

Rechargeable alkaline zinc batteries: Progress and challenges

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Abstract: The ever-growing demands for energy storage motivate the development of high-performance batteries. Rechargeable alkaline Zn batteries get increasing attractions due to their remarkable performance, high safety, low cost, and environmental friendliness. However, the research is in the early stage with challenges that hinder the road of commercialization, such as the unsatisfactory utilization of active materials and poor stability. Recently, some excellent works are performed to boost the development of alkaline Zn batteries from the electrode optimization to electrolyte exploration and structure design. Herein, this article provides a timely spotlight on the breakthroughs in the performance and structure of well-developed Zn batteries such as Zn-Ag and Zn-Ni batteries, as well as some new types of Zn batteries like Zn-Co, Zn-Cu, and Zn-Bi batteries. The reaction mechanisms of different positive electrodes are first introduced, followed by the summary on positive electrodes, Zn electrodes, and electrolytes. Moreover, current issues and possible strategies are also highlighted.

Graphical abstract:



Keywords: alkaline zinc batteries, positive electrodes, zinc electrodes, electrolytes, performance improvements

1. Introduction

With the ever-increasing demands for high-performance and low-cost electrochemical energy storage devices, Zn-based batteries that use Zn metal as the active material have drawn widespread attention due to the inherent advantages [1,2]. Firstly, Zn is one of the most abundant elements on the earth and has a low price. Secondly, the theoretical capacity is up to 820 mAh g^{-1} [3]. Thirdly, the potential of Zn in alkaline solutions can reach -1.26 V versus standard hydrogen electrode (SHE), which promises a high voltage region [4]. Finally, the intrinsic safety can be guaranteed owing to the aqueous electrolytes [5].

In light of the positive electrode reaction mechanisms, Zn-based batteries can be generally divided into two categories. One is the Zn-ion battery (ZIB) in which the positive electrode reaction is the intercalation/extraction process of Zn ions, similar to the lithium-ion batteries, and neutral or slightly acidic electrolytes are usually implemented [6]. The other is that using transition metal compounds or air as the positive electrode materials, such as Zn-Ni, Zn-Ag, and Zn-air batteries [7–11], in which aqueous alkaline electrolytes are mainly used, contributing to a more negative electrode potential (-1.26 V vs. SHE) than the one in neutral

or acid electrolytes (-0.76 V vs. SHE) [4,6].

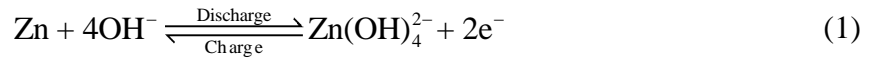
Although the rechargeable Zn-air battery owns the highest discharge capacity among Zn batteries, issues from the half-open system are challenging, such as carbon dioxide poison and electrolyte evaporation [12]. To this end, the closed systems are more suitable for various applications. Zn-Ag and Zn-Ni batteries have been developed for a long history and breakthroughs have been accomplished. Very recently, some new types of rechargeable alkaline Zn batteries have also been proposed [10,13,14]. For example, Zn-Co batteries exhibit a much higher theoretical capacity than that of Zn-Ni batteries [10]. In Zn-Cu batteries, the Cu electrode can possess a theoretical capacity of 844 mAh g⁻¹, which is even higher than the Zn electrode [13]. Zn-Bi batteries can deliver an ultra-stable discharge plateau, which is striking for applications [14]. Aimed at high electrochemical performance, efforts have been made in Zn-based batteries, such as enhancing the conductivity and utilization of active materials, suppressing Zn dendrite and passivation, and designing multifunctional electrolytes. To date, excellent reviews on Zn-ion batteries have been bloomed [15–17]. However, to our best knowledge, an elaborate summary of the recent progress in rechargeable alkaline Zn batteries has not been reported yet.

Herein, this article tries to give a timely spotlight on the development of rechargeable alkaline Zn batteries. The reaction mechanisms of Zn batteries with different positive materials are introduced, followed by a comprehensive presentation of the advances from the positive electrode to the Zn electrode and electrolyte. Finally, the remaining challenges and possible strategies in the materials, configurations, and test methods are discussed. Hopefully, this work can motivate the further development of Zn batteries and other high-performance energy storage systems.

2. Reaction mechanisms and positive electrode materials

For all kinds of rechargeable alkaline Zn batteries, Zn deposition and dissolution

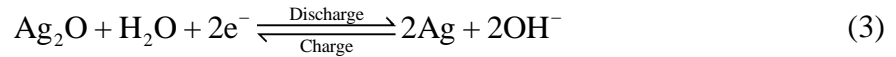
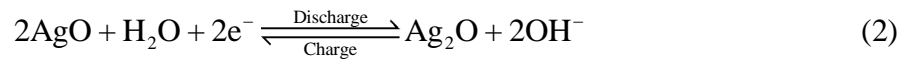
processes occur on the negative electrode:



During discharge, Zn metal gradually dissolves and combines with hydroxide ions in the alkaline solution to form zincate ions. When the concentration reaches the saturation value, zinc oxide (ZnO) will precipitate out of the solution. During charge, zincate ions reduce on the negative electrode surfaces to form Zn. For the positive electrode, the active materials and the corresponding reactions are introduced below, and the battery performance is summarized in Table 1.

2.1 Zn-Ag batteries

Zn-Ag batteries are one kind of mature batteries with hundreds of years [18]. The reversible electrochemical reactions on the positive electrode are:



which involves two steps in discharge: AgO is firstly reduced to Ag₂O (i.e., Ag²⁺ → Ag⁺), and then Ag₂O is reduced to Ag (Ag⁺ → Ag). Therefore, a Zn-Ag battery can exhibit two discharge voltage platforms (~1.85 and ~1.60 V), corresponding to a high energy density of up to 300 Wh kg⁻¹ [7,18]. However, the high price of Ag [19], separator degradation [20], migration of Ag ions [21], and oxygen evolution at a high voltage region (i.e., >1.85 V vs. Zn) limit its performance [22]. Recent advances thus focus on the electrode structure and material to meet further applications.

