Progress of carbon-based electrocatalysts for flexible zinc-air batteries in the past 5 years: recent strategies for design, synthesis and performance optimization

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Abstract
The increasing popularity of wearable electronic devices has led to the rapid development of flexible energy conversion systems. Flexible rechargeable zinc-air batteries (ZABs) with high theoretical energy densities demonstrate significant potential as next-generation flexible energy devices that can be applied in wearable electronic products. The design of highly efficient and air-stable cathodes that can electrochemically catalyze both the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) are highly desirable but challenging. Flexible carbon-based catalysts for ORR/OER catalysis can be broadly categorized into two types: (i) self-supporting catalysts based on the in situ modification of flexible substrates; (ii) non-self-supporting catalysts based on surface coatings of flexible substrates. Methods used to optimize the catalytic performance include doping with atoms and regulation of the electronic structure and coordination environment. This review summarizes the most recently proposed strategies for the synthesis of designer carbon-based electrocatalysts and the optimization of their electrocatalytic performances in air electrodes. And we significantly focus on the analysis of the inherent active sites and their electrocatalytic mechanisms when applied as flexible ZABs catalysts. The findings of this review can assist in the design of more valuable carbon-based air electrodes and their corresponding flexible ZABs for application in wearable electronic devices.

Keywords: Flexible zinc-air batteries, Carbon-based electrocatalysts, Electrocatalytic mechanism, Air cathode

Introduction
The current excessive usage of non-renewable energy has raised concerns regarding the energy crisis. Therefore, to alleviate the current energy shortage, more efficient and environmentally friendly power supply devices need to be established. In addition, the emergence and popularization of stretchable, foldable and bendable wearable electronic devices have instigated the rapid growth and development of flexible energy storage systems [1–3]. Zinc-air batteries (ZABs) exhibit a theoretical energy density of 1086 Wh kg\textsuperscript{-1}, which is approximately five times that of the widely used rechargeable lithium-ion batteries. Moreover, zinc has the advantages of abundant reserves and wide availability [4, 5]. Typical ZABs utilize zinc as the negative electrode, oxygen as the positive electrode and potassium hydroxide as the electrolyte. Owing to the introduction of highly stable zinc anodes and water-based electrolytes, ZABs are non-toxic, environmentally friendly and safe and have received widespread attention as promising energy storage systems [6].
The basic working principle of ZABs involves an electrochemical reaction between zinc on the negative electrode of the battery and the OH\(^{-}\) in the electrolyte solution resulting in the release of electrons. Simultaneously, the catalysts in the gas diffusion electrode or air cathode reaction layer come in contact with the electrolyte and the oxygen in the air, and then the charge transfer occurs. During the operation of rechargeable ZABs, the conversion between oxygen and water occurs on the air electrode; this includes the ORR and OER, both of which are multi-electron recombination processes. The specific reactions that occur in alkaline solutions are as follows:

\[
\text{ORR : } \ce{O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-} \tag{1}
\]

\[
\text{OER : } \ce{4OH^- \rightarrow O_2(g) + 2H_2O(l) + 4e^-} \tag{2}
\]

Various kinetic models have been developed to understand the reaction pathways involved during the ORR. The first model, developed by Damjanovic et al. [7, 8], involves the formation of hydrogen peroxide in a reaction pathway parallel to that in which O\(_2\) is reduced to water without the formation of hydrogen peroxide as an intermediate. This is schematically represented by Eq. 1 and 2.

\[
\text{O}_2 \rightarrow^{I_1} \text{H}_2\text{O} \tag{1}
\]

\[
\text{O}_2 \rightarrow^{I_2} \text{H}_2\text{O}_2 \rightarrow^{I_3} \text{H}_2\text{O} \downarrow^{I_4} \text{to solution and ring electrode} \tag{2}
\]

Hydrogen peroxide, formed as a reaction intermediate in pathway 2, is partially reduced at the same disk electrode as water and partially transferred from the disk electrode to the solution and ring electrode by convective diffusion. I\(_1\), I\(_2\) and I\(_3\) represent the respective currents. I\(_4\) represents the rate at which hydrogen peroxide diffuses away from the disk electrode as a current. However, the generated peroxide intermediate is unstable, which may complicate the reaction process, damage the electrolyte membrane and reduce the activity of the catalyst, as well as the output voltage and energy conversion rate of the fuel cell [9]. Therefore, the direct 4e\(^{-}\) pathway (Eq. 1) is considered to be the ideal pathway for the ORR, as it has a higher output voltage and energy conversion than the 2e\(^{-}\) pathway (Eq. 2).

