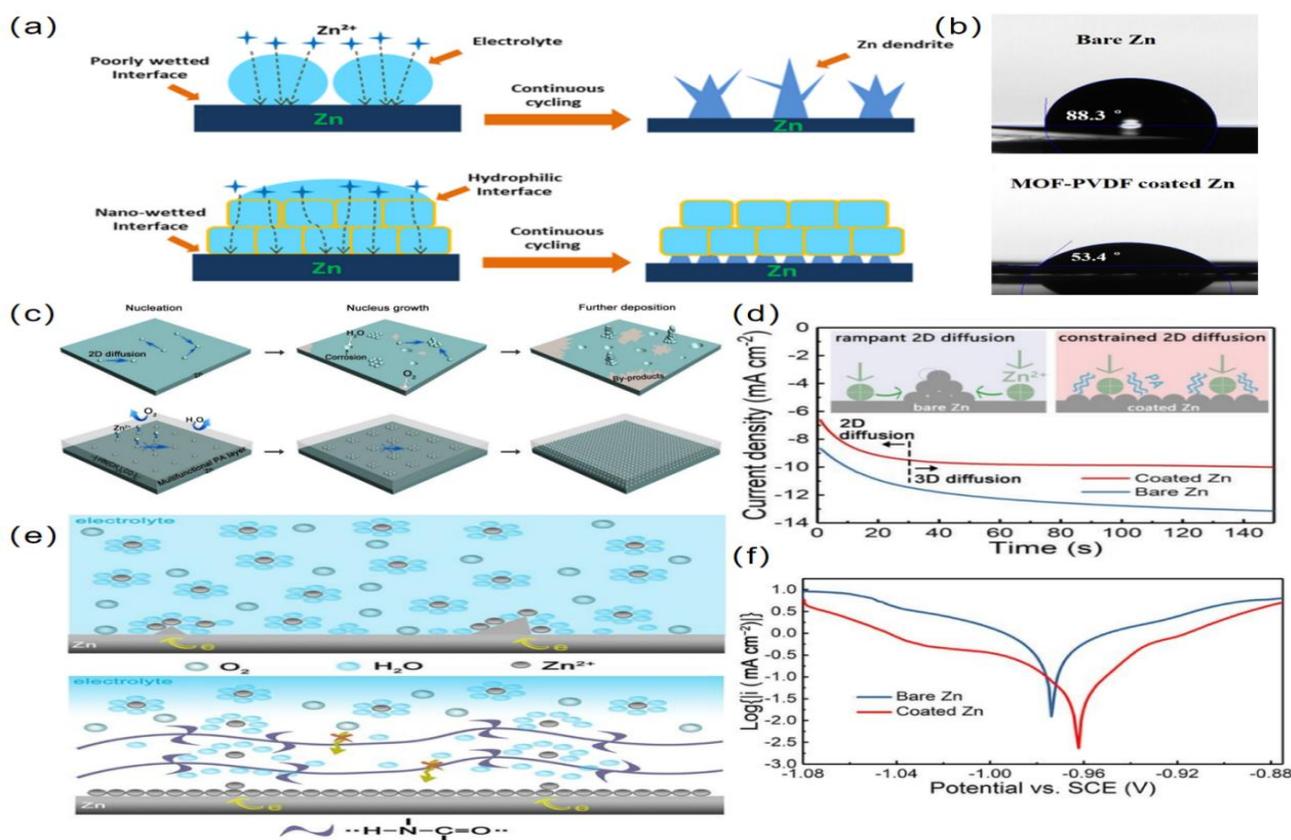


Figure 5. (a) Scheme of Zn Plating Mechanisms on Bare Zn and MOF–PVDF-Coated Zn.[65]. (b) Images of contact angles between the electrolyte and different anodes(Bare Zn and MOF–PVDF-Coated Zn).[65].Copyright 2019 ACS Applied Materials & Interfaces .(c) Schematic diagrams for Zn deposition, corrosion, byproducts on bare Zn and the PA coated Zn.[65]. (d) Chronoamperograms (CAs) of bare Zn and the PA coated Zn at -150 mV overpotential. Insets: schematics of the Zn^{2+} diffusion and reduction processes on bare and coated Zn electrodes, showing that the 2D diffusion is constrained on coated Zn.[65]. (e) Schematic diagrams for Zn deposition on the bare Zn and the PA coated Zn.[65]. (f) Linear polarization curves showing the corrosion on bare Zn and the PA coated Zn.[65]Copyright 2019 ACS Applied Materials & Interfaces

Unlike Li, Na, and other alkali metal anodes, which can form solid electrolyte interface (SEI), zinc anode has poor wettability with electrolyte, which will lead to the formation of local currency on

the anode surface, thus promoting the growth of dendrites. Liu [65] formed a composite coating layer of nanosized metal-organic framework (MOF) containing polyvinylidene fluoride (PVDF) on the anode surface to improve the poor wetting effect of electrolyte on it. In this layer, With the help of its own special nanowetting effect (**figure 5a**), MOF nanoparticles can achieve supersaturated electrolyte adsorption, which can significantly improve the wettability of the zinc anode surface (**figure 5b**). This helps to reduce the charge transport resistance and promote the uniform distribution of current on the anode surface which inhibits the formation of dendrites.