As a mature battery system, Zn-Ag batteries are attractive for flexible electronics. To this end, designs of flexible materials or integrated with soft supports are required [23]. A 2D planar flexible Zn-Ag battery based on the stretchable Ag nanowire (AgNW) electrode (Fig. 1a) was presented by Yan et al., in which the AgNW elastic conductors were embedded on a

soft polydimethylsiloxane (PDMS) substrate (Fig. 1b) [24]. This electrode demonstrated excellent functional stability even at 80% strain and could be cycled up to 1000 cycles with nearly 100% capacity retention. In addition to the 2D planar structure, wire-shaped flexible batteries can offer omnidirectional flexibility (Fig. 1c) and can be wrapped around the body like a necklace and weaved into fabrics (Fig. 1d) [25]. For this structure, dip coating the silver nanoparticle solution on the conductive stainless steel thread is commonly applied to construct the Ag electrode [26]. To guarantee the stable adhesion between the active material and the substrate, Berchmans et al. developed a new skin-worn Zn-Ag tattoo battery based on an electrodeposited Ag electrode, which revealed a capacity in the range of 1.3-2.1 mAh cm⁻² [27].

The formation of resistive Ag₂O species is one of the reasons for capacity degradation. Thus, rGO [28] and acetylene black [29] are added into the Ag electrode to increase the conductivity. However, conductive additives can cause large contact resistance, deteriorating the specific capacity and rate performance. Alternatively, a combination of metal-organic framework (MOF) and Ag nanowires (Fig. 1e) to grow on carbon cloth (Ag-MOF/CC) as a binder and conductive additives-free electrode could effectively avoid the contact resistance [30,31]. A Zn-Ag battery with this electrode delivered a capacity of 1.245 mAh cm⁻² and a remarkable power density of 2.8 mW cm⁻². Further, through covering a protective layer of poly(3,4-ethylenedioxythiophene)poly(styrenesulfonate) (PEDOT:PSS) to suppress the structural pulverization and alleviate the migration of Ag ions, the electrode composed of carbon nanotube fiber (CNTF), nitride-doped nanocarbon array (NCA), and Ag₂O (Fig. 1f) improved the capacity retention from 81.6% after 70 cycles (Ag-MOF/CC) to 79.55% after 200 cycles [32].

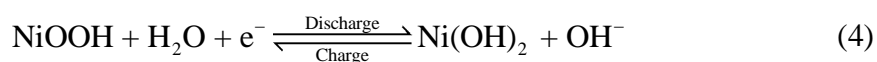
Restricted by the oxygen evolution reaction (OER) during the charge region from Ag₂O to AgO, a cut-off voltage of ~1.8 V is usually applied. Consequently, only the Zn-Ag₂O

reaction region is used, leading to the low utilization of active material and low energy density. To solve this problem, a hybrid battery integrating the Zn-Ag and Zn-air battery has been developed by Tan et al. [33], in which Ag nanoparticles could act as both the active material in Zn-Ag reactions and the effective catalyst in Zn-air reactions. Correspondingly, the hybrid battery delivered a remarkable energy density of 944 Wh kg⁻¹ with a capacity retention ratio of 55.7% after 500 cycles and a utilization ratio of 70.3% at 20 mA cm⁻². Although the half-open architecture can address the oxygen evolution issue and enable a high energy density, an additional OER catalyst was needed owing to the poor OER activity of AgO. Besides, the half-open system is vulnerable to humidity and carbon dioxide factors [12]. Hence, more investigations should be performed to improve the utilization of AgO, such as exploring the catalysts to inhibit the OER. The short cycle life caused by the migration of Ag ions is also challenging, which might be addressed by applying a mild ZnCl₂ electrolyte which demonstrated remarkable capacity retention of 93.2% after 1300 cycles [34]. In addition, effective additives and better protective layers should be further innovated.

2.2 Zn-Ni batteries

Nickel-based materials have been applied in Zn batteries since 1899 [35]. The major barriers of Zn-Ni batteries are the irreversibility (e.g., α -Ni(OH)₂ is easy to turn to the β phase over several cycles [36]) and poor conductivity of Ni-based materials, as well as the self-corrosion and dendrite of Zn electrodes, which lead to the unsatisfactory cycling stability [37]. Recently, through constructing nanostructures, combining with conductive carbon materials, and doping with other transition metal ions, the electrochemical performance of Ni-based material has been improved greatly [38]. Besides, effective strategies on the Zn electrode design have also been reported, such as the 3D sponge Zn electrode that can successfully solve the dendrite [39]. Thus, Zn-Ni batteries have attracted more research attention and exhibited potentials for further applications. For a typical alkaline Zn-Ni battery using

Ni(OH)₂ as the positive electrode material, the reaction occurred on the positive electrode is:
[40]



which can output a high working voltage of ~1.8 V and a theoretical energy density of 340 Wh kg⁻¹ [41]. Recent progress in Zn-Ni batteries focuses on the positive electrode material optimization and the phase transformation prohibition [38].

Chen et al. constructed a new Ni@Ni(OH)₂ fiber electrode based on an impregnation-dyeing method, and a Zn-Ni battery based on that delivered a discharge capacity of 704 μAh cm⁻³ with 75% capacity retention from 0.5 to 5 A g⁻¹ [42]. However, subject to the high molecular weight, Ni(OH)₂ has a lower theoretical capacity (290 mAh g⁻¹) than NiO (360 mAh g⁻¹). Hence, NiO has also been applied in Zn-Ni batteries, while the poor electronic conductivity limits its performance [43]. To address this issue, Wang et al. anchored the NiO nanosheet on carbon nanotubes (CNTs). Benefiting from the better conductivity, thinner nanosheet, and higher crystallinity, the battery showed a high capacity of 155 mAh g⁻¹ and an excellent energy density of 228 Wh kg⁻¹ [9]. Besides growing on conductive carbon materials, a binder-free NiO electrode based on 3D carbon cloth-carbon nanofiber substrate has been reported by Liu et al [44]. This electrode had a mesoporous structure and rendered the facilitation of electrolyte infiltration and fast species transport, leading to a high capacity of 203 mAh g⁻¹ and 41.6% capacity retention after the current density increased 40 times. To further improve the electronic conductivity, metallic Ni nanoparticles have been introduced to NiO nanosheets, through which 96.6% capacity retention was obtained after 10000 cycles [11]. Besides, non-interconnected Ni-MOF-74 [Ni₂(dhtp)(H₂O)₂·10H₂O] cone-shaped nanoarrays on CNT fiber with 1D hexagonal channels were fabricated.[45] Due to the remarkable affinity, the low electrical resistance and high mechanical reliability could be achieved simultaneously. As a result, a solid-state battery with the 90°-bending electrode