Because a considerable over-potential of the ORR is required to overcome the energy barriers associated with multi-step electron transfer [10], the main challenge faced in developing flexible rechargeable ZABs that can be applied on a large scale is the use of air cathodes in the ZABs that exhibit excessive potential [11] and poor oxygen reversibility caused by the slow ORR and OER during charge and discharge [12]. The Pt/C electrodes demonstrate the best catalytic performance for the ORR, whereas IrO\(_2\)/RuO\(_2\) demonstrates an excellent catalytic performance in the OER. However, these catalysts also suffer from several drawbacks, such as scarce reserves, high cost, single catalytic activity and poor stability, which severely hamper their application on a large scale [13]. Thus, the development of a catalyst with excellent bifunctional ORR/OER catalytic performances that is affordable is vital for the commercialization of flexible ZABs. Non-noble metals, particularly transition metals, have attracted widespread attention owing to their high activity and excellent thermal stability. In addition, carbon-based catalysts possess significant advantages, including structural flexibility, excellent electrical conductivity, good chemical and thermal stability and simple chemical functionalization, in addition to being lightweight. Thus, they are regarded as promising candidate materials for use in wearable electronic products. There exist several excellent CC (carbon cloth)-based air cathodes; however, one of the main challenges is the identification of materials with excellent conductivity that can uniformly grow on CC. If the materials grow in a disorderly fashion on the CC, the number of active sites on the catalyst are reduced. Traditional ZABs use an aqueous solution as the electrolyte, which cannot meet the requirements of solid-state flexible ZABs. Thus, most solid-state ZABs that exhibit excellent performances use gel electrolytes to conduct electricity, such as polyvinyl alcohol, polyethylene oxide (PEO), polyacrylamide (PAM) and polyacrylic acid (PAA). These gel electrolytes are increasingly used in ZABs, as they possess strong plasticity and good conductivity. Specifically, sodium polycrylate is stable in the practical application of water-based gel electrolytes, owing to its buffering effect in alkaline electrolytes [1].

In recent years, the number of studies on flexible ZABs has increased, providing some theoretical basis for the practical production and application of flexible ZABs. Although Zhu et al. published a detailed review of one-dimensional batteries [14] and Shi et al. introduced bifunctional catalysts in detail [15], the recent progress, particularly in the past five years, of flexible ZABs containing carbon-based catalysts has not been reported. Therefore, this work summarizes the strategies for the synthesis of carbon-based catalysts and the optimization of their electrocatalytic performances in air electrodes, with a significant focus on the analysis of their inherent active sites and their electrocatalytic mechanism when applied as flexible ZABs catalysts.
**Designer carbon-based electrocatalysts**

Carbon-based materials are widely used in ZABs catalysts owing to their excellent properties. These materials are mainly graphene-based materials (including functionalized graphene and graphene profiles); however, graphite, fullerene and carbon nanotubes (CNTs) are also used [16]. Nevertheless, carbon-based materials still suffer from many defects during the practical application of ZABs. Thus, it is necessary to optimize the treatment applied to carbon materials. An example of this is N-doped porous carbon materials, which exhibit exceptional bifunctional electrocatalytic performances in the ORR and OER [17, 18]. Among the variety of methods used to modify carbon materials, doping with single atoms, such as N, P and S, can significantly improve the catalyst activity. In view of this, some researchers have used N and P co-doping and found that the co-doped catalyst has excellent activity. In addition, other methods, such as single metal doping, bimetal doping and nanomaterials, have a definite positive effect on the catalyst performance optimization of carbon materials. However, methods to develop high-performance electrocatalysts for ZABs have been scarcely explored. Studies have shown that modifying carbon materials, such as graphene and CNTs, through doping can optimize the surface properties of the carbon materials. The most typical strategy to optimize the catalyst performance is to combine heteroatom-doped carbon nanomaterials with transition metal-based material (oxides, chalcogenides such as Ni-based sulfides, etc. [19–21], transition metal phosphides (TMP [22]) and nitride) composites. As ZABs electrocatalysts still have numerous shortcomings, it is vital to optimize their catalytic structure. Currently, electronic structure adjustment, oxygen defects, metal–oxygen bonds, interface strain and atomic doping have been widely used in the design of ZABs catalysts.