Zhao [66] constructed a polyamide coating, which mainly consists of polyamide (PA) and zinc trifluoromethanesulfonate ($\text{Zn}(\text{TFO})_2$). The coating not only has a unique hydrogen bond network and strong coordination ability with metal ions but also can improve the nucleation barrier and limit the 2D diffusion of Zn^{2+} (**figure 5c and d**), which results in a uniform distribution and deposition of Zn^{2+} . In addition, the coating acts as a buffer layer to separate the internal metal zinc from the external electrolyte, thus inhibiting the corrosion and passivation of zinc anode (**figure 5e and f**).

The modification of the anode surface also has many points that are not mentioned in the above methods. For example, if the bonding between coating and anode is strong enough to keep the coating from dissociating to the electrolyte. And the coating also needs enough mechanical strength to suppress dendrite without being destroyed or pierced.

3.3 modification of electrolyte

In addition to the modification of anode, the modification of electrolyte is also an effective way to solve the dendrite problem. Generally, the electrolyte used in zinc ion batteries is some zinc salts, such as ZnSO_4 [67], ZnCl_2 [68], $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ [69], $\text{Zn}(\text{NO}_3)_2$ [70], and so on. Among them, ZnSO_4 is the most used because of its good stability, low price, environmental friendliness, and compatibility with electrodes, but the ZnSO_4 can not inhabit the dendrite growth. So, there would be some new electrolyte to replace the original one for the dendrite-free anode. And the modification of electrolyte includes many aspects, on the one hand, by adding the additive to realize dendrite-free, for example, Chang [71] proposed to add trace metal ion Pb^{2+} to achieve a cathodic polarization for zinc plating and Huang [72] achieved a smoother surface by adding fumed silica (FS) to immobilize the water molecules and fatty methyl ester ethoxylate (FMEE) to homogenize the electrolyte and improve the electrolyte's wetting on the zinc surface (**figure 6a and b**). On the other hand, the types of the electrolyte can be changed, For one thing, there are different zinc salts, for instance, $\text{Zn}(\text{TFSI})_2$ and LiTFSI [73, 74] mixed in proper proportion can isolate the water and zinc ion to alleviate the water-induced corrosion, $\text{Zn}(\text{TFSI})_2$ and acetamide(ACE)[75] were composed to achieve solid electrolyte interphase (SEI) layer on anode surface (**figure 6c**), and some organic electrolytes were also used in the zinc ion batteries, such as triethyl phosphate (TEP)[76], trimethyl phosphate (TMP)[77] and so on. For another, hydro-gel electrolytes are widely used for their excellent ionic conductivity and mechanical properties. For example, Xiong[78] used fumed silica gel to improve the electronegativity of the electrode surface and achieved multiple nucleation sites. In addition, Tang[79] developed a three-dimensional Zn^{2+} -conductor gel electrolyte (Alg-Zn) via a directly ion crosslinking method (**figure 6e**) to achieve dendrite-free anode through its

confinement effect (figure 6d).

