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Bifunctional electrocatalysts for rechargeable Zn-air batteries

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ABSTRACT

Zn-air batteries have attracted extensive attention for their unique features including high energy density, safety, low cost and environmental friendliness. However, due to their poor chargeability and low efficiency, the practical application remains a challenge. The main obstacles are the intrinsic slow reaction kinetics on air cathodes, including oxygen reduction reaction during the discharging process and oxygen evolution reaction during the recharging process. Searching for efficient bifunctional oxygen electrocatalysts is key to solve these problems. In this review, the configuration and fundamental oxygen electrochemical reactions on air cathodes are briefly introduced for Zn-air batteries first. Then, the latest bifunctional oxygen electrocatalysts are summarized in detail. Finally, the perspectives are provided for the future investigations on bifunctional oxygen electrocatalysts.

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1. Introduction

With the development of human society, the demand for energy is growing sharply. However, the excessive consumption of energy has sounded the alarm for mankind. Sustainability has attracted widespread attention and quickly became the focus of modern society [1]. Great efforts have been made towards the development of green and sustainable energy resources, which greatly promote the progress of electrochemical energy storage and conversion technologies [2–6]. Currently, lithium-ion batteries are leading the field of energy storage. However, the insufficient energy density of rechargeable lithium-ion batteries (the theoretical value is about 400 Wh kg⁻¹, and the actual value is 200–250 Wh kg⁻¹) limits their further applications and development [7]. The theoretical energy density of metal-air batteries is several times larger than that of the

most advanced lithium-ion batteries, making them a good substitute for lithium-ion batteries with widespread attention [8]. Metal-air batteries can be classified into several different types depending on the metal anode [9]. Lithium-air batteries and zinc-air batteries are the most promising ones [10,11]. However, lithium-air batteries have some potential dangers, since lithium metal is active, and organic electrolytes are flammable [12]. The cost of lithium metal is relatively high and lithium resource occurs only in unusual natural mineral deposits and salt lakes [13]. These shortcomings hinder the commercialization process and large-scale application of lithium-air batteries in the future.

Zn-air batteries are by far one of the best options for their unique features including relatively high specific energy (1370 Wh kg⁻¹), safety, low cost [14], and environmental friendliness. However, due to their poor chargeability and low efficiency,

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their practical application remains a challenge. The main obstacles are the intrinsic slow reaction kinetics on air cathodes, including oxygen reduction reaction (ORR) during the discharging process and oxygen evolution reaction (OER) during the recharging process [15]. Currently, the common electrocatalysts for ORR/OER are noble metal-based materials, such as Pt and its alloys for ORR and RuO₂/IrO₂ for OER. However, high cost, low reserves in the earth, and inferior durability greatly hinder their large-scale applications [16]. In addition, noble metal-based materials commonly have single catalytic function toward either ORR or OER, which would cause poor recharge ability [17]. Therefore, it is urgently needed to develop efficient and inexpensive bifunctional electrocatalysts for both ORR and OER.

There have been some reviews summarizing single functional cathode catalysts for Zn-air batteries, but the specific summary of bifunctional catalysts for Zn-air batteries has rarely been reported. In this review, we focus on the latest advances in bifunctional electrocatalysts for air cathodes in Zn-air batteries. The aim is to provide better understanding of the electrocatalysis in Zn-air batteries and rational guidance for further investigation and design of bifunctional electrocatalysts. The configuration and fundamental oxygen electrochemical reactions on air electrodes are briefly introduced for Zn-air batteries first. Then, recently reported ORR/OER bifunctional electrocatalysts are summarized specifically and systematically. Finally, the challenges facing the development of bifunctional electrocatalysts are highlighted, together with further research directions and perspectives.

2. Working principles of Zn-air batteries

2.1. Configuration of Zn-air batteries

A rechargeable Zn-air battery (RZAB) consists of a metal Zn anode, a separator and an air cathode, which are packaged together with the aqueous alkaline electrolyte [1], as illustrated in Figure 1. The generation of electricity in rechargeable Zn-air batteries is realized through redox reactions between the an-

Fig. 1. Schematic of a typical Zn-air battery.

ode and cathode, i.e., oxidation and reduction of the Zn anode, ORR and OER on the air cathode, respectively [18].

