Nanoscale Design of Zinc Anodes for High-Energy Aqueous Rechargeable Batteries

Tzu-Ho Wu§, Yamin Zhang§, Zachary D. Althouse, and Nian Liu*

School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332, USA
*Correspondence: nian.liu@chbe.gatech.edu
§These authors contributed equally to this work.
Abstract

Rechargeable zinc-based aqueous batteries have attracted increasing attention due to the merits of inherent safety, high capacity (820 Ah kg\(^{-1}\) and 5854 Ah L\(^{-1}\)), and cost effectiveness. However, the poor rechargeability of Zn anodes limits their development in next-generation batteries, which is attributed to the dendrite growth, shape change, passivation, and hydrogen evolution issues in the zinc anodes. Nanomaterial design of Zn anodes provides a pathway to tackle these long-standing challenges to develop electrically rechargeable Zn anodes. In this review, we summarize the most recent advances in various strategies for improving zinc electrochemical performance, including 3D high surface area electrode structure, core/shell structure with surface coatings and nanocomposites with highly conductive materials. Additionally, the concepts of molecular design of the aqueous electrolytes with confined water molecules and high salts concentration are introduced. Finally, future opportunities and challenges with zinc-based aqueous batteries are discussed.

*Keywords: aqueous batteries; Zn anodes; rechargeable; nanomaterial; molecular engineering*
1. Introduction

Environmental concerns of fossil fuels drive people to develop clean energy economy [1]. Rechargeable batteries are regarded as a green energy storage system and have great potential to alleviate the energy and environmental problems. Their benefits of convenience, low cost, and reliability are the ‘enablers’ for their use in mobile electronic devices, electric vehicles and grid energy storage [2–4]. A key aspect of any future battery technology development is safety. Although lithium-based batteries are ubiquitous, there are still challenges related to their energy density, cycle life, cost and safety [5–8]. In regard to safety, compared with organic electrolyte, aqueous rechargeable batteries may provide a safer alternative for reliable, low-cost and large-scale energy storage systems. As seen from the penetration test in Fig. 1a-1b, the battery with organic electrolyte catches fire, yet the battery with aqueous electrolyte is relatively safe [9]. Moreover, aqueous batteries have high ion conductivity and cost effectiveness [10–17]. Generally, the cell voltage and energy density of aqueous batteries are lower than those of organic-based batteries (e.g. Li-ion) because of the relatively smaller electrochemical stability window of water. Among all the metals that are stable in water, zinc is the most active and has the lowest possible operating potential [9]. This means using Zn anode can increase overall cell voltage of aqueous batteries. Moreover, zinc is globally available, inexpensive (3.19 USD kg\(^{-1}\) [18]), and has high capacity (820 Ah kg\(^{-1}\) and 5854 Ah L\(^{-1}\)). Zinc-based aqueous batteries also possess the stability to be operated in ambient air. Accordingly, Zn aqueous rechargeable batteries are promising to become a safer energy storage system [19–28]. In Fig. 1c, we compare the theoretical specific and volumetric capacities of Li and Zn rechargeable batteries. Among zinc-based aqueous batteries, Zn-air batteries have high theoretical volumetric energy density [29–33], which is around three times that of conventional Li-ion batteries (LIB).

Zinc-based aqueous batteries consist of zinc metal anodes, aqueous electrolyte, and cathodes [31,34–36]. Generally, the rechargeability of zinc-based aqueous batteries is greatly limited by the zinc anode. The poor rechargeability of Zn anode is ascribed to the dendrite growth, dissolution, passivation and hydrogen evolution problems, which significantly impede its development for use in next-generation batteries. In this review, we first overview the Zn anode reactions and the corresponding challenges for electrical rechargeable Zn electrodes in Section 2. Then, we review (Fig. 1d) the most recent advances in various strategies for nanoscale design of Zn anodes in aqueous electrolyte, including nanocomposites with highly conductive materials, 3D high surface area electrode structure, and structures with surface coatings. Finally, we summarize the new electrolyte technologies that can improve zinc anode efficiency, such as “water in salt”, which involves molecular engineering and design. To fulfill the goal of better energy storage of Zn-based batteries, the strategies of novel nanomaterials design and structural modifications are recommended to provide promising Zn electrodes (> 50% DOD\(_{Zn}\)) with good cycle stability (> 400 cycles with > 80% Columbic efficiency).
Fig. 1. Battery penetration test to investigate the safety property of organic electrolyte (a) and aqueous electrolyte (b). (c) Theoretical specific and volumetric energy density of Li and Zn batteries. LiC₆ and CoO₂ are used to calculate energy densities of LIB. (d) Schematic of nanoscale design of Zn anodes and electrolyte in zinc-based aqueous batteries.

2. Challenges of Rechargeable Zn Anodes

Zn-based batteries have been known to the scientific community, since the Voltaic pile was first discovered to generate continuous current in the nineteenth century. Commercial Zn primary batteries have been available since they emerged in the 1930s [37]. Currently, they are most notable for being the predominant energy source for hearing aids, navigation lights, and railway signals [38]. In regard to rechargeable Zn anodes, the zinc active material must be able to convert back to Zn metal upon recharging. However, despite past efforts dedicated to making rechargeable Zn anodes, creating stable Zn electrode with satisfactory cycle life in practical cells
remains a challenge [39,40]. In this review, we summarize Zn anode reactions and the long-standing limits that have impeded Zn rechargeability.