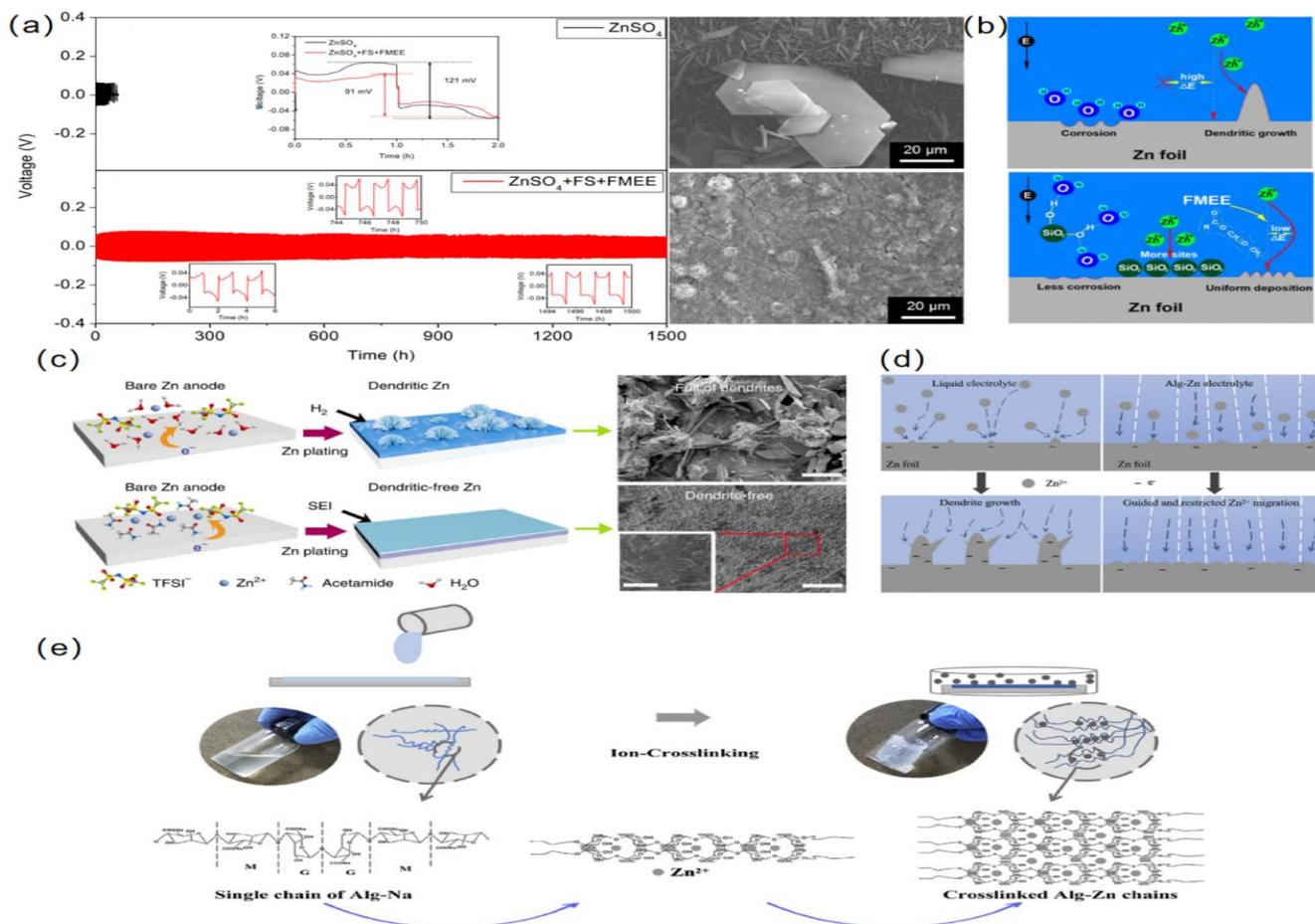


Figure 6. (a) Galvanostatic Zn plating/stripping in a Zn/Zn symmetric cell with ZnSO₄ electrolyte and ZnSO₄+FS+FMEE electrolyte at a current density of 0.2 mA cm⁻² and their SEM images of Zn metal surface after cycling.[75]. (b) Illustration of the schemes of the electrochemical processes of Zn metal in the reference ZnSO₄ electrolyte and the ZnSO₄+FS+FMEE electrolyte.[75].Copyright 2020 Energy Storage Materials (c) Scheme of Zn deposition with/without the generation of SEI and their SEM images of Zn anode surface after deposition.[75].Copyright 2019 nature communications.(d) The mechanism for the deposition behaviors of Zn²⁺ in ZnSO₄+MnSO₄ aqueous electrolyte and Alg-Zn electrolyte.[75]. (e) Schematic diagram of the preparation of Alg-Zn electrolyte by ion crosslinking method.[75].Copyright 2020 Energy Storage Materials

Recently, some innovative methods of electrolyte modification have been proposed. A hybrid electrolyte was reported by Hong .[80] In their work, a phase-filed simulation was used to analyze a porous polymer/aqueous ZnSO₄ electrolyte and found out the dendrite could be suppressed by utilizing both the mechanical suppression effect from the polymer framework and the high diffusivity from the aqueous electrolyte. And the ideal polymer was designed from bulk modulus and porosity, for one thing, higher bulk modulus has better dendrite suppression (**figure 7a** and **b**). But the ideal porous polymer's bulk modulus is about 1 GPa (for instance polymer of intrinsic microporosity PIM), which leaves the

control to porosity. For another, a lower porosity leads to lower diffusivity which favors dendrite growth, while higher porosity leads to lower mechanical suppression (figure 7c and d). So, according to the two-dimensional mapping of AGF (anisotropic growth factor: more the dendrite, higher the AGF) (figure 7e), we learned that the bulk modulus of the PIM between 0.67GPa to 2GPa, porosity between 30% to 60% is the reasonable design range (figure 7f and g).

