Recent progress and challenges of co-based compound for aqueous Zn battery

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Abstract
Aqueous Zn battery turns to be a rational approach for next-generation energy storage devices due to the high abundance, admirable theoretical capacity and excellent safety. As an emerging candidate of the ideal cathode material for Zn battery, Co-based compounds have drawn increasing attentions because of the high output voltage, remarkable theoretical capacity and excellent redox property. In this review, a summary of recent developments of Co-based cathodes in aqueous Zn batteries is presented, including Co3O4, Co(OH)2, NiCo2O4 and other Co-based compounds. In addition to charge storage mechanisms, smart strategies including structural modulation, composition regulation, and defect engineering are systematically introduced, and their structure-performance relationships are discussed in depth. Finally, limitations and proposed future work are demonstrated.

KEYWORDS
aqueous battery, cathode, cobalt, Zn battery

1 INTRODUCTION
Meeting the requirements of booming economy, the intensive usage of fossil fuels becomes a necessity for transportation and power supply, inevitably generating pollutants released to the environments, specifically, the uncontrolled carbon emission.1–7 It is of great importance to explore a convenient, controlled and sustainable solution to generate and store the renewable energy, in order to reduce the exhaust emission and protect the environment. Relative speaking, installation cost is lower for energy storage in an electrochemical way.8–9 In recently years, extensive studies have been conducted to develop various types of electrical energy storage and generating devices, such as supercapacitors, batteries and fuel cells.10–24 Therein, batteries that build the bridge between supercapacitors...
and fuel cells realistically store and deliver the energy to satisfy the human needs in modern society.\[8\]

A ideal battery needs to meet several requirements, such as safety, environmental friendliness, energy/volume density, rate ability and abundance of raw materials.\[25\] Li ion batteries (LIBs) have attracted tremendous efforts due to the light weight and high energy density. However, major drawbacks of LIBs hinder the large-scale applications, including high flammability, high cost and mechanical inflexibility.\[25-27\] Conversely, multivalent ion batteries such as Al, Mg, and Ca ion batteries have attracted considerable attentions recently.\[28-30\] As the representative multivalent ion battery, aqueous Zn ion batteries (ZIBs) become competitive owing to the high theoretical capacity of Zn anode, high safety and low cost.\[18,31-34\] Moreover, ZIBs are characterized with the two-electron transfer mechanism and long history of being applied in alkaline electrolytes. Furthermore, easy recyclability and high abundance promote the wide application.\[26,35-40\]

To realize the long-term stability and high specific capacity of ZIBs, great efforts have been expended to explore an ideal cathode material, including inorganic and organic compounds.\[36-37,39,41-48\] Therein, V-based, Mn-based and Prussian blue analogues (PBA)-based compounds are the most studied cathode materials. Specifically, the large tunnels in V-based compounds promote the accommodation of Zn\(^{2+}\) ions during the charge/discharge process. However, the structure degradation caused by the repeated intercalation of Zn\(^{2+}\) through the layered structure impedes the deeper development of V-based compounds as the cathode materials.\[18-19,49-78\] Mn-based compounds, as another representative, possess tunable morphologies, nontoxicity, high purity, high voltage, low cost, and high density.\[16-17,41,65,79-105\] However, they suffer from the cathode dissolution and intrinsic poor electrical conductivity, leading to the rapid decay of the electrochemical performances.\[106\] Differently, PBA-based compounds with a 3D open framework offer a fast ion transfer and high output voltage.\[107-114\] But their applications are limited by the poor intrinsic capacity, short lifescan and low rate capability.\[115\] In addition to the above cathode materials, newly explored inorganic compounds have been emerged in recent years, including Co-based,\[116-117\] Mo-based,\[43,116,118-122\] sulfates,\[118,123-124\] and polyanion compounds.\[33,120,125-122\]

Besides the inorganic compounds, organic compounds benefit from their flexibility, mechanical strength, multiple electron reactions, sustainability, and chemical richness.\[133-137\] Chen and his coworkers\[136\] firstly applied quinones as a organic cathode in ZIBs and achieved an impressive capacity of 335 mAh g\(^{-1}\) at 20 mA g\(^{-1}\) with a 87% capacity retention over 1000 cycles. Based on the experimental and theoretical results, carbonyl groups in quinones were responsible for the superior electrochemical performances. To enlarge the working temperature window, Wang and high coworkers\[138\] assembled a zinc-organic battery using phenanthrenequinone macrocyclic trimer as the cathode material and DMF as the electrolyte. An excellent cycling stability of nearly zero capacity decay over 20,000 cycles and a wide temperature window from -70 °C to 150 °C were realized. To further enhance the specific capacity and rate capability, Lu and his coworkers\[47\] developed a novel organic cathode based on a aromatic molecular crystal with a strengthened $\pi$-$\pi$ stacking interaction. Owing to the enhanced electron and ion transfer, the assembled battery exhibited a superior rate performance of 62.6% retention after a 162.75-fold current density increase. Despite the recent achievements, however, the relatively sluggish ionic conductivity and low mass loading limit the energy density and rate performance of organic cathodes. In addition, the membrane used to prevent the unwanted reactions between soluble products and Zn anode is too expensive to possibly hinder the commercialization.\[106,139\]

Among the various cathode materials, great progress of Co-based compounds as the ZIB cathodes have been seen in recent years because of the excellent redox property, high theoretical capacity (446 mAh g\(^{-1}\)), good reversibility and high potential.\[140-143\] For example, Shang et al.\[144\] prepared porous nanowire Co\(_2\)O\(_4\) structures, which was assembled with Zn plate to form a Zn-Co batteries, exhibiting a 230 mAh g\(^{-1}\) specific capacity at 0.5 A g\(^{-1}\). Shang et al.\[145\] fabricated NiCo\(_2\)O\(_4\) nanowire spinel structures with a intricate control of hydrothermal temperatures. Outstanding rate capability was presented that 73.8% retention was reserved after 16-fold current density increase.\[145\] Despite the developments made in Co-based compounds as the ZIB cathodes, the recent reviews are mainly focused on V-based,\[146\] Mn-based\[40\] and organic cathode materials.\[147\] A review on the Co-based cathode materials benefits the rational design of the battery and promotes the development of energy storage device in future. Therefore, we herein summarize the recent progress of Co-based compounds as a cathode material in Zn-based batteries, including the charge storage mechanisms, the smart designs of the cathodes and the structure-performance relationships.