Like typical secondary batteries, rechargeable Zn-air batteries can be recharged by applying an external potential to reverse the electrochemical reactions in the cell [19]. During discharging, electrons which are released by zinc oxidation travel through an external circuit to the air cathode [20], simultaneously, oxygen from the atmosphere diffuses and adsorbs into the air cathode, which is reduced through ORR to form hydroxide ions (eqn (1)) at three-phase boundaries among oxygen, the electrolyte, and the active materials. The generated hydroxide ions migrate to the zinc electrode, forming zincate ions (Zn(OH)₄²⁻) (eqn (2)), which further decompose to insoluble zinc oxide (ZnO) (eqn (3)) when becoming supersaturated in the electrolyte. The diffusion of zincate ions from the zinc anode to the air cathode causes increased polarization and decreased cycling efficiency; therefore, a separator is used between two electrodes to allow the flow of hydroxide ions while block zincate ions. The overall reaction is summarized in eqn (4), with an equilibrium potential of 1.65 V [20].

Air cathode:

Zinc anode:

Overall reaction:

To charge the battery, the aforementioned electrochemical reactions are reversed, in which zinc is deposited at the zinc electrode (eqn (5,6)) and oxygen is released through OER at the electrolyte-electrode interface (eqn (7)). The overall reaction is summarized in eqn (8).

Zinc anode:

Air cathode:

Overall reaction:

2.2. ORR and OER reaction mechanisms

2.2.1. ORR

As mentioned above, ORR and OER are the basic electrochemical reactions at the air cathode, corresponding to the process of discharging and charging, respectively. In alkaline Zn-air batteries, ORR can be described as the following steps: oxygen first diffuses to the catalyst surface from the atmosphere and adsorbs on it, then the oxygen bond is subsequently weakened and broken by electrons transferred from the anode, and finally the hydroxyl ion product is released from the catalyst surface into the electrolyte [21]. There are several steps in the electrochemical reaction as shown below [22].

ORR may proceed via a four-electron route as shown in eqn (9) or a two-electron route as shown in eqn (10). In the 2e pathway, peroxide species are produced, either the reduction of the peroxide (eqn (11)) or a chemical disproportionation of the peroxide (eqn (12)) will subsequently occur. This process can be denoted as a serial $2 \times 2\text{e}$ pathway. The ORR pathway depends on the configurations of oxygen adsorption that exist on the active sites of the catalyst [23]. There are two types of oxygen adsorption: bidentate O_2 adsorption (two O atoms coordinated with the catalyst) and end-on O_2 adsorption (one O atom coordinated perpendicularly to the catalyst). The bidentate adsorption contributes mainly to the direct 4e pathway, while the end-on adsorption mainly results in a 2e pathway with peroxide formation. The peroxide species generated during the 2e pathway are corrosive and detrimental to the stability of the battery [7]. For practical battery applications, catalysts that can facilitate ORR through the direct four-electron reduction pathway are highly preferred. The ORR pathways and mechanisms vary with different catalysts and are associated with the specific crystal structure, electronic structure, or experimental parameters.

2.2.2. OER

The reaction mechanisms of OER are also extremely complex and vary with different catalysts. Oxygen molecules are easier to be evolved from metal oxides, rather than pure metals. A multivalence characteristic of metal cations is essential because the electrochemical reaction is induced from the interaction between metal cations and oxygen intermediates, with the formation of a bond by transforming the valence state [7]. The site geometry of metal ions has huge impact on the reaction process because it affects the adsorption energy of the oxygen species, the activation energy for the oxidation state, and the relevant coordination number. The OER route in an alkaline electrolyte is described as follows [19,24]. M represents the active site on the surface of the catalyst, and “ads” represents the substance adsorbed on the surface of the catalyst. All mechanisms begin with the coordination of hydroxides to the active sites in the alkaline environment. Then the next reaction proceeds mainly through two ways. The first pathway occurs through the process of (13)→(14)→(15), direct coupling reaction between the two M-O_{ads} intermediates produces oxygen. The second pathway occurs through the process of (13)→(14)→(16)→(17), M-O_{ads} and OH^- react to generate intermediate $\text{M-OOH}_{\text{ads}}$, and then $\text{M-OOH}_{\text{ads}}$ react with OH^- to produce O_2 . The barrier of the first reaction pathway is bigger than that of the second pathway [25].