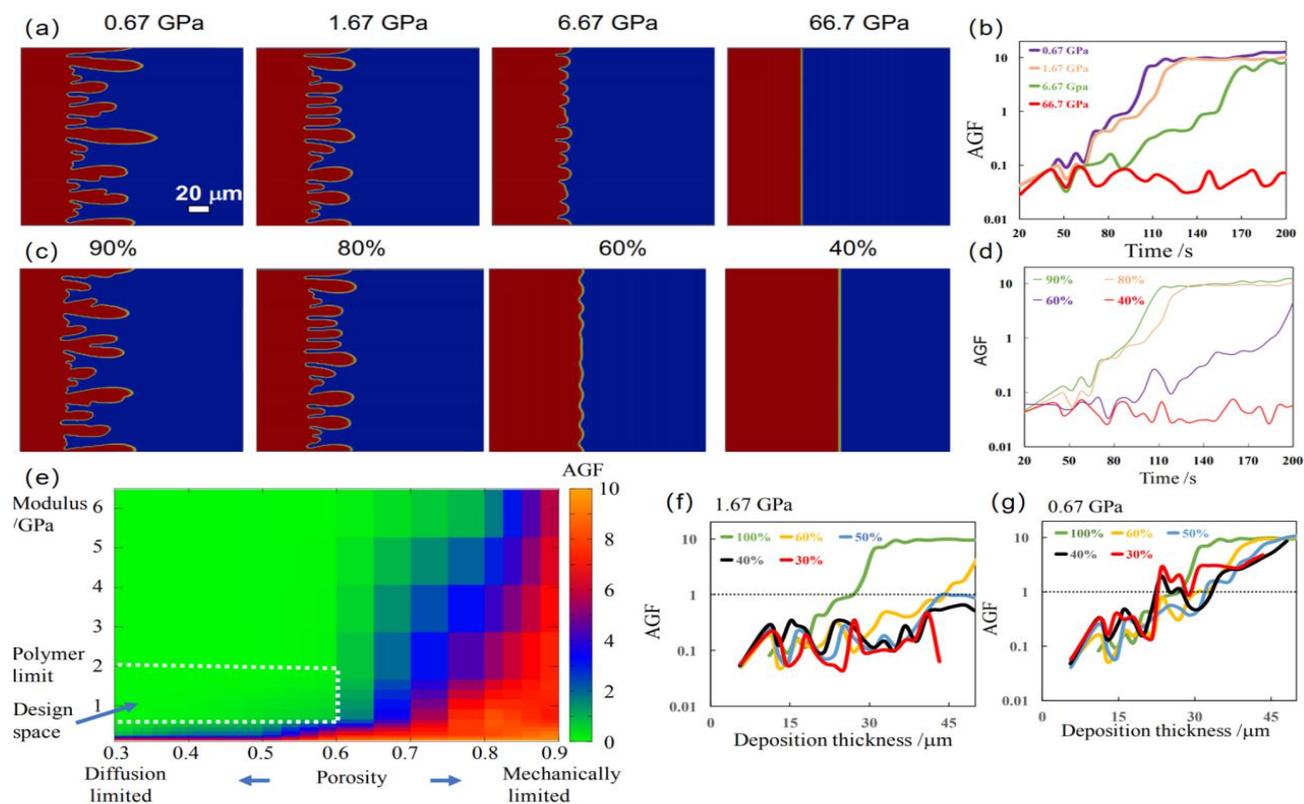


Figure 7. (a) Influence of the bulk modulus of the polymer framework on electrodeposition stability.[80]. (b) The anisotropic growth factor (AGF) with respect to electrodeposition time for different electrolyte bulk modulus.[80] (c) Influence of the porosity of the polymer framework on electrodeposition stability.[80]. (d) Evolution of AGF for different porosities.[80]. (e) Two-dimensional mapping of the AGF after electrodeposition of 120 s as a function of porosity and modulus.[80]. (f) (g) Evolution of AGF for different porosity with a bulk modulus of 1.67 GPa and 0.67GPa.[81].Copyright 2020 ACS Energy Letters

The modification of electrolyte is the most extensive among the three modification methods, which is mainly owing to the variety of electrolyte types and forms. The most widely used additives are organic electrolyte additives, which inevitably need to consider its flammability and toxicity. Also, the consumption of additives in the process of battery charging and discharging is also a point that needs to be considered.

3.4 others

All the methods mentioned above need to be supported by additional equipment. Is it possible to get rid of the substrate, coating, or electrolyte additive and by design to get a dendrite-free battery? Yang [81] solved this problem perfectly by designing an electrohealing methodology to in situ eliminate already-formed Zn dendrites. Firstly, They found the two major factors that affect dendrite growth—current density and capacity. The higher the current density, the more dendrite growth, and the less lifespan (figure 8a-e). While the capacity corresponding to the cathode loading mass affects the nucleation and growth of zinc dendrite. Then, through practice, it is found that the Zn dendrites may not be a problem at low current densities and small capacity (figure 8f). In brief, the electrohealing process is mainly aimed at the elimination of existing dendrites, and the specific step is to charge and discharge the battery slowly and repeatedly by applying a very small current density ($\leq 1 \text{ mA cm}^{-2}$), thus eliminating dendrites in situ (figure 8g and h). According to figure 8i, the sharp tips of Zn dendrites were passivated into smooth edges firstly, and gradually deposit a smooth anode surface after about 3h electrohealing. The advantage of this method is that it can maintain and prolong the life of the battery without disassembling it.