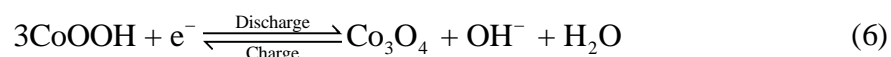
displayed 5.7% capacity decay after operating 1000 cycles. In addition to carbon materials, Li et al. got a cellulose nanofiber (CNFs) from sustainable biomass, which is suitable for the adsorption of Ni^{2+} ion owing to the plentiful hydroxyl and carboxyl functional groups [37]. Benefiting from the interfacial tension and hydrogen bond, the Ni/NiO nanoparticles distributed uniformly, leading to the enlarged surface area and considerable active sites. After assembled into a battery, it empowered a capacity of 256 mAh g^{-1} , 68.5% capacity retention after increasing 40-time current density, and 12.5% decay after 2000 cycles. Apart from the oxide and hydroxide, sulfide and phosphide have also been applied considering their higher electronic conductivity. Hu et al. constructed a 3D Ni_3S_2 nanosheets structure, which achieved a capacity of 150 mAh g^{-1} and 46% capacity retention after the current density increased 10 times [46]. Li et al. embedded carbon nanoparticles into the surface of N_2P particles to inhibit their agglomeration, and obtained a capacity of 176 mAh g^{-1} with 6.2% decay after 1500 cycles [47].

Generally, $\text{Ni}(\text{OH})_2$ can be classified in different phases based on their different crystal structures [36]. Unfortunately, the often applied $\alpha\text{-Ni}(\text{OH})_2$ in Zn-Ni batteries can spontaneously turn to thermodynamically stable β phase over several cycles, decreasing the capacity [48]. To solve this problem, a variety of strategies have been used, and introducing other elements is an effective method [49]. Gong et al. reported a Zn-Ni battery using NiAlCo-layered double hydroxide (LDH) on CNT [50]. Benefiting from the combined effect of aluminum and cobalt co-doping, the nanoplate size could be reduced while exorbitant oxidation of Ni^{2+} could be prevented, inhibiting the decay of $\alpha\text{-Ni}(\text{OH})_2$. This battery exhibited a maximum energy density of 324 Wh kg^{-1} and capacity retention of ~90% after 600 cycles. Xu et al. electrodeposited the Co-doped $\text{Ni}(\text{OH})_2$ into nickel nanowire on Ti foil [51]. The introduction of Co dopant was proposed to be favorable for the generation of defects and disorder structure, in which the stress upon multiple cycles could be alleviated.

When served in a Zn-Ni battery, an ultra-high capacity of 247 mAh g⁻¹ and ~88% capacity retention after 5000 cycles could be achieved. To get optimal battery performance, a comprehensive strategy combining carbon/Ni interconnection and element doping may be applied, which is worth further investigations.

2.3 Zn-Co batteries

Cobalt-based materials (e.g., Co₃O₄) have attracted attention due to the great electrochemical redox performance and stable crystal structure [52,53]. The reactions are proposed as follows: [54]



where Co₃O₄ transforms to CoOOH and further to CoO₂ upon charging, and the reverse reactions occur upon discharging. Owing to the capability of oxidation to Co⁴⁺, Co₃O₄ owns a high theoretical capacity of 446 mAh g⁻¹.

The first rechargeable Zn-Co battery was reported by Wang et al., in which a mesoporous Co₃O₄ electrodeposited on nickel foam was constructed [10]. Based on this positive electrode and electrodeposited Zn as the negative electrode, a discharge voltage of ~1.8 V, capacity of 162 mAh g⁻¹, and 20% capacity decay after 2000 cycles were achieved. However, the practical capacity was much lower than the theoretical value, leading to an unsatisfactory utilization ratio (i.e., 36.2%). To improve the utilization, efforts have been made in tuning the morphology and microstructure, changing the surface state, and introducing other elements [55–58].

Tan et al. constructed a Co₃O₄ nanowire-cluster structure directly grown on Ni foam with improved electronic conductivity and large electrochemical surface [59]. A battery with this electrode delivered a considerable capacity of 173.6 mAh g⁻¹ and capacity retention of 84.1%

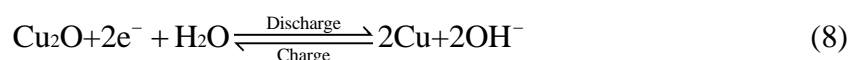
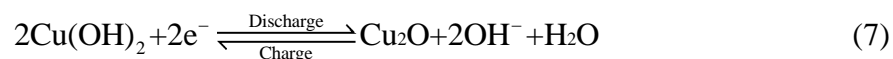
after 1000 cycles. Later, Shang et al. fabricated a Co_3O_4 electrode with a heterogeneous porous nanowire structure through tuning the pore size distribution and obtained a discharge capacity of 230 mAh g^{-1} with 62.6% retention after the current density increased 20 times [60]. It is postulated that the relatively high utilization ratio (51.6%) benefited from fast species transfer due to the abundant pore structures and enlarged reaction active area. Further, Lu et al. modified the surface state by introducing oxygen-defects into Co_3O_4 nanosheets [61]. They found that the surface with oxygen vacancy boosted the OH^- adsorption capability, therefore enhancing the reactivity. Fig. 2 shows the results of a battery utilizing this electrode. As depicts in Fig. 2a, a much higher capacity of 240.8 mAh g^{-1} was achieved compared to the pristine electrode (19.7 mAh g^{-1}). The improvement may come from relatively lower charge transfer resistance ($\sim 4.3 \Omega$) than the pristine one ($\sim 60 \Omega$), as shown in Fig. 2c. For the rate performance, the battery delivered an average capacity from 258 to 105.7 mAh g^{-1} when the current density changed from 0.525 to 10.5 A g^{-1} (Fig. 2b and 2d), demonstrating higher capacity retention of 40.8% than the pristine one (10.5%). Besides, the battery could work with almost no capacity decay even after 10000 cycles, illustrating superior cycle stability (Fig. 2e and 2f). As doping other transition metals in the Co_3O_4 lattice can provide more ion diffusion channels and increase the electrical conductivity [62], Wang et al. fabricated a nickel-cobalt hydroxide nanosheet electrodeposited on carbon cloth with a highly stable octahedral structure and good conductivity, which delivered the energy density of 172 and 210 Wh kg^{-1} under -20 and $50 \text{ }^\circ\text{C}$, respectively [63]. A battery with a mesoporous NiCo_2O_4 nanowire electrode also showed a capacity of 230.1 mAh g^{-1} , improving the utilization of Co-based materials [64].

