Research progress on the cathode and anode of aqueous zinc ion battery

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Abstract. Electrochemical energy storage problems become a worldwide research direction. Now Lithium-ion batteries (LIBs) are the most common battery product. However, LIBs still has many shortcomings such as, safety problems, a scarcity of lithium, and high price. Rechargeable aqueous-based zinc ion batteries (AZIBs) with lower costs, fewer safety risks as well as abundant zinc reserves have attracted extensive research interest. For the current electrode materials of AZIBs, for example, Mn-based materials, V-based materials and metallic zinc, scientists have done in-depth research to develop the performance of the materials, but complex processes are still inevitable. As a result, sustainable and scalable manufacturing technology and electrode materials with high capacity and the longer service life is the research direction.

1. Introduction
In nowadays society, energy problems have become a problem that hinders human development, which has led to the development of batteries. Currently, LIBs dominate the market due to its excellent performance. However, its high production cost and flammability have also affected its development. [1-4]. Now, scientists are interested in rechargeable aqueous batteries because they are less expensive, have fewer security risks, and have higher ion diffusion rates. Rechargeable aqueous batteries are also far more suitable for large-scale energy systems than traditional batteries.[2]. On the other hand, because of plentiful supply, minimal toxicity, and high stability of metallic zinc, rechargeable aqueous zinc ion batteries (AZIBs) have emerged as one of the promising battery technologies.

For AZIBs, zinc ions can be swiftly deposited and dissolved on the Zn anode and could also be inserted or extracted in the manganese dioxide tunnel. In addition to the typical AZIBs, many different materials were utilized in the electrode material, therefore this article will summarize and examine numerous anode and cathode materials suitable for AZIBs.

2. The cathode of AZIBs

2.1 Mn-based cathodes

2.1.1 $\alpha$-MnO$_2$
α-MnO₂ has been studied the most among cathode materials. As illustrated in Figure 1a, its crystal structure is a one-dimensional 2×2 tunnel (4.6×4.6Å). α-MnO₂ will experience structural changes throughout the reaction, converting into spinel-like trivalent manganese phase, layered bivalent manganese phase, and tunnel-type bivalent manganese phase. Finally, 3 distinct phases coexist. These phase changes of MnO₂ during cycling may cause large volume changes, leading to the breakdown of the electrode structure and capacity degradation. In a zinc ion battery system with α-MnO₂ as the cathode, the cycle discharge capacity can reach 205 mAh/g. Pan et al. also prepared α-MnO₂ nanofibers by hydrothermal method and used it as the cathode material of AZIBs. At the same time, the sample also showed high capacity and high reversibility, and the capacity retention rate was 92%.

2.1.2 β-MnO₂
β-MnO₂ has a [1×1] tunnel (2.3×2.3Å) structure and has outstanding zinc storing capability, as illustrated in Figure 1b.

2.1.3 δ-MnO₂
Because the 2D layer birnessite δ-MnO₂ has a high interlayer distance (7.0Å) in the application of AZIBs, it has a lot of room to improve its electrochemical performance. But Alfaruqi et al. revealed that the capacity of layered δ-MnO₂ was found to be considerably reduced. At 0.1 A g⁻¹, the layered manganese dioxide electrode's reversible discharge capacity fell fast from 233 mAh g⁻¹ to 99 mAh g⁻¹ after 50 cycles. Kim et al. synthesized flaky δ-MnO₂ through thermal decomposition and used it as the cathode of systems. The system showed a discharge capacity of 250 mAh g⁻¹. However, capacity attenuation is inevitable, and further research is needed.

