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Progress in Modification of Aqueous Zinc-Ion Batteries

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Abstract. Aqueous zinc-ion batteries get a lot of attention for grid-scale storage because they're safe, relatively cheap, and easier on the environment than many alternatives. The problem is they still stumble in the two places that matter most for real-world use: they don't last long enough over repeated cycling, and they struggle when you try to charge or discharge them fast. This review pulls together the latest progress on approaches that try to fix both issues at once—longer cycle life and better rate performance—in aqueous zinc-ion batteries (AZIBs). On cycling stability, it focuses on how protective layers and interface tuning at both the cathode and anode can suppress side reactions and slow degradation, and it explains the mechanisms behind the improvements. On rate capability, it covers tactics like defect engineering, morphology control, ion doping, adjusting interlayer spacing, adding conductive coatings, and other interface treatments, with an emphasis on how these changes speed up ion movement and improve electronic conductivity.

Keywords: Zinc-ion Batteries, Cycle Life, Rate, Ion doping, Interface

1. Introduction

Aqueous zinc-ion batteries got their real starting point in 1986, when Yamamoto and Shoji [1] built a rechargeable Zn|ZnSO4|MnO2 cell using a mildly acidic ZnSO4 electrolyte. Since then, most work in the area has chased two goals: faster charge/discharge (rate capability) and longer life (cycle stability). That chase has produced a steady stream of material and interface tweaks.

One often-cited example is Kundu et al. (2016), who used a hydrothermal route to make vanadium oxide with zinc ions and water molecules already sitting between the layers. That layer structure leaves open pathways for ions to move, which is why it can deliver about 300 mAh g^{-1} and keep running for roughly 1000 cycles. A lot of papers, though, still treat rate and lifetime like separate problems: push one hard, and the other tends to get less attention [2]. We have plenty of individual results, but fewer reviews that lay out—side by side—how people can improve both at once, or what trade-offs keep showing up. That makes it harder to see the real link between rate behavior and cycling failure, and it slows down the design of cells that are genuinely good on both fronts.

This review looks at rate performance and cycling stability together. It pulls together the main modification strategies, explains the mechanisms people think are at work, and points out practical rules of thumb for tuning performance. The goal is to give readers a useful map of the field—what tends to help, what tends to backfire, and where "synergy" is actually real rather than just a nice word.Rate Performance Modulation Strategies

2. Rate performance modulation strategies

2.1. Defect engineering and morphology control

Oxygen-vacancy engineering is an effective way to boost ion transport in vanadium-based cathode materials. Yang et al. [3] improved the electrochemical performance of VO using KOH activation. After treatment, the surface roughness increased by 1.24 and the specific surface area by 1.35, which suggests the formation of a large number of oxygen vacancies.

Controlling how the material assembles, and in turn how the tunnels line up, is a practical way to speed up ion transport. To get around the slow kinetics that tunnel type vanadium oxides often suffer from, He et al. proposed a "tunnel oriented" strategy. Using a hydrothermal method, they made two kinds of VO(B) nanobelts with (00l) facets [4]. When they changed the mass ratio of VO to glucose from 1.0:0.4 to 1.0:1.0, the product shifted between two morphologies: a more dispersed form (VO-D) and a more aggregated one (VO-A).

VO-D spreads more evenly across the electrode surface, so its transport tunnels tend to line up along the c axis. VO-A, by contrast, stacks in a more random way, with tunnels pointing in mixed directions. Structural analysis confirmed that VO-D shows a stronger (00l) facet orientation, and it also delivered a higher Zn diffusion coefficient (on the order of 10^−10 cm^2 s^−1) than VO-A. In electrochemical testing, VO-D performed better overall.

