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Review on the suppression of Zn dendrite for high performance of Zn ion battery

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Abstract

Researchers are paying more attention to the environmentally friendly and low-cost energy storage devices, due to the environmental issues and energy crisis caused by current commercial energy storage technologies. Zinc ion battery (ZIB) is one of the new, environment-friendly and low-cost energy storage technologies, which is the most promising alternative technology to replace the lithium ion battery applications. However, one of the challenges-dendrite growths during cycling of Zn anode is still limited its practical applications. In this review, the recent progress on suppression of Zn dendrite in various electrode design, electrolyte additives, and separator modifications for ZIBs is summarized.

1. Introduction

Nowadays, the renewable energy sources include solar, geothermal, tidal, and wind are used extremely widely. However, the sun does not always shine, and the wind does not blow on command, the effectiveness of these renewable sources depends on energy storage devices when renewable sources are not available [1]. Battery, a storage device used extensively, is the one of energy storage devices taken to develop pragmatically due to its excellent energy efficiency [2]. The rechargeable batteries have attracted more and more interests as an electrochemical energy storage device system [3]. The lithium-ion batteries (LIBs) have taken over the rechargeable battery market and they are the first choice of energy storage devices because of their high capacity features and energy density. However, they have many issues include low abundance of lithium resources, safety concerns, high cost, and low environmental friendliness which are extremely limit its further development [4]. Therefore, it is urgent to find another type battery for further development.

Zinc-ion batteries (ZIBs), one of rechargeable batteries, since their low cost, environmental friendliness, high abundance of Zn resources, a high theoretical gravimetric capacity of 820 $mAh \cdot g^{-1}$, and a high theoretical volumetric capacity of 5855 $mAh \cdot cm^{-3}$, which has attracted wide concern in the recently years [5,6]. Nevertheless, one of the biggest challenges for ZIBs is the poor electrochemical reversibility of zinc anode in aqueous electrolytes. The "hostless" zinc metal anode dissolves in the electrolyte upon discharge and plates back during charging, and the dendritic metallic Zn may grow on the surface of anode during the process, which can finally cause a short circuit of the battery [7]. To date, some methods have been developed for inhabiting the dendrite growth and improving the cycle performance, like the modification of the electrodes, electrolyte, and separator. Herein, we summarize the recent progress of the suppression of zinc dendrites and future strategies on designing a dendrites-free zinc ion battery with superior electro-chemical performance.

2. Suppression of zinc dendrites

The formation of the zinc dendrites can cause many problems, like increasing the surface area, which facilitate the corrosion and hydrogen evolution, and severe dendrite growth may even puncture separators and short circuit the batteries. Therefore, it is vital to develop the modification strategies to inhabit the formation of the zinc dendrites. As shown in Figure 1, the Zn-symmetric battery is a simple model that facilitates the study of battery lifespan, it is clearly seen that the coin cell mainly contains anode, cathode, separator and electrolyte. Therefore, the modification of electrodes, electrolytes and separators has become the most practical method for dendrite-free zinc anodes.

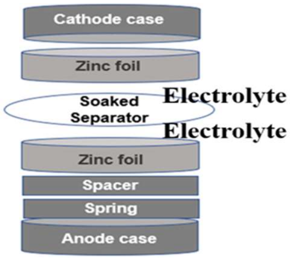

Figure 1. The components of Zn- symmetric batteries.

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2.1 Electrode

It is widely known that the conductivity and wettability play important roles in the performance of the electrode. The conductivity is a key factor of the zinc growth during the nucleation process, and it determined the electric field distribution [8]. Another factor, the wettability determines the degree of contact between the electrolyte and the electrode, and further determines the transmission rate of electrons and ions at the interface.

Zeng et al. prepared a flexible 3D carbon nanotube (CNT) framework as a Zn plating/stripping scaffold is constituted to achieve a dendrite-free Zn anode (Figure 2(a)) [9]. Compared with the pristine deposited Zn electrode on carbon cloth (CC), the as-fabricated Zn/CNT anode affords lower Zn nucleation overpotential (Figure 2(b)) and more homogeneously distributed electric field, thus being more favorable for highly reversible Zn plating/stripping with satisfactory Coulombic efficiency rather than the formation of Zn dendrites or other byproducts. The Zn is plated homogeneously on the surface of each carbon fiber with voids of random CNT arrays filled and no dendrite formation is observed form the SEM images (Figure 2(b)). As expected, the Zn/CNT electrode can maintain stable after 200 cycles, while the Zn/CC are short circuit after about 50 cycles under the same test condition, indicates that the good electric conductivity endows the anode with distinct advantages including limited local current density, low nucleation overpotential of Zn as well as homogeneous electric field distributions, and thus achieve a dendrites-free anode (Figure 2(c)).