## 2 | CO\(_3\)O\(_4\)-BASED CATHODE MATERIALS

Owing to its high theoretical capacity of 446 mAh g\(^{-1}\) and high output voltage (1.78 V) with Zn anode, Co\(_3\)O\(_4\) has been intensively studied as cathode in Zn-based batter-
The energy storage mechanism of Co₃O₄-based ZIBs in alkaline electrolytes are shown in Figure 1.[143,148–150] During the charging, Co₃O₄ is converted to CoO₂ in two steps with CoOOH as the intermediate by reacting with OH⁻ from the alkaline electrolyte; meanwhile, Zn(OH)₄²⁻ gains electrons to form metal Zn and release OH⁻ into the electrolyte simultaneously. During the discharging, Zn(OH)₄²⁻ is generated from the reaction between Zn and OH⁻ in the electrolyte; simultaneously, CoO₂ gains electrons to transform back to Co₃O₄ in two steps.[149] Enlightened by this mechanism, small amounts of Zn(Ac)₂ was added into the electrolyte to increase the OH⁻ concentration due to the hydrolysis of CH₃COO⁻ ions, which promoted the reversible conversion of Zn and Zn(OH)₄²⁻ and enhanced the cycling performance.[151]

Positive electrode

$$\text{Co}_3\text{O}_4 + \text{OH}^- + \text{H}_2\text{O} \leftrightarrow 3\text{CoOOH} + \text{e}^- \quad (1)$$

$$\text{CoOOH} + \text{OH}^- \leftrightarrow \text{CoO}_2 + \text{H}_2\text{O} + \text{e}^- \quad (2)$$

Negative electrode

$$\text{Zn(OH)}_4^{2-} + 2\text{e}^- \leftrightarrow \text{Zn} + 4\text{OH}^- \quad (3)$$

2.1 Structure modulation

Currently, the major barriers for the applications of Co₃O₄ as advanced cathode is its intrinsic poor conductivity, limited active sites, and large volume change. To figure out these issues, plenty of efforts have been made to exploit various Co₃O₄-based nanostructures as cathodes since nanostructured materials can exhibit a higher surface area and more abundant active sites as well as shorter electron/ion transport pathways than the bulk one. So far, varieties of Co₃O₄ nanostructures such as nano cluster, nanowire, nanosheet and 3D hierarchical structures[144,149,152–154] have been synthesized and delivered good electrochemical performance. For example, uniform Co₃O₄ nanosheets were grown on Ni foam via a facile electrodeposition method and exhibited a mesoporous structure (Figure 2A).[149] The Co₃O₄ nanosheets underwent a two-step redox reaction in 1 M KOH electrolyte, as revealed by the redox peaks located at 0.37/0.286 and 0.464/0.415 V in cyclic voltammetric (CV) curves (Figure 2B). When coupling a Zn deposited on carbon fibers (Zn@CF) electrode, a large potential difference of 1.844 V was observed, which means the full battery would deliver a high discharge voltage platform. Figure 2C are the galvanostatic charge-discharge (GCD) curves of the as fabricated Zn@CF//Co₃O₄ battery at various current densities, showing two high discharge voltages of 1.73 and 1.83 V. Moreover, a high specific capacity of 162 mAh g⁻¹ at 1 A g⁻¹ (based on Co₃O₄ mass) and good rate capability (over 48.1% capacity retention from 1 to 10 A g⁻¹) were obtained for this battery. Additionally, as shown in Figure 2D, this Zn@CF//Co₃O₄ battery could maintain 80% retention of initial capacity was achieved over 2000 cycles at 1 A g⁻¹ and nearly 100% Coulombic efficiency, demonstrating a high reversibility and long lifespan (Table 1). Similarly, Shang et al. reported a porous Co₃O₄ nanowires on Ni foam as a binder-free cathode, and the assembled Zn/Co₃O₄ battery reached a large capacity of 230.0 mAh g⁻¹ and an excellent energy density of 308.8 Wh kg⁻¹ (based on the whole electrode materials).[144]

2.2 Oxygen defects

Besides the structural modulation, the creation of oxygen defects is a new and available strategy to boost the capacity and rate capability of Co₃O₄ materials.[150,152–157] On the one hand, the introduced oxygen defects can well tune the electronic states and surface properties of Co₃O₄, thus enhancing the intrinsic electrical conductivity and redox reaction kinetics. On the other hand, these oxygen defects can also directly function as active sites for surface redox reaction, resulting in high electrochemical performance. Lu and his coworkers prepared an ultrathin Co₃O₄ nanosheet followed by solvothermal reduction by ethylene glycol to form oxygen-defect-rich Co₃O₄ cathode materials (seen in Figure 3A).[156] As for the advantages
of oxygen vacancies, Figure 3B suggested a much lower charge transfer resistance with the introduction of oxygen vacancies, thus facilitating the electron transport. On the other hand, the redox reaction among Co species was affected by the adsorption of OH\(^-\). Based on DFT calculation, the adsorption energy of OH\(^-\) was only -4.44 eV with one oxygen vacancy, much lower than -2.97 eV for the perfect surface of Co\(_3\)O\(_4\), indicating a promotional effect of oxygen vacancies on the redox kinetics. Owing to the enhanced electrical conductivity and redox reaction kinetics, a good specific capacity of 240.8 mAh g\(^{-1}\) and almost zero capacity decay over 10,000 cycles were delivered shown in Figure 3C and D.

In addition to the solvothermal reduction, inert gas treatment is effective in introducing oxygen vacancies. Xu et al. synthesized Co\(_3\)O\(_4\) nanoparticles dispersed on nitrogendoped mesoporous carbon (N-MC) derived from a new coordination polymer [Co(dpdc)(dpphen)]n-2nH\(_2\)O, followed by heat treatment under N\(_2\) to generate oxygen vacancies.\(^{[150]}\) Owing to the large amounts of oxygen vacancies originating from coordination polymers, the transport of electrons turned to be more rapid, achieving a high specific capacity of 213.7 mAh g\(^{-1}\) at 1A g\(^{-1}\). Besides calcination under N\(_2\) gas, Ar plasma is also applied to engrave Co\(_3\)O\(_4\) to generate abundant oxygen vacancies.\(^{[155]}\) The introduction of oxygen vacancies enlarged the surface area for redox reaction between Co-O and Co-O-H, thus enhancing the electrochemical performance, delivering a superior cycling stability of 1600 cycles at 2 A g\(^{-1}\).