Designing new polyanionic-type materials and constructing open tunnel frameworks are effective ways to improve high-rate performance. Zhao et al. via a one-step solvothermal method prepared a novel polyanionic sodium vanadium oxyfluorophosphate ($Na(VO)_2(PO_4)_{1.5}F_{0.5}\cdot 0.4H_2O$) cathode material. The material features an open tunnel-like framework structure [5], created through vertex-sharing connections among VO_5F octahedra and PO_4 tetrahedra, which results in ample channels facilitating ion transport. When the current density was increased to 2 A g^{-1}, the discharge capacity stayed stable at 41.5 mAh g^{-1}, which shows a very good rate tolerance.

Electrochemical kinetic analysis indicated that the material exhibits both surface capacitive and diffusion-controlled characteristics. The Zn^{2+} diffusion coefficient was 6.51×10^{-12}~9.65×10^{-10} cm^2 s^{-1}. The fast ion transport kinetics provided a solid guarantee for the high-rate performance.

2.2. Ion doping and interlayer spacing regulation

Ion doping to form interlayer pillars can regulate the interlayer distance. Sun et al. synthesized K^+-doped vanadium oxide (KVO) using a simple one-step hydrothermal method. This material possesses a unique microscopic morphology [6], consisting of nanospheres self-assembled from nanobelts (Figure 1). By acting as interlayer pillars, introduced K^+ ions not only widened the interlayer spacing of vanadium oxide but also enhanced its electrical conductivity, thereby optimizing Zn^{2+} diffusion kinetics. The material demonstrated outstanding rate performance in electrochemical tests, with discharge specific capacities of 372 mAh g^{-1}.

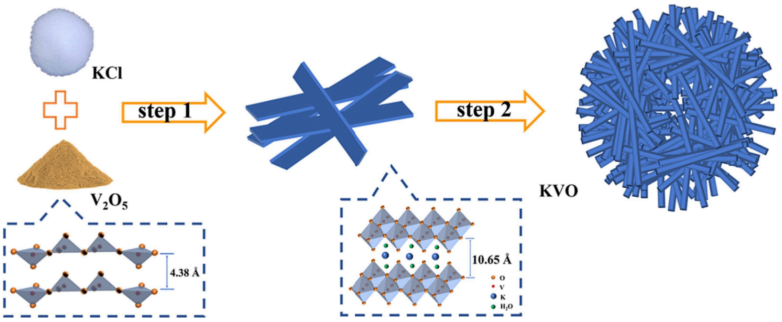

Figure 1. Preparation of the interlayer pillar material $K_{0.5}V_2O_5\cdot nH_2O$

Cheng et al. proposed a synergistic engineering strategy for interlayer structure and interface [7], combining sodium ion pre-intercalation and nitridation treatment to successfully prepare a high-performance nitrogen-doped $Na_2Mn_3O_7$ cathode material. XRD tests showed that after N-doping, the main phase remained NMO, and the layered structure was not destroyed, with only small amounts of $NaMnO_2$ and MnO phases appearing. Some Mn^{4+} was reduced to Mn^{3+} and Mn^{2+}. XPS tests detected an N 1s characteristic peak at 399.5 eV, and the Mn 2p peak shifted to lower binding energy, confirming successful N-doping and the formation of Mn-N bonds.

Pre-intercalated sodium ions did two useful things at once: they pushed the layers farther apart (so Zn can move through faster) and they also worked like little pillars that keep the structure from collapsing. On top of that, the nitridated surface layer improved electronic conductivity and helped prevent the cathode from dissolving.

To address the sluggish reaction kinetics and poor structural stability during cycling of the δ-MnO_2 cathode, Wang et al. proposed a molybdenum (Mo) pre-intercalation modification strategy. They prepared Mo-preintercalated δ-MnO_2 (Mo-MnO_2) cathode material via a one-step hydrothermal method [8]. During preparation, manganese sulfate, potassium permanganate, and ammonium heptamolybdate were mixed and dissolved, followed by hydrothermal reaction at 160°C for 16 hours. The product was obtained after centrifugation, washing, and vacuum drying at 60°C for 10 hours. Pure δ-MnO_2 without ammonium heptamolybdate served as the control sample.