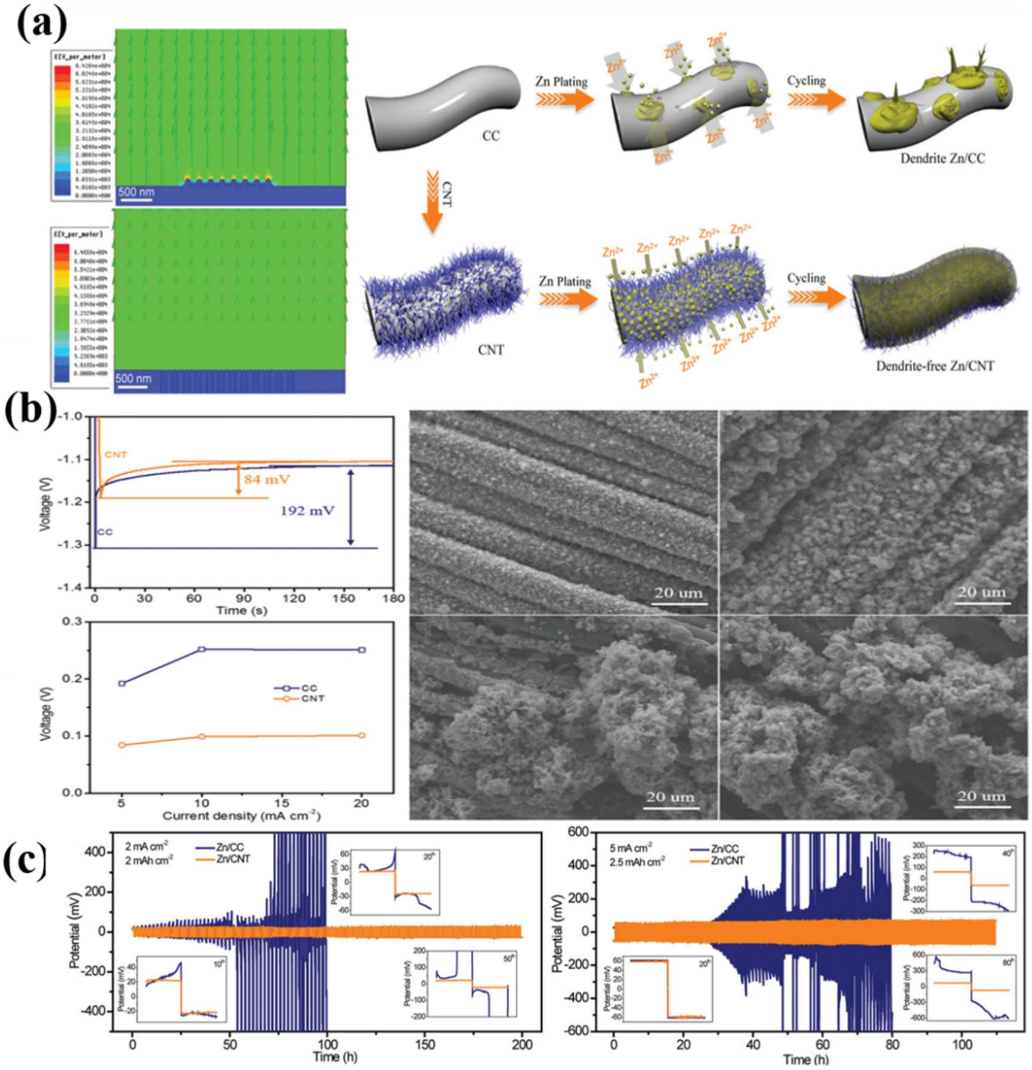

Figure 2. (a) The schematic illustration of Zn/CC electrode and a Zn/CNT electrode; (b) The voltage- time curves, Zn nucleation overpotentials, SEM images of CNT and CC after plating Zn; (c) Voltage profiles of symmetric cells based on Zn/CC and Zn/CNT anodes at 2 mA·cm^{-2} and 5 mA·cm^{-2}. Reproduced with permission from [9] Copyright 2019, Wiley-VCH.