### 2.1. Zn anode reactions

For Zn-air batteries, Zn metal is oxidized to Zn\(^{2+}\) on the anode and delivers electrons to cathode through external circuit upon discharge (eqn (1)). Then, zincate ions (Zn(OH)\(_4^{2-}\)) are formed due to the abundant hydroxide ions in alkaline medium (eqn (2)). When the Zn(OH)\(_4^{2-}\) reaches its solubility limit, zinc oxide (ZnO) is precipitated on the electrode surface (eqn (3)). The overall reaction of Zn electrode can be summarized as eqn (4), for which the standard reduction potential is \(-1.26\) V vs standard hydrogen electrode (SHE) at pH of 14.

\[
\text{Electro-oxidation: } \text{Zn(s)} \rightarrow \text{Zn}^{2+}(aq) + 2e^- \\
\text{Complexation: } \text{Zn}^{2+}(aq) + 4\text{OH}^- \rightarrow \text{Zn(OH)}_4^{2-}(aq) \\
\text{Dehydration/Precipitation: } \text{Zn(OH)}_4^{2-}(aq) \rightarrow \text{ZnO(s)} + \text{H}_2\text{O(l)} + 2\text{OH}^-(aq) \\
\text{Overall reaction: } \text{Zn(s)} + 2\text{OH}^-(aq) \rightarrow \text{ZnO(s)} + \text{H}_2\text{O(l)} + 2e^- 
\]

On the other hand, the highly reversible plating/stripping of Zn metal can be obtained in mild electrolytes (pH \(\sim\)4), such as ZnSO\(_4\), Zn(CF\(_3\)SO\(_3\))\(_2\) and Zn(NO\(_3\))\(_2\) [41–48]. Post-mortem analysis of cycled Zn electrode reveals a dense and dendrite-free surface morphology after 280 h of repeated Zn plating/stripping cycles [15]. In mild electrolytes, the highly reversible Zn metal can serve as the anode, which can couple with other cathode materials, such as manganese oxides, vanadium oxides, iron oxides, to realize energy storage. Recent efforts have been made to achieve outstanding performance of Zn/MnO\(_2\) batteries (e.g. \(-130\) mAh g\(^{-1}\) at 5C for 5000 cycles [14]). Nonetheless, developing rechargeable Zn-air batteries in mild electrolyte faces great challenges due to the lack of efficient catalysts under mild conditions. Therefore, it is important to develop rechargeable Zn anodes in alkaline media.

### 2.2. Historical challenges of rechargeable Zn electrodes

Although the concept of mechanically rechargeable Zn batteries (replacing the exhausted Zn electrode with a fresh Zn anode) was proposed to bypass the issue of poor Zn reversibility, the high costs of setting up a network of Zn supplying stations [29,35] and long-term habits of users encourage the development of electrically rechargeable Zn anodes to meet the requirements of next-generation batteries. Ideally, these Zn electrodes would be capable of high-efficiency recharging, possess a major proportion of utilizable active material and have high capacity retention over long time periods. In this review, we focus on the challenges and nanomaterial design for electrically rechargeable Zn. Different from conventional intercalation electrodes in lithium ion batteries, the solid-solute-solid transformation of zinc electrodes inherently
represents a series of challenges. The long-standing constraints that have impeded implementing Zn in next-generation batteries are its poor rechargeability, where the performance-limiting phenomena are attributed to dendrite growth, shape change, passivation and hydrogen evolution (as shown in Fig. 2).

2.2.1 Dendrite growth
The formation of Zn dendrites is one of the major challenges in secondary alkaline Zn-based batteries [49–51]. According to the reactions expressed by eqn (1-3), the formed zincate ions should completely return to metallic Zn during charge in alkaline electrolyte. Unfortunately, a concentration gradient of zincate ions leads to concentration-controlled Zn electrodeposition, where Zn dendrites arise when the deposition reaches beyond the boundary of the diffusion-limited region [52]. Accordingly, dendritic morphologies are formed with repeated cycles, when Zn(OH)$_4^{2-}$ and/or Zn$^{2+}$ ions are deposited faster growth along energetically favorable crystallographic directions [53]. Zn dendrites are sharp, needle-like metallic protrusions reaching hundreds of micrometers in length [54] that can puncture the separator and make contact with the cathode, resulting in internal short circuit and catastrophic failure of Zn-based batteries [36].

The formation of zinc dendrites is mainly controlled by the concentrations of zincate ions and hydroxide ions, the mass transfer process of the electrolyte and current density distributions during charge and discharge [55]. It was reported that dendritic growth arises when the current density was larger than a certain critical value [56]. For instance, cycling Zn electrodes at a current density greater than 10 mA/cm$^2$ easily induces dendrite formation is easily induced in alkaline electrolyte [57]. Nonetheless, it is worth mention that dendrites can also form at lower deposition overpotentials under a long period of time for initiation [56]. Therefore, strategies that can effectively control the dendrite formation must be developed.

2.2.2 Shape change
Zn electrode shape change, the redistribution of Zn material over the electrode after repeated charge-discharge cycles, has been identified as one of the main life-limiting factors for alkaline
Zn-based batteries [58]. It occurs when the dissolved Zn(OH)$_4^{2-}$ and/or Zn$^{2+}$ ions are redeposited onto different locations of Zn electrode during the charge process, resulting in densification of the electrode at specific regions over many charge/discharge cycles. This causes the loss of usable capacity after repeated cycles. The mechanism is attributed to uneven current distribution within the reaction zones, and convective flows when electro-osmotic forces across the battery [59–62].

Although the deposited Zn structures can be tuned by using specific additives and applied current density [63], Zn shape change is also affected by the concentration of alkaline electrolyte. In typical Zn alkaline batteries, 6–7 M KOH is used due to the maximum electrolyte conductivity [64]. However, the solubility of the discharge product (i.e. ZnO) also increases with increasing electrolyte concentration [65,66]. Therefore, a large amount of Zn dissolves and re-deposits under non-uniform conditions, resulting in a severe shape change of Zn electrode and a poor cycle life [65].