**Growing high-efficiency catalysts on flexible electrodes**

The flexible electrode is represented by the gas diffusion layer in flexible ZABs. The air cathode is formed by directly growing a high-efficiency catalyst on the flexible electrode, which has the advantages of being self-supporting and having a large electrode contact area and strong foldability. Self-supporting indicates that no non-conductive adhesive is required, thereby avoiding the deterioration of the electrode performance and loss of the catalyst during repeated deformation of the electrode. Furthermore, the reduction in active sites and increase in interface impedance is avoided by using non-conductive adhesives. Growth of the catalyst on the expandable electrode can be combined with other methods, such as electrodeposition, the hydrothermal method and room temperature vulcanization. Commonly used flexible electrodes include nitrogen-doped carbon foam, carbon fiber cloth, carbon paper and carbon felt, which possess excellent electrical conductivity.

**Growth of high-efficiency catalysts on carbon fiber cloth**

Carbon fiber cloth, a woven fabric constructed from carbon fibers, is the most commonly used flexible substrate material. Growing high-efficiency catalysts directly on carbon fiber cloth is a simple and effective method, which can be achieved through solution reactions (Fig. 1a–c), electrodeposition and a combination of other methods, such as confined space, heat treatment [2] (Fig. 1d, e), carbonization-oxidation CC and ligand-assisted calcination (preparation of an ultrathin CoOx layer [23]). An example of carbonization-oxidation includes the growth of different crystals structures, morphologies and particle sizes of 3D and 2D cobalt-based catalysts [24]. The nanofiber network is rooted on CC in a nitrogen atmosphere to obtain a bifunctional air cathode with an excellent catalytic performance and remarkable flexibility [25]. Although the electrodeposition method has been widely used to prepare electrode materials, owing to the inherently poor conductivity of Co3O4, conventional electrodeposition methods exhibit limitations in forming a Co3O4 layer with a large contact area on a conductive carrier. Co3O4 can be grown in situ on the carbon fiber cloth to form a uniformly grown ultrathin Co3O4 layer. In particular, the ultrathin Co3O4 layers have a maximum contact area on the conductive support, facilitating rapid electron transport and preventing aggregation of the ultrathin layers during the electrode preparation process [26]. Moreover, Co3O4 can be converted into a nano-microarray with a layered structure [24], as depicted in Fig. 1f. This ultrathin cobalt oxide layer can also be used as an electrocatalyst in ZABs [23], as depicted in Fig. 1g.

**Growth of efficient catalysts on self-made foam materials**

Self-made foam materials mainly refer to carbon foam and nickel foam. Pan et al. used a melamine sponge annealed at a temperature of 800 °C to form a flexible foamed carbon material, which was then used as a working electrode to electrodeposits the precursor for Fe-Co3O4NWS@NCFs via a scalable electrodeposition method. Consequently, the flexible foamed carbon material could be applied in all-solid sponge batteries [27], as shown in Fig. 1h. The nickel foam material is a type of reticulated metal sponge. Jiang et al. indicated that growing catalyst electrodes in situ on a flexible substrate would cause disorder and form
dense irregular areas, which would reduce the catalytic activity. Therefore, they constructed an ordered multidimensional array of 1D CNTs decorated with 0D cobalt nanoparticles (called MPZ-CC@CNT) and 2D carbon nano-ridges on a nickel foam material. During the pyrolysis of the 2D ZnCo bimetallic coordination framework, CNTs containing a high content of N-doping were grown in situ from the highly dispersed cobalt, thereby forming an open and ordered array [28], as depicted in Fig. 2a.

Synthesis of high-efficiency catalysts on carbon felt
Carbon felt is a non-woven fabric. Yu et al. [29] developed a novel strategy for synthesizing Co–N–C nanosheets supported on carbon felt (Co/Co–N–C), containing Co nano-islands with a 3D-layered structure, as illustrated in Fig. 1c.
in Fig. 2b. This unusual structure results in good contact between the Co nano-islands and Co–N-C nanosheets. Additionally, the coexistence of Co\(^0\) and Co\(^{2+}\) enhanced the electrocatalytic performance of the bifunctional (ORR/OER) catalyst. Therefore, the overall unique layered structure can further promote effective electron/ion transport in ORR and OER [29]. In addition to growing 3D nanoelectrodes on carbon felt, a nanoscale ultrathin cobalt oxide (CoOx) layer can also be fabricated on carbon felt (i.e., a metal Co/N-doped graphene substrate) [23]. This ultrathin structure provides favorable conditions for application in ZABs.