Characterization backed up the modification pretty cleanly. XRD showed Mo was actually incorporated into the lattice, and the interlayer spacing widened from 0.631 nm to 0.676 nm. XPS and EPR also pointed the same way: Mo pre-intercalation created more oxygen vacancies in MnO, which pushed the average Mn valence down.

Mechanistically, Mo sits between the layers and acts like a brace. That lowers the resistance to ion insertion/extraction and helps the structure hold together during cycling. The larger spacing also gives Zn2+ (and H+) an easier path in and out. On top of that, the oxygen defects add extra storage sites. Put together, those changes speed up the reaction kinetics.

Electrochemically, Mo-MnO derivable 327 mAh g^{-1} at 20 mA g^{-1}, about 31.3% higher than pristine δ-MnO. After 100 cycles at 10 mA g^{-1}, it still held 159 mAh g^{-1}, corresponding to 76.8% retention. Ex situ tests suggested a stepwise, reversible Zn and H insertion/extraction process, with no obvious phase transformation, and a Coulombic efficiency of 98.8% at the 101st cycle.

The impedance data matched the performance: EIS showed a charge-transfer resistance of 10.2 Ω, much lower than 26.3 Ω for δ-MnO. GITT gave ion diffusion coefficients on the order of 10^{-10} to 10^{-12} cm^2 s^{-1}, which supports the idea that Mo pre-intercalation improves both structural stability and kinetics.

2.3. Conductive layer coating and interface engineering

Adding a conductive coating is a straightforward way to boost high-rate performance, mostly because it cuts down charge-transfer resistance. Xu et al. [9] took that idea and built a flexible composite electrode around it. They started with carbon cloth, which works as a bendable, conductive backbone. On top of that, they grew ultrathin, two-dimensional NHVO nanosheets directly on the cloth using an in situ hydrothermal process. NHVO has a naturally open, layer structure, so it already gives Zn ions decent "lanes" to move through. Then they coated the NH4V4O10 nanosheets with a dense polypyrene layer via chemical polymerization. The polypyrene ends up clumping into a popcorn-like porous texture. That matters for a few reasons: it helps electrons move more easily, it exposes more active sites, it lowers the barrier for Zn insertion and extraction, and it adds extra space for ion storage. In other words, it doesn't just make the electrode more conductive; it also makes the electrochemistry less cramped. The impedance data back this up. EIS shows the composite's charge-transfer resistance is about 12 Ω, much lower than the uncoated material, which helps explain why it can keep up under high current. GITT results suggest a Zn-ion diffusion coefficient on the order of 10^{-10} to 10^{-9} cm^2 s^{-1}, higher than bare NHVO, so ion transport is less likely to bottleneck when the rate goes up.

Performance-wise, the fully charged cell derivable 551.1 mAh g^{-1} at 0.1 A g^{-1}. During stepwise rate testing from 0.1 to 1 A g^{-1}, the capacity bounced around a bit, but it removable after returning to the lower current, which points to good rate reversibility. Overall, the polypyrene layer acts like a conductive scaffold and a kinetic booster, while also helping hold the structure together and slowing the loss (dissolution) of active material.

Interface engineering (for example, building core–shell structures and heterostructures) can improve electron transport. Xu et al. addressed two persistent problems in MnO-based cathodes—low conductivity and slow ion diffusion—by fabricating a TiN@MnO nanowire array on carbon cloth (TiN@MnO NWAs/CC). In this design, the carbon cloth acts as a flexible substrate [10].

They first prepared TiO nanowire array precursors by a hydrothermal method, then converted them into highly conductive TiN nanowire cores through nitridation. After that, MnO nanosheets were deposited uniformly onto the TiN surface by electrochemical deposition, creating a three-dimensional, self-supporting hierarchical core–shell structure.

Even after extended high-rate cycling, the electrode maintained a high capacity, suggesting that the core–shell architecture helps electrons move more easily while also shortening ion diffusion paths.