2.2.3 Passivation

Passivation is one of the challenges to develop electrochemically rechargeable Zn anode. During the discharge process, active Zn is transformed to relatively insulating ZnO, leading to an increase in the internal resistance of the Zn electrode [67–69]. The key factor causing passivation in rechargeable Zn anodes is attributable to the surface concentration of the reaction product [70,71]. This phenomenon inhibits further discharge processes due to the formation of an insulating ZnO film on Zn surface. Besides, precipitation of ZnO on the surface of porous Zn electrodes might reduce the pore volume of these electrodes, leading to the blockage of migration of the hydroxide ions and/or discharge products [72]. This causes the loss of energy efficiency for the charge-discharge cycles (i.e., voltage losses during discharging and voltage increases during charging). This significantly restricts the development of rechargeable Zn-based batteries with high energy density. It is noteworthy that zinc utilization (depth of discharge, DOD) is a common metric used to evaluate the electrochemical rechargeability of Zn anodes [73]. Although the zinc utilization for conventional powder-based electrodes was reported to range from 60–80% [74], it is important to develop Zn anodes that can be operated deeply discharged over repeated cycles. Therefore, it is important to reduce the passivation effect of Zn anodes by adopting the strategies of material design.

It is worth mentioning that dendrite growth, shape change, and ZnO passivation are closely interconnected. Dendrite growth and shape change are attributed to the inhomogeneous deposition of Zn on electrode surface, which is closely associated with the Zn ion transport kinetics at Zn electrode surface in both liquid phase and ZnO passivation layer. In the recharge process, the ion transport in ZnO passivation layer on Zn electrode surface would be the rate-determine step of the entire charge-transfer process. This means ZnO passivation is a key factor for the morphologies of deposited Zn. This phenomenon is similar to the influences of SEI layer on charge-transfer kinetics of Li deposition on Li metal anode used in Li-ion batteries.
2.2.4 Hydrogen evolution

As mentioned previously, the standard reduction potential of Zn/ZnO in eqn (4) is -1.26 V (vs SHE at pH of 14), which is lower than that of the hydrogen evolution reaction (HER, eqn (5), -0.83 V vs SHE at pH of 14).

Hydrogen evolution reaction: $2H_2O(l) + 2e^- \rightarrow 2OH^-(aq) + H_2(g)$

Self-discharge: $Zn(s) + 2OH^-(aq) + 2H_2O(l) \rightarrow Zn(OH)_4^{2-}(aq) + H_2(g)$

This means hydrogen evolution is thermodynamically favored and inevitably takes place during the operation of Zn-based alkaline batteries. H$_2$ evolution (eqn (6)) also causes self-discharge of Zn anodes. Thus, Zn electrodes cannot be charged with 100% coulombic efficiency, since the H$_2$ evolution consumes some of the electrons provided to the Zn electrode during charging. Moreover, it generates H$_2$ gas on the surface of Zn particles in aqueous media by consuming electrolyte during cycling, resulting in battery swell. The rate of H$_2$ evolution was found to be associated with applied current density and electrolyte concentration [75]. The undesired side reactions can lead to capacity fade and shortened life span of Zn anode [76,77]. Thus, strategies to inhibit H$_2$ evolution are in great demand to improve the rechargeability of Zn anodes. To briefly summarize, the main challenges of rechargeable Zn electrodes are dendrite growth, shape change, passivation and hydrogen evolution.

Past efforts have been dedicated to improving rechargeability of Zn anodes by using additives for Zn electrode and electrolyte. The former includes polymer additives (e.g. carboxymethyl cellulose [78], polyvinyl alcohol [79], poly(vinylidene fluoride) [80], etc.) to alleviate shape change of Zn electrodes and inorganic corrosion inhibitors (e.g. In [81], Bi [82], Pb [63], etc.) to suppress hydrogen evolution. The latter utilizes specific additives (e.g. Bi$_2$O$_3$ [83], polyethylene glycol [53], etc.) to control the morphologies and suppress dendrite formation on Zn electrodes. These additives have been demonstrated to improve the rechargeability of Zn anodes. However, the above approaches might raise other potential issues. For instance, polymeric additives are generally not electrically conductive and thus increase the internal resistance of the developed Zn electrode. In addition, heavy metals are not preferred in the perspective of environmental concerns. Therefore, to achieve long cycle life, high capacity and coulombic efficiency of Zn anodes, it is imperative to design and prepare novel Zn electrodes to overcome the aforementioned challenges.

3. Nanoscale design of zinc anodes

The emergence of nanotechnology was the invention of the scanning tunneling microscope and atomic force microscope in the 1980s, which provides unprecedented atomic-level visualization [84]. Since then, atomic-level characterization and experimental synthesis techniques have fueled the nanoscale research community. Recently, employing nanoscale materials has been successfully demonstrated in rechargeable batteries [5,85–91]. Nanotechnology has revived
interest in battery technologies that were thought impossible. Protection of the graphite anode [92] has been achieved using nanocoatings. Si nanostructured electrodes, including nanoparticles [93,94], nanowires [88,95], and nanotubes [96,97] have shown highly improved electrochemical cycling performance and have solved the problem of rapid reversible capacity loss of Si. Nanostructured sulfur electrodes [98,99] also achieved high sulfur utilization by mitigating dissolution and increasing conductivity. In addition, the nanoscale electrode design of Li metal anode [100], LiFePO$_4$ cathode [101], and so on, have been successfully demonstrated to improve electrochemical performance. Accordingly, it is believed that the rechargeability of zinc anodes can be improved by using nanoscale material design.