**Synthesis of high-efficiency catalysts on carbon paper**

Carbon fiber paper (CFP) is composed of carbon fiber and produced through the papermaking process. CFP can be used to improve the ORR and OER performances of non-metallic electrocatalysts, such as g- C\(_3\)N\(_4\). G-C\(_3\)N\(_4\) has a high nitrogen content and can thus provide a sufficient number of active sites for electrocatalytic reactions and reduce the ORR potential [30]. However, its electrocatalytic performance is significantly limited owing to its non-conductivity leading to a poor electron transfer ability [30]. G-C\(_3\)N\(_4\) with different morphologies can be prepared using different heat treatment methods [30]. The ORR and OER performances of the catalyst can be optimized by applying treatments to g-C\(_3\)N\(_4\), such as 1) synthesizing a high-efficiency catalyst using g-C\(_3\)N\(_4\) as a template [31, 32], 2) applying a g-C\(_3\)N\(_4\)-assisted pyrolysis strategy [33–35], or 3) introducing g-C\(_3\)N\(_4\) into carbon. Phosphorus-doped g-C\(_3\)N\(_4\) can directly grow on CFP, which can be designed as a flexible oxygen electrode. This is the first non-metallic ORR/OER bifunctional electrocatalyst formed by the combination of flower-like P\(_8\)-C\(_3\)N\(_4\) composed of thin nanosheets of g-C\(_3\)N\(_4\) and CFP. The electrocatalyst contains a 3D hybrid network with a high N content and a large amount of P-doping, which produces an excellent ORR and OER activity and

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**Fig. 2** a Schematic of the preparation process for MPZ-CC@CNT [28]. b Synthesis of the Co/Co–N-C catalyst [29]. c Schematic of the preparation of the Fe\(_3\)O\(_4\)@PCN catalysts [40]. d Scheme depicting the Co\(_3\)O\(_4\)/N-p-MCNTs composite catalyst synthesis [41]. e Scheme of the fabrication procedure for the MH paper air cathode, along with its photograph [43]. f Schematic representation of the fabrication procedure for the NCNF and photographs of the resultant flexible NCNF [44].
durability [36], and a good charge and discharge performance, even in the case of bending deformation.

**Synthesis of high-efficiency catalysts in confined spaces**

The synthesis of high-efficiency catalysts in confined spaces can increase doping efficiency, reduce heat loss and increase mesoporous properties, thereby improving their ORR performance. The confined spaces can be molecular sieve nanochannels, such as montmorillonite, 2–4–6 tripyridyl triazine, CNTs, carbon nanosheets and doped carbon layers. Numerous experiments have also demonstrated that catalysts prepared in confined spaces exhibit an improved catalytic effect. Doping transition elements and non-metallic elements in confined spaces can significantly enhance catalytic efficiency. N and S co-doping [13], N and P co-doping [12], two-dimensional nitrogen doping [37, 38], etc. have been reported. Furthermore, it has been established that if a plasma-assisted strategy is used for doping in a confined space, the etching effect of the plasma can endow porosity to the confined space, thereby exposing more active sites, which is conducive to the long-term durability and effective electron transport of the electrocatalyst [39]. Zhang et al. used a soft membrane method to prepare Fe₃O₄ wrapped in a porous carbon nano-bowl, demonstrating excellent catalytic performance and long-term durability [40], as shown in Fig. 2c. The Co₃O₄ nanoparticles were anchored on the partially exfoliated multi-walled CNTs doped with nitrogen, resulting in an outstanding catalytic performance [41], as shown in Fig. 2d.