Liu et al. modified the zinc anode with an artificial composite protective layer consisting of nanosized metal-organic frameworks (MOFs) to improve the poor wetting effect of aqueous electrolytes on the Zn anode, and the Zn/electrolyte interface is reconstructed (Figure 3(a)) [10]. The hydrophilic MOF nanoparticles serve as interconnecting electrolyte reservoirs enabling nano-level wetting effect. This zincophilic interface exhibits significantly reduced charge-transfer resistance (Figure 3(b)). As a result, stable and dendrite-free Zn plating/stripping cycling performance is achieved for over 500 cycles under the current densities of 1 mA·cm^{-2} and 3 mA·cm^{-2} (Figure 3(d)), and no obvious zinc dendrites grow on the MOF-coated Zn foil.

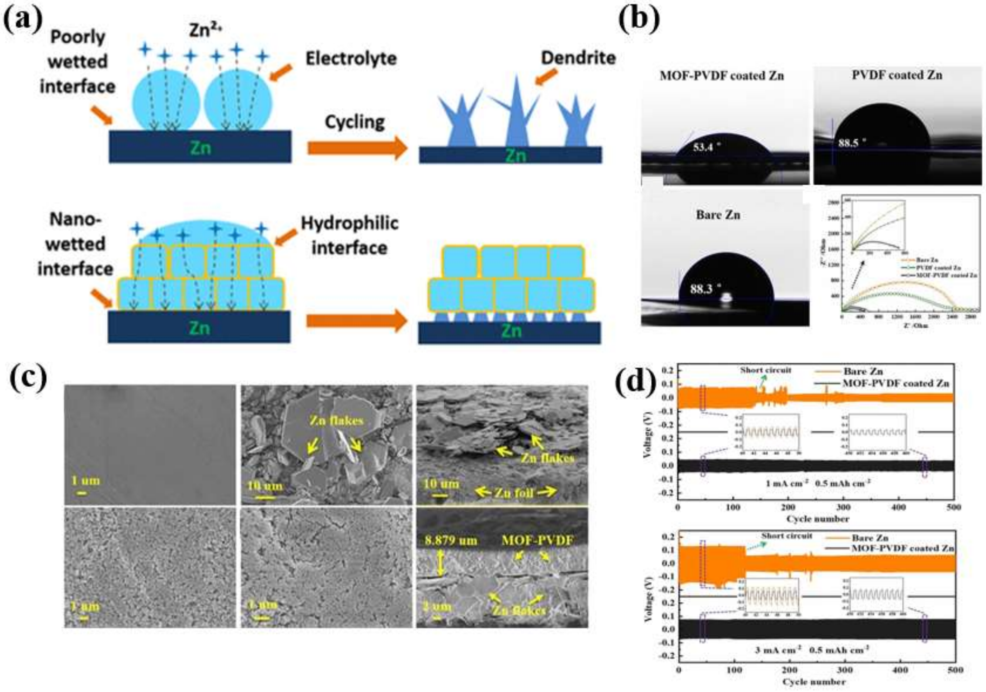

Figure 3. (a) The schematic illustration of Zn Plating Mechanisms on Bare Zn and MOF–PVDF-Coated Zn; (b) Images of contact angles and electrochemical impedance spectra of Zn-symmetric cells with different anodes; (c) SEM images of bare Zn foil and MOF-coated Zn foil before cycling and after cycling; (d) Voltage profiles of galvanostatic Zn plating/stripping for different Zn electrodes at 1 mA·cm^{-2} and 3 mA·cm^{-2}. Reproduced with permission from [10] Copyright 2019 American Chemical Society.

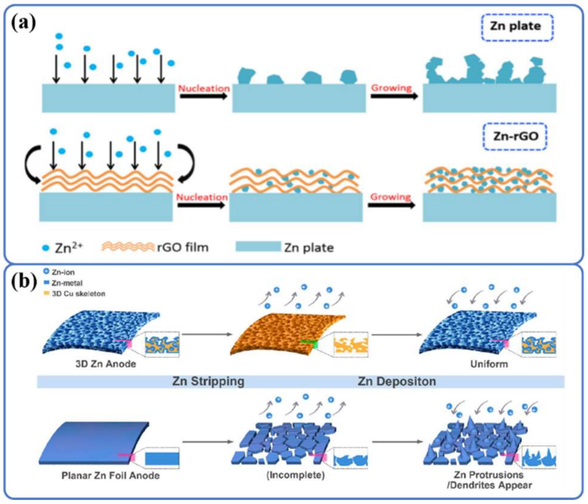

Figure 4. The schematic illustration of the mechanism of the suppression of the zinc dendrites on (a) Zn/rGO anode. Reproduced with permission from [11] Copyright 2019 Elsevier. (b) 3D porous copper skeleton