In addition to using cobalt oxides, Zhang et al. fabricated a core-shell Co_3S_4 nanosheet to enhance the adsorption of OH^- and electrical conductivity [65], resulting in an ultrahigh capacity of 317 mAh g^{-1} and an energy density of 507 Wh kg^{-1} . Furthermore, a mild

electrolyte composed of 2 M ZnSO₄ and 0.2 M CoSO₄ has been applied in a Zn-Co battery. Equipped with the Co³⁺-rich Co₃O₄, a higher discharge voltage of ~2.2 V could be delivered, and only 8% capacity dropped after even 5000 cycles [66]. It is worth noting that even though the utilization of Co₃O₄ has been improved in recent years, the maximum obtained capacity of Co₃O₄ in alkaline solutions (~250 mAh g⁻¹) is still away from the theoretical value (446 mAh g⁻¹). Hence, the intrinsic mechanism and improvement method should be further explored.

2.4 Zn-Cu batteries

Zn-Cu primary batteries have been invented for centuries. Attributed to the two-electron transfer, Cu actually can deliver a higher theoretical specific capacity of 844 mAh g⁻¹ than Ag, Ni, and Co [31,67,68]. However, the irreversibility of Cu in acidic and neutral electrolytes makes the secondary Zn-Cu battery impossible. Inspired by the low solubility of Cu(OH)₂ in alkaline solutions, Zhu et al. first proposed a rechargeable Zn-Cu battery by using the aqueous KOH solution as the electrolyte and waterweed-like Cu clusters deposited on a Ti substrate as the positive electrode, in which the reaction can be expressed as follows: [13]



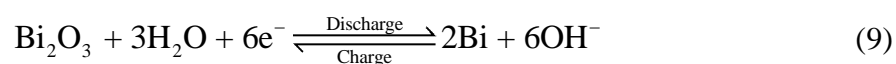
During charge, Cu is first oxidized to be Cu⁺ at about 1.0 V and then oxidized to Cu²⁺ at 1.2-1.5 V. While in the discharge process, Cu²⁺ is reduced to Cu⁺ at 0.8 V and further reduced to Cu. Fig. 3a presents that a Zn-Cu battery using the KOH solution has better reversibility and higher discharge capacity than the one using the neutral ZnSO₄ solution. The ex-situ XRD patterns and in-situ Raman spectra prove the two-step reactions, as shown in Fig. 3b and 3c, respectively. Fig. 3d presents the discharge capacity at different current densities. At 0.1 A g⁻¹, the capacity and voltage plateau reached 718 mAh g⁻¹ and 0.76 V, respectively. When the current density increased to 0.5, 1, and 2 A g⁻¹, the capacity decreased to 592, 530, and 401

mAh g⁻¹, correspondingly, demonstrating good rate capability. In the long-term cycle stability test, the charge capacity decreased from 538 to about 300 mAh g⁻¹ after 20 cycles at 1 A g⁻¹, but this value was maintained for 200 cycles, as demonstrated in Fig. 3e. In addition, the discharge capacity is almost identical to the charge capacity at the same cycle, confirming the good reversibility. Furthermore, it is found that a Cu foil electrode can undergo a self-activation process to form Cu nanowires in an alkaline solution, which can deliver a high capacity of 9.4 mAh cm⁻² and superior stability of 500 cycles without capacity decay at 1 mA cm⁻².

To increase the operating voltage, a decoupled structure may be applied, which has been applied in many kinds of batteries with improved performance (e.g., Li-air, W-air, and Zn-MnO₂ batteries) [69–72]. Recently, Zhong et al. reported a rechargeable Zn-Cu battery with a three-chamber structure [69]. By using a cation- and anion-exchange membrane, the Zn and Cu electrodes could work in alkaline and acidic electrolytes, respectively, connected by the middle neutral chamber. Benefiting from this design, the Cu electrode has a more positive potential, which leads to a Zn-Cu battery with a high discharge voltage plateau of 1.5 V. Although rechargeable Zn-Cu batteries present striking advantages of high capacity, facile fabrication, and cost-effectiveness, the research is in a preliminary stage and in-depth investigations are required.

2.5 Zn-Bi batteries

More recently, Bi₂O₃ has been used as the electrode material in alkaline solutions based on the reaction: [14]



When paired with a Zn electrode, the theoretical voltage can be 0.795 V. Benefiting from the six-electron transfer, the theoretical capacity of Bi₂O₃ can be 345 mAh g⁻¹. Fig. 4a and 4b provide the XRD patterns of the α-Bi₂O₃ electrode at different stages, indicating the

transformation from Bi_2O_3 to Bi during discharge and the reverse reaction during charge. A Zn-Bi battery thus exhibited an operating voltage of 0.789 V and a high discharge capacity of 325 mAh g^{-1} at 0.1 A g^{-1} . More importantly, the discharge curve showed an ultra-flat plateau with a much low slop of $\sim 0.1 \text{ V per Ah g}^{-1}$ [6]. To further study the reaction mechanism, the equilibrium potential was measured through the galvanostatic intermittent titration technique (GITT). As illustrated in Fig. 4c, the ultra-stable equilibrium plateau suggested a first-order phase transformation with the two-phase (Bi_2O_3 and Bi) coexistence. Furthermore, the small potential difference of 0.032 V also illustrated the high reversibility (Fig. 4d). Fig. 4f sheds light on the pure transition mechanism between $\alpha\text{-Bi}_2\text{O}_3$ and Bi upon discharging and charging, which contributes to the ultra-plat plateau. As for the rate performance, when the current density increased 200 times to 20 A g^{-1} , the capacity still reached 155 mAh g^{-1} (Fig. 4e). Hence, a Zn-Bi battery can achieve a high capacity, ultra-stable discharge plateau, and remarkable rate capability. However, restricted by the **severe** structure collapse at low current densities, this battery had poor cycling stability with the capacity retention of less than 50% after only 100 cycles at 1 A g^{-1} , which should be overcome in further research. **Besides, the theoretical potential in the alkaline solution is low, limiting the room for improvement. It is noted that the potential is related to the pH value, and thus a suitable alkaline concentration or hybrid alkaline/acidic electrolytes can be applied to further improve the voltage.**