Besides the treatment by inert gas/plasma, ion doping is adopted in the synthesis of Co\(_3\)O\(_4\) cathode to generate abundant oxygen vacancies, thus enhancing the charge/discharge rate, specific capacity and intrinsic conductivity. Li et al.\(^{[152]}\) doped Zn\(^{2+}\) into Co\(_3\)O\(_4\) nanowires to initiate the insulator-metal transition. Based on the DFT calculations, Co\(^{2+}\) ions were located in the tetrahedrons and Co\(^{3+}\) ions were located in the octahedrons. Different from the pristine Co\(_3\)O\(_4\) which was an inert material, doping of Zn into the lattice would replace both Co\(^{2+}\) and Co\(^{3+}\) ions and distort the lattice structure, enhancing electrical conductivity. Moreover, Co\(^{3+}\) ions were partially substituted by Zn\(^{2+}\) to generate oxygen vacancies proven by the higher intensity of O\(_I\)/O\(_{II}\) ions in XPS spectra, where O\(_I\) ions were oxygen deficient while O\(_{II}\) ions were with full complement. Owing to the Zn\(^{2+}\) doping, a much higher rate performance was delivered at a series of current densities in a mild electrolyte. Specifically, after a
## Table 1: Electrochemical performances of Co-based cathodes in aqueous Zn batteries

| Cathode                  | Anode          | Electrolyte                                 | Capacity [mAh g⁻¹] or Capacity retention [%] / current density [A g⁻¹] | Stability capacity [mAh g⁻¹] / cycle number / current density [A g⁻¹] | Ref |
|--------------------------|----------------|---------------------------------------------|------------------------------------------------------------------------|--------------------------------------------------------------------------|-----|
| Co₃O₄ NW/NF              | Zn plate       | 6 M KOH and 0.2 M Zn(CH₃COO)₂                | 230/0.5                                                                | 66.8/3000/2                                                              | 144 |
| Co₃O₄ NS/CC              | Zn foil        | 6 M KOH and 0.02 M Zn(CH₃COO)₂               | 792/1 mA cm⁻²                                                          | 70/200/1 mA cm⁻²                                                          | 148 |
| Co₃O₄ NW/NF              | Zn/CF          | 1 M KOH and 0.01 M Zn(CH₃COO)₂               | 162/1                                                                  | 80/2000/1                                                                | 149 |
| Co₃O₄/MCN                | Zn slice       | 4 M KOH                                     | 213.7/1                                                               | N.A.                                                                     | 150 |
| Co₃O₄/CC                 | Zn/CC          | 2 M ZnSO₄ and 0.2 M CoSO₄                   | 180.6/0.5                                                              | 94.6/2000/2                                                               | 5   |
| Zn-Co₃O₄ NWs/CNTF         | Zn NS/CNTF     | ZnSO₄, CoSO₄, and CMC gel                   | 1.47 mAh cm⁻²/1 mA cm⁻²                                                | 93.8/5000/20 mA cm⁻²                                                      | 152 |
| Co₃O₄ₓ/CFC               | Zn plate/CFC   | 6 M KOH and 0.2 M Zn(CH₃COO)₂               | ~800/10 mA cm⁻²                                                        | 93.6/1600/2                                                               | 155 |
| Co₃O₄/CC                 | Zn plate       | 6 M KOH and 0.5 M Zn(CH₃COO)₂               | 240.8/2 mA cm⁻²                                                        | ~zero decay/10000/40 mA cm⁻²                                               | 156 |
| Co₃O₄ₓ/NF                | Zn foil        | 6 M KOH and 0.2 M Zn(CH₃COO)₂               | 384/1                                                                 | Constant/60000/10                                                         | 157 |
| CoSe₂₋ₓ@C/CC             | Zn foil        | 5 M KOH and 0.02 M Zn(CH₃COO)₂               | 10.4 mAh m⁻²/6 mA cm⁻²                                                 | 0.02% decay cycle-1/4000/10 mA cm⁻²                                      | 158 |
| Co(OH)₂ NS/Co foam       | Zn plate       | 6 M KOH and 0.5 M Zn(CH₃COO)₂               | 0.21 mAh cm⁻²/1 mA cm⁻²                                                | 83.3/10000/20 mA cm⁻²                                                     | 160 |
| CoₓAl₀.₂-LDH             | Zn foil        | 6 M KOH saturated with ZnO                  | 316/1.8                                                                | 96/8000/10                                                               | 162 |
| NCHO/Co-Ni foam          | Zn plate       | 6 M KOH and 0.5 M Zn(CH₃COO)₂               | 2.13 mAh cm⁻²/8 mA cm⁻²                                                | ~90/30000/40 mA cm⁻²                                                      | 163 |
| NiCo DH/NF               | Zn foil        | 2.5 M KOH saturated with ZnO                | 329/0.5 mA cm⁻²                                                        | 73/850/6 mA cm⁻²                                                          | 164 |
| NCHO NS/SS yarn          | Zn/SS yarn     | 6 M KOH and 0.2 M Zn(CH₃COO)₂               | 16.6 mAh cm⁻³/31 mA cm⁻²                                               | 60/1000                                                                  | 165 |
| NiCo₂O₄ NS/CC            | Zn NS/CC       | ZnSO₄, Na₂SO₄, H₂BO₃                        | 183.1/1.6                                                              | 82.7/3500/6.4                                                            | 38  |
| NiCo₂O₄ NW/NF            | Zn plate       | 6 M KOH and 0.1 M Zn(CH₃COO)₂               | 230.1/0.5                                                              | 63.23/1000/10                                                            | 145 |
| P-NiCo₂O₄ₓ NS            | Zn plate       | 1 M KOH and 0.05 M Zn(CH₃COO)₂              | 361.3/3                                                                | ~73.6/5000/25.3                                                          | 166 |
| P-CoMoO₂ NS/NS            | Zn plate       | 6 M KOH and 0.2 M Zn(CH₃COO)₂               | 431.4/10                                                               | 80/12000/60 mV s⁻¹                                                        | 31  |
| Co₃S₄ NS/NF              | Zn plate       | 3 M KOH and 0.1 M Zn(CH₃COO)₂               | 317/1                                                                  | Constant/5000                                                            | 159 |
| NF-NCO@CMO@CO            | Zn plate       | 2 M KOH and 0.02 M Zn(CH₃COO)₂              | 2.51 mAh cm⁻²/2 mA cm⁻²                                                | 73/2000/10 mA cm⁻²                                                        | 167 |