To overcome the formation of Zn dendrite, our group also developed the co-electrodepositon of nano TiO_2 into Zn coatings as the anode of zinc ion battery [13]. It can be found that the Zn-TiO_2//Zn-TiO_2 symmetric cell displays a flat voltage plateau comparing with the Zn//Zn cell, while the overpotential between plating and stripping of Zn//Zn cells slightly increases (Figure 5(a)). The compact and smooth surface can be obtained for the Zn/TiO_2 coatings anode, while the gaps around the granular boundaries and sharp needle can be observed on the surface of Zn coatings anode without the TiO_2 nanoparticles (Figure 5(b)). And the cycling performance of the Zn/TiO_2//MnO_2 full battery is also more excellent than Zn//MnO_2 full battery (Figure 5(c)). Because the Zn coatings have many defects such as sharp edges, coarse surface, and big gaps around the granular boundaries, the distribution of current will be not uniform on the coarse surface of Zn coatings. The sharp points with high current area tend to deposit faster and much coarse than other flat area, resulting in the dendrite formation on the Zn coatings electrode. While the Zn/TiO_2 coatings exhibit a compact and smooth surface, the current distribution would be uniform and then can keep flat surface during the cycle process.

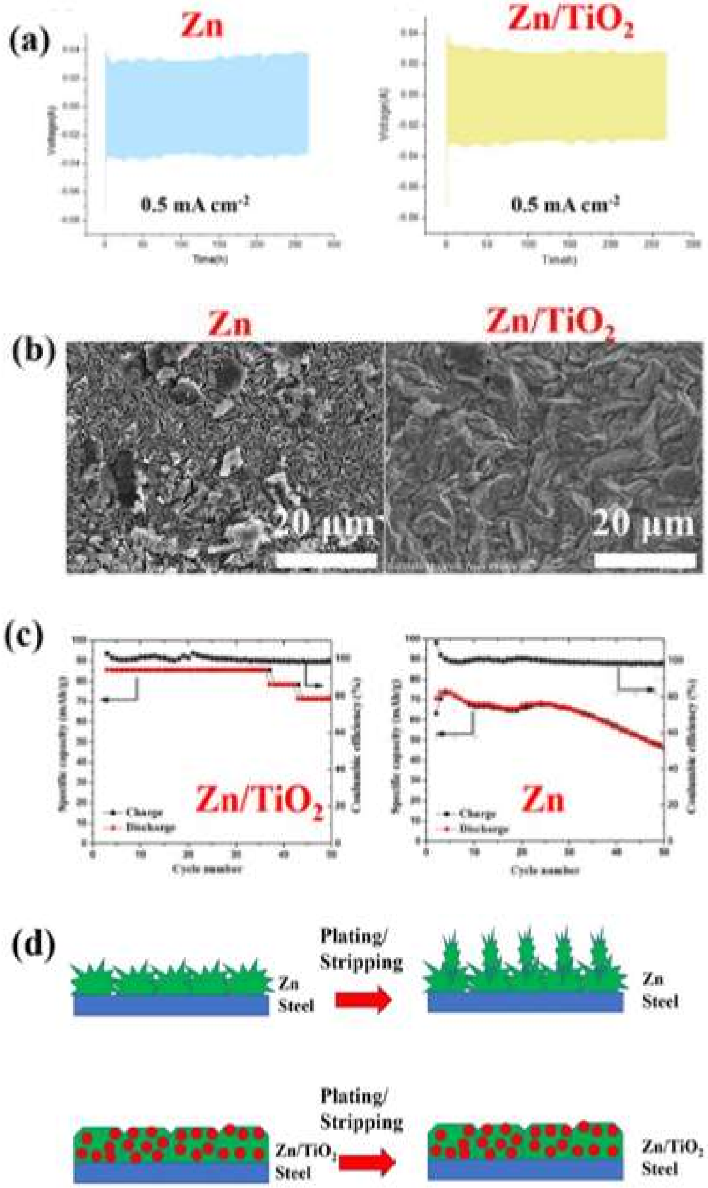

Figure 5. (a) Plating/stripping performance of Zn//Zn and Zn-TiO_2//Zn-TiO_2 symmetric cells at a current density of 0.5 mA·cm^{-2} (b) SEM images Zn and Zn/TiO_2 after cycling; (c) cycling performance of the Zn/TiO_2//MnO_2 full battery and Zn//MnO_2 full battery; (d) The schematic illustration of Zn Plating Mechanisms on different anodes. Reproduced with permission from [13] Copyright 2019 J. Met. Mater. Miner.

