

Progress of Interfacial Modified Layer in Zinc Anode Protection

Xu Zheng*

School of Materials and Chemistry, the University of Shanghai for Science and Technology, 516 Jungong Road, Shanghai 200093, China

*Corresponding author Email: zhxureal@gmail.com

Abstract

With the expansion of the use of electronic equipment and the increasing consumption of non-renewable fossil energy, zinc-ion energy storage devices represented by zinc-ion batteries and zinc-ion hybrid supercapacitors have become the most promising energy storage systems because of their high safety and low-cost advantages. However, the uncontrolled dendrite growth, hydrogen evolution and a series of side reactions such as corrosion and passivation occur in the process of charging and discharging zinc anodes, which hinder their practical application. This review summarizes the problems encountered by zinc anodes, and the strategy of zinc anode protection is discussed from the direction of interface modification layer. Finally, the challenges faced by zinc anode are prospected, and the future development direction of zinc anode protection is discussed.

Keywords

Zinc-ion Batteries; Zinc-ion Hybrid Supercapacitors; Zn Anode; Interface Protective Layer.

1. Introduction

With the increased use of numerous portable electronic devices and electric vehicles, the energy storage systems (ESSs) with excellent electrochemical properties such as long cycle life and high capacity play a vital role in modern society [1]. Electrochemical energy storage as one of the most efficient energy storage methods has received great attention. Lithium-ion batteries have high energy density and good stability, but their high cost and safety risks limit their large-scale development. Zinc has a higher electrode potential (-0.76 V vs. standard hydrogen electrode, SHE) and a higher volumetric specific capacity (5855 mA h cm⁻³), which means that zinc can be used directly as an anode [2]. Therefore, zinc-ion energy storage systems, mainly represented by zinc-ion batteries [3-5] and zinc-ion hybrid supercapacitors [6, 7], have been widely concerned because of their safety and economy.

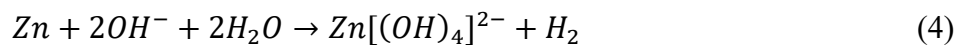
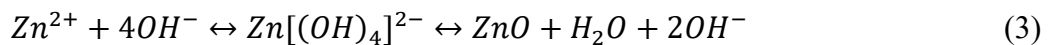
Zinc foil has the advantages of rich REDOX reaction, low flammability, flexibility and low cost, is a suitable zinc anode material commonly used in zinc-ion batteries and zinc-ion hybrid supercapacitors. However, similar to the lithium dendrites in lithium-ion batteries, uncontrollable zinc dendrites can also grow on the exposed zinc foil surface, greatly reducing the cycle life, which may pose a potential safety hazard to electronic devices [8]. In addition to dendrites, the unavoidable side reactions such as corrosion and hydrogen evolution caused by the contact between anode and water molecules in the electrolyte during charge and discharge greatly affect the Coulomb efficiency and hinder its practical application. Zinc anodes undergo Zn/Zn²⁺ deposition/stripping reaction during charge and discharge, and the reaction equation can be expressed as equation (1):



During the charging process, because the electrode surface can not be absolutely smooth, when there are some prominent places on the surface, there will be uneven distribution of electric field intensity E , resulting in uneven zinc deposits and the appearance of dendrites on the surface. Since the hydrogen evolution potentials in $\text{PH}=4$ and $\text{PH}=10$ environments are -0.236 V and -0.59 V, respectively, and the reduction potentials of Zn^{2+}/Zn are -0.76 V (vs SHE), hydrogen evolution reactions must occur during the charging process of the zinc anode. Hydrogen evolution reaction changes the electrolyte environment by consuming solvent water in the electrolyte, and also increases the internal pressure for a closed energy storage system. The reaction equation can be expressed as eq (2):



The increase of OH^{-} concentration in the electrolyte caused by hydrogen evolution reaction will combine with Zn^{2+} in the electrolyte to form zinc oxide, passivating the electrode surface, and OH^{-} will also react directly with the Zn anode, corroding the zinc anode to produce hydrogen. The reaction equation can be expressed as eq (3, 4):



The upward growth of dendrites increases the reaction area of zinc anode, which accelerates the occurrence of hydrogen evolution reaction, and the passivation and corrosion of zinc anode caused by hydrogen evolution reaction will reduce the active site on the zinc surface and make the zinc surface more uneven, thus intensifying the formation of dendrites. These problems about zinc anodes are promoted by mutual circulation, so when one or several of these problems are suppressed, the overall protection of zinc anodes can be improved.