Abbreviations: CC, carbon cloth; CCH, Co(CO₃)₀.₅(OH)ₓ⋅0.₁₁H₂O; CF, carbon fibers; CFC, carbon fiber cloth; CMC, carboxymethyl cellulose sodium; CMO, CoMoO₄; CNTF, carbon nanotube fiber; CO, Co₃O₄; DH, double hydroxide; MCN, mesoporous carbon nanosheets; N.A., not available; NCHO, Ni-Co hydroxide; NCO, NiCo₂O₄; NF, nickel foam; NIV-LDH, Nickel-vanadium layer double hydroxide; NS, nanosheets; NW, nanowires; NWA, nanowire array; SS, stainless steel.

20-fold current density increase, Zn-doped Co₃O₄ cathode still maintained 65.3% of the capacity while only 38.1% was retained in the pristine counterpart. Due to the oxygen vacancies and intrinsic conductivity, an excellent cycling performance of 93.8% retention over 5000 cycles and 98.4% Coulombic efficiency were achieved in the assembled fiber-shaped and all-solid-state Co₃O₄-based aqueous rechargeable Zn battery.
2.3 Combined structure and defect engineering

In addition to the standalone oxygen defect engineering, a combined strategy of tuning both the structure and defects are developed to realize a synergy. The oxygen vacancies would promote the charge transport, enhance the intrinsic electrical conductivity and facilitate the surface redox reaction. On the other hand, 3D ordered mesoporous structure would benefit the ion transport and electrolyte permeation, and prevent the volume change during the charge/discharge cycle. Teng et al.\textsuperscript{157} fabricated a 3D nanostructured Co\textsubscript{3}O\textsubscript{4} by applying nanocasting method under 300 MPa using KIT-6 as a hard template. Combining the N\textsubscript{2} heat treatment and doping with P element with Na\textsubscript{2}H\textsubscript{2}PO\textsubscript{4}+H\textsubscript{2}O steam, a 3D mesoporous Co\textsubscript{3}O\textsubscript{4} cathode with abundant oxygen vacancies were formed where Co\textsuperscript{2+} and Co\textsuperscript{3+} coexisted in the lattice (seen in Figure 4A). As shown in Figure 4B, the pie shape morphology and ordered mesopores of Co\textsubscript{3}O\textsubscript{4} was maintained after reduction treatment, suggesting a strong interaction among the Co\textsubscript{3}O\textsubscript{4} nanoparticles. DFT calculations and experimental results showed an facilitated ion and electron transport, stable structure, strong hydroxyl group adsorption and large active surface area. Benefiting from these merits, a superior specific capacity of 384 mAh g\textsuperscript{-1} at 1.0 A g\textsuperscript{-1} was delivered in Figure 4C, outperforming the counterparts (150 mAh g\textsuperscript{-1} for mesoporous Co\textsubscript{3}O\textsubscript{4}, 80 mAh g\textsuperscript{-1} for oxygen deficient Co\textsubscript{3}O\textsubscript{4} and 50 mAh g\textsuperscript{-1} for pristine Co\textsubscript{3}O\textsubscript{4}), suggesting the synergetic effects of porous structure and oxygen defects. Owing to the synergy, an extraordinary cycling performance of zero decay of capacity after 60,000 cycles at 10 A g\textsuperscript{-1} was achieved.

2.4 Abundant Co\textsuperscript{3+} ion stabilization

It is well known that a higher operating voltage generates a higher energy density. Co-based cathodes are generally deemed as a high voltage cathode material in alkaline electrolytes. However, the low potential of Co\textsuperscript{2+}/Co\textsuperscript{3+} limits the output voltage up to only 1.419 V, which can be
enhanced by introducing Co-species with a higher valence state, such as Co^{3+}/Co^{4+} pairs. But the reluctant activation and rapid degradation of this redox pair retard the application. To solve this issue, metal selenides are considered due to their admirable intrinsic electrical conductivity and reversible metal-Se bond. Particularly, they can stabilize Co^{3+} ions in Co selenides, rendering a great potential for being a cathode in Zn-based battery.\textsuperscript{158} Metal sulfides display nanoporous structures accommodating OH\textsuperscript{-} ions which reversibly intercalated into the active materials. Moreover, they possess a fast charge transfer and low OH\textsuperscript{-} adsorption free energy.\textsuperscript{159} Therefore, doping Se into Co\textsubscript{3}O\textsubscript{4} is a promising strategy to enlarge the operating voltage. Tang et al. annealed the ZIF-67 on CC to form an intermediate Co@C/CC, which subsequently selenized into CoSe\textsubscript{2-x}@C/CC as shown in Figure 5A.\textsuperscript{158} Co\textsuperscript{3+}/Co\textsuperscript{4+} redox pair with a higher potential (1.95 V vs Zn anode than 1.419 V for Co\textsuperscript{2+}/Co\textsuperscript{3+}) expanded the operating voltage window from 0.8–1.7 V to 0.75–2.05 V. Owing to the enlarged potential window, as shown in the CV curves from 0.75 to 2.05 V at 5 mV s\textsuperscript{-1} (Figure 5B), the areal capacity was greatly enhanced with Se doping as suggested by the 1.92-fold increase of the integrated area compared with the counterpart. Moreover, O\textsubscript{2}/R\textsubscript{2} pair referred to the Co\textsuperscript{3+}/Co\textsuperscript{4+}, which exhibiting a much larger area than that of O\textsubscript{1}/R\textsubscript{1} pair belonging to Co\textsuperscript{2+}/Co\textsuperscript{3+}. This suggested a stabilizing effect of Se doping on the Co\textsuperscript{3+} species in alkaline electrolytes. In detail, the CoSe\textsubscript{2-x} transformed into Co\textsubscript{x}O\textsubscript{y}Se\textsubscript{z} species in the first few cycles where Co\textsuperscript{3+} was effectively stabilized (not easily reduced to Co\textsuperscript{2+}), thus promoting the Co\textsuperscript{3+}/Co\textsuperscript{4+} redox reaction. This promotional effect was further proven by the 1.8–1.9 V voltage plateau shown in the discharge curves of Se-doped Co\textsubscript{3}O\textsubscript{4} at 6 mA cm\textsuperscript{-2} in Figure 5C, in consistent with the oxidation peak in Figure 5B. To confirm the role of Se in determining the electrochemical performance, a series of Se contents were measured at corresponding cycles to be compared with the capacity values respectively (seen in Figure 5D). It is obviously that the capacity dropped with the decrease of Se amount in the cathode as the cycles continued, presenting
FIGURE 5  A. A potentially higher voltage plateau of Co$^{3+}$/Co$^{4+}$ redox pair compared with Co$^{2+}$/Co$^{3+}$ counterpart and the triggered Co$^{3+}$/Co$^{4+}$ redox pair enabling a widened operating voltage. B. CV curves, (C) GCD curves of Co$_3$O$_4$/Se@C/CC and CoO@C/CC. D. capacity retention of samples cycled different cycles and atomic content of Se in such samples. Reproduced with permission: Copyright 2020, Wiley [158]