2.2 Electrolyte

Zinc deposition is highly reactive and very unstable in aqueous electrolytes because hydrogen or oxygen generated from water decomposition cannot precipitate on anode surface to form the solid electrolyte interphase (SEI). Therefore, some other strategies are developed to regulate zinc deposition. The most commonly used is introducing functional additives into electrolyte or increasing Zn^{2+} concentration.

Wan et al. found the addition of Na_2SO_4 into the $ZnSO_4$ electrolyte to inhibit the Zn dendrite deposition synchronously [14]. A large number of vertical and harsh Zn dendrites formed on the surface of Zn negative electrode (Figure 5(a)), while 1 M Na_2SO_4 was added into the $ZnSO_4$ electrolyte as the electrolyte additive in our Zn/$NaV_3O_8 \cdot 1.5H_2O$ (NVO) system, As expected, the addition of Na_2SO_4 in $ZnSO_4$ electrolyte could effectively avoid the growth of Zn dendrites (Figure 6(b)), and the cyclic performance of Zn/NVO has been significantly enhanced (Figure 6(c)). According to electrostatic shield mechanism, the dendrite deposition during charge process would be avoided by adding other positive ions with lower reduction potential into electrolyte (Figure 6(d)).

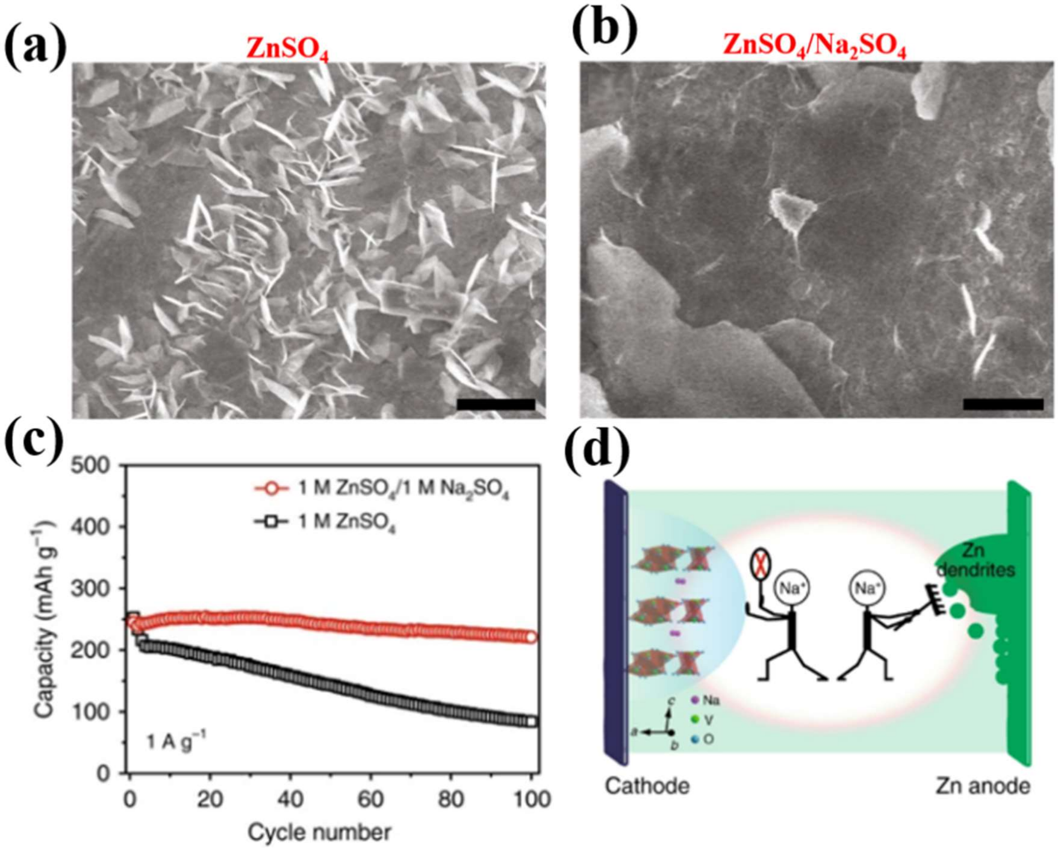

Figure 6. SEM images of the Zn negative electrode surface after cycle in (a) $ZnSO_4$ and (b) $ZnSO_4$/Na_2 SO_4 electrolytes; (c) cycling performance of Zn/NVO battery; (d) The schematic illustration of the mechanism of Na_2SO_4 electrolyte additive. Reproduced with permission from [14] Copyright 2018, Springer Nature.