**Combination of high-efficiency flexible catalysts**

A combined catalyst comprises a single functional catalyst composed of the same material in different shapes or a bifunctional catalyst composed of different materials. Xu et al. achieved a single-function ORR air cathode by simultaneously designing aligned, cross-stacked and porous CNT sheets, where the CNT sheets functioned as a gas diffusion layer, a catalyst layer and a current collector, and synthesized a new fibrous, flexible and stretchable ZABs [42]. The air cathode catalyst in flexible ZABs typically exhibits insufficient ORR/OER catalytic activity and requires harsh synthesis conditions, including high temperatures/high pressures and acid (or alkaline) solutions. In addition to the problems of bifunctional air catalysts, the mechanical properties of the air cathode strongly depend on the mechanical properties of its substrate, resulting in a lack of shape diversity and deformability in the air cathode sheet. On this basis, Lee et al. used a combined high-efficiency flexible catalyst for the OER and nitrogen-doped CNTs for the ORR [43], as shown in Fig. 2e. The monolithic hetero-nano-mat paper air cathode comprises a 1D bifunctional catalyst mixture, cellulose nanofibers and polytetrafluoroethylene nanoparticles, with no need for conventional current collectors and gas diffusion layers [43]. Zhang et al. synthesized a new type of NiCo₂O₄/N-doped carbon nano-mesh bifunctional electrocatalyst composed of hollow NiCo₂O₄ nanospheres and N-doped carbon nano-mesh [40]. The bifunctional electrocatalyst was synthesized through a liquid-phase synthesis and subsequently heat treated, after which it was assembled into a battery.

**Home-made flexible cathode film**

Liu et al. prepared a nanoporous carbon nanofiber film (NCNF) by pyrolyzing an electrospun polyimide (PI) film under an Ar atmosphere. As shown in Fig. 2f, the NCNF possesses flexibility and high mechanical and tensile strength. The tensile strength of the NCNF is 1.89 MPa, and the tensile modulus is 0.31 GPa. NCNF exhibits a 3D nanoporous carbon network structure and a large specific surface area, which can provide short and fast electron/ion paths and abundant gas diffusion channels. More importantly, the electrode design also has the advantages of eliminating polymer binders and simplifying the manufacturing process, minimizing battery size and cost. The flexible all-solid rechargeable ZABs containing the NCNF air cathode exhibits a high discharge voltage (~1.0 V @ 2 mA cm⁻²), low charging voltage (~1.8 V @ 2 mA cm⁻²), high energy density of 378 Wh kg⁻¹ and excellent mechanical and cyclic stability. These results suggest the possibility of large-scale applications of the ZABs [44].

**Optimization strategies for ZABs catalyst performance**

In the past few years, research on inexpensive and highly efficient electrocatalysts for ORR and OER has developed rapidly. Although there are many controversies regarding the specific catalytic process occurring during electrocatalysis, it is certain that a greater number of effective active sites in the catalyst leads to better catalytic activity. In the process of optimizing the performance of ZABs catalysts, atomic doping on carbon can lead to synergy and structural defects as well as adjustment of the electronic structure, coordination environment and catalyst structure. Therefore, the electrocatalytic effect of the catalyst can be improved by doping the carbon materials with specific atoms. Atomic doping can be categorized into single-atom doping and multi-atom doping, wherein the atoms can be either metal atoms or heteroatoms. Both single-atom doping and multi-atom doping can improve the electrocatalytic performance of the catalyst.

**Atomic doping**

Through compositional analysis and density functional theory calculation, Yu et al. established that N-doping
can effectively improve the conductivity and oxygen absorption capacity of the catalyst; however, excessive N-doping causes a decrease in the reaction kinetics [45]. Synergistic effect and structural defects can be achieved by heteroatom doping.

**Single-atom doping**

Heteroatoms (N, P, S, etc.) and metals (Fe, Co, Mn, etc.) can be used for single-atom doping. Among them, N-doping is the most commonly used single-atom doping on carbon. N-doping can increase the electron transport efficiency and oxygen adsorption strength, as well as improve the reaction kinetics of the catalyst, resulting in defects and the exposure of more active sites. For example, Yu et al. demonstrated that N-doping can significantly improve the electronic conductivity and O$_2$ adsorption capability of Co$_3$O$_4$ nanowires through experimental investigations and density functional theory (DFT) calculations [45]. Owing to the gap between the sheets, transition metals, such as Co [5], Ni, Mn [46, 47] (as shown in Fig. 3b, c), Fe and Cu, can be doped on active substrate materials, such as carbon materials (graphene, CNTs, etc.). It has also been confirmed that 2D heteroatoms exhibiting unique structures and physical and chemical properties, such as N, P, S [22, 48] and B [49–54] (as shown in Fig. 3d, e), can improve the electrochemical and electrocatalytic performances of the catalysts.