or

There are several important parameters to evaluate the catalytic activity of oxygen electrocatalysts. The performance of the as-prepared catalysts is usually investigated by a standard three-electrode system, containing rotating disk electrode

(RDE) and rotating ring disk electrode (RRDE). Typically, a graphite rod is used as the counter electrode and a saturated calomel electrode (SCE) is implemented as the reference electrode. On the linear sweep voltammetry (LSV) curve of ORR, the onset potential (E_{onset}) is defined as the potential at 0.1 mA cm^{-2} [26]. Superb ORR catalysts require a high onset potential. The half-wave potential ($E_{1/2}$) is the electrode potential when the current density is equal to one-half of the limiting current density. In the OER process, the potential at 10 mA cm^{-2} is an important indicator for evaluating catalytic performance. Additionally, the potential difference ΔE ($\Delta E = E_{j=10} - E_{1/2}$) between the potential under the OER current density of 10 mA cm^{-2} and the half-wave potential of ORR is used to evaluate the overall activity of a bifunctional catalyst. The smaller the ΔE value, the better the catalytic activity of the bifunctional catalyst.

3. Bifunctional electrocatalysts for Zn-air batteries

The multi-electron reactions of ORR and OER can occur on the carbon electrode without any other catalyst, but they are very slow. Although two single-function catalysts can be combined to achieve dual-function catalysis, this combination increases the cost and the difficulty of preparation processes [21,27–33]. Therefore, bifunctional catalysts are very important for Zn-air batteries. The development of bifunctional catalysts has been so urgent that many groups have explored the preparation and performance of bifunctional catalysts [34–39]. In this section, bifunctional electrocatalysts such as heteroatom doped carbon materials, metal/metal oxides and carbon hybrid materials and metal organic framework (MOF)-derived materials are summarized. Electrocatalytic performances of recently reported bifunctional electrocatalysts for ORR and OER are compared in Table 1.

3.1. Metal-free bifunctional electrocatalysts

3.1.1. Heteroatom doped carbon materials

Carbon materials are considered to be candidates for metal-free catalysts due to their catalytic activity, stability and cost-effective characters [40]. Moreover, the catalytic activity can be improved by heteroatom (N, S, P, or B) doping or structural engineering adjustment [26,36,41–43], and heteroatom doped carbon materials are effective metal-free electrocatalysts [44]. Through the doping of heteroatoms, carbon materials can benefit the formation of hydroxide ions through a four-electron process, thereby promoting the occurrence of ORR. Unfortunately carbon materials are commonly used as single-functional ORR catalysts because their OER catalytic activity is generally poor [45]. However, by doping heteroatoms in carbon materials, the OER activity can also be improved. The catalyst obtained by this method exhibits excellent bifunctional catalytic activity and stability.

For instance, nitrogen-doped graphene was prepared by Cui et al. [41] with a molten salt assisted method (Figure 2). Density functional theory (DFT) computations reveal that arm-chair-graphitic N and zigzag-pyridinic N are more favorable for ORR and OER, respectively. Because of matched N catalytic

Table 1

Electrocatalytic performance of recently reported bifunctional electrocatalysts for ORR and OER.