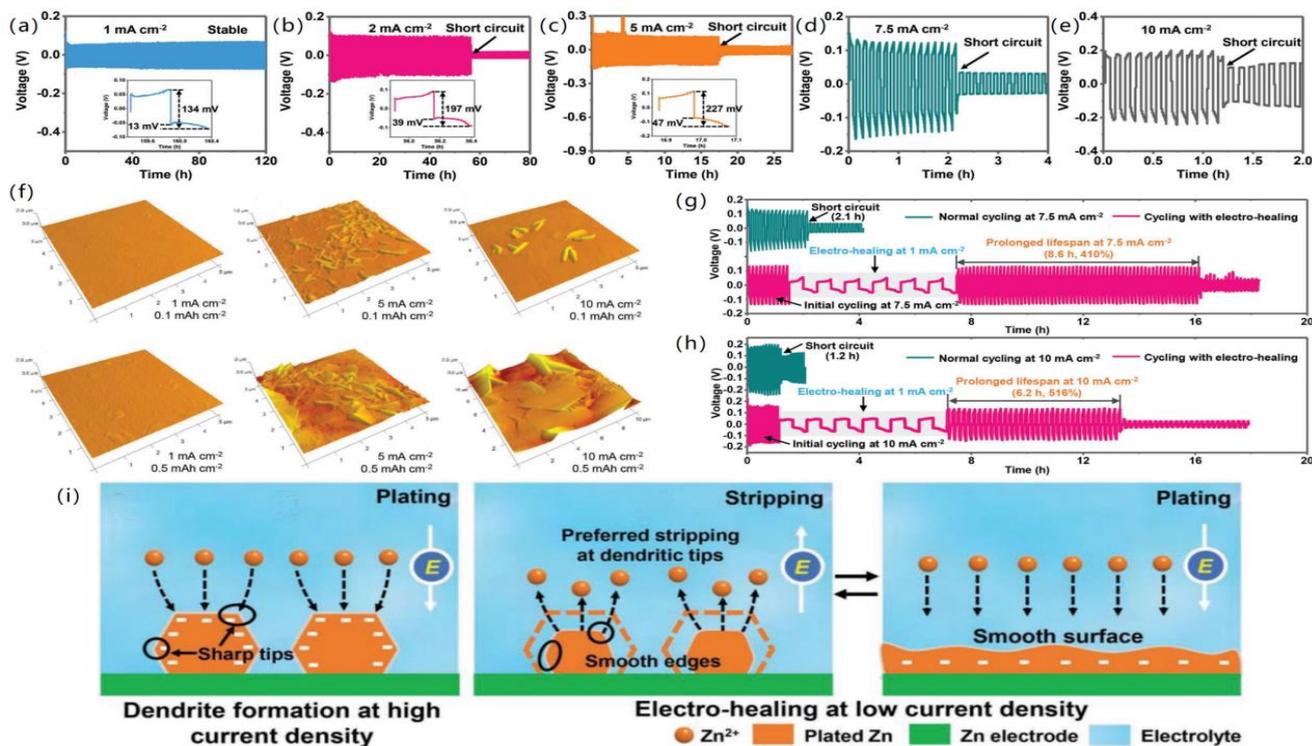


Figure 8. (a–e) Voltage–time curves recorded at various areal current densities of 1–10 mA cm⁻². [81]. (f) AFM images of Zn electrodes cycled at 1, 5, 10 mA cm⁻² with a constant capacity of 0.1 mAh cm⁻² and 0.5 mAh cm⁻². [81]. (g–h) Comparison of voltage–time profiles between the normal cycling and the electrohealing mode: 7.5 mA cm⁻² and 10 mA cm⁻². [81]. (i) Schematic illustration of the electrohealing process. [81]. Copyright 2019 Adv Mater.

4. SUMMARY AND PERSPECTIVES

As a kind of green and environmental battery, ZIB is an indispensable direction of the energy storage industry in the future. And owing to the nonnegligible shortcomings of LIB and the distinctive features of ZIB, ZIB has been seen as the most competitive candidate for the LIB in the secondary battery industry. However, there are still some problems that hinder the development of zinc ion batteries, and in this review, we firstly present the issues of zinc metal anode in three main parts, which are zinc dendrite, zinc corrosion, and zinc passivation. And in three of them, the zinc dendrite is the most serious problem in the anode surface, which is the focus of this paper. The main culprit of zinc anode corrosion is H_2O , $(\text{Zn}-(\text{H}_2\text{O})_6)^{2+}$ with strong binding force can be formed between Zn and H_2O , which not only hinders the deposition behavior of Zn^{2+} on the anode surface but also easily generates hydrogen in the deposition process, which causes corrosion of zinc anode. And the zinc anode passivation generally follows the zinc corrosion, because the excess OH^- produced by the corrosion side reaction would react with Zn^{2+} adsorbed on the anode surface to generate a ZnO passivation layer, which impedes the supply of electrons to the anode surface. Lastly, The dendrite problem of zinc anode is the most difficult to avoid, and the formation of zinc dendrite is mainly affected by tip effect and concentration polarization. However, the real mechanism of dendrite formation is not very clear at present, and it is likely to be controlled by many factors. Superficially, the main reasons for the formation of dendrites are the uneven morphology of the anode surface, the dendrite growable orientation of the surface crystal plane, the large concentration polarization, the high surface charge transport resistance, the generation of localized current, the uncontrolled 2D ion diffusion on the anode surface and so on. Then, according to the factors that relate to dendrites, the strategies of dealing with the zinc dendrite to improve the cycle performance and lifespan in recent three years were summarized to mainly three aspects, which are the modification of anode structure, the modification of anode surface and the modification of electrolyte. The mechanisms of those strategies to achieve dendrite-free anode are investigated in this work, as well as their advantages and disadvantages. Although many methods and strategies have been proposed to prevent dendrite growth, these methods have limitations, and some methods have obvious defects. So, if zinc ion battery aims to be as mature as the lithium-ion battery, there is still a long way to go, and the challenges are also continuing. Therefore, according to the summary of the methods put forward by predecessors, the prevention and control of zinc dendrite in the future can be improved from the following aspects:

1 Now many methods are stuck in the above three aspects of modification, but innovation is an essential part, and future methods can break the shackles of the above framework. We can try to start from the diaphragm or some additional conditions, or we can consider the problems by combining the above aspects, instead of the single anode structure, surface, or electrolyte modification.