2.6 Performance comparisons of Zn batteries

Fig. 5 summarizes the numbers of electron transfers and theoretical capacities of metallic Zn, Ag, Ni, Co, Cu, Bi, and their oxides/hydroxides. In terms of the reaction mechanism, Ag has two valence states from Ag to Ag^+ and Ag^{2+} , and thus delivers two different discharge voltage plateaus. Ni oxide or hydroxide only has one valence state from Ni^{2+} to Ni^{3+} . Although Co oxide has two valence states from Co^{2+} to Co^{3+} and Co^{4+} , the voltages for the two reactions are close [59]. Similarly, Cu exhibits two discharge voltage plateaus due to the

two valence states from Cu to Cu⁺ and Cu²⁺. Bi₂O₃ exhibits an ultra-flat discharge voltage based on a first-order phase transition process from Bi³⁺ to Bi with 6e⁻ transfer in total. Thus, the theoretical capacities are 248 and 497 mAh g⁻¹ for Ag → Ag₂O and Ag → AgO, 360 and 290 mAh g⁻¹ for NiO and Ni(OH)₂, 446 mAh g⁻¹ for Co₃O₄, 844 mAh g⁻¹ for Cu, and 345 mAh g⁻¹ for Bi₂O₃. As for the battery performance, restricted by the migration of Ag ions dissolved in the alkaline solution, the cycle life of Zn-Ag batteries should be further improved. Owing to the poor intrinsic electrical conductivity of Ni(OH)₂ and Co₃O₄, some conductive carbon materials may be included in the Ni and Co-based electrodes. Further, Co₃O₄ has high stability of cobalt ions in the spinel crystal structure and leads to the low capacity utilization of less than 50%, which should be well considered [73]. As for Zn-Cu and Zn-Bi batteries, their discharge voltages are relatively low (~0.8 V) and the capacity drop is severe, which should be further improved.

3. Zn electrode development

In plenty of works, a Zn plate or foil was utilized to fabricate the full battery due to its convenience [9,25,33,37,61]. However, the pristine planar Zn electrode confronts critical issues during operation, including dendrite growth during cycles, surface passivation, and hydrogen evolution [74]. As indicated in Reaction 1, zincate ions are reduced to metallic Zn during charge, which is controlled by the transport of zincate ions [75,76]. The consumption of zincate ions leads to severe polarization between the electrode surface and the bulk electrolyte. Due to the higher local current density, zincate ions are more likely to immigrate to the protrusions of the electrode surface, which serve as the nucleation sites for zinc dendrites [75,76]. With the charge-discharge cycles go by, the dendrite gradually grows, which can result in the electrochemical performance decay and even the short-circuit, reducing the cycle life and causing safety problems. The passivation caused by the deposition of ZnO is another remaining issue that needs to be conquered for Zn-based batteries. During

discharge, when the local concentration of zincate ions becomes saturated, the insoluble and insulating ZnO deposits from the solution and tightly adheres to the Zn electrode, leading to the decay of surface area and the loss of active material [77]. The hydrogen evolution reaction (HER) refers to the hydrogen generation resulted from both chemical and electrochemical reactions. On the one hand, Zn can react spontaneously to generate hydrogen in concentrated alkaline electrolytes [78]. On the other hand, the HER potential (-0.83 V vs. SHE) is less negative than the Zn reduction potential (-1.26 V vs. SHE) in the alkaline electrolyte, which makes the HER thermodynamically inevitable during operation [79]. The HER consumes Zn and charge energy, causing the capacity decay. Besides, the accumulated hydrogen is harmful to the battery package, resulting in the electrolyte leakage [76]. In order to eliminate the critical issues, many feasible strategies have been proposed, mainly including structure designs, surface modifications, and additive incorporations. Owing to the scope of this work, we mainly introduce the progress in rechargeable alkaline Zn batteries.

3.1 Structure designs

Structural designs mainly focus on the use of electrode with a high specific surface area and/or a porous structure to replace the pristine planar electrode. For one thing, a higher specific area contributes to the reaction rate. For another, the electrode with a suitable structure provides accommodation for the deposited Zn, suppressing the dendrite formation. The commonly applied Zn electrodes are composed of Zn nanoparticles, active additives, and binders, such as polytetrafluoroethylene (PTFE), polyvinyl alcohol (PVA), polyethylene oxide (PEO), and polyvinylidene fluoride (PVDF) [28,29]. Braam et al. fabricated a printed Zn-Ag battery using Zn particles mixed with binders and acetylene black as the conductive additive [29]. Ozgit et al. developed a rechargeable Zn-Ag battery that employed reduced graphene oxide (rGO) as a high-surface-area conductive additive to load the Zn nanoparticles with PTFE [28]. The use of rGO contributed to the formation of a stable continuous 3D conducting

network, which not only increased the electrochemical performance but also served as the accommodation for the product ZnO. Thus, the capacity of the battery with rGO was about 100 mAh g⁻¹, higher than the pristine electrode without rGO (65 mAh g⁻¹). More importantly, the lifetime was increased dramatically from 4 to 160 cycles. Recently, Zheng et al. found that a graphene substrate could regulate the morphology of deposited Zn, in which an epitaxial electrodeposition process was presented [80]. Zn first nucleated on the graphene surface and grew parallel to the surface. When the graphene surface was covered, Zn continued to grow in parallel on the deposited Zn surface layer. By this, Zn dendrite was well suppressed, enabling over 1000 stable cycles with coulombic efficiency of higher than 99% in a Zn-Mn battery.