Catalyst	ORR performance vs RHE	OER performance vs RHE $E_{j=10}$ (V)	ΔE ($E_{j=10} - E_{1/2}$) (V)	Ref.
N-G	$E_{\text{onset}} = 0.95$ V, $E_{1/2} = 0.78$ V, $J_L = -4.3$ mA cm $^{-2}$	1.69	0.91	[39]
P-CN	$E_{\text{onset}} = 0.92$ V, $E_{1/2} = 0.85$ V, $J_L = -4.5$ mA cm $^{-2}$	1.59	0.74	[41]
N,S-C	$E_{\text{onset}} = 0.99$ V, $E_{1/2} = 0.85$ V, $J_L = -5.8$ mA cm $^{-2}$	1.69	0.81	[40]
P,S-CNS	$E_{\text{onset}} = 0.97$ V, $E_{1/2} = 0.87$ V, $J_L = -7.1$ mA cm $^{-2}$	1.56	0.69	[51]
S-C ₂ NA	$E_{\text{onset}} = 0.98$ V, $E_{1/2} = 0.88$ V, $J_L = -6.6$ mA cm $^{-2}$	1.53	0.65	[54]
FeCo-N _x -CN	$E_{\text{onset}} = 0.95$ V, $E_{1/2} = 0.89$ V, $J_L = -6.3$ mA cm $^{-2}$	1.67	0.78	[57]
PBSCF-NF	$E_{1/2} = 0.73$ V, $J_L = -4.5$ mA cm $^{-2}$	1.53	0.80	[32]
NiO/CoN PINWS	$E_{\text{onset}} = 0.89$ V, $E_{1/2} = 0.68$ V, $J_L = -4.7$ mA cm $^{-2}$	1.53		[67]
Co ₃ O ₄ /NPGC	$E_{\text{onset}} = 0.97$ V, $E_{1/2} = 0.84$ V, $J_L = -5.8$ mA cm $^{-2}$	1.68	0.84	[72]
NCNT/CoO-NiO-NiCo	$E_{\text{onset}} = 0.97$ V, $E_{1/2} = 0.83$ V, $J_L = -4.3$ mA cm $^{-2}$	1.50		[76]
NC-Co ₃ O ₄	$E_{\text{onset}} = 0.91$ V, $E_{1/2} = 0.87$ V	1.59	0.72	[79]
MnO@Co-N/C	$E_{1/2} = 0.83$ V, $J_L = -5.3$ mA cm $^{-2}$	1.76	0.93	[82]
NiFe@NC _x	$E_{\text{onset}} = 1.03$ V, $E_{1/2} = 0.86$ V, $J_L = -5.9$ mA cm $^{-2}$	1.46	0.60	[83]
N,P-C	$E_{\text{onset}} = 0.92$ V, $E_{1/2} = 0.82$ V			[84]
NPSC	$E_{\text{onset}} = 0.93$ V, $E_{1/2} = 0.77$ V, $J_L = -4.76$ mA cm $^{-2}$	1.56	0.79	[85]
Co ₃ O ₄ -C	$E_{\text{onset}} = 0.95$ V, $E_{1/2} = 0.83$ V	1.54	0.71	[87]
CoFe/N-GCT			0.88	[88]
CoO _x @NGCR	$E_{\text{onset}} = 0.91$ V, $E_{1/2} = 0.80$ V, $J_L = -4.9$ mA cm $^{-2}$			[89]
FeCo/N-C	$E_{\text{onset}} = 0.89$ V, $E_{1/2} = 0.81$ V	1.62	0.81	[90]
CoPi/NPGA	$E_{\text{onset}} = 0.91$ V, $E_{1/2} = 0.80$ V	1.57	0.77	[91]

Fig. 2. (a) Schematic representation of the fabrication method for 3D holey N-doped graphene (HNG). (b) Scanning electron microscope (SEM) image of HNG-900. (c) N₂ adsorption-desorption isotherm curve of HNG-900; the inset is pore distribution curve. (d) LSV curves of different catalysts for both ORR and OER in 0.1 mol L⁻¹ KOH at 1600 rpm [41]. © 2018 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

active sites, large specific surface area, and special hierarchical porous structure, the catalyst exhibits good bifunctional catalytic activity. Phosphorus is another important doping atom. Lei et al. [26] reported the preparation of 2D phosphorus-doped carbon nanosheets with adjustable porosity by a multifunctional template method. The high phosphorus doping content makes it have superior electrochemical properties. The catalyst shows well-balanced catalytic activity for both ORR and OER, which is comparable to that of commercial Pt/C and Ir/C counterparts in half-cell testing. Pei et al. [42] developed a facile one-pot synthetic method utilizing in situ reactions to fabricate N and S co-doped carbon catalysts (CNS). This catalyst exhibits excellent ORR/OER bifunctional activity and durability, even