Nanoengineering offers a novel and exciting opportunity to enhance electrochemical performance by providing proper architecture, shortening the ion transport paths, and relaxing the strain generated during battery cycling [86,102,103]. In order to tackle the long-standing limits of rechargeable Zn electrodes, investigators attempt to overcome the raised issues by nanoscale design of Zn anode. Studies on rechargeable Zn anodes have regained great interest by downsizing particle sizes, moving to nanoscale composites, or designing new electrode concepts. It is noteworthy that the thickness of the ZnO passivation layer was identified as ~ 2 µm after discharging [104], which means the nanomaterial design of Zn electrodes are essential to significantly alleviate the ZnO passivation issue. Moreover, with nanoscale material design, preparation of coating layers with controllable pore sizes was demonstrated to act as ion-sieving layer to block larger zincate ions inside the coating and allow smaller hydroxide ions to penetrate [105]. Thus, the micro- and nano-structured Zn anodes can improve the rechargeability and fulfill the goal of deeply discharge. Recent efforts focused on developing performance-improved Zn electrodes can be categorized into three different approaches.

### 3.1. Nanocomposites with highly conductive materials

Ideal rechargeable Zn anode requires active materials that fully discharge and convert back to Zn metal upon charging. The current bottlenecks are the surface reaction of Zn dissolution into the electrolyte and the formation of poor electrically conductive ZnO onto the anode surface during discharge, resulting in exacerbated passivation of electrodes. Because of the introduction of nanoscale carbon-based materials into zinc electrodes, the overall electrical conductivity improves due to the increased availability of electron pathways after discharge, leading to better Zn utilization during cycling. For instance, carbon nanotubes (CNTs) have been used to improve electron transport and reduce overall resistance of Zn-based electrodes, which effectively improves the capacity of Zn anodes [106,107].

In addition to good electrical conductivity, reduced graphene oxide (RGO) also has suitable surface adsorption properties [108,109] and could be used to form ZnO/RGO nanocomposites with good electron conductivity. Sun et al. [110] use in situ solution synthesis method to grow uniform ZnO coating on an RGO surface (Fig. 3a). The ZnO@RGO composite shows significant capacity improvements in charge/discharge cycling in comparison with commercial ZnO (Fig.
Stable discharge performance of Ni-Zn secondary battery was achieved with 510 mAhg\(^{-1}\) after 300 cycles. Yan et al. [111] grew vertical ZnO nanoplates on graphene layers, which provides ZnO/graphene composites with long free path and facile diffusion channels for electron transport. As a result, ZnO/graphene composites exhibit lower internal resistance and better electrical conductivity in comparison with pure ZnO. The ZnO/graphene composites were used as anode material in a quasi-solid-state (Polyvinyl alcohol (PVA) gel electrolyte) Ni-Zn secondary battery system, where the performance can reach 297 mAhg\(^{-1}\) and good cycle stability for 86.69\% retention after 400 cycles. Thin and uniform graphene oxide (GO) coating can effectively stabilized the Zn anode. Zhou et al. [112] demonstrated a facile solution casting method to modify Zn mesh (~15 µm) with GO. The morphology of the Zn@GO anode successfully remained after cycling. The GO layer was proved to slow down the Zn intermediates from dissolving into the electrolyte which enhanced utilization and rechargeability of Zn anode. Moreover, recent attempts used carbon cloth as substrate to support the loading of active material (ZnO). The carbon cloth substrate (Fig. 3c) has the merits of highly conductive architecture and high surface area [113–115] that allow the intimate deposition of nanosized ZnO and enable fast electron transport and rapid ion diffusion. Liu et al. [116] successfully prepared atomic layer conformal deposition of ZnO nanoparticles on a hierarchical carbon cloth-carbon nanofiber (CC-CF) substrate (Fig. 3d), which was demonstrated as good anode material for both aqueous and polymer-gel electrolyte (Fig. 3e-f). Li et al. [117] exhibited dendrite-free and long-durability performance of a tri-layer 3D CC-ZnO@C-Zn anode, which was prepared by \textit{in situ} growing ZIFs (Zeolitic-imidazolate frameworks) derived ZnO@C core–shell nanorods on carbon cloth followed by Zn deposition. The finely crafted skeleton of core-shell CC-ZnO@C nanorod arrays combined with Co-based cathode can deliver specific energy and power of 235 Wh kg\(^{-1}\) and 12.6 kW kg\(^{-1}\), respectively with high durability (71.1\% after 5000 cycles).

![Diagram](image)

**Fig. 3.** (a) Schematic of the growth strategy of ZnO@RGO. (b) High rate discharge performances of ZnO@RGO and ZnO at different C-rates. (c) SEM images of ALD ZnO coated CC-CF. (d) TEM image of ZnO coated on CC-CF. (e) Charge–discharge curves and (f) rate performance of aqueous Ni–Zn
batteries. (a, b) Reprinted from [110] with permission from Copyright (2016) American Chemical Society. (c-f) Reprinted from [116] with permission from Wiley-VCH.