To protect and improve zinc anodes, a number of dendrite suppression methods have been designed, including interfacial modified[9, 10], Electrolyte Optimization [11-13], and structural design [14-16]. Because the formation of zinc dendrites is related to the uneven electric field intensity caused by the uneven surface of zinc, constructing a modified layer on the surface of zinc is a simple and practical strategy. The interfacial modification layer can not only uniform the electric field between the zinc anode and the electrolyte, but also prevent the H_2O molecule from contacting the zinc anode and protect the zinc anode from many aspects. In this paper, the research progress of novel zinc anode interfacial protective modification layer in recent years is reported from three directions.

2. Inorganic Oxide

Inorganic materials are abundant in nature, and many of these inorganic oxides are widely favored for their unique nanostructures and charge properties. Inorganic materials are abundant in nature, and many of these inorganic oxides are widely favored for their unique nanostructures and charge properties. The inorganic oxides of nanostructures are in various forms, including nanoparticles, nanowires, nanotubes, nanofilms, etc. The size effects and interface effects of these nanostructures can modify and regulate the zinc anode interface well. It is particularly important to find inorganic oxides with high specific surface area and porous nanostructure as modification layers. Peng et al. mitigated zinc dendrite growth and side reactions on zinc anodes by growing ultra-fine and interleaved ZnO nanowires arrays on zinc foils using a horizontal potentiostatic anodizing technique

[17]. The electroactive surface area and conductivity of zinc metal anode were significantly increased by the structure of intertwined ZnO nanowires array, and the local current density was reduced, which promoted the uniform distribution and electroplating of Zn ions on the anode surface. The nucleation overpotential of Zn deposited on ZnO@Zn electrodes (49 mV) is much lower than that of bare Zn (98 mV), indicating a significantly boosted Zn nucleation process, which is due to the significantly increased active nucleation sites on ZnO@Zn. Correspondingly, ZnO@Zn//ZnO@Zn can be tested for long-term cyclic symmetry at a high current density of 1 mA cm^{-2} for about 450 h, while the bare Zn electrode shows unfavorable voltage drop and poor stability after only 80 h, which is caused by short circuit caused by the growth of Zn dendrites. This work uses ZnO nanowires arrays to even the surface electric field of zinc anodes, which plays an important role in protecting zinc anodes and improving their electrochemical performance.

Yu et al. designed a SiO₂ coating on the surface of the zinc foil [18]. Nano silica has high dielectric constant and low conductivity. Zinc foil has good electrical conductivity and low dielectric constant. Under the action of applied electric field, the surface of nano-silica is prone to Maxwell polarization. As a result, a large amount of negative charge appears on the surface of the coating, providing more controllable nucleation sites for Zn²⁺. Zn@SiO₂//Zn@SiO₂ symmetric cells exhibit stable cycles of more than 500 cycles at 1 mA cm^{-2} , while bare zinc symmetric cells exhibit high overpotential and short cycle life. The specific capacity of assembled zinc-ion hybrid supercapacitors at different current densities is higher than that of bare zinc batteries. When the current density is 0.2 A g^{-1} , the specific capacity reaches 263.1 mAh g^{-1} .

3. Metal Organic Frameworks

Metal-organic frameworks (MOF) as unique organic materials have been widely used in energy and catalysis because of their abundant pores, regular pore size and large specific surface area, moreover, the size and morphology of MOF nanocrystals are controllable [9]. MOF materials have excellent electrochemical activity, can store and release ions quickly in the pores, and its structure and pores can be purposefully changed by different synthesis methods. Changing the chemical structure of organic ligands can also regulate electrochemical activity and stability, which gives researchers a broad platform for designing different ideas. In interfacial modification, they are used as functional materials to regulate the diffusion, nucleation and deposition of Zn²⁺ to achieve highly reversible dendrite-free zinc plating/stripping.