3. Cycling performance

Whether an aqueous zinc ion battery can cycle cleanly over and over comes down to what happens at the interfaces. The zinc anode is where the usual headaches show up: dendrites, hydrogen bubbling off, and plain old corrosion. On the cathode side, you run into a different set of problems, like the material swelling and shrinking during cycling and manganese slowly dissolving into the electrolyte. Put it all together and the battery's capacity fades faster than it should.

That's why people lean so hard on interface engineering. If you can tweak what the electrode surface is made of and how it's structured, you can help zinc ions move the way you want them to, while blocking the reactions that chew up the electrodes. In practice, the work usually falls into two buckets: fixing the zinc anode interface and fixing the cathode interface. Each targets its own failure modes, but the goal is the same—longer cycle life for AZIBs.

3.1. Zinc anode interface modification

3.1.1. Electrolyte additives for regulating the interfacial microenvironment

Adding functional additives to standard electrolytes is a straightforward way to change how Zn^{2+} is solvated and to build a protective adsorption layer on the zinc surface, so you cut down side reactions where they start. Zeng et al. [11] did this by adding sodium lactate (SL) to a conventional electrolyte. In their work, SL helps in three main ways: it changes the Zn^{2+} solvation environment, suppresses parasitic reactions, and guides how zinc deposits (Figure 2).

SL has plenty of oxygen-containing groups, so it coordinates strongly with Zn2+ and also interacts with nearby water molecules. This interaction partly replaces water in the usual [Zn(H2O)x] solvation shell. Once some of that water is pushed out, the solvation structure becomes looser and there are fewer "active" water molecules directly tied to Zn^{2+}. That matters because it reduces the likelihood that water participates in the hydrogen evolution reaction (HER).

SL also improves zinc anode stability in more direct electrochemical terms. The corrosion current drops, the HER onset shifts to more negative potentials, and the formation of by-products such as Zn4SO4(OH)6·5H2O is suppressed. In practice, that means less buildup of insulating or bulky side products that chew up active sites and physically disrupt the electrode over time.

On top of all that, SL molecules tend to adsorb on the zinc surface on their own, forming a fairly uniform electrostatic "shield." This evens out charge distribution, limits lateral Zn^{2+} diffusion along the surface, and weakens the tip effect that drives uneven growth. The result is denser, more uniform zinc plating, with less dendrite formation and a lower risk of dendrites piercing the separator during cycling.

Put together, the takeaway is simple: SL helps the zinc anode behave itself—less corrosion, less HER, fewer by-products, and smoother deposition—which translates into better long-term cycling for aqueous zinc-ion batteries (AZIBs).

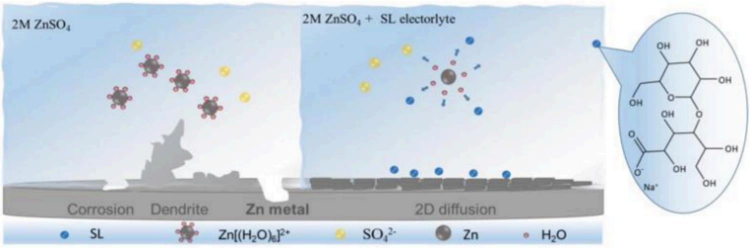

Figure 2. Mechanism of SL action

3.1.2. Constructing artificial interface protective layers

The construction of a robust and compact artificial protective layer with high ionic conductivity on the zinc surface is to physically isolate the electrode from electrolyte corrosion, homogenizing ion flux. Wu et al. [12] took a trivalent chromium conversion film (TCCF) and made it a protective layer on the zinc anode by a straightforward room-temperature immersion process. The TCCF has several critical functions underlying its modification mechanism. It provides strong zinc-affinity anchoring sites, because the binding energy of Zn atoms on TCCF surface is significantly higher than that on bare zinc. This promotes uniform desolvation and oriented deposition of $[Zn(H_2O)_6]^{2+}$, resulting in a compact, dendrite-free zinc layer. Moreover, TCCF acts as a physical barrier, effectively blocking direct electrolyte–electrode contact, which significantly reduces hydrogen evolution and corrosion, while also limiting the formation and accumulation of loose by-products. Moreover, TCCF coating has excellent adhesion to zinc substrate, so it stays intact during long charge–discharge cycling, preserving its interfacial regulation function. Electrochemical evaluations clearly show that this modification strategy is effective: under the demanding condition of $4Ag^{-1}$, after 120 cycles, the capacity retention reached 78.3%.