a positive mutual relationship between the capacity retention and Se content. Specifically, after 6000 cycles when Se was missing in the structure, a sharp decrease of the capacity was presented from 92.0% to 72.4% retention value.

Despite the high voltage in alkaline electrolytes, their corrosive property renders them not environmentally friendly. Moreover, the formation of irreversible species like ZnO and Zn(OH)$_2$ and Zn anode dendrites limits the rechargeability and cycling stability. Therefore, it is of great value to explore a Co(III)-rich Co$_3$O$_4$ cathode material to be applied in mild electrolytes to enhance the operating voltage. When mild electrolyte replaces the alkaline KOH solution, the reaction mechanism is changed to the following. [5,152] During the discharge process, a high concentration of Co$^{3+}$ promotes the formation of CoO; also, the intercalation of H$^+$ derived from water dissociation converts Co$_3$O$_4$ into CoO. Simultaneously, OH$^-$ reacts with Zn$^{2+}$ in the electrolyte to form ZnSO$_4$·[Zn(OH)$_2$]$_x$·xH$_2$O, maintaining the neutral charge of electrolytes. In the anode, different from the alkaline system, reversible reaction between Zn and Zn$^{2+}$ takes place, which inhibits the formation of irreversibly discharged ZnO, Zn(OH)$_2$ and carbonates; meanwhile, Zn anode dendrite formation is alleviated. [5,152]

Cathode:

$$\text{H}_2\text{O} \leftrightarrow 2\text{H}^+ + \text{OH}^- \quad (4)$$

$$\text{Co}_3\text{O}_4 + 2\text{H}^+ + \text{e}^- \leftrightarrow 3\text{CoO} + \text{H}_2\text{O} \quad (5)$$

Anode:

$$\text{Zn} \leftrightarrow \text{Zn}^{2+} + 2\text{e}^- \quad (6)$$

Based on this mechanism, modifications are made to enhance the Co$^{3+}$ concentration. Ma et al. adopted ZnSO$_4$/CoSO$_4$ mixture as a mild electrolyte and hydrothermally prepared Co(III)-rich Co$_3$O$_4$ with 1D nanorod morphology homogeneously anchored on carbon cloth as the cathode (Figure 6A). [5] To investigate the Co content on the surface, XPS spectrum of Co(III)-rich Co$_3$O$_4$ (Figure 6B) was fitted to present a high Co$^{3+}$/Co$^{2+}$ ratio of 1.696, much higher than 0.998 of the counterpart, suggesting a possibility of realizing a large potential window in a mild electrolyte. As shown in Figure 6C, an ultrahigh voltage of 2.0 V was delivered in 2 M ZnSO$_4$ and 0.2 M CoSO$_4$ electrolyte, higher than 1.8 V in 1 M KOH electrolyte, suggesting an enhancement effect of Co$^{3+}$/Co$^{2+}$ on the widening of operating voltage. Interestingly, a higher discharge capacity was shown in mild electrolyte than that in alkaline KOH electrolyte. To further investigate the influence of Co$^{2+}$ additive on the electrochemical performance, a GCD test was conducted, which presented that owing to the high output voltage, the Co(III)-rich Co$_3$O$_4$ delivered a capacity of 158 mAh g$^{-1}$ at 1 A g$^{-1}$, outperforming the 91 mAh g$^{-1}$ for well-balanced Co$_3$O$_4$ as shown in Figure 6D. Moreover, in the rate performance test in Figure 6E, Coulombic efficiency was maintained nearly 100%; more importantly, Co(III)-rich
Co$_3$O$_4$ maintained the initial capacity when the current density increased to 8 A g$^{-1}$ and shifted back to 0.5 A g$^{-1}$, demonstrating an outstanding rate performance resulting from the stabilization of Co$^{3+}$ and fast redox kinetics.

In summary, various strategies to modify the Co$_3$O$_4$ cathodes have been introduced, including oxygen vacancy generation by thermal treatment and doping, structure modulation (nanowire and nanosheet) and enhancement of operating voltage by increasing or stabilizing Co$^{3+}$ ions in the cathode. More efforts can be put into the exploration of Co$_3$O$_4$ cathode materials applied in mild electrolytes.