In addition, binder-free Zn electrodes are extensively used in all kinds of Zn-based batteries, especially for flexible batteries [10,24,26,27,31,32,44,51,63]. A convenient and effective strategy is to electroplate Zn on the electrode substrates or current collectors. For example, Berchmans et al. constructed a Zn-Ag printable tattoo battery with a deposited Zn electrode, which could be used in wearable electronics [27]. Alla et al. used Zn-deposited tin-coated copper current collector as the negative electrode to fabricate a wire-shaped Zn-Ag battery based on helical band springs, which showed good stability and flexibility [26]. The substrate materials that have large surface areas such as carbon fibers [10], metal wires [24], and carbon cloth [63] are commonly used. Yan et al. presented a Zn-Ag battery based on the stretchable Ag nanowire electrode constructed by a lithographic filtration method [24]. Similarly, Xu et al. proposed a Zn-Ni battery using nickel nanowire arrays (NNA) as the substrate for the deposited Zn, which was rooted in the Ti foil vertically to work as the current collector and the substrate (Fig. 6a) [51]. During the deposition process, Zn plated on the NNA surface discretely, through which the dendrite formation was considerably suppressed. As a result, 5000 cycles were achieved with only about 12% capacity loss, as shown in Fig. 6b. Besides, carbon fiber is a suitable substrate material for the deposited Zn due to the good

conductivity and large surface area. Wang et al. employed carbon fibers as the Zn electroplating substrate (Zn@CF) to fabricate a Zn-Co battery for wearable and portable electronic devices [10]. Compared with the Zn plate, a battery with Zn@CF demonstrated the capacities of 162 and 78 mAh g⁻¹ at the current densities of 1 and 10 A g⁻¹, respectively, which were higher than those with the Zn plate (160 and 48 mAh g⁻¹). More importantly, the dendrite was suppressed for even 2000 cycles.

To further optimize the Zn electrode performance, nano-structured Zn was introduced to the electrode. Li et al. deposited the Zn nanoflakes on the carbon cloth as the negative electrode of a quasi-solid-state flexible Zn-Ag battery [31]. Due to the microstructure of the Zn nanoflakes, the electron transfer of the electrode was dramatically improved. Later, the same group used nanosheets electroplated on a carbon nanotube fiber (CNTF) nitride-doped nanocarbon array (NCA) as the negative electrode [32]. In addition to depositing Zn on the substrate, ZnO was also selected as the additive. Ullah et al. synthesized ZnO nanorods with a high surface area, uniform geometry, and well-aligned direction [20]. The characterization results revealed that the size of the nanorods is below 500 nm with an aspect ratio of greater than 20, which permitted lower solubility and better structural stability compared with the commercial ZnO powder. The capacity of a Zn-Ag battery using commercial ZnO powder declined to below 80% after 15 cycles, while the one with ZnO nanorods operated stably for 18 cycles. Liu et al. deposited ZnO directly on 3D N-doped carbon fiber arrays coated on the carbon cloth, which dramatically enhanced the electric conductivity, alleviated the shape change, suppressed the Zn dendrite growth, and ameliorated ion diffusion [44]. In a Zn-Ni battery, the capacity retention reached 91.45% and 72.90% after 1000 and 2400 cycles, respectively. Besides using conductive substrates, a 3D sponge Zn electrode was developed by Parker et al., which demonstrated a monolithic, porous, aperiodic architecture [39]. In a Zn-Ni battery with this sponge Zn electrode, the discharge capacity reached 743 mAh g⁻¹_{Zn}

and could be recharged to over 95% capacity after the deep discharge at 10 mA cm^{-2} . Besides, the battery demonstrated well capability as a start-stop battery for microhybrid vehicles, and over 50000 duty cycles were achieved with minimal shape change and no dendrites in the Zn electrode.

3.2 Surface modifications

Surface modifications, which use coating materials to form a protective layer on the Zn surface [81–84], are widely used in Zn-based batteries to suppress passivation and the HER, as well as adjust the deposited Zn morphology. For example, Schmid et al. developed Zn particles with silica coatings as the negative electrode materials to reduce the passivation and the HER [81,82]. They found that the silica coatings could react in the alkaline solution and form a gel Si(OH)_4 layer, which not only reduced the direct contact between the Zn electrode and the alkaline solution but also controlled the zincate and OH^- ions diffusion. As a result, the Zn utilization rate with silica coatings was up to 69%, higher than the pristine Zn electrode (52%). Additionally, the HER was reduced by 40% with the silica coatings. Later, the same group developed $\text{Bi}_2\text{O}_3\text{-ZnO-CaO}$ as the coatings for Zn particles [83]. In the cycle tests, the Zn electrode coated with 3.2 wt% $\text{Bi}_2\text{O}_3\text{-ZnO-CaO}$ could operate for 20 cycles, while the uncoated Zn failed after the 1st cycle due to the passivation. Besides the effects on suppressing passivation, it has been reported that Bi_2O_3 also has evident effects on suppressing the dendrite and the HER [85,86]. Kim et al. used CuO nanoparticles to modified the Zn particles by the sol-gel technique [87]. The cycle ability of the Zn electrode with and without 0.1 wt% CuO was 26.33 h ($658.25 \text{ mAh g}^{-1}$) and 18.16 h (454 mAh g^{-1}), respectively. Apart from oxides, carbon-based materials have also been investigated as the modified materials. Zhou et al. used graphene oxide (Zn@GO) to modify the Zn mesh electrode by a facile solution casting method [88]. As shown in Fig. 6c, the GO layer not only accelerated the electron transfer but also protected the Zn from passivation. Fig. 6d shows that the

Zn@GO electrode presented better recyclability after 10 cycles. In the first 200 cycles, the accumulated discharge capacity with the Zn@GO electrode was 61.5 mAh cm^{-2} , which was higher than the one with the bare Zn mesh electrode. Besides, other coating layers such as nano-ZrO₂, 3D nanoporous ZnO, and polyamide/Zn(TfO)₂ layer have been applied to neutral Zn batteries, which can also be tested in alkaline Zn batteries [89–91].