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Zhang et al. proposed a synergistic method to fabricate three-dimensional dendrite-free zinc anode by combining Cu-Zn solid solution interface and zinc-oriented polyacrylamide (PAM) electrolyte additive (Figure 7(a)) [15]. The copper mesh can not only provide the structural support for zinc but also promote the zinc nucleation by the Cu-Zn solid solution formed in situ. PAM served as the guiding intermediary to induce the uniform zinc deposition at both the electrode preparation and charge-discharge process. It is shown that the Cu-Zn solid solution exhibits excellent zinc affinity and zinc ion has strong selective adsorption on the acyl group of PAM and can be transferred along the polymer chains, leading to the homogeneous distribution of zinc on the surface of the electrode. And the battery with PAM electrolyte shows a lower reduction potential (Figure 7(b), Figure 6(d)) and excellent cycling performance (Figure 7(c)). And the dendrites-free zinc anode is achieved (Figure 7(e) and Figure 7(f)).

It can be clearly noticed that it is difficult to completely inhibit the formation of dendrites with only one modification strategy and combining electrolyte additives and electrode surface modification would be a promising strategy in the future

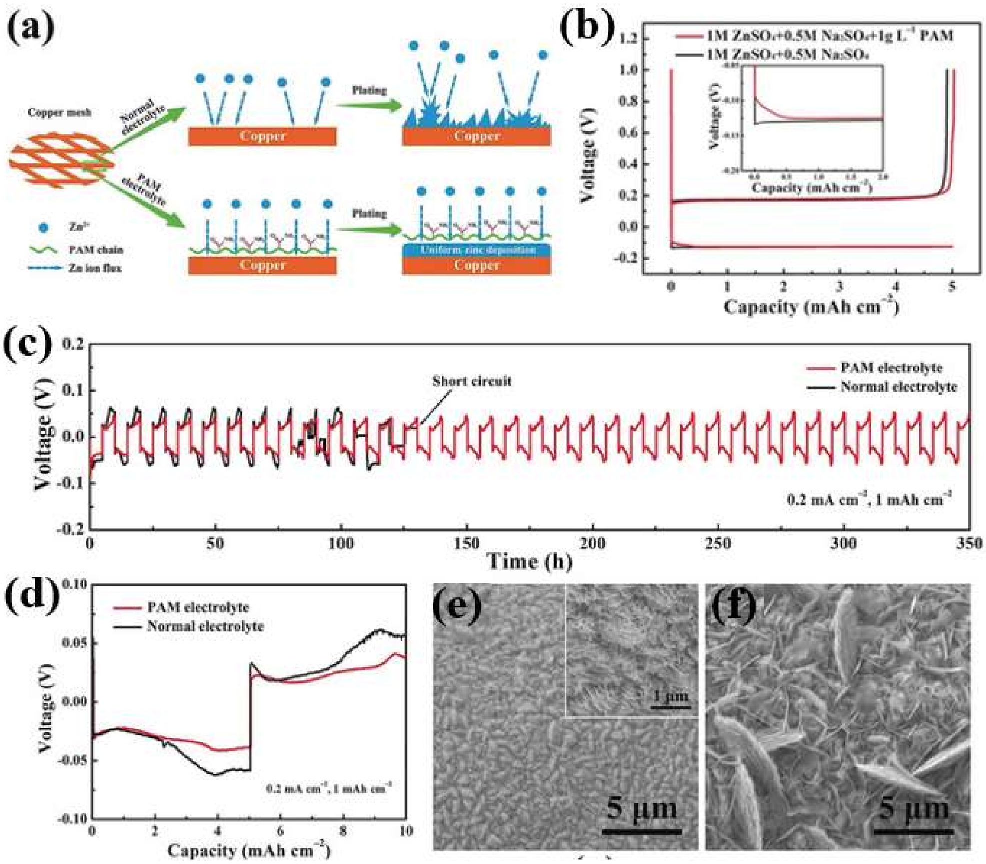

Figure 7. (a) The schematic illustration of the mechanism of Cu-Zn solid solution interface and zinc- oriented polyacrylamide (PAM) electrolyte additive; (b) Voltage profiles of a zinc plating/stripping cycle; (c) Cycling performance; (d) the corresponding voltage profiles in the 5th cycle; SEM images of the zinc anode with (e) PAM electrolyte and (f) normal electrolyte at 20 mA·cm^{-2}. Reproduced with permission from [15] Copyright 2019, Wiley-VCH.