Xiang prepared dense and uniform MOFs films (ZIF-8) with a precise thickness of 150 ~ 600 nm on zinc foil by pre-oxide gas deposition (POGD) method [19]. Under the protection of the optimal thickness (600 nm) of MOF layer, zinc corrosion, hydrogen evolution and dendrite growth on the surface of zinc are inhibited. The symmetric cell based on Zn@ZIF-8 anode exhibits exceptional cyclicality for over 1100 h with low voltage hysteresis of $\approx 38 \text{ mV}$ at 1 mA cm^{-2} . Even at current densities of 50 mA cm^{-2} with an area capacity of 50 mAh cm^{-2} (85% Zn utilization), the electrode can keep cycling for >100 h. Zhao et al. construct a missing-linker bifunctional MIL-125(Ti)-Zn as the interface modification layer of zinc metal anode [20]. The symmetric cell based on MIL-125(Ti)-Zn@Zn anode exhibits favorable cyclicality for over 2100 h with voltage hysteresis of $\sim 80 \text{ mV}$ at 1 mA cm^{-2} , showing the nearly incremental quantity of eleven and fortyfold in cycle life compared with MIL-125(Ti)@Zn anode and bare Zn anode, respectively. This MIL-125(Ti)-Zn@Zn anode also releases a high CE of 99.01 % at 1 mA cm^{-2} . They analysis that the excellent performance of the MIL-125(Ti)-Zn is due to the missing-linker in the MOF skeleton, which constructs electron-rich oxygen sites, substantially lowering the diffusion barrier of Zn²⁺, so as to accelerate Zn²⁺ diffusion kinetics and effectively uniform the flux distribution of Zn²⁺. Moreover, electron-rich oxygen sites enhance the adsorption of H* and acquire a less thermoneutral ΔG_{H^*} , reducing the harm of HER side reaction, thus improving the cycling life of Zn anode.

4. Carbon-based Materials

Compared with inorganic oxides and MOF materials, the excellent electronic conductivity of carbon-based materials can provide a strong and uniform interfacial electric field, effectively avoiding the accumulation of charge. Moreover, the relatively low density has little effect on the energy density, has been widely used in interface protective layer materials to solve the dendrite problem.

Due to its high electrical conductivity and abundant active sites, graphene can adjust the deposition location of Zn^{2+} , thus achieving uniform zinc deposition. Zhang et al. obtained a long cycle life graphene@Zn anode by coating a zinc sheet with graphene [21]. The cyclic life of graphene@Zn anode in ZHS at 1 A g^{-1} reaches at least 10,000 cycles, 200-fold higher than that of Zn foil anode.

In addition to conventional carbon materials, the introduction of functional groups with adsorption (such as nitrogen, sulfur, hydroxyl, etc.) on the surface of carbon materials can enhance their long-term stability. Zhou group reported a novel one-step synthesized process of nitrogen-doped graphene@zinc anodes by Langmuir–Blodgett method [22]. By using the amphiphilic nature of NGO materials, the ultrathin and parallel NGO film was spontaneously transferred to the Zn foil by slowly lifting the vertically placed Zn foil. It was found that the parallel coating with N functional groups guided the directional deposition of Zn on the (002) crystal plane, while the ultra-thin (120 nm) coating at the interface improved the diffusion kinetics of Zn^{2+} and inhibited HER and the side reactions of $Zn_4(OH)_6SO_4$ in the mild acidic electrolyte. NGO@Zn//NGO@Zn Symmetric battery achieves 1200 h stable cycle at a current density of 1 mA cm^{-2} with only 48 mV overpotential. This simple method provides a new direction for the synthesis of ultra-thin interface modification and is expected to promote the large-scale application of zinc-based water-based batteries.

5. Conclusion

In summary, inorganic oxides, metal organic frameworks and carbon materials as interfacial modification layers can all uniform the electric field strength on the surface of zinc anode at different angles, regulate and constrain the deposition of zinc ions, and play a key role in inhibiting the formation of dendrites. However, it has to be admitted that the interface modification layer on the surface of the zinc anode will increase the interface impedance, Therefore, in future development, the in-situ bonding of the zinc anode and the modified layer should be strengthened, and a balance between surface modification and impedance reduction should be sought by improving the conductivity and thickness of the modified layer.

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