better than that of transition-metal and noble-metal catalysts, and the potential difference ΔE ($E_{j=10} - E_{1/2}$) value of the best sample was only 0.72 V in 1 mol L⁻¹ KOH, superior to the values reported for metal-free catalysts so far. Besides, the performances of rechargeable Zn-air batteries based on the optimized catalyst substantially outperform those afforded by a benchmark Pt/C catalyst (Figure 3). The author thinks that the suitable active sites introduced by N and S elements account for the outstanding ORR activity of the catalysts, whilst the OER catalytic activity of the catalysts originates primarily from the oxygen and pyridinic N species in the carbon skeleton, in addition to a little contribution from S atoms.

DFT computations could predict the catalytic performance

Fig. 3. (a) Illustration of the one-pot fabrication process of doped porous carbon materials. (b) Charging and discharging polarization curves of the 1100-CNS and Pt/C catalysts. (c) Cycling tests of Zn-air batteries with the 1100-CNS or Pt/C sample as the catalyst at 10 mA cm^{-2} . (d) Photograph showing the lighting of a LED by two Zn-air batteries with 1100-CNS catalysts in series [42]. © 2017 The Royal Society of Chemistry.

of heteroatom-doped carbon materials and guide experiments. Zhao et al. [46] explored an intrinsic descriptor which could directly demonstrate the ORR/OER activities of heteroatom doped carbon materials. Based on their intrinsic activity and doping species in carbon materials, they established a volcanic pattern to predict the bifunctional catalytic activity of the catalyst. This work indicates that doping near the edge of graphene nanoribbons is an effective strategy to develop highly active carbon-based bifunctional catalysts.

3.1.2. Heteroatom doped carbon nitride materials

Further improvement of the content and the uniform distribution of nitrogen in carbon-based materials may lead to more excellent catalytic performance, and this strategy has attracted great attention [47]. Carbon nitride-based materials may exhibit superior performance over nitrogen-doped carbon materials due to higher nitrogen content. For example, graphitic carbon nitrides ($\text{g-C}_3\text{N}_4$) is another promising metal-free bifunctional catalyst because of the high nitrogen content (theoretically up to 60 wt.%) and adjustable structure. The $\text{g-C}_3\text{N}_4$ contains a large amount of graphitic and pyridinic N species to promote the occurrence of ORR and OER [48,49]. However, poor conductivity limits its use as an oxygen electrocatalyst. Heteroatom doping can change its surface polarity and electronic properties to improve conductivity and further enhance catalytic activity [50,51]. In addition, reasonable structural design can increase the specific surface area, accelerate electron transfer, and improve chemical stability. Shinde et al. [52] developed a phosphorus and sulfur co-doped carbon nitride sponge (P,S-CNS) by the polymerization and pyrolysis of aminoguanidine. Through this method, a stable carbon-nitrogen material could be obtained with bifunctional electrocatalytic

activity, and exhibits excellent charge and discharge performance in Zn-air batteries. DFT calculations reveal that the heteroatom-induced charge and spin density polarization affects and amends the sorption free energies involving reaction intermediates at the N- and defect-rich sites, facilitating excellent ORR and OER activities. Their work provides an effective method to develop metal-free bifunctional electrocatalysts from nonmetal polymeric and carbonaceous materials as a substitute for precious metal catalysts for energy storage and conversion. In practical applications, especially at high voltages, disordered pore characteristics and unstable structures tend to limit the chemical behavior of the catalyst. Covalent organic frameworks (COFs) gradually enter people's vision because of their relatively ordered porous and π -conjugated structures, which help us understand the direct relationship between compositional structure and chemical performance [53]. Especially, carbon- and nitrogen-based COFs (holey C_2N) have attracted huge attention because of stable pore characteristics, adjustable electronic/chemical functionalities, robust covalent linkages coming from their building blocks, and ultrahigh cross-linking density, which greatly elevate the stability of the structure and the flexibility of the material, promoting the improvement of bifunctional catalytic activity [54]. Based on the above advantages, Shinde et al. [55] presented the hierarchical 3D sulfur-modulated holey C_2N aerogels by the amination and polymerization of chloroanilic acid (Figure 4). The combination of aerogels and COFs with continual and ordered porous structures has great significance. Benefiting from the continual and ordered porous, sulfur-doped carbon-nitrogen structure and ultrahigh surface area, S- C_2N aerogels reveal outstanding bifunctional catalytic activity ($\Delta E = 0.65 \text{ V}$), outperforming noble metal (Pt/C and RuO_2) benchmarks in terms of current density,