**Table 1** Electrochemical performance of the recent developed rechargeable Zn-based batteries.

<table>
<thead>
<tr>
<th>Material</th>
<th>Cathode</th>
<th>Specific capacity (mAh g(^{-1}))</th>
<th>Cyclability (mAh g(^{-1}))</th>
<th>Electrolyte</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nanocomposites with highly conductive materials</td>
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<tr>
<td>ZnO/RGO</td>
<td>Ni(OH)(_2)</td>
<td>510 at 0.6 A g(^{-1}) cycles</td>
<td>510 after 300 cycles</td>
<td>6M KOH with saturated ZnO</td>
<td>[110]</td>
</tr>
<tr>
<td>ZnO/graphene</td>
<td>Ni-Al layered double hydroxide</td>
<td>297 at 1 A g(^{-1}) cycles</td>
<td>249 after 400 cycles</td>
<td>~4.5M PVA + 6M KOH with saturated ZnO</td>
<td>[111]</td>
</tr>
<tr>
<td>ZnO/CC-CF</td>
<td>NiO</td>
<td>~130 at 2.6 A g(^{-1}) cycles</td>
<td>~95 after 2,400 cycles</td>
<td>~3.2M PVA + 6M KOH with saturated ZnO</td>
<td>[116]</td>
</tr>
<tr>
<td>3D high surface area electrode structure</td>
<td></td>
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<tr>
<td>Zn sponge*</td>
<td>AgO</td>
<td>164 at ~0.02 A g(^{-1}) cycles</td>
<td>~82 after 36 cycles</td>
<td>6M KOH</td>
<td>[118]</td>
</tr>
<tr>
<td>Zn sponge*</td>
<td>NiOOH</td>
<td>328 at ~0.55 A g(^{-1}) cycles</td>
<td>~164 after 141 cycles</td>
<td>6M KOH + 1M LiOH</td>
<td>[57]</td>
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<td>Structures with surface coatings</td>
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<tr>
<td>ZnO@C*</td>
<td>Ni(OH)(_2)</td>
<td>~350 at ~0.658 A g(^{-1}) cycles</td>
<td>~300 after 40 cycles</td>
<td>4M KOH, 2M K(_2)CO(_3)</td>
<td>[105]</td>
</tr>
<tr>
<td>ZnO@TiN</td>
<td>Ni(OH)(_2)</td>
<td>~525 at 0.33 A g(^{-1}) cycles</td>
<td>~525 after 640 cycles</td>
<td>4M KOH with saturated ZnO</td>
<td>[9]</td>
</tr>
<tr>
<td>Zn-pome*</td>
<td>Ni(OH)(_2)</td>
<td>~375 at 0.658 A g(^{-1}) cycles</td>
<td>~300 after 50 cycles</td>
<td>4M KOH, 2M K(_2)CO(_3)</td>
<td>[119]</td>
</tr>
<tr>
<td>ZnO lasagna*</td>
<td>Ni(OH)(_2)</td>
<td>~586 at 0.658 A g(^{-1}) cycles</td>
<td>~565 after 150 cycles</td>
<td>4M KOH, 2M K(_2)CO(_3)</td>
<td>[120]</td>
</tr>
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* Tested in lean electrolyte (limited amount of electrolyte) condition, with ZnO-free electrolyte.

In short, significant improvements in electrochemical performance have been achieved by designing nanostructured Zn electrodes comprised of highly conductive materials that alleviate passivation issues and Zn/ZnO. However, this approach generally cannot effectively confine the zincate ions within a limited space to avoid dendrite formation. More importantly, good mechanical stability of nanostructured Zn electrodes is also required to maintain the structure after conducting long-term deeply charge-discharge cycles.
3.2 3D high surface area electrode structure

One of the most practical methods for improving the electrochemical performance of the Zn anode is to increase the surface area through the modification of zinc particles, which provides more efficient electrochemical reaction of Zn in the alkaline electrolyte. Moreover, increasing the surface area of Zn electrodes can minimize the likelihood of dendrite formation upon charging, since a lower zinc-deposition overpotential can be achieved by a lower current density. Therefore, approaches for using high surface area of zinc electrodes have successfully demonstrated enhanced electrochemical performance. Zhang [121] reported solid fibrous Zn anodes have suitable porosity and effective surface area with good electrical conductivity and mechanical stability and can provide 20% more capacity in alkaline cells at high discharging currents in comparison with commercially available cells. Parker et al. [118] investigated a novel 3D-wired Zn architecture which can be operated over 80 charge–discharge cycles at high currents without visible dendrite growth. Fig. 4a depicts the schematic of ZnO electrodeposition in a conventional powder-bed electrode and 3D-wired Zn sponge electrode during charge/discharge. Powder-composite electrodes have regional high local current density and can form dendrite morphologies due to the loss of interparticle connectivity during cycling. This is in contrast with the 3D Zn sponge architecture that maintains its structure after charge-discharge cycles. The ZnO that is formed is well distributed within the void space in all three dimensions of the Zn, preventing shape change upon cycling. Nearly 90 hours continuous charge-discharge cycling of a symmetrical cell comprising Zn//Zn@ZnO sponge were conducted (Fig. 4b), indicating good stability of the Zn sponge. In regard to full-cell performance, 3D Zn-Ni battery to 40% DOD<sub>Zn</sub> can persist for 85 and 65 cycles with an average energy efficiency of 84% at recharge rate of 5 and 10 mA cm<sup>-2</sup>, respectively, and the post-cycled electrodes exhibit no obvious changes in dimension, shape, or monolithicity (Fig. 4c-e) [57]. It is worth mentioning that the tests were conducted in a Nylon cell with a limited amount of electrolyte, which can better represent real operating conditions. Recently, Ko et al. further improved volumetric capacity and power capability by engineering the solid volume fraction of Zn sponge to increase the degree of metallic connectivity and boost mechanical integrity of the electrode [122].