2.3 Separator

To date, various methods have been developed to suppress the formation of the zinc dendrites and improve the cycle performance, and most of the work focus on the modification of the electrolyte and electrodes, few works study around the battery separator. Recently, a novel separator modified by graphene oxide (GO) has been applied to zinc ion battery in our group [7]. The modified separator is fabricated via vacuum filtered the GO onto the commercial glass fiber (GF) separator (GF/GO1), and the GF/GO1 separator can be cycled for 500 cycles at the current densities from 0.5 to 20 mA·cm^{-2}. However, the Zn//Zn batteries with ordinary GF separator are short circuit after about 50 and 40 cycles under the same test conditions. It can be seen that the overpotential of Zn plating/peeling in the battery with GF/GO1 separator is lower than that of the battery with GF separator in all current densities from the inset pictures of Figure 8, which indicates that the interfacial charge-transfer resistance has been decreased after the GF separator was modified by GO.

After cycling, the flat, uniform and hexagonal Zn deposits can be seen on the surface of zinc anode when using GF/GO1 separator in Figure 9(b) and Figure 9(f), and the Zn flakes and Zn dendrites can be found when using GF separator in Figure 9(d) and Figure 9(h). As for the mechanism of the dendrite-free behavior of GF/GO1 separator, the crystal plane preferential growth orientation of the zinc metal with GF/GO separator has been identified as the main reason via the *ex situ* XRD and *in situ* optical observation of the zinc anode. The dominance of (002) plane and the absence of (101) plane when using GF/GO1 separator lead to a dendrites-free zinc anode due to the difference in growth direction between the two planes (Figure 9(i)-9(k)). Another reason is that the GF/GO1 separator can reduce the nucleation overpotential of the zinc ions during the charging/discharging process (Figure 9(m) and Figure 9(n)).

This novel method for inhibiting Zn dendrites growth and improving batteries cycle stability is developed by modified the separator with the GO. And the method i is simple, low cost and pollution-free, making the modification of separator a promising strategy. More importantly, this will make a great contribution to the further development of the practical application of ZIBs and other batteries.

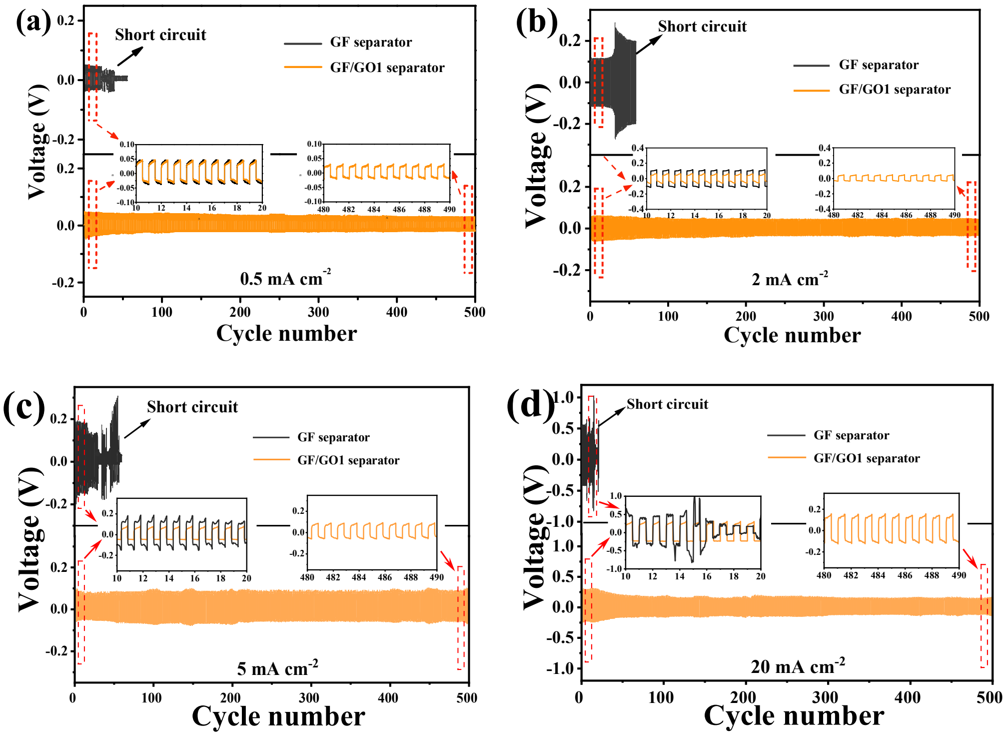

Figure 8. Voltage curves of galvanostatic Zn plating/stripping in Zn symmetrical batteries using different separators at (a) 0.5 mA·cm^{-2}; (b) 2 mA·cm^{-2}; (c) 5 mA·cm^{-2} and (d) 20 mA·cm^{-2}. Reproduced with permission from [7] Copyright 2020 The Royal Society of Chemistry.