**Multi-atom doping**

Multi-atom doping includes both heteroatom co-doping (N-S, N-P, N-B, etc.), and heteroatom and metal co-doping [55] (Fe-Co–N [56], Mn-N [57], Fe–N [58], Co–Fe–N–P [12], Co–Fe–N [39], Co–Mn–N–P [59], Co–Cu–N [60, 61], Co–Cu–P, etc.). On the one hand, heteroatom doping can effectively generate synergistic defect effects in the catalyst, leading to a higher catalytic activity [62, 63]. On the other hand, it has been confirmed that co-doping with transition metal atoms and heteroatoms can effectively improve the oxygen reduction performance of the catalyst [64, 65]. In addition, there exists a synergistic effect between multi-metals and heteroatoms that increases the electrocatalytic activity of the catalyst. Multi-metals can improve the conductivity and oxidation state of the catalyst, thereby increasing the amount of charge transfer of the catalyst [66] and the electrocatalytic performance of the catalyst [60]. For example, Diao et al. established through DFT that Cu-doping can lead to more positive sites adjacent to Co and weaken the binding force between the surface active sites and the adsorbed intermediates, thereby increasing the mass and charge transfer rates and the exposure of active sites [61]. As shown in Fig. 3a, in Cu-doped Co$_2$P, clear electron depletion occurs on the Co sites neighboring the Cu atoms, indicating that Cu-doping can change the electron distribution of Co$_2$P [22].

**Synergistic effect**

A synergistic effect in catalysis can be defined as a significant enhancement in the catalytic activity when several elements (metals or non-metals) or compounds are combined, in comparison with when these elements or compounds are used on their own. The synergistic effect can assist in the regulation of the electronic structure of the catalyst substrate, enhancing the electrocatalytic activity [37, 67], and can produce a strong coordination to produce more active sites [56]. This collaboration can be classified into the following categories:

Highly active metal/non-metal groups experience synergism with the conductive doped carbon/nitrogen substrates. One example of this category is metal-nitrogen-carbon (M–N–C) compounds [68–70], such as Co–N–C compounds. Co–N–C active sites can exist on the interface between Co and the N-doped carbon, which may facilitate the formation/deposition of O$. Moreover, it has been shown that the Co-Nx sites and the N embedded in the carbon matrix are active sites in non-noble metal ORR hybrid catalysts [68]. Other examples include transition metals (Co and Fe) on N-doped carbon [39, 71, 72], pyridine-N [58], graphitization-N [71], Co-azo species [71], N, P co-doped materials, lay-
ered N-doped heteroporous carbon nanofibers that possess excellent electron transport paths and a high specific surface area [10] and graphene nanocomposites. Graphene nanocomposites have been synthesized through the in situ hydrothermal growth of CoSe and nickel selenide nanoparticles on graphene nanosheets (GNs). The synergistic effect between the composite nanoparticles and graphene enhances the electrochemical performance of the catalyst [73, 74]. Most importantly, it has been proved that the strong coordination between the metal center and pyridine- N can promote the formation of pyridine-NM active sites, and the electron-rich pyridine-N can effectively accelerate the charge transfer to the metal center, thereby greatly improving the ORR activity [75, 76]. The synergy between metals endows the catalysts with an alloying effect that adjusts the electronic structure of the system and optimizes the combination of oxygen [74, 77]. The synergistic effect of bimetallic active sites on oxygen electrocatalysis has previously been studied. For the NiCo2S4@g-C3N4-CNT integrated flexible electrode, electrons are transferred from the bimetallic Ni/Co active site to the abundant pyridine-N in g-C3N4 and cooperate with the coupled conductive CNT to promote reversible oxygen electrocatalysis. Theoretical calculations indicate that the pyridine metal-N species (Ni, Co-N2) has a unique co-activation effect on the bimetallic Ni/Co atom. It reduces its d-band center and facilitates the adsorption/desorption of oxygen intermediates, thereby accelerating the reaction kinetics. In a Co-doped Fe-O4N@NC nanosheet array, the metal center can generate a strong coordination effect with the pyridine-N, and the Fe and N co-doping significantly promotes the formation of a large number of pyridine-N-M active sites in the ORR [78–81]. In hybridized porous Co3O4 anchored on MnO2, Co and Mn generate a coupling effect, thereby accelerating the electron transport rate, forming a buffer zone and accelerating the separation of the catalyst surface products [82]. Another example is Cu and Co-modified N-doped GNs with Co nanoparticles [60]. Furthermore, the excellent electrocatalytic activity of Co3P@CNF can be explained by the strong interaction between the Co3P nanocrystals and the porous carbon coating co-doped with CoNx and N and P, resulting in an enhanced interfacial charge transport and regulation of the Co3P electrocatalytic activity [83]. A new 2D MoSe2-Ni(OH)2 material has also been prepared through a simple one-step hydrothermal synthesis. The 2D MoSe2-Ni(OH)2 nanohybrid, with a unique vertical orientation nanosheet structure, provides a large amount of electroactive specific surface area, shortening the diffusion length of the electrolyte ions and thereby improving the electrochemical reaction kinetics [84].