2.2 V-based cathodes
2.2.1 V₂O₅
V₂O₅ typically has a 2D layered crystal structure, with the formula V₂O₅·nH₂O. These crystal fluids are usually found in the V₂O₅ interlayer, resulting in a wider interlayer gap that is favorable for zinc ion insertion. However, problems such as volume change caused by the insertion of Zn²⁺ ions still

Figure 1. (a) Crystal structures of α-MnO₂ [3]; (b) Crystal structures of the β-MnO₂ [2]
haunt the development of this $V_2O_5$. Zhang et al. [12] showed a Zn/$V_2O_5$ battery system in a Zn(CF$_3$SO$_3$)$_2$ electrolyte. The high concentration of Zn(CF$_3$SO$_3$)$_2$ electrolyte can effectively inhibit side reactions and improve cycle stability.

2.2.2 $VO_2$ (b)
The edges of $[VO_6]$ octahedrons are shared to produce VO$_2$ (b). It is the most researched of the VO$_2$ phases due to its unusual structure. This massive lattice tunnel structure allows metal ions to be inserted and de-intercalated quickly [13]. Researchers have created plenty of high quality batteries that employ VO$_2$ as the cathode in recent years. Wei et al. [14] created a kind of cathode out of VO$_2$ nanoribbons. As demonstrated in Figure 2, the test results revealed that, at 0.1 A g$^{-1}$, the capacity could reach 274 mAh g$^{-1}$. Furthermore, the battery has exceptional cycle stability.

![Figure 2. Cycle performances at 0.5 and 10 A g$^{-1}$ [16]](image)

2.2.3 $H_2V_3O_8$
$H_2V_3O_8(V_3O_7\cdot H_2O)$ is a vanadium oxide with mixed valences. Due to the crystal water in the structure, $H_2V_3O_8$ has a wider interlayer spacing than oblique $V_2O_5$, and this structure results in a higher electrical conductivity, $H_2V_3O_8$ is more conductive than other vanadium oxides due to its mixed valence [15]. Cao et al., [16] developed the $V_3O_7\cdot H_2O$ nanogrid as the cathode material of AZIBs using in-situ electrochemical oxidation reaction. At 0.1 A g$^{-1}$, it can reach a high reversible specific capacity of 481.3 mAh g$^{-1}$.

3. The anode of AZIBs
Due to the excellent electrical properties of metallic Zn, there is an outstanding research prospect for it. At present, it has been extensively researched as an AZIB anode material.s.

3.1. Metallic zinc's benefits
(a) Metal zinc is environmentally friendly and will not pollute the environment when used in battery manufacturing and practical applications.
(b) Zinc is a resource-rich metal with a cheap cost. Metal zinc is an excellent conductor of electricity. It also easy to deal with and helps to minimize production costs.
(c) Metallic zinc has higher stability and corrosion resistance in water than metals like aluminium, salt, and magnesium, which helps to increase the battery's safety and stability. Metallic zinc also has a great theoretical specific capacity, a large volume capacity, and a high energy density, all of which might help batteries operate better electrochemically [1].

3.2 Metallic zinc's drawbacks.
(a) Zn$^{2+}$ dissolves and deposits on the surface of metallic Zn during the reaction process of AZIBs, forming dendritic deposits. Deposits will continue to build and produce zinc dendrites as the reaction proceeds.
progresses. Battery short circuits and electrode deformation are frequently caused by these zinc dendrites.

(b) The Zn electrode would progressively corrode and be consumed during the continuous charging and discharging operation, lowering the zinc usage rate and battery capacity.

(c) Passivation will be applied to the zinc electrode. The natural dissolution of Zn could be affected and the reaction surface area of the Zn is diminished, resulting in polarization and a reduction in the battery's cycle performance.