3 | CO(OH)$_2$-BASED CATHODE MATERIALS

3.1 | Single Co(OH)$_2$ facile synthesis

In addition to Co$_3$O$_4$, Co(OH)$_2$ is also considered as an emerging cathode material in Zn-based batteries due to the multiple oxidation state, high electrochemical activity and good thermodynamic stability. However, the synthetic procedures of nanostructured Co(OH)$_2$ are mostly complicated and uncontrolled. It would be attractive if a highly efficient and low cost method is exploited to fabricate a high-performance Co(OH)$_2$ cathode material.\cite{160} To solve this issue, Lu and his coworkers applied a facile ultrasound-assisted method to synthesize a Co(OH)$_2$ nanosheet onto a Co foam (CF) (shown in Figure 7A).\cite{160} The oxidation of CF was initiated by HCl treatment under ultrasound, generating Co$^{2+}$ ions on the active layers, which reacted with surface water and air to form Co(OH)$_2$. This synthetic route was simple, scalable and inexpensive, potentially producing 3D electrode materials in large scale. Owing to the enhanced ionic diffusion/electrical conductivity and increased surface active sites on the in-situ formed Co(OH)$_2$ nanosheet, a good capacity of 0.21 mAh cm$^{-2}$ at 1 mA cm$^{-2}$ was achieved as presented in Figure 7B, outperforming the CF electrode (0.022 mAh cm$^{-2}$) by nearly 10-fold increase.
Furthermore, 29.3% of the initial capacity was retained even after a 60-fold current density increase (as shown in Figure 7C), demonstrating an admirable rate performance.

### 3.2 Synergy of Co-based double hydroxides

On the basis of standalone Co(OH)$_2$, owing to the synergistic effect of components and abundant active sites, Co-based layered double hydroxides (LDH) has attracted much interest as a promising cathode material in Zn-based batteries. Specifically, trivalent Al$^{3+}$ ions can fix the metal ions in the CoAl LDH by accommodating the active sites in the stable scaffold, thus enhancing the redox reaction kinetics.[161] He et al. prepared ultrathin CoAl LDH nanosheets in-situ grown on NF by hydrothermal method.[162] HR-TEM image in Figure 8A presented the lattice fringe spacing of CoAl LDH as 0.362 nm, symbolizing the successful synthesis of the layered double hydroxides structure. To investigate the diffusion kinetics, Figure 8B and C compared the Al-doped and pristine Co hydroxides using galvanostatic intermittent titration technique. Obviously, Co$_{0.8}$Al$_{0.2}$-LDH facilitated the OH$^{-}$ transport due to a high ion transfer coefficient during the titration process. Moreover, as shown in EIS results Figure 8D, the lowest charge transfer resistance (0.37 Ω) was obtained by Co$_{0.8}$Al$_{0.2}$-LDH (smallest semicircle in high frequency range in Nyquist plots), followed by other Al-doped LDH and Co(OH)$_2$. Owing to fast OH$^{-}$ diffusion and charge transfer through the large interlayer space and 3D conductive network when Al was doped into the Co-LDH, the rate performance was greatly improved. As shown in Figure 8E, 74.5% retention was achieved for Co$_{0.8}$Al$_{0.2}$-LDH even after a 36-fold increase of current density, much outperforming 51.3% of Co(OH)$_2$. Interestingly, Co$_{0.7}$Al$_{0.3}$-LDH only exhibited a 50.3% capacity retention, suggesting that excess Al led to the recession of the performance possibly due to the prolonged ion migration route in a thicker electrode.

Besides CoAl-LDH, CoNi-LDH deposited on Ni foam (NF) draws increasing attentions due to the intrinsic high charge and ion conductivity and large surface area available for electrolyte access. Limited by the complex synthetic procedures or weak interaction between active materials and NF, the large-scale fabrication and electrochemical performances are retarded. To overcome this challenge, Lu and his coworkers fabricated a CoNi composite hydroxides by ultrasonic treatment with the help of hydrochloric acid.[163] With this facile and scalable method, the assembled battery exhibited a superior capacity of 2.13 mAh cm$^{-2}$ at 8 mA cm$^{-2}$ and an outstanding cycling stability of 90% retention over 30,000 cycles.

To achieve a more hierarchical design, different from the
ultrasonic method, an in situ etching–deposition–growth mechanism was adopted by Chen et al. to synthesize NiCo LDH by growing Co-based metal-organic framework (Co-MOF) onto the NF followed by chemical etching as shown in Figure 9A. In detail, H\(^+\) released from the hydrolysis of Ni\(^{2+}\) consumed the linkers in Co-MOF structure, generating Co\(^{2+}\) ions to be hydrolyzed to release H\(^+\), driving a continuous chemical etching process. Ni(OH)\(_2\) and Co(OH)\(_2\) formed during the hydrolysis intergrew into an nanosheet structure. Herein, Co-MOF acted as both a source of Co and a skeleton for deposition; micro-skeleton arrays and ultrathin nanosheets were both vertically aligned and possessed suitable interspaces. As shown in Figure 9B, this hierarchical structure enabled a fast electron transport from active materials to NF and a facilitated access and diffusion of electrolyte ions within the active materials. Benefiting from the above merits, an admirable specific capacity of 303.6 mAh g\(^{-1}\) at 2 mA cm\(^{-2}\) was delivered by NiCo-90 (reaction time was 90 minutes) with a superior rate capability of 80% retention after a 20-fold increase of current density (seen in Figure 9C), outperforming the single hydroxides and other NiCo-LDH treated over different durations. Moreover, the assembled NiCo-90/Zn battery maintained 99.5% of the Coulombic efficiency and 73% of the initial capacity over 850 cycles. Also, the real-life application was proven by the successful powering a digital clock with three batteries in series as shown in Figure 9D.

Besides the design of hierarchical structures to promote ion/electron transfer, the morphology of NiCo DH can be controlled by coating the active materials onto the conductive substrate (current collector) to increase the potential of Zn-based batteries for wearable electronics. Huang et al. electrodeposited NiCo DH onto conductive yarns made by high temperature spinning of stainless steel 316 L followed by a twist-bundle-drawing technique. Owing to the high surface area and fast ion/electron transport, a high capacity of 5 mAh cm\(^{-3}\) and energy density of 8 mWh cm\(^{-3}\) were achieved. The enhanced electrochemical performance of bimetallic hydroxide was also attributed to the synergy of Ni and Co, that is, the detrimental Jahn-Teller distortion of Ni\(^{3+}\) was accommodated by Co\(^{3+}\), thus stabilizing the framework.