**Structural defects**

Defects, including lattice distortion, broken stripes and edge sites at the corners, are considered to have a positive effect on catalytic activity. It has been established that defects at the edges of DG (defective graphene) can reduce the free-energy changes of ORR and OER, thereby improving the catalytic activity and conductivity of DG [85]. For example, the introduction of P atoms into the N-doped carbon matrix can effectively produce a synergistic defect effect and N-P structure, thereby optimizing the catalytic performance in the OER and ORR [12]. Meanwhile, H2 [86] and Ar plasma etching can also be used to form materials with rich defect structures.

**Adjusting the electronic structure and coordination environment**

Regarding the electronic structure of the catalyst, it has been widely estimated that the surface charge distribution of the catalyst can be adjusted by introducing defects, such as doped heterometallic cations. The defects, including oxygen vacancies (VO) [77], can increase the number of catalytic active sites or provide the catalyst with new catalytic activity [87]. VO can be achieved by Ar plasma etching [88]. In alkaline media, an efficient ORR catalyst should be able to completely reduce oxygen to hydroxide through the four-electron reduction process, whereas a weaker ORR catalyst terminates the reaction sequence in the middle of the two-electron transfer process. For example, Lian et al. proved that a 3D orbital configuration of the metal center promotes the ORR by adjusting the oxidation state and electronic state of the metal center. Additionally, local coordination can further accelerate the conversion rate of the target redox substances [10]. Co atoms also have excellent activity owing to their different possible valence states. Co2+ and Co3+ occupy the tetrahedral and octahedral sites of Co3O4, respectively, which helps in promoting electron transfer in the OER [11]. Furthermore, the deposition of ultrathin NiFe-layered double hydroxides (NiFe LDHs) on the surface of Co3O4 can adjust the surface chemical valence of Co, Ni and Fe by changing the electron donor and/or electron absorption effect, resulting in the balance and optimization of the ORR and OER performance [89], as shown in Fig. 3f.

**Increasing the number of pore structures**

Nanostructured materials have rich pore structures and large numbers of mesoporous channels, which play a
vital role in modifying oxygen transmission channels \[11\], extending the capture time of oxygen molecules and enhancing their interaction with the catalytic active sites. Some nanostructured materials exhibit a 2D/3D structure \[90\], which has a larger specific surface area and increases the number of three-phase interfaces. By rational design, a nanostructured porous material with a large surface area and high conductivity can be constructed to ensure that more nanoparticles are in direct contact with the electrolyte, resulting in a lower resistance between the active material and the electrolyte \[83\]. A rich pore structure can accelerate charge transfer and diffusion between charges and increase mass transfer, thereby improving the performance of the catalyst \[11, 39\]. The surfaces of nanostructured materials have a stable low-refractive-index and can exhibit oxygen adsorption energies similar to the surface of Pt \[91\]. This feature is part of the conditions required for catalyst’s highly efficient catalytic performance. Nanostructured materials that can be used as the air cathode of ZABs include Ni$_3$C/NC nanosheets (2D), Ni$_3$S$_2$/Ni nanosheet arrays \[1\] (as shown in Fig. 3g), uniform porous Co$_3$O$_4$ nanoparticles/nanosheets \[11, 45\], N-doped CNTs (usually used as an active substrate), hollow NiCo$_2$O$_4$ nanospheres, N-doped CNTs \[92\], and MoSe$_2$/G nano-hybrids \[93\].