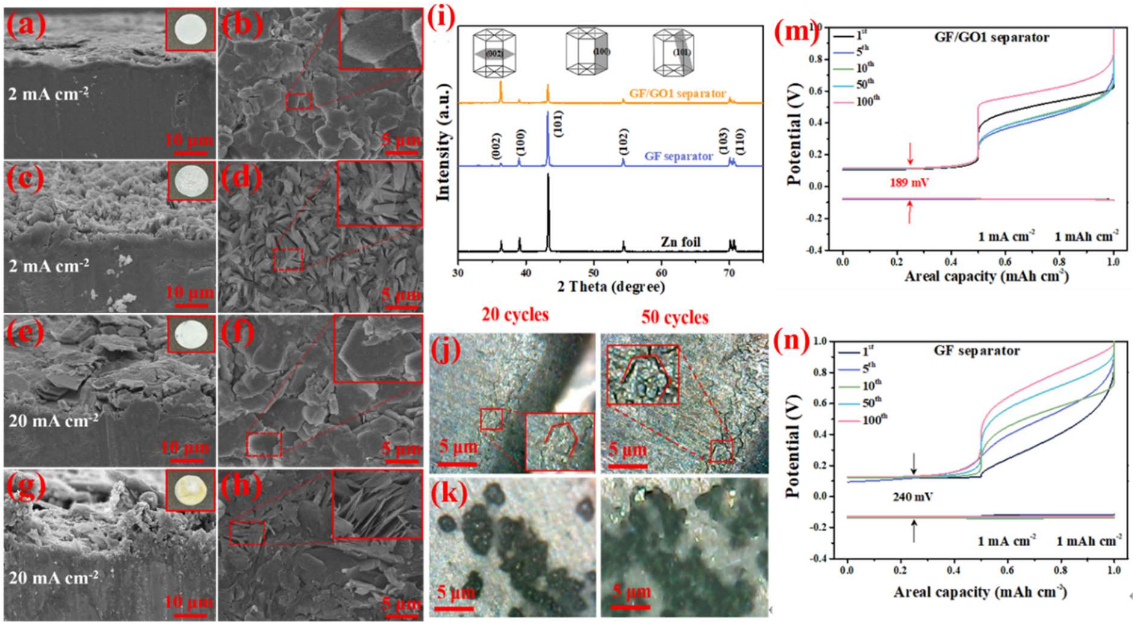

Figure 9. SEM images of the surface of Zn anode after cycling at a current density of 2 mA·cm^{-2} with (a-b) GF/GO1 separator and (c-d) GF separator; SEM images of the surface of Zn anode after cycling at a current density of 20 mA·cm^{-2} with (e-f) GF/GO1 separator and (g-h) GF separator; (i) *Ex situ* XRD pattern of Zn foil and Zn anode after cycling; The *in situ* observation images of Zn anode in the batteries with (i) GF/GO1 separator and (k) GF separator; GCD profiles of zinc-titanium half-batteries with (m) GF/GO1 separator and (n) GF separator at 1 mA·cm^{-2} with the total capacity of 1 mAh·cm^{-2}. Reproduced with permission from [7] Copyright 2020 The Royal Society of Chemistry.

3. Conclusion and Outlook

In summary, zinc anodes have attracted widespread attention in recent years and are ideal anode candidates for large-scale energy storage system. For a dendrites-free anode, the first suppression strategy is modification of the electrode, which enables the high conductivity and wettability, and these properties can produce a better electric field distribution and excellent contact between the electrolyte and electrode. The second method is electrolyte additive, which has been proved to reduce reduction potential and ensure the homogeneous distribution of zinc. The last strategy is modifying the separator, which controls the ion diffusion and charge transfer, GO is an excellent modified material since it can induce zinc ions to prefer non-protruding crystal planes during nucleation.

In the future, for further inhabiting the formation of the zinc dendrites to improve the cycling performance of the zinc ion battery, the researchers still need to pay more attention on the optimization of the electrode, electrolyte, and separator. However, the optimization in only one aspect is cannot eliminate the dendrites, like electrode, electrolyte, and most of the electrolyte additives are toxic, expensive, or difficult to synthesize. Accordingly, the combination of both surface modified electrode and easily available electrolyte additives can be an effective strategy to mitigate the impacts of the dendrites. Moreover, few researches on the modification of the separator, in the future, the research on the modification of the separator of the zinc ion battery will become popular.

4. Acknowledgements

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