Fig. 4. (a) Schematic illustration depicting the development of 3D holey S-C₂N aerogel bifunctional catalysts through amination and polymerization processes and (b) their reaction mechanism. (c) Optical image of the fabricated 3D holey S-C₂N aerogel; the inset shows the ultralight aerogel suspended on a dandelion. (d, e) SEM images of the S-C₂N aerogel catalyst [55]. © 2017 American Chemical Society.

overpotential, and stability. DFT calculations revealed the bifunctional catalytic activity originates from dual doping and efficient mass/charge transfer.

3.2. Metal-based bifunctional electrocatalysts

Currently, the commonly used electrocatalysts for ORR/OER are noble metal-based materials such as Pt and its alloys for ORR and RuO₂/IrO₂ for OER [16]. However, high cost, low reserves in the earth and inferior durability greatly hinder their large-scale applications; therefore, looking for non-precious metals as bifunctional catalysts has become an urgent task. Compared with precious metals, transition metals are relatively inexpensive and abundant in the earth. Due to the multiple valence states, transition metals can form various oxides with different crystal structures, which impart active electrochemical reaction characteristics to transition metal oxides [7]. In this aspect, metal-based bifunctional catalysts can be classified into three types depending on the composition or preparation method, namely metal and carbon hybrid materials, metal oxide and carbon hybrid materials and metal-organic framework (MOF)-derived materials. Bifunctional non-precious electrocatalysts are summarized and compared in this section.

3.2.1. Metal and carbon/nitrogen hybrid materials

The combination of transition metal particles and carbon materials for use as ORR and OER bifunctional catalysts exhibits stimulating properties. In such composites, the transition metal can not only increase the graphitization of the carbon materials during carbonization, but also contribute to the transfer of electrons. The carbon materials wrapped on the surface can effectively prevent the metal from being oxidized or corroded by acids; moreover the carbon surface can prevent metal agglomeration to ensure dispersion [56]. The addition of nitrogen to the carbon matrix not only adjusts the electronic structure of adjacent carbon atoms but also forms bonds with the metal (M-N_x-C), thereby greatly improving the catalytic activity of the catalyst. These materials are generally prepared by pyrolysis of metal salts and carbon-containing chemicals at high temperatures. Co has been widely studied as the efficient oxygen electrocatalyst through the direct carbonization of a powdery mixture of gelatinized amylopectin, melamine and cobalt nitrate. Tang et al. [57] reported that a graphene catalyst was prepared with atomically dispersed Co-N_x-C active sites. In addition, the abundant defective edges of graphene promote the coordination of Co atoms with pyridinic N species, resulting in highly dispersed Co-N_x-C structure. As a result, Co-N_x-C, N-doping, and oxygen functional groups adjust the charge distribution on the *sp*²-conjugated carbon matrix, thereby increasing the selectivity of chemisorption and promoting the

transfer of electrons. In combination with the above advantages, Zn-air batteries assembled with the catalyst exhibit excellent performance in relation to open-circuit voltage, charge/discharge voltage gap and energy efficiency. Increasing the metal species in the composite is an effective attempt to increase catalytic activity. Li et al. [58] developed a method to prepare Fe, Co-N_x-CN with the assistance of metal salts and silica nanoparticles (Figure 5a–c). The combination of Fe and Co with N-doping can modulate the electronic properties and surface polarities, thus improving the activity of the catalyst. Due to rich pore structure, abundant oxygen catalytic sites and uniform dispersion of single metal atoms or very small metal clusters, Fe, Co-N_x-CN reveals outstanding bifunctional catalytic activity, outperforming noble metal benchmarks (Figure 5d).