4. Investigation and development of electrodes

4.1 Mn-based materials

4.1.1 Hybridization with carbon materials
Mn-based cathodes, such as manganese dioxide, are suitable cathode materials for AZIBs, however throughout the charge and discharge process, the phase transition process of MnO$_2$ resulting in a significant reduction in capacity. Furthermore, MnO$_2$ development is hampered by low electrical conductivity. Hybridization using carbon materials is a viable solution to the issue. Electrochemical performance can be improved by combining electrode materials with graphite. Scientists [17] utilized mechanical ball milling of MnO$_2$ and graphite nanosheets to generate a particular structure of MnO$_2$/graphite (MG) hybrids by fixing tiny and highly scattered manganese dioxide particles with a special structure on graphite nanosheets. MnO$_2$ particles and graphite will form a 3D conductive network with great reaction kinetics. MnO$_2$/graphite hybrid had a capacity of 230 mAh g$^{-1}$ at 0.1 A g$^{-1}$, whereas manganese dioxide only reached 113 mAh g$^{-1}$, according to the testing findings. In terms of cycle performance, the sample has an 80.8 percent retention rate after one thousand cycles at 1 A g$^{-1}$, that is substantially superior than manganese dioxide's 51.2 percent.

Carbon materials may be used in a number of ways on Mn-based products, except graphite. Scholars [18] made hollow-structure spherical composites through growing manganese dioxide particles on the surface of N-doped hollow porous carbon nanospheres (NHCSs). The nitrogen-doped HCSs with an integrated conductive frame may substantially minimize electron and ion transfer resistance, resulting in high rate capability. In 650 cycles of 0.5 A g$^{-1}$, the sample can reach a capacity of 98.3 percent, demonstrating the material's high cycle stability (Figure 3a and b).

![Figure 3](image_url)

Figure 3. (a) Electrical properties of Zn//NHCSs@MnO$_2$ system (b)cyclic performance of Zn//NHCSs@MnO$_2$ battery [18] (c) Rate performance of electrodes [19]

4.1.2 Defect engineering
Another successful approach is defect engineering. Defect engineering is used to induce oxygen vacancies into MnO$_2$ to enhance the cathode's electronic structure, which improves conductivity and electrochemical performance. Zhang et al. [19] created a novel N-doped MnO$_2$-x (N-MnO$_2$-x) branch array with a significant number of oxygen vacancies using a low-temperature (200°C) NH$_3$ processing technique. The quicker reaction kinetics, higher capacity, and better cycle performance of N-MnO$_2$-x
were also demonstrated in subsequent tests. The battery capacity could achieve 285 mAh g\(^{-1}\) with 0.2 A g\(^{-1}\). At the same time, at 1 A g\(^{-1}\), the battery retention rate reached more than 85 percent after 1000 cycles, which was greater than control groups (Figure 3c).

4.2 Vanadium-based materials

4.2.1 Insert metal ions
Researchers generally introduce a range of metal ions into vanadium oxide to extend the layer spacing for developing the electrical performance of V-based materials. This technique improves the structural stability of materials by promoting the movement of reversible Zn\(^{2+}\).

Li et al. [20] utilized the pyrolysis technique to create porous ZnV\(_2\)O\(_4\) particles covered with nitrogen-doped carbon and used it as the cathode material for testing. The battery's specific discharge capacity was 301 mA h g\(^{-1}\) and 207 mA h g\(^{-1}\) for 3 hundred mA g\(^{-1}\) and 5 hundred mA g\(^{-1}\). The battery's initial discharge specific capacity was 95 mA h g\(^{-1}\) with 2 A g\(^{-1}\), and the maximum capacity could achieve 147 mA h g\(^{-1}\) (Figure 4).