2 Many methods and strategies are only in the laboratory stage. For commercialization and industrialization, much more aspects need to consider, such as cost, process technology, raw materials, etc. Therefore, the method in the future will start from low cost, mass production, simple process, and high performance to lay the foundation for the future industrialization, rather than just stay in the laboratory or even articles.

3 Although many strategies were proposed to solve the zinc dendrite problem. Surprisingly, there

has been relatively little research about the mechanism of zinc dendrite growth. It is still unclear how the metal zinc grows to dendrites. Therefore, more work needs to be devoted to the study of the essential mechanism. Only when the essence is explored can the dendrite problem be solved thoroughly.

Reference

1. B.Obama, *Science*, 355 (2017) 6321.
2. S.Chu, Y. Cui, N.J.N.M. Liu, *nature materials*, 16 (2016) 1.
3. Y.Wu, N.J.C. Liu, *Chem*,4 (2018) 3.
4. Larcher, J-M, T.J.N. *nature chemistry*, 17 (2015) 29.
5. J.-S. Lee, S.-T.Kim, R.Cao, N. S.Choi, M.Liu, K.-T. Lee, J.J.A.E.M. Cho, *Advanced Energy Materials*, 1 (2011) 1.
6. N. Liu, Z. Lu, J. Zhao, M.-T. Mcdowell, H. WLee, W. Zhao, Y. Cui, J.N.N, *Nature nanotechnology*, 9 (2014) 3.
7. Y. Jin, B. Zhu, Z. Lu, N. Liu, J.J.A.E.M. Zhu, *Advanced Energy Materials*, 7 (2017) 23.
8. D. Lin, P.-Y. Yuen, Y. Liu, W.N. Liu, R.-H. Dauskardt, Y. Cui, J.A.M, *Advanced Materials*, 30 (2018) 32 .
9. A.J.W, A.J.X, B.D.G.M, A.W.B, B.Z.B, C.Y.C.A.J.M.T.N, *Materials Today Energy*, 4 (2018) 1.
10. B. Dunn, H. Kamath, J.M.J.S. Tarascon, 334 (2011) 6058.
11. C. Xu, B. Li, H.Du, F.J.A.C.I.E. Kang, *Adanced Energy material*, 10 (2012) 34.
12. Xu.Wangwang, Letters, W.J.N.M, *Nano- Micro Letters* volume, 11 (2019) 04.
13. B. Jiang, C. Xu, C. Wu, L. Dong, J. Li, F. Kang, *Electrochimica Acta* 229(2017) 422-428.
14. Y. Fu, Q. Wei, G. Zhang, X. Wang, J. Zhang, Y. Hu, D. Wang, L. Zuin, T. Zhou, Y. Wu, *Advanced Energy Materials*, 8(2018)26.
15. A.H.Z, A.J.W.A, Q. L, A, W. H, A, Z. L, A, X. Z, C, M. Y. A, A, Y. T, B, X. L. A, *Energy Storage Materials*, 21 (2019) 154-161.
16. M. Yan, P. XHe, Y. Chen, S. Wang, Q. Wei, K. Zhao, X. Xu, Q. An, Y. Shuang, Y. Shao, *Advanced Materials*, 30(2017)1.
17. Y. Yang, Y. Tang, G. Fang, L. Shan, J. Guo, W. Zhang, C. Wang, L.Wang, J. Zhou, S. Liang, *Energy & Environmental science*, 11(2018)11.
18. S. Deng, Z. Yuan, Z. Tie, C. Wang, L. Song, Z. Niu, *Angewandte Chemie International Edition*, 59(2020)49.
19. L. Zhang, L. Chen, X. Zhou, Z. Liu, *Advanced Energy Materials*, 5 (2015)2.
20. L. Zhang, L. Chen, X. Zhou, Z. Liu, *Rep*, 5(2015)18263.
21. A. Paolella, C.Faure, V.Timochevskii, S.Marras, G.Bertoni, G. Abdelbast, *Journal of Materials Chemistry A*, 10(2017)1039.
22. Q. Zhao, W. Huang, Z. Luo, L. Liu, Y. Lu, *science Advances*, 4(2018) 3.
23. H.-Y. Shi, Y.-J. Ye, K. Liu, Y.S ong, X. Sun, *Angewandte Chemie*, 130 (2018) 50.
24. Kundu, Dipan, Oberholzer, Pascal, Glaros,Christos, Bouzid, Assil, Tervoort, Elena, *Chemistry of Materials A Publication of the American Chemistry Society*, 30 (2018) 11.
25. F. Wan, L. Zhang, X. Dai, X. Wang, Z. Niu, J.J.N.C. Chen, 9 (2018) 1.
26. W. Yu, W. Shang, P. Tan, B. Chen, Z. Wu, H. Xu, Z. Shao, M. Liu, M. Ni., *Journal of Materials Chemistry A*, 7(2019) 47.
27. H. Jianhang, W. Zhuo, H. Mengyan, D. Xiaoli, L. Yao, W. Yonggang, X. Yongyao, *Nature Communications*, 9 (2018) 1.
28. V. Verma, S. Kumar, W. Manalastas, R. Satish, M. Srinivasan, *Advanced Sustainable Systems*, 3 (2019) 1.