3.1.3. Anode microstructure design

Changing the physical morphology of the zinc anode is another effective method to optimize the deposition behavior. Sha's research team [13] successfully built a three-dimensional cracked zinc (Crack Zn) anode by creating a lot of micron- or submicron-scale cracks and protrusions on the zinc foil surface. The modification increases the electrode's specific surface area, so Zn plating shifts from isolated "point deposition" to more uniform "surface deposition." That spreads out the local current, weakens the "tip effect," and keeps zinc from growing straight up into dendrites.

Inside the microcracks, the voids work like a little expansion joint. They absorb volume changes during Zn plating/stripping, which makes the zinc layer less likely to crack. That, in turn, cuts down on "dead zinc" and slows the loss of active material.

Cracking also lowers the cell's charge transfer impedance. The activation energy for Zn desolation drops from 44.041 kJ mol in pristine Zn to 29.615 kJ mol. Faster desolation helps explain the better cycling stability and rate performance.

3.2. Cathode material modification

Keeping the cathode structurally stable as zinc ions move in and out is one of the main ways to extend a battery's overall lifespan.

3.2.1. Ion doping and crystal engineering

Hetero-ion doping can both modify the crystal structure and optimize the electronic structure. Wang [14] gave an efficient crystal engineering modification strategy, which involves preparing aluminum (Al)-doped MnO_2 (AlMO) cathode by a one-step hydrothermal method. Al^{3+} doping resulted in a synchronous crystal phase transformation and the formation of a doped superlattice structure (as shown in Figure 3). The undoped product was β-MnO_2 with a [1×1] tunnel structure, while the introduction of Al^{3+} caused it to transform into α-MnO_2 with a [2×2] tunnel structure. The ionic radius of Al^{3+} is 53.5 pm, which is very close to that of Mn^{4+} (53 pm), so it can be embedded into MnO_2 tunnels and form strong Al-O bonds with oxygen atoms, effectively stabilizing the tunnel structure. Al doping simultaneously caused a substantial expansion of the lattice spacing, resulting in a unique doped superlattice structure with interplanar spacing of 1.08 nm, which is significantly higher than the typical interplanar spacing of ordinary α-MnO_2 (0.69 nm).