4.2.2 Structure optimization
Unlike previous techniques, Researchers [21] created an amorphous V\(_2\)O\(_5\) and carbon material (a-V\(_2\)O\(_5@C\)) metal-organic-frame-derived composite material using an in-situ electrochemical induction method. Because of its amorphous form, V\(_2\)O\(_5\) has more isotropic Zn\(^{2+}\) diffusion routes and active sites, leading to a higher ion migration rate and specific capacity. At 0.3 A g\(^{-1}\), the battery's reversible capacity can reach 620.2 mAh g\(^{-1}\). Furthermore, the capacity retention rate could get more than 90 percent after 2 thousand cycles with 40.0 A g\(^{-1}\) (Figure 5).
4.2.3 Defect engineering
Vanadium-based materials can also benefit from defect engineering. When cycling is highly steady, the VO$_2$ cathode has a high specific capacity, but when Zn$^{2+}$ ions are transferred, the specific capacity gradually decreases. For solving this issue, Zhang et al. [22] used defect engineering to induce vacancies in the cathode material, allowing for additional electrochemical energy storage sites. They produced VO$_{2-x}$ rich in oxygen vacancies using a simple solution process involving NaBH$_4$ solution reduction. The test findings revealed that the VO$_{2-x}$ cathode’s CV curves considerably overlapped. It demonstrates that the sample is reversible when charging and discharging. There is an increase in electrochemical performance at 0.1 A g$^{-1}$. The VO$_{2-x}$/Zn system, on the other hand, has a greater specific capacity and cycle stability (Figure 6). This suggests that the oxygen vacancy of VO$_{2-x}$ can offer a higher specific empty capacity, demonstrating that defect engineering is a useful method.

Figure 6. Cycling performance of VO$_{2-x}$/Zn battery [22].

4.3 Zinc electrodes
4.3.1 optimizing the electrode structure
Optimizing the electrode structure in AZIBs is an effective method for improving the characteristics of metal zinc. The specific surface area of a modified Zn anode might grow, resulting in more Zn deposition sites. On the other hand, it may stop zinc dendrites from growing and improve reaction kinetics. The 3D Zn anode was created on a porous copper framework by scientists. Scientists utilized
a mix of chemical etching and electrodeposition to achieve their results. Zinc may be deposited/dissolved uniformly during battery cycling due to the porous copper framework's fantastic electrical conductivity and frame structure. According to the findings of the tests, the 3D Zn anode could decrease polarization, enhance stability and coulomb efficiency. After 300 cycles at 0.4 A g⁻¹, the 3DZn/MnO₂ system still contains 173 mAh g⁻¹, significantly more than the 50 mAh g⁻¹ specific capacity of Zn/MnO₂ [23].

4.3.2 Functional protection layer
Producing a protective layer on Zn flakes via electrodeposition methods or directly coating is the most common method for forming a functional protection layer. The protective layer might improve the kinetics and the manner Zn is deposited. It may also promote homogeneous zinc deposition/dissolution and prevent zinc dendrite development. To make the Zn@TiO₂ anode, scientists employed the atomic layer deposition (ALD) technique for building an amorphous TiO₂ protective layer on the zinc sheet. The capacity of α-MnO₂/Zn@TiO₂ battery may achieve more than 230 mAh g⁻¹ after 60 cycles at 0.1 A g⁻¹. The specific capacity of the α-MnO₂/Zn battery, on the other hand, drops dramatically to 155 mAh g⁻¹ [24].

Cao et al. [25] utilized a high-efficiency electrodeposition technique for creating Zn phosphorus solid solution alloy (ZnP) coated on Zn foil (Zn@ZnP). The zinc-phosphorus alloy employed has electrical characteristics that benefit the battery's current density, and the P atoms in the coating will aid in Zn²⁺ transfer. Furthermore, the electrochemical deposition method is simple to use, has a cheap cost, produces little pollution, and may be used on a wide scale. The produced Zn@ZnP anode exhibits outstanding cycle performance during the test (Figure 8).

Figure 7. The rate performance of Zn@ZnP and bare Zn anode [25]

5. Conclusions
AZIBs is a promising technology for its enormous capacity, security, low-cost manufacture, and environmentally friendly. Mn-based materials, V-based materials, and PBAs are now the most widely utilized materials for AZIB cathodes. In addition, the anode is made of metallic zinc. These materials, however, offer their own benefits, such as great capacity and low cost. Its progress, however, has been hampered by flaws such as reduced capacity and poor reaction kinetics. Scientists have offered a number of solutions to difficulties, such as flaw engineering, but the process's complexity and high cost remain obstacles to AZIBs industrialisation. As a result, future research will focus on sustainable and scalable production technologies, as well as electrode materials with higher capacity and extended service life.

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