29. D.Kundu , B.-D.Adams, V.Duffort, S.-H.Vajargah, L.-F.Nazar, *Nature Energy* ,1 (2016) 10.
30. Z.-L. Wang, D. Xu, J.-J. Xu, X.-B. Zhang, *Cheminform*, 43 (2014) 22.
31. F. Guozhao, Z. Jiang, P. Anqiang, L.Shuquan, *ACS Energy Letters*,3 (2018) 10.
32. Z.-W.Seh, J. Kibsgaard, C.-F.Dickens, I.-B. Chorkendorff, J.-K. Norskov,T.-F.Jaramillo, *science* 355 (2017) 6321.
33. J.F. Parker, C.N. Chervin, I.R. Pala, M. Machler, M.F. Burz, J.W.Long, D. R.Rolison, *science* ,356 (2017) 6336.
34. A.Gavrilovic-Wohlmuther, A.Laskos, C.Zelger, B.Gollas, A. H.Whitehead, *Energy and Power Engineering*, 9 (2015) 11.
35. K.-I.Popov, M.-D.Maksimović, J.-D. Trnjančev, M.-G.Pavlović, *Journal of Applied Electrochemistry* ,11 (1981) 2.
36. Z. Zhao, X. Fan, J. Ding, W. Hu, J. Lu, *ACS Energy Letters*, 4 (2019) 9.
37. Y.-F.Yuan, J.-P.Tu, H.-M. Wu, S.F. Wang, W. K.Zhang, H.Huang, *Journal of Applied Electrochemistry*, 37 (2007) 2.
38. K.-E.-K. Sun, T.-K.-A. Hoan, T.-N.-L. Doan, Y. Yu, X. Zhu, Y. Tian, P. Chen, *ACS Applied Materials & Interfaces*, 9 (2017) 11.
39. G.Wranglén, Dendrites and growth layers in the electrocrystallization of metalsJ.. *Electrochimica Acta*, 2 (1960) 130-143.
40. Enze, Physics, L.J.J.o.P.D.A, 19(1989)1.
41. A.-R. Despic, J. Diggle, J.-O.-M. Bockris, *Journal of the Electrochemical Society*, 115 (1968) 5.
42. J.-W.Diggle, A.-R.;Despic, J.-O.-M.Bockris, *Journal of the Electrochemical Society* ,116 (1969) 11.
43. A.-R. Mainar, L.-C. Colmenares, J.-A. Blázquez, I. Urdampilleta, *International Journal of Energy Research*, 42 (2017) 3.
44. R.-E.-F.Einerhand, W.-H.-M.Visscher, E.Barendrecht, *Journal of Applied Electrochemistry* ,18 (1988) 6.
45. J. Fu, Z.-P. Cano, M.-G .Park, A. Yu, M. Fowler, Z. Chen, *Advanced Materials*, 29 (2017) 7.
46. M.-B.Liu, *Journal of the Electrochemical Society* ,128 (1981) 8.
47. Baugh, L.-M. Baugh, A .Higginson, *Electrochimica Acta*, 30 (1985) 9.
48. Z.Kang, C.Wu, L. Dong, W. Liu, J. Mou, J. Zhang, Z. Chang, B. Jiang, G. Wang, F.Kang, *ACS Sustainable Chemistry & Engineering*, 7(2019)3.
49. C. Li, X. Shi, S. Liang, X. Ma, M. Han, X. Wu, J. Zhou, *Chemical Engineering Journal* ,379(2020) 122248.
50. J. Yu, F. Chen, Q.Tang, T.-T. Gebremariam, J. Wang, X. Gong, *ACS Applied Nano Materials* ,2(2019)5.
51. Y. Zeng, X. Zhang, R. Qin, X. Liu, P. Fang, D. Zheng, Y. Tong, X. Lu, *Adv Mater* ,31(2019)36.
52. Q. Guan, Y. Li, X. Bi, J. Yang, J. Zhou, X. Li, J. Cheng, Z. Wang, *Advanced Energy Materials* , 9(2019)41.
53. Y. Yin, S. Wang, Q. Zhang, Y. Song, N. Chang, Y. Pan, H.Zhang, X. Li, *Adv Mater* ,23 (2020) 6.
54. J. Zheng, Q. Zhao, T. Tang, J. Yin, C.-D. Quilty, G.-D. Renderos, X. Liu, L. Wang. 366(2019)6465.
55. Z. Wang, J.Huang, Z.Guo, X. Dong, Y. Liu, Y. Wang, Y. Xia, *Joule* ,3(2019)5.
56. J.-H. Lee, R. Kim, S. Kim, J. Heo,H. Kwon, J.-H.Yang, H.-T. Kim, *Energy & Environmental Science* , 13(2020) 2839-2848.
57. S. Wang, Q. Ran, Q. Yao, H. Shi, Z. Wen, M. Zhao, X.-Y. Lang, *Nature Communications*, 11(2020)1 .
58. L.Kang, M.Cui, F. Jiang, Y. Gao, H. Luo, J. Liu, W. Liang, *Advanced Energy Materials* , 8(2018)25.
59. C. Zhang, X. Xie, J. Han, Y. Tang, J. Gao, C. Liu, X. Shi, J. Zhou, S. Liang, *Advanced Functional Materials* , 30(2020)21.