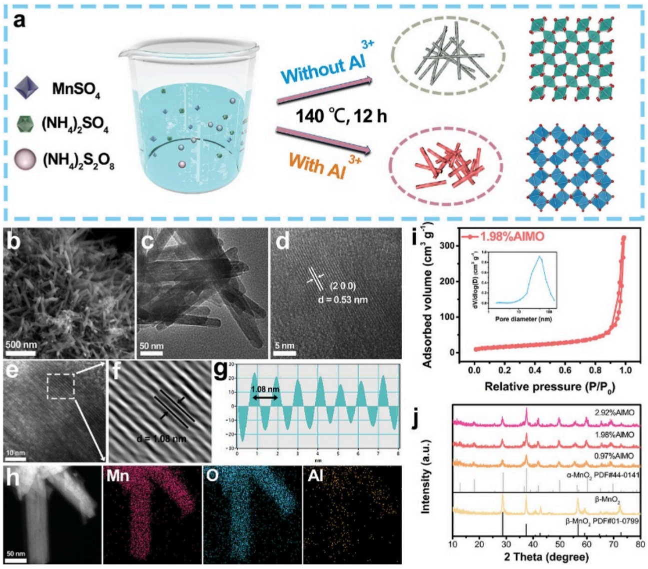

Figure 3. (a) A schematic representation of the as-prepared material. b) SEM image of 1.98%AlMO. (c) TEM image of 1.98%AlMO. (d,e) HRTEM images of 1.98%AlMO. (f) Inverse FFT lattice images of 1.98%AlMO. (g) Interplanar spacing profile of 1.98%AlMO. (h) EDS element mapping images of 1.98%AlMO. (i) Nitrogen adsorption-desorption isotherm (insert-image: pore distribution of the 1.98%AlMO) and (j) X-ray diffraction patterns of β-MnO_2, 0.97%AlMO, 1.98%AlMO, and 2.92%AlMO

3.2.2. Novel stable structure design and electrolyte synergy

Developing new materials with intrinsically stable tunnel or layered structures is a major direction. Ran et al. successfully made tunnel-structured sodium vanadate (NaV_6O_{15}) nanosheet cathodes by using a molten salt method. The material's unusual crystal structure, plus a two steps zinc storage process, clearly helped its cycling stability and capacity retention. Vanadium can switch between V^{4+} and V^{5+}, which opens up plenty of sites for Zn^{2+} to insert and come back out.

A big part of the stability comes from the sodium that's already sitting between the VO layers. Those pre intercalated Na+ ions work like little structural props: they keep the layers from collapsing inward when zinc goes in, so the framework stays intact.

In rate tests, the electrode derivable 63.16 mAh g^{-1} at 5 A g^{-1}. When the current density was lowered back to 0.1 A g^{-1}, the discharge capacity rebounded to 318.07 mAh g^{-1} (a 1.51% recovery relative to the earlier value). Ex situ XPS backed up the structural argument: the Na peaks did not shift in either the fully charged or fully discharged state, which suggests the sodium stays put and the structure remains stable.

Put together, the tunnel like framework and this sodium "pillar" effect explain why the cathode can cycle for so long. More than anything, it's a useful design cue for building sturdy cathode materials for aqueous zinc ion batteries.

4. Conclusion

Aqueous zinc-ion batteries have a performance optimization task, which requires the coordinated development of cathode, anode, and electrolyte systems. This review makes a simple point that's easy to miss: cycle life and rate performance don't live in separate boxes. They're tied together by two things that keep showing up no matter what chemistry you look at—how stable the electrode/electrolyte interface stays over time, and how fast ions can actually move.

A lot of recent work has stopped obsessing over "the perfect electrode material" in isolation and has shifted toward electrolyte engineering, with the idea that you design the electrolyte and the cathode/anode interfaces as a set. In that framing, the electrolyte isn't just a passive liquid you pour in. It does double duty: it's the battery's "lifeblood," but it's also a functional medium that can be tuned to steer reactions in the right direction.

On the practical side, you can push the electrolyte to do real work by adding functional additives (like SL) or moving to high concentration and dual-salt recipes. That kind of formulation can reshape the Zn solvation sheath, cut down the number of "active" water molecules coordinated to Zn, and stop parasitic reactions closer to the source. At the same time, it can nudge Zn to deposit more evenly by changing the kinetics, not just the thermodynamics.

But the electrolyte also sets the stage for what the interface becomes in the first place. Its composition and inherent properties feed directly into the chemistry and structure of the electrode–electrolyte interface. And those interfacial processes—SEI formation on the anode inside the cell, or ion exchange and surface reconstruction on the cathode—end up controlling transport impedance and whether the electrode structure holds up or slowly falls apart.

That's why "miracle" interface fixes don't reliably behave like miracle fixes. Even strong strategies—say, putting a TCCF artificial layer on the anode or using nitridation coatings on the cathode—only pay off when they match the electrolyte they're paired with. If the electrolyte fights the coating (or forms the "wrong" interphase on top of it),the benefits get watered down fast.

So, the real takeaway is blunt: the electrolyte is the hub. If you want the next jump in performance, you don't treat electrolyte choice as an afterthought—you treat it as the thing that links, enables, and sometimes limits every interfacial engineering trick you try.

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