In summary, in addition to the in-situ formation of single Co(OH)\(_2\) on Co foam, double hydroxides are also promising due to the synergy between components to
enhance the intrinsic conductivity and surface area. Moreover, surface coating on current collector can promote the application in flexible device. More attentions may be paid to the facile and large-scale synthesis of hydroxide cathode materials.

4 | NICO₂O₄-BASED CATHODE MATERIALS

Owing to an excellent electrical conductivity and electrochemical performance in LIBs and supercapacitors, spinel nickel cobaltite (NiCo₂O₄) has also achieved an admirable specific capacity and energy density in Zn-based batteries. The charge storage mechanism is shown as below:

\[ \text{Cathode: } \text{NiCo}_2\text{O}_4 + \text{OH}^- + \text{H}_2\text{O} \leftrightarrow \text{NiOOH} + 2\text{CoOOH} + \text{e}^- \]  
\[ \text{CoOOH} + \text{OH}^- \leftrightarrow \text{CoO}_2 + \text{H}_2\text{O} + \text{e}^- \]

In detail, NiCo₂O₄ in cathode reacted with OH⁻ in the electrolyte to form NiOOH and CoOOH by releasing one electron; subsequently, the formed CoOOH further transformed into CoO₂; in the anode, a reversible conversion between Zn(OH)₂²⁻ and Zn metal occurred.

4.1 | Freestanding NiCo₂O₄ and modifications

To enhance the flexibility, Zhang et al. hydrothermally coated a layer of porous NiCo₂O₄ nanosheets onto CC to fabricate a self-supported NiCo₂O₄/CC cathode. Benefitting from the fast charge transfer, high conductivity and mechanical strength, the assembled Zn-based battery exhibited an impressive specific capacity of 183.1 mAh g⁻¹ and a remarkable rate performance of over 52.5% capacity retention after a 20-fold increase of current density. To further enhance the electrical conductivity and generate abundant active sites for redox reaction, oxygen vacancy as a shallow donor can be introduced into the spinel structure to facilitate the charge transfer and promote the surface redox reaction. On the other hand, doping of phosphate ions can weaken the interaction with Ni and Co.
ions in the spinel structure because of the low electronegativity and long bond length compared with O$^{2-}$, thus accelerating the reaction kinetics. Enlightened by these findings, Zeng et al. applied a facile phosphating strategy to create oxygen vacancies and modulate the surface of NiCo$_2$O$_4$ by introducing the phosphate ions. Figure 10A presented the XPS spectra of Co 2p, where the ratio of Co$^{3+}$/Co$^{2+}$ intensities was smaller in P-doped NiCo$_2$O$_4$ than that of pristine NiCo$_2$O$_4$, suggesting a reduction of Co$^{3+}$ to Co$^{2+}$ when phosphate ions were doped. Due to the oxygen vacancy and P doping, the surface reactivity and redox reaction kinetics were greatly enhanced based on the smaller Brunauer–Emmett–Teller surface area of P-NiCo$_2$O$_4$. Moreover, as shown in Figure 10B, the much smaller semi-circle in the high-frequency region indicated a much lower charge-transfer resistance and an improved electrical conductivity resulting from the oxygen vacancies. Owing to increased amounts of surface active sites and reduced resistance for electron transport, as presented in Figure 10C, an admirable specific capacity of 365.8 mAh g$^{-1}$ at 3.0 A g$^{-1}$ was achieved, outperforming the 52.9 mAh g$^{-1}$ for pristine NiCo$_2$O$_4$. Moreover, an excellent rate capability was presented for P-NiCo$_2$O$_4$ with a 90.9% retention after 250 cycles. Long-term stability was demonstrated in Figure 10D that 96.4 mAh g$^{-1}$ was still preserved after 5000 cycles at an super-high current density of 25.3 A g$^{-1}$, with nearly 100% Coulombic efficiency, demonstrating a remarkable durability.

Apart from controlling the surface active sites and structural defects, the morphology of NiCo$_2$O$_4$ exerts an effect on the electrochemical performance in Zn-based batteries. Shang et al. successfully synthesized three types of nanostructured NiCo$_2$O$_4$ on NF, including nanosheet, nanowire, and nanoplate at a series hydrothermal reaction temperatures. Compared with the counterparts, NiCo$_2$O$_4$ nanowire//Zn battery electrode delivered the best performance, that is, a discharge capacity of 230.1 mAh g$^{-1}$ at 0.5 A g$^{-1}$ and 63.23% capacity retention after 1000 cycles. This remarkable electrochemical reactivity originated from the proper pore volume, hierarchical porous structure, high surface area and efficient utilization of active materials.

### 4.2 Multi-component structures

Different from the standalone NiCo$_2$O$_4$, a rational design of a multi-component hierarchical structure can effectively take advantages of the synergy among the active materials to enhance the mass loading, electrical conductivity and electrochemical performance. Xie et al. applied a MOF-involved strategy to integrate NiCo$_2$O$_4$, CoMoO$_4$ and Co$_3$O$_4$ into an arrayed structure in-situ grown on NF as shown in Figure 11A. In detail, NiCo$_2$O$_4$ nanowires were hydrothermally grown on NF, followed by growing CoMoO$_4$ nanosheets and ZIF-67 onto the composites.
successively. Owing to this rational hierarchical design, the mass loading of active materials reached 9.6 mg cm\(^{-2}\). In the meanwhile, this binder-free cathode material possessed a fast electron transfer kinetics and good structural stability due to the intimate contact between active materials and NF, facilitated ion diffusion and electrolyte penetration through abundant open space and plentiful active sites for redox reaction. Compared with the single or binary phase cathodes in Figure 11B, the assemble Zn battery with a ternary-phase material cathode exhibited an excellent capacity at 8 mA cm\(^{-2}\) outperforming the counterparts by 2–5 times. Moreover, benefiting from the synergetic effects of the 3D design and stable structure, an impressive cycling performance of 73% retention over 2000 cycles at 10 mA cm\(^{-2}\) and nearly 100% Coulombic efficiency were achieved (seen in Figure 11C).

In summary, spinel phase NiCo\(_2\)O\(_4\) can be modified by introducing defects and more active sites by doping; also, 1D structure such as nanowire can enhance the utilization of active materials; finally, multi-component structures could take the merits of synergy to facilitate the charge transfer and ion diffusion, and strengthen the structure during cycling. More efforts could be put into the improvement of electrical conductivity of spinel structure.