60. P. Liang, J. Yi, X. Liu, K. Wu, Z. Wang, J. Cui, Y. Liu, Y. Wang, Y. Xia; J. Zhang, *Advanced Functional Materials*, 30(2020)13.
61. X. Xie, S. Liang, J. Gao, S. Guo, C. Wang, G. Xu, X. Wu, G. Chen, J. Zhou, *Energy & Environmental Science*, 2(2020)13.
62. J. Hao, B. Li, X. Li, X. Zeng, S. Zhang, F. Yang, S. Liu, D. Liu, C. Wu, Z. Guo, *Adv Mater*, 32 (2020)
63. Y. Cui, Q. Zhao, X. Wu, X. Chen, J. Yang, Y. Wang, R. Qin, S. Ding, Y. Song, J. Wu, K. Yang, Z. Wang, Z. Mei, Z. Song, H. Wu, Z. Jiang, G. Qian, L. Yang, F. Pan, *Angew Chem Int Ed Engl*, 59 (2020) 38.
64. Q. Yang, Y. Guo, B. Yan, C. Wang, Z. Liu, Z. Huang, Y. Wang, Y. Li, H. Li, L. Song, J. Fan, C. Zhi, *Advanced Materials*, 32 (2020) 25.
65. M. Liu, L. Yang, H. Liu, A. Amine, Q. Zhao, Y. Song, J. Yang, K. Wang, F. Pan, *ACS Applied Materials & Interfaces*, 11 (2019)35.
66. Z. Zhao, J. Zhao, Z. Hu, J. Li, J. Li, Y. Zhang, C. Wang, G. Cui, *Energy & Environmental Science*, 12 (2019)6.
67. Y. Zhang, H. Li, S. Huang, S. Fan, L. Sun, B. Tian, F. Chen, Y. Wang, Y. Shi, H. Y. Yang, *Nano-micro letters*, 12 (2020) 1.
68. L. Zhang, I. A. Rodríguez-Pérez, H. Jiang, C. Zhang, D. P. Leonard, Q. Guo, W. Wang, S. Han, L. Wang, X. Ji, *Advanced functional materials*, 29 (2019) 30.
69. Z. Ning, *Journal of the American Chemical Society*, 138 (2016) 39.
70. C. Xu, B. Li, H. Du, F. Kang, *Angewandte Chemie International Edition*, 51 (2012) 4.
71. G. Chang, S. Liu, Y. Fu, X. Hao, J. J. A. M. I. Hu, *Advanced Materials Interfaces*, 6 (2019) 23.
72. J. Huang, X. Chi, Q. Han, Y. Liu, Y. Du, J. Yang, Y. J. J. o. T. E. S. Liu, *Journal of the Electrochemical Society*, 166 (2019) 6.
73. F. Wang, O. Borodin, T. Gao, X. Fan, W. Sun, F. Han, A. Faraone, J. A. Dura, K. Xu, C. J. N. M. Wang, *Nature materials*, 17 (2018) 543-549.
74. J. Zhao, J. Zhang, W. Yang, B. Chen, L. J. N. E. Chen, *Nano Energy*, 57 (2018) 625-634.
75. H. Qiu, X. Du, J. Zhao, Y. Wang, J. Ju, Z. Chen, Z. Hu, D. Yan, X. Zhou, G. J. N. C. Cui, *Nat Commun*, 10 (2019) 5374.
76. A. Naveed, H. Yang, J. Yang, Y. Nuli, J. J. A. C. Wang, *Angewandte Chemie International Edition*, 58 (2019) 9.
77. A. Naveed, H. Yang, Y. Shao, J. Yang, N. Yanna, J. Liu, S. Shi, L. Zhang, A. Ye, B. J. A. M. He, *Advanced Materials*, 31 (2019) 36.
78. W. Xiong, D. Yang, T. K. A. Hoang, M. Ahmed, J. Zhi, X. Qiu, P. J. E. S. M. Chen, *Energy Storage Materials*, 15(2018)131-138.
79. Y. Tang, Liu, C. Liu, H. Zhu, Xie, X. Xie, J. Gao, C. Deng, M. Han, S. Liang, J. Zhou, *Energy Storage Materials*, 27 (2020) 109-116.
80. Z. Hong, Z. Ahmad, V. Viswanathan, *ACS Energy Letters*, 5 (2020) 2466-2474.
81. Q. Yang, G. Liang, Y. Guo, Z. Liu, B. Yan, D. Wang, Z. Wang, X. Li, J. Fan, *Adv Mater.*, 31 (2019) 8