It is worth mentioning that the metallic zinc array can be prepared by a facile electrodeposition method [123]. Chao et al. [124] successfully prepared a Zn array anode supported by a conductive porous graphene foam. The nanoarray structure with ca. 20 nm in thickness and 400 nm in width can be operated to 66% DOD<sub>Zn</sub> without noticeable dendrite growth. Furthermore, the concept of ‘Zn-less anodes’, where a stable structure with the ability to accommodate Zn electrodeposition as nanoparticles in Zn-contained alkaline solution, was demonstrated. Li et al. [125] utilized a host material, 3D lithium doped TiO<sub>2</sub> nanotube-array fiber-shaped electrode, Li-RTiO<sub>2</sub>, served as the anode for electrochemical deposition and dissolution of Zn during charge/discharge process. The long-term durability of Zn@ Li-RTiO<sub>2</sub> in Zn-contained alkaline solution is ascribed to the ordered nanotube-array architecture which is largely enhancing transformation efficiency of anodic Zn/ZnO<sub>2</sub> couple by confining Zn as the form of nanoparticle to TiO<sub>2</sub> nanotubes rather than bulk dendrite morphologies. Combined with
Mn-NiO$_x$ cathode, the full-cell battery shows the maximum volumetric energy density of 0.034 Wh cm$^{-3}$, power density of 17.5 W cm$^{-3}$, high energy efficiency of 91% and ca. 5% capacity loss after 20,000 cycles.

However, the high surface area in 3D structures will increase the rate of the hydrogen evolution reaction, which is not only deteriorates the coulombic efficiency of charging batteries but also raises the self-discharge rate when batteries are not operating. Thus, approaches to reduce hydrogen evolution in high surface area Zn electrodes have drawn increasing attention.

![Fig. 4](image)

**Fig. 4.** (a) Schematic of the dissolution-precipitation of ZnO in (left) conventional powder-bed electrodes and (right) the 3D-wired Zn sponge electrode. (b) The charge-discharge cycles of a symmetrical cell consisting of Zn sponge at ±24 mA cm$^{-2}$ to a DOD$_{Zn}$ of 23%. SEM images of (c) pre-cycled and (d, e) post-cycled Zn sponges after >100 cycles. (a, b) Reprint from [118] with permission from Royal Society of Chemistry. (c-e) Reprint from [57] with the permission from American Association for the Advancement of Science.

### 3.3. Structures with surface coatings

In alkaline electrolyte, Zn anodes undergo a solid-solute-solid mechanism (Zn-Zn(OH)$_4^{2-}$-ZnO), which may cause dendrite, shape change and passivation issues. By using nanostructured Zn anodes, the ZnO passivation problem can be overcome. Uniform and thorough coating on zinc
anodes can mitigate the migration of dissolved zincate ions. Wu et al. [105] reported an ion-sieving carbon nanoshell coated ZnO nanoparticle anode (Fig. 5a). Ion-sieving is a separation process of ions. In this work, the ion-sieving coating was used to block larger zincate ions ($\text{Zn(OH)}_4^{2-}$) inside the coating and allow smaller hydroxide ions ($\text{H}_2\text{O}$ and $\text{OH}^-$) to penetrate (Fig. 5b). From inductively coupled plasma (ICP) analysis, the dissolution rate of core/shell nanostructured Zn anodes was found to be lower than that of bare ZnO nanoparticles, indicating the ion-sieving coating effectively constrains the zincate ions in the structure. This design successfully prevented the dissolution and shape change of anodes. Thus, such ion-sieving carbon nanoshell coated ZnO nanoparticle anode shows improved specific capacity in comparison with Zn foil and a bare ZnO anode. In addition, this manuscript points out that lean electrolyte system should be used to test the true performance of anodes instead of a large amount of ZnO saturated electrolyte in flooded or beaker cells. Furthermore, Zhang et al. [9] synthesized a core/shell ZnO@TiN$_x$O$_y$ nanorod structured anode (Fig. 5c) through a hydrothermal method followed by atomic layer deposition of TiN$_x$O$_y$. The surface morphologies of uncoated ZnO and ZnO@TiN$_x$O$_y$ anodes before and after charge were examined (Fig. 5d). The electrode shape of uncoated ZnO anode dramatically changed, and ZnO nanorods detached from the carbon paper substrate. On the contrary, the surface morphology of the ZnO@TiN$_x$O$_y$ anode maintained its structure after charge (Fig. 5e). The results clearly demonstrate that the TiN$_x$O$_y$ coating layer can protect the Zn electrode and slow down the dissolution of zinc anodes. Instead of coating on ZnO, which is the discharged state of zinc anodes, efforts with coating on metallic Zn were also demonstrated. Schmid et al. [126] reported that coating metallic zinc particles with silica (Fig. 5f) can control the dissolution of zinc, precipitation of zincate, thus reduce the ZnO passivation layer formation (Fig. 5g). Silica coated zinc particles exhibit an improved discharge capacity compared with as-received zinc.
Fig. 5. Core/shell structured zinc anodes with individual coating. (a) Schematic of carbon nanoshell coated ZnO nanoparticle anode. (b) Ion size calculations of hydroxide and zincate. (c) Schematic of uncoated ZnO and ZnO@TiN$_x$O$_y$ nanorod anodes during cycling. (d) SEM image of the uncoated ZnO and ZnO@TiN$_x$O$_y$ anodes before and after charge. (e) SEM image and EDS elemental mappings of the ZnO@TiN$_x$O$_y$ anode after charge. (f) Schematic of as-received zinc and silica coated zinc nanoparticles. (g) Schematic of zincate precipitation for as-received zinc and silica coated zinc nanoparticles during cycling. (a, b) Reprint from [105] with the permission from Wiley-VCH. (c-e) Reprint from [9] with the permission from Elsevier. (f) Reprint from [126] with the permission from Elsevier.