5 OTHER CO-BASED CATHODE MATERIALS

Recently, a number of novel Co-based materials have been developed into an effective cathode in Zn-based battery. Metal molybdates, especially CoMoO\(_4\) has been utilized in both catalysis and energy areas due to the good electrical conductivity and multiple redox reactions. CoMoO\(_4\) integrates the high electrochemical activity of cobalt oxide and the reversible small-ion storage and rich polymorphism of molybdenum oxide.\(^{[31]}\) Enlightened by these properties, Shen et al. hydrothermally prepared CoMoO\(_4\) nanosheets, followed by phosphating CoMoO\(_4\) under inert gas and NaH\(_2\)PO\(_4\) \(\cdot\) H\(_2\)O.\(^{[31]}\) The doping of P enriched oxygen
vacancies and enhanced the electrical conductivity. Also, the activation energy of redox reaction was lowered. Furthermore, CoP nanoparticles in-situ formed on CoMoO₄ increased surface active sites and promoted the charge transfer. Owing to these advantages, the assembled battery exhibited an impressive energy density of 679.4 Wh kg⁻¹ and a ultra-long lifespan of 80% retention over 12,000 cycles, suggesting a great potential for application of wearable and portable electronics. Based on the good electrochemical performance of CoMoO₄ as a cathode, Li et al. took advantages of the 3D hierarchical design and integrated CoMoO₄ (CMO) with Co(CO₃)₀.₅(OH)ₓ∙0.₁₁H₂O (CCH) to form a branch-like binder-free cathode material via a two-step hydrothermal reaction, which was clearly shown in Figure 12A where the diameter of CCH nanowire was about 50 nm.[154] Compared with standalone CC-CCH cathode, the CC-CCH@CMO 3D structure delivered a remarkable capacity of 0.71 mAh cm⁻² at 1 mA cm⁻², outperforming that of CC-CCH (0.20 mAh cm⁻² at 4 mA cm⁻²), which resulted from the enhanced charge transfer, larger redox potential separation and faster redox kinetics. Owing to these merits, the assembled fiber-shaped Zn-Co battery (shown in Figure 12B) delivered an outstanding capacity of 3 mAh cm⁻³ at 25 mA cm⁻³ based on the whole volume (seen in Figure 12C).

Besides CoMoO₄, CoₓSᵧ has been explored as an effective cathode material in Zn-based batteries because the nanoporous structure can allow OH⁻ diffusion reversibly in amply amounts; also, a large barrier density originating from the density of states and bank structures lead to an enhanced electrical conductivity compared with Co₃O₄. Therefore, S can be doped into the Co-based cathode to improve the performance. Zhang et al. fabricated Co₃S₄ nanosheets by substituting O ions in Co₃O₄ by Na₂S using simple ion exchange method.[159] DFT calculations was adopted to explore the surface adsorption properties. Results in Figure 12D showed that Co₃S₄ (311) possessed a much lower OH⁻ adsorption Gibbs free energy than Co₃O₄ (311) (2.83 vs 3.49 eV), suggesting a facilitated adsorption of OH⁻ ions which accelerated the redox reaction. This lower adsorption energy possibly originated from the charge transfer from Co to OH and more delocalization areas in Co₃S₄. Owing to these merits, the assembled battery delivered an admirable capacity of 317 mAh g⁻¹ at 1 Ag⁻¹ and exhibited a high rate performance of 119.6 mA h g⁻¹ at 10 A g⁻¹, both outperforming the counterpart (shown in Figure 12E). Moreover, single battery could power a 1.5 V electronic clock, which was still powered well under a bending of 90° as shown in Fig. 12(F-I), suggesting a superior flexibility and high discharge voltage. The
6 | CONCLUSIONS AND PROSPECTS

In this review, recent development of Co-based cathode materials are covered, including the charge storage mechanisms in alkaline and neutral electrolytes, the advanced designs of the cathodes and the structure-performance relationships. In detail, the discussion of Co-based compounds are classified into four categories: Co$_3$O$_4$, layered double hydroxides, NiCo$_2$O$_4$ spinel and other emerging Co-based materials. To enhance the electrochemical performances, several strategies can be applied as below: doping with heteroatoms to create oxygen vacancies, improve electrical conductivity and promote the redox reaction; optimizing the morphology to increase the utilization of active materials; integrating different materials to exert a synergetic effect. Despite the great progress of this field, there is still some room for further improvement:

1. Oxygen vacancies can be introduced into the Co-based active materials via ion doping and thermal/chemical treatments, which accelerate the charge transfer, change the electronic states of active materials, increase the amount of active sites, thus promoting the surface redox reaction and enhancing the intrinsic electrical conductivity.$^{[150,152]}$ However, more efforts are suggested to put into the elucidation of the detailed mechanisms of the modulation effect of oxygen vacancies on the physicochemical properties and electrochemical performances.

2. A high operating voltage is desirable for achieving a high-performance battery in real-life applications. In both alkaline and neutral electrolytes, a large potential window can be realized if Co species with a high valence state are dominant in the active material.$^{[5,38]}$ However, the activation and rapid degradation of Co$^{3+}$/Co$^{4+}$ pair become the hindrance. Thus, it is of importance to develop a facile strategy to stabilize the redox pair.

3. An energy storage device with both a high output voltage and specific capacity simultaneously is quite challenging for a single type of battery. Hybrid battery systems combining Zn-air and Zn ion batteries are a promising solution, which incorporates oxygen evolution reaction, oxygen reduction reaction and redox reactions.$^{[148]}$ The cathode materials satisfying this system should possess a good electrical and ionic conductivity, large surface area and abundant active sites. Despite the progress made recently, many works are expected to be conducted to explore a robust and efficient electrode material suitable for both battery types in a single system.

4. To alleviate the side reactions of Zn anode such as passivation and dendrite formation, additives, surface modifications and hierarchical structure can be applied as a combination. Moreover, anode cycling stability can be further enhanced by using anode operating at a low potential. It is also meaningful if in-situ removal of side products on Zn anode is realized.

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