3.3 Additive incorporations

Based on alkaline solutions, plenty of additives have been incorporated to improve the electrochemical performance of the Zn electrode, mainly including metal oxides and organic additives. In the alkaline solution, metal oxides dissolve into metal ions (Sn²⁺, Pb²⁺, Bi³⁺, etc.), which have less negative potentials than Zn [92–94]. During reduction, the introduced ions deposit on the surface of the electrode before Zn and thus affect the later Zn deposition process [74]. Kim et al. investigated the impacts of SnO as the electrolyte additive to adjust the Zn deposition in the alkaline solution [92]. In the absence of SnO, the microscopic images revealed that the dendrite formation was very severe at the current density of 40 mA cm^{-2} . However, the deposited Zn became dramatically uniform after increasing the content of SnO to $3 \times 10^{-3} \text{ M}$, indicating that a higher additive content contributed to the greater inhibition of dendrite formation, but excess SnO led to rough and crumbling deposited Zn due to the excess Sn formation. Organic additives are other commonly used additives, mainly including surfactants [95,96], alcohols [97], and polymers [98]. The organic additives can be absorbed on the electrode surface to form a protective layer, which can reduce the direct contact between the electrode and electrolyte and regulate the deposited zinc morphology [99]. For example, Liu et al. investigated the dodecyltrimethylammonium bromide (DTAB) surfactant as the corrosion and passivation inhibitor for the Zn electrode [96]. A uniform and fluffy protective layer was formed on the surface of the electrode due to the well absorption and moisture retention of DTAB, which not only reduced the direct contact between the electrode

and the electrolyte but also contributed to the diffusion of ions and solution reactions. Besides the absorption, some organic additives also have effects on the electrode reaction. Lee et al. investigated the effects of alkoxide and acetate ions on the inhibition of passivation [97]. As shown in Fig. 6e, in the alkaline solution, alcohols changed into alkoxide ions, which replaced some hydroxide ions in the zincate ions to form Zn alkoxide complexes $\text{Zn}(\text{OH})_{4-n}(\text{OR})_n^{2-}$ (OR represented alkoxide ions). The decomposition reaction rate of $\text{Zn}(\text{OH})_{4-n}(\text{OR})_n^{2-}$ was slower than that of zincate ions, indicating that the ZnO formation was slowed down. The effects of isopropyl alcohol (IP), ethylene glycol (EG), glycerol (GL), and meso-erythritol (ER) were also compared in the work. As shown in Fig. 6f, it was found that the discharge capacities with alcoholic additives were higher than the one without additives through 10 cycles. The discharge capacity with ER (42.2 mAh g^{-1}) was about five times than that with IP (8.2 mAh g^{-1}) at 10th cycle.

Apart from the aforementioned works, flowing electrolytes, pulsed charging protocols, using hydrogel electrolytes, and changing the types of electrolytes have also been proposed as effective strategies to improve the Zn electrode performance. The flowing electrolyte can effectively suppress dendrite and passivation through accelerating ion transfer and bringing out the products and by-products [2]. Pulsed charging protocols can regulate the zinc deposition through introducing a relaxation time after a short $\text{Zn}(\text{OH})_4^{2-}$ reduction period to re-establish the concentration of $\text{Zn}(\text{OH})_4^{2-}$ at the electrode surface [100]. In the hydrogel electrolytes, limited water molecules and their limited movement can suppress the HER to a certain extent [101]. In a neutral electrolyte composed of $1 \text{ mol kg}^{-1} \text{ Zn}(\text{TFSI})_2 + 20 \text{ mol kg}^{-1} \text{ LiTFSI}$, Zn^{2+} is surrounded by TFSI^- instead of water. To this end, the HER is effectively suppressed, leading to the Coulombic efficiency of nearly 100% [102]. The proper combination of the aforementioned multiple strategies is probably a promising way to accelerate the commercialization of the Zn electrode.

4. Electrolyte development

Among alkaline electrolytes, the KOH solution has considerable solubility of zinc salt and higher conductivity than NaOH and LiOH [4]. Table 1 summarizes the electrolytes applied in recent reported Zn batteries, the majority of which utilizes the KOH electrolyte with different concentrations. As a rule, increasing the concentration of KOH can improve conductivity, thereby enhancing the electrochemical performance. However, the viscosity of the electrolyte and growth of ZnO can also be enhanced dramatically, which accelerate the Zn dendrites and damage cycling stability [17]. To this end, 6 M KOH is generally applied in alkaline Zn batteries. Besides, to guarantee the reversible reaction of the Zn electrode, Zn(Ac)₂ is usually added into the KOH solution instead of ZnO due to its higher solubility [103]. However, the leakage of liquid alkaline electrolytes is a severe issue for applications. To solve this problem, a sealed membrane is crucial for the battery [104]. For example, Ugalde et al. designed a double-membrane with different pore morphologies in a Zn-air battery, which reduced the water loss in the electrolyte under high humidity levels and increased the water absorption by 12 times [105].

For the feasible applications in flexible devices, hydrogel and gel polymer electrolytes which consist of the abundant frame and functional groups, have been developed owing to their decent flexibility, simple constructing process, and considerable ionic conductivity (10^{-3} S cm⁻¹) [106,107]. Moreover, they can prevent the leakage of liquid electrolytes and reduce the Zn dendrite to some extent. Among them, PVA is a promising one that can soak with aqueous electrolytes under high temperatures [33]. Besides, polyacrylic acid (PAA) can also mix with K⁺ to be gel electrolyte. Wang et al. constructed a PVA and PAA copolymer film with a ratio of 2:1 soaked in 1 M KOH and 10 mM Zn(Ac)₂, which could balance ion transportation and mechanical stability [10]. When served into a flexible Zn-Co battery, a single battery could light a light-emitting diode (LED) in the potential range of 1.7-2.3 V no