We summarize the above nanostructured Zn anodes as ‘particle-level coating’, which means that every single nanoparticle/nanorod is coated by a protective layer individually. In addition, coatings can also be applied to micro-sized secondary particles and capsules. Inspired by the ion-sieving carbon nanoshell coated ZnO nanoparticle anode [105], Chen et al. [119] fabricated a nanoscale, pomegranate-structured Zn anode (Zn-pome, Fig. 6a), where ZnO secondary particles are coated with carbon layers. As shown in Fig. 6b, compared with carbon nanoshell coated ZnO nanoparticle anode, Zn-pome has a smaller contact area between the anode and electrolyte. With this design, the dissolution rate of anode active materials can be significantly reduced. To verify the ion-sieving ability of the carbon coating, samples of ZnO nanoparticles, carbon nanoshell coated ZnO nanoparticles and Zn-pome containing equal amounts of zinc were immersed in 1 mL of 4 M KOH solutions. The dissolved zinc concentration in the solutions of these three samples were analyzed by ICP (Fig. 6c). Zn-pome significantly reduced the portion of dissolved Zn in KOH (1.05%) in comparison with ZnO NPs (30.8%) and ZnO@C NPs (11%). This effect
is attributed to the synergistic function of carbon nanoshell and secondary structure in Zn-pome. As a result, Zn-pome achieved better performance than the ZnO nanoparticles anode. In addition, with nanoscale material design, Yan et al. [120] reported a lasagna-inspired Zn anode consisting of 100 nm ZnO nanoparticles encapsulated by graphene oxide (Fig. 6d), which can effectively alleviate the passivation and dendrite formation of Zn anode. In detail, GO framework allowed the free-transportation of electron, OH\(^-\) and H\(_2\)O to support the anode reaction, but blocked the resulting Zn(OH)\(_4\)^{2-} inside the lasagna capsule. The effectiveness of restraining the diffusion of zincate ions from lasagna structure was confirmed by ICP-AES (Fig. 6e). Accordingly, the discharge capacity can reach above 565 Ah kg\(^{-1}\) for 150 cycles.

Applying a carbon coating on the large-size zinc foil has also been demonstrated to suppress dendrite formation and shape change of Zn electrodes [127]. The zinc foil was coated thoroughly with a porous carbon layer (Fig. 6f), which serves as the nucleation site and reservoir of Zn ions. This anode demonstrated a stable Zn plating/stripping, which is ascribed to the uniform charge distribution and abundant space for zinc deposition with the existence of carbon coating layer (90 \(\mu\)m). Besides, Zhao et al. [128] introduced a conformal and conductive TiO\(_2\) protective layer on the zinc plate (Fig. 6g) by using atomic layer deposition technique. The TiO\(_2\) protective layer is ultrathin (8 nm). It acts as the passivation layer to avoid the direct contact between the zinc metal and the electrolyte. At the same time, the TiO\(_2\) layer can suppress the hydrogen evolution and zinc corrosion. As a result, Zn plate with the TiO\(_2\) protective layer showed an enhanced electrochemical performance in both Zn symmetric cells and Zn–MnO\(_2\) full cells. Moreover, Stock et al. [129] coated anion-exchange ionomer on the zinc sponge, which can stabilize the entire pore system during cycling.
Fig. 6. Coatings on secondary particles, capsules, and zinc electrodes. (a) SEM image of Zn-pome. (b) Schematic of Zn-pome anode. (c) Inductively coupled plasma results showing dissolved zinc proportions in 4M KOH for ZnO nanoparticles, carbon nanoshell coated ZnO nanoparticles, and Zn-pome. (d) Schematic of ZnO lasagna microstructure comprising ZnO nanoparticles and carbon black encapsulated by GO sheets (top), and a single capsule inside the ZnO lasagna electrode. (e) Percentages of ZnO that were dissolved in 4M KOH solution over time, measured using ICP-AES. (f) SEM images of Zn foil and carbon coated zinc foil. (g) Schematic of Zn plate and TiO$_2$ coated Zn plate during cycling. (a-c) Reprint from [119] with the permission from Royal Society of Chemistry. (d, e) Reprint from [120] with the permission from American Chemical Society. (f) Reprint from [127] with the permission from American Chemical Society. (g) Reprint from [128] with the permission from Wiley-VCH.

All of the works above are related to structures with surface coatings, which mainly focus on solving the dissolution and shape change of Zn anodes. However, hydrogen evolution is still an issue that must be addressed. A hydrogen suppressive coating could be an effective way to tackle the hydrogen evolution problem.
4. Molecular design of electrolytes

The performance of batteries is highly associated with the electrolyte environments. As discussed above, zinc metal in aqueous electrolyte suffers from dendrite growth and hydrogen evolution issues. Hydrogen evolution is thermodynamically favored and inevitably takes place during the operation of Zn-based alkaline batteries. This side reaction deteriorates Columbic efficiency of zinc anodes. In addition to nanoscale design of zinc anodes, molecular engineering of electrolytes with reduced side reaction is an alternative approach to improve Zn anode performance. Even though completely using organic electrolyte can avoid hydrogen evolution issue, Zn-based batteries would lose their advantage (against Li-based batteries) of operating in non-flammable aqueous electrolytes. Recently, new concepts have been revealed to reduce the side reaction of water by using electrolyte additives, highly concentrated salts, or inert solvents [130,131].