**Adjusting the catalyst structure**

A catalyst with a reasonable structure is required to catalyze a reaction. Transition metal oxides with a spinel structure can help reduce overpotentials, thereby improving the energy conversion efficiency of the catalyst \[82, 94\]. The 2D/3D structure of the catalyst can result in an excellent catalytic activity owing to the enlarged contact area between the active site and the electrolyte. For example, Co-doped NiO nanoporous flowers, in which the synergistic effect between the 2D hexagonal frame and a large number of nanopores on the side of the nanosheet increases the number of effective catalytic active sites for O$_2$ adsorption/diffusion \[5\]; and the unique 3D-layered Co/Co-NC system structure that can provide an efficient number of active sites \[29\]. Other examples include a new graphene hydrogen/B-doped quantum dot composite material that has a unique 3D structure, high porosity and large specific surface area, which exhibits an abundance of catalytically active sites and enhanced electrolyte mass transport and ion diffusion \[95\], and a 2D Co-MOF that is grown directly on CC providing the 3D Co-MOF growth sufficient space to form a layered 3D-on-2D MOF system structure. In comparison with an exclusively 3D or 2D MOF, more catalytically active sites are exposed \[24\]. Furthermore, the 3D framework facilitates full penetration of the electrolyte and promotes electron transport in the porous network structure \[41\]. In addition, miniaturizing the volume of the catalytic material can also improve catalytic efficiency. For example, at the atomic scale, an ultrathin CoO$_x$ layer effectively accelerates electron conduction and provides abundant active sites. This is owing to the introduction of Co oxidation in the nanosheets that can increase the number of exposed active centers \[23\]. Another example includes a 2D La(OH)$_3$/graphene nanohybrid, prepared by a simple and economical solvo-thermal reduction technique, which is electrostatically anchored on 2D GNs to prevent the aggregation of lanthanum hydroxide and provide several electroactive centers for the reaction \[96\].

**Conclusions and future prospects**

Although the current research on ZABs has made some substantial progress, there are still extensive challenges, including the development of new methods for synthesizing self-supporting flexible cathodes, exploring electrocatalytic mechanisms and identifying suitable materials to synthesize flexible cathodes with excellent catalytic performance. As one of the important catalyst materials for ZABs, carbon-based catalysts have attracted significant attention owing to their large specific surface area, abundant active centers and good electrical conductivity. However, carbon materials still suffer from some disadvantages, such as uncertain toxicity of CNTs, higher cost than other flexible electrocatalyst materials and poor repeatability on different substrates; carbon materials derived from natural biomaterials have relatively poor flexibility and conductivity, which limits the performance of the wearable electronic devices in which they are applied. An extensive study regarding the catalyst microstructure and effect of atomic doping, as well as the internal relationship between the electronic distribution of the catalyst and its electrocatalytic oxygen reduction performance, is expected to play a vital role in effectively identifying the actual role of metal ions, N, S and P, and other doping elements on the active sites and deepen the understanding of the carbon catalyst electrocatalysis ORR process. We expected to contribute to the development of affordable, high-performance carbon-based non-noble metal ORR catalysts. A carbon-based flexible electronic products have been used to detect the human pulse and breathing rate \[97\]. It is believed that more multifunctional flexible electronic devices based on carbon-based flexible ZAB catalysts will be commercialized in the future.

**Abbreviations**

ZABs: Zinc-air batteries; ORR: Oxygen reduction reaction; OER: Oxygen evolution reaction; CC: Carbon cloth; PEO: Polyethylene oxide; PAM: Polyacrylamide; PAA: Polyacrylic acid; CNTs: Carbon nanotubes; TMP: Transition metal oxides; PVDF: Polyvinylidene fluoride; PDA: Polydopamine; PVP: Polyvinylpyrrolidone; TCP: Transition metal hydroxides; PAM: Polyacrylamide; PAA: Polyacrylic acid; LPE: Long period polyelectrolyte; PEO: Polyethylene oxide; PAM: Polyacrylamide.
phosphides; CFP: Carbon fiber paper; DFT: Density functional theory; DG: Defective graphene; VO: Oxygen vacancies; NiFe LDHs: NiFe-layered double hydroxides.

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Authors’ contributions
CZG, YS and TTZ conceived the topic and supervised the whole paper. YQ, ZHO, CLX, ZBZ, JY, Yi and JYW wrote the manuscript. All authors read and approved the final manuscript.

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Declarations

Competing interests
The authors declare that they have no competing interests.

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