matter bent, twisted or folded. Zamarayeva et al. reported a Zn-Ag wire battery using a PVA-KOH polymer electrolyte [25], which showed a specific discharge capacity of 1.4 mAh cm^{-1} at 0.5C, a slight capacity loss of 2% after 170 cycles, and no significant capacity change under multiple bending conditions. Further, sodium polyacrylate hydrogel (PANa) has been applied [63], which can absorb much more water than PVA and PAA and maintain good mechanical stability soaked with a high concentration of KOH. Fig. 7 shows a PANa polyelectrolyte with 6 M KOH and 0.2 M $\text{Zn}(\text{Ac})_2$, which can manipulate under a wide temperature range [63]. As depicts in Fig. 5a, after fused with evaporated ions, it could stretch 14 times under -20 and 50 °C. Even at an ultra-low temperature of -50 °C, the stretchability could still reach 9 times. In comparison, it freezes below 0 °C and fractures under 50 °C after saturated with water. Thereby, the high concentrated solution contributed to the decreased freezing point and much low water content. Besides, the much higher ion conductivity of 0.057 and 0.163 S cm^{-1} could be achieved under both low (-20 °C) and high (50 °C) temperatures than other polymer electrolytes (Fig. 7b). As illustrated in Fig. 7c, with an increase in temperature, micropores become larger, which facilitates rapid ion transport, leading to high ionic conductivity. Consequently, a flexible Zn-Co battery with this electrolyte delivered an energy density of 172 Wh kg^{-1} and capacity retention of 87% after 10000 cycles under -20 °C, while the values changed to 210.1 Wh kg^{-1} and 58% under 50 °C.

Through the exploration of electrolytes, the applications of alkaline Zn batteries have been expanded largely. However, many practical issues are still challenging. For example, the polymer electrolytes may break after repetitive deformations when used in wearable devices, which can be solved by adding Fe^{3+} to obtain the seal-healing ability [108]. Besides, the interface contact of the gel electrolyte to the solid electrode is usually poor, which should be well addressed in the future.

5. Summary and perspective

In this article, recent progress in rechargeable alkaline Zn batteries is reviewed, including their reaction mechanisms, positive electrodes, electrolytes, and Zn electrodes. Focused on the well-developed Zn batteries such as Zn-Ag and Zn-Ni batteries, breakthroughs in the performance and structures are obtained. In addition, innovations on the new types of batteries like Zn-Co, Zn-Cu, and Zn-Bi have also been reported. These achievements have greatly encouraged the development of high-performance, cost-effective, and intrinsic safe alkaline Zn batteries. For further commercialization, there still remain some issues that need to be addressed imperatively.

First, exploring new positive electrode materials is significant to promote rechargeable Zn batteries. The relatively low practical utilization ratio of positive materials leads to unsatisfactory capacity. For example, Ag generally oxide to Ag_2O in an alkaline environment, which limits the further utilization of AgO. Although Co_3O_4 is proposed to be oxidized to CoO_2 during charge, considering the achieved capacity that is away from the theoretical value, the reaction mechanism is still under debate. Although Zn-Cu and Zn-Bi batteries have great potential to get high specific capacities, the operating voltages are less than 0.8 V, resulting in low power and energy density. In addition to the capacity and discharging voltage, cycling stability is also very vital for the application. The cycling performance decay is usually ascribed to the Zn electrode issue, while the effects on the positive electrode are hardly studied [10,51,59]. To counter the above issues, some feasible work may be carried out, such as decreasing the particles to nanoscale through changing the microstructures, embedding the nanoparticles into carbon materials, constructing hierarchical structures, and changing the surface state through introducing some defects or doping. Furthermore, to improve the contact interfaces between electrode and electrolyte, the design of electrode structures like increasing the hydrophilic properties is also essential.

Second, the stability and durability of the zinc electrode should be enhanced. For the batteries using liquid electrolytes, the use of a porous electrode structure combining with the pulsed charging protocols may be an effective strategy to regulate Zn deposition [100]. The porous electrode can provide accommodations for Zn deposition, but the real capacity decreases due to the existence of substrate materials. Additionally, the substrate materials with better stability should be developed. Flowing the electrolyte is a feasible approach to suppress both the dendrite and passivation, which is especially practical for a large-scale energy storage device [3]. While for the small-scaled battery, how to introduce the flowing system is still absent in research. Focusing on hydrogen evolution, the key is to explore effective additives that can suppress the reaction, which is still on the road.

Third, the research of electrolytes, including the solvent, salt concentration, and additive, is also crucial. Due to the water electrolysis upon dissolution and deposition of metallic Zn, abundant oxygen and hydrogen can release in alkaline electrolytes, thereby causing the leakage. Besides, aqueous electrolytes cannot operate normally at subzero temperatures because of the inevitable freeze of water. To address these issues, it may be useful to add effective hydrogen evolution inhibitors, use optimal electrolyte concentration to decrease the freezing point [109], apply the flowing electrolyte, and set air vent to release the pressure timely. Apart from alkaline electrolytes, using neutral electrolytes may be a promising strategy to address the Zn dendrite. Besides, constructing an acid-alkaline dual electrolyte through a reasonable ion-exchange member can also improve the operating voltage [110]. As for the solid-state electrolytes, the poor ionic conductivity limits the whole electrochemical performance. Subject to the weak adhesion between the solid-state electrolyte and two electrodes, the interfacial resistance is high. Moreover, the electrolyte may run out quickly under various deformation, which also deteriorates the cycling behavior. Hence, for the feasible application on a wearable device, it is necessary to further increase the ionic

conductivity to the level of aqueous one ($10^{-1} \text{ S cm}^{-1}$), adjust the interface contact through modifying electrode surface structure, and enhance the self-healing capability [108].

Finally, the battery configuration and performance evaluation require considerable attention. Among the battery assembly, the high internal resistance from the poor contact waste the capacity, especially in the stack, and the sealing level determines the possibility of leakage. Hence, novel configurations that can assemble easily and prevent the short-circuit are in great need. Besides, the performance tests under bent, stretched, and/or twisted operations are also important for flexible batteries [111]. More importantly, since the cycling stability tests are usually continuous, the self-discharge performance is still lacking, and different operating conditions (e.g., operating temperatures) should also be considered.

In short, many challenging works should be carried out aiming at the practical capacity, rate capability, cycling stability, etc. It is believed that rechargeable alkaline Zn batteries can be promising in the near future.

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