Chen et al. [44,132,133] indicated that the electrolyte additive Zn(CF$_3$SO$_3$)$_2$ benefits reactivity and stability of Zn anode. Compared with sulfate and alkaline electrolytes, Zn(CF$_3$SO$_3$)$_2$ electrolyte shows higher stability of Zn plating/stripping because the bulky CF$_3$SO$_3^-$ anion could decrease the number of water molecules surrounding Zn$^{2+}$ cations. Using Zn(CF$_3$SO$_3$)$_2$ salt, they further reported a self-healing integrated all-in-one zinc-ion battery [128] with poly(vinyl alcohol)/Zn(CF$_3$SO$_3$)$_2$ hydrogel electrolyte. Besides, Wang et al. [129] demonstrated a ‘water in salt’ aqueous electrolyte with high concentrations of Zn and lithium salts (20 m lithium bistrifluoromethanesulfonimide (LiTFSI) and 1 m Zn(TFSI)$_2$). By using the developed electrolyte, nearly 100% coulombic efficiency and dendrite-free Zn plating/stripping can be achieved. The performance of Zn-based batteries consisting of LiMn$_2$O$_4$ cathode (Fig. 7a,b) was demonstrated. The good reversibility is ascribed to the effective suppression of hydrogen evolution by severely confining water molecules within the Li$^+$ solvation structures and by diminishing water in the vicinity of Zn$^{2+}$. Also, they presented molecular dynamics simulations to study Zn$^{2+}$-solvation-sheath structure (Fig. 7c), indicating Zn$^{2+}$ is occupied primarily by TFSI with six coordinating oxygens all from TFSI anions. The obtained Zn/LiMn$_2$O$_4$ batteries can deliver 180 Wh kg$^{-1}$ while retaining 80% capacity for over 4,000 cycles. Nonetheless, the high cost of fluorinated-salt-based electrolytes may limit their practical viability. Zhang et al. [130] introduced another “water in salt” electrolyte based on inexpensive ZnCl$_2$ at 30 m at room temperature. It also achieved high coulombic efficiency and a dendrite-free Zn metal anode. Zhao et al. [131] reported a “water-in-deep eutectic solvent” electrolyte (Fig. 7d), which involves ~6 wt.% (~30 mol.%) water into a eutectic mixture of urea/LiN(SO$_2$CF$_3$)$_2$/Zn(N(SO$_2$CF$_3$)$_2$)$_2$. Water molecules participate in the internal interaction network of deep eutectic solvents. Thus, the zinc interaction with water is significantly suppressed (Fig. 7e), which enables a stable and reversible Zn plating/stripping phenomenon (Fig. 7f).
To briefly summarize, electrolyte has a big influence on the electrochemical performance of Zn anodes in both alkaline and neutral electrolytes. In alkaline electrolyte, Zn anode undergoes a ‘Zn-Zn(OH)$_4^{2-}$-ZnO’ mechanism. In neutral electrolyte, Zn exists in forms of Zn element and Zn$^{2+}$. Both ions (Zn(OH)$_4^{2-}$ and Zn$^{2+}$) are in the electrolyte, thus molecular engineering of electrolyte may provide an effective way to suppress hydrogen evolution. The developed electrolytes enable dendrite-free Zn plating/stripping at nearly 100% coulombic efficiency, and the rechargeability of Zn anodes is significantly improved. It opens a viable route to the development of Zn-based batteries that are reliable, high energy, and very safe. It is highly recommended to further develop low-cost advanced electrolytes.
5. Summary and Outlook

As a promising energy storage device, rechargeable zinc-based aqueous batteries have attracted increasing attention due to inherent safety, high capacity (820 Ah kg\(^{-1}\) and 5854 Ah L\(^{-1}\)), and cost-effectiveness. However, its poor rechargeability greatly limits its development in next-generation batteries. In this review, we overview the challenges that plague the rechargeability of Zn anodes. The poor rechargeability of Zn anodes is attributed to the dendrite growth, shape change, passivation and hydrogen evolution problems. Extensive research has been carried out to improve the rechargeability and utilization of Zn electrodes. This review highlights recent advances in nanomaterial design of Zn electrodes, categorized into 3D high surface area electrode structure, core/shell structure with surface coatings and nanocomposites with highly conductive materials. These strategies utilizing nanostructured Zn anodes were demonstrated to tackle the aforementioned challenges. Accordingly, nanoscale design of Zn anodes is an effective and promising approach to develop electrically rechargeable Zn anodes for long-term battery operation. Moreover, the concepts of molecular engineering/design of the aqueous electrolytes with confined water molecules and high salts concentration (such as “water in salt” electrolyte) have been demonstrated to improve the electrochemical performance and stability of zinc anodes.

Although much progress has been achieved in nanoscale Zn anode design for aqueous rechargeable batteries, there is still room for further advancement of electrically rechargeable Zn electrodes. Future research is recommended to deal with the following perspectives.

1. To fulfill the goal of better energy storage of Zn electrodes, it is required to further design the Zn anodes with high zinc utilization (> 50% DOD\(_{Zn}\)), capable of operating deeply discharge and recharging with high Columbic efficiency (> 400 cycles with > 80% efficiency) under practical operating conditions. The strategies of novel nanomaterials design and structural modifications are recommended to provide promising Zn electrodes with good cycle stability. Besides, the device-level Zn-based batteries by integrating Zn anode with positive electrode can serve as an indicator of technology readiness level. It is encouraged to appropriately translate materials- and component-level performance into device-level metrics [73].

2. The testing conditions should be clearly stated in the publications. The zinc anode electrochemical performance is related to many parameters, including electrolyte volume, electrolyte additives, electrode material, electrode capacity, current collector, testing device, current density, degree of charge and discharge of the Zn anode, and so on. Thus, without detailed experiments conditions, the cycling performance may fall into the “hype cycle” category, which has the inherent danger of “breakthrough” cynicism. Lean electrolyte with a limited amount of electrolyte (e.g. electrolyte: electrode ~ 10: 1 in 2032 coin cells) should be used rather than beaker cell or flooded cell with excess electrolyte (electrolyte: electrode ~ 1000: 1), because
coin cells better represent real operating conditions.

(3) Current understanding of zinc battery chemistries is deficient. Considering multiple reactions occur simultaneously during battery operation, more investigations on the mechanisms related to zinc anode reactions should be explored in order to further solve the dendrite growth, shape change, passivation, and hydrogen evolution issues. Advanced techniques, such as \textit{in situ} and \textit{in operando} techniques [132,133] are encouraged to conduct in-depth studies.
Conflict of interests

The authors declare no competing financial interest.

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