3.2.2. Metal oxide and carbon hybrid materials

Transition metals are considered to be effective alternatives to precious metal catalysts because of their abundant reserves, low cost, easy preparation, environmental friendliness and chemical reactivity in alkaline electrolytes. Transition metals can produce a variety of oxides with different crystal structures due to their various valence states. Therefore, the electrocatalytic activity of transition metals depends on the conversion between different valence states, and the formation of redox couples at the ORR and OER potential is critical [59]. The chemical constitution, oxidation state, texture, morphology, and crystal structure have been adopted as functional adjustment of the electrocatalytic activity [21]. Among the metal oxides, perovskite and pyrochlore are known to be promising candidates as electrocatalysts [60]. Especially, ABO₃-type perovskite oxides, composed of rare-earth or alkali metal at the A-site and transition-metal at the B-site, have been used as catalysts for air batteries. The performance of perovskite oxides can be adjusted by substituting the cation of the A site or the B site to achieve special structure, oxygen content, and electrocatalytic capability. The ORR/OER catalytic performance can also be enhanced by cation doping, surface optimization, nanostruc-

ture and composites [61]. For example, Bu et al. [34] reported the excellent ORR/OER catalytic performance of cation-ordered perovskite oxide PrBa_{0.5}Sr_{0.5}Co_{2-x}Fe_xO_{5+δ} ($x = 0, 0.5, 1, 1.5$, and 2) nanofibers as a bifunctional catalyst for alkaline Zn-air batteries. The well-controlled B-site metal ratio and large surface area of mesoporous nanofiber result in high performance of the oxygen reduction reaction and oxygen evolution reaction and stability in Zn-air battery. In addition to perovskite oxides, many transitional-metal spinel oxides, such as Co₃O₄, MnO₂, MnCo₂O₄, and NiCo₂O₄, are used as bifunctional catalysts for Zn-air batteries [62,63]. NiCo₂O₄ is a representative spinel compound and NiCo₂O₄ nanowires are widely used in electrocatalysis [64–66]. However, the electrocatalytic performance of NiCo₂O₄ nanowires is limited by the structure and lack an effective method to adjust the structure. Doping heteroatoms, especially nitrogen atoms, can effectively change the structure of low-dimensional materials and improve their catalytic performance [67]. The doped nitrogen can promote the adsorption of oxygen species and can generate more active sites, thereby effectively increasing the catalytic activity. In-situ nitrogenization of NiCo₂O₄ nanowire arrays is an effective method. Yin et al. [68] reported a strategy for preparing NiO/CoN porous interface nanowire arrays (NiO/CoN PINWs) as bifunctional electrocatalysts. The catalyst exhibits excellent performance for OER with a low overpotential of 300 mV at 10 mA cm⁻² and outstanding stability of 48 h. They are also active for boosting ORR with a half-wave potential of 0.68 V (Figure 6). The remarkable electrocatalytic performance of NiO/CoN PINWs is attributed to the porous nanowire structure, the reduction of coordination number for cobalt, the improved oxygen vacancies from the nanointerface, and robustly coupled interface from NiO and CoN.

The use of transition metals as bifunctional catalysts has undergone a lot of research and development; however, the catalytic activity and stability are still limited by low conductivity and agglomeration of metal oxide nanoparticles. The combination of transition metal oxides and carbon-based materials

Fig. 5. (a) Illustration of the preparation of active salt/silica-templated 2D meso/micro-FeCo-N_x-CN. (b, c) SEM images of meso/micro-FeCo-N_x-CN-30. (d) E_{gap} difference of micro-FeCo-N_x-CN and meso/micro-FeCo-N_x-CN [58]. © 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

Fig. 6. (a) LSV of NiO/CoN PINWs, NiCo₂O₄ NWs, CFP, and Ir/C (20%) for OER. (b) Tafel plots of NiO/CoN PINWs, NiCo₂O₄ NWs, CFP, and Ir/C (20%). (c) The differences in current density ($\Delta j = j_a - j_c$) at 1.04 V vs RHE plotted against the scan rate fitted to a linear regression allow for the estimation of C_{dl} . (d) LSV of NiO/CoN PINWs and Ir/C (20%) before and after CV cycles. The inset in (d) shows the chronoamperometric response at a constant potential of 1.53 and 1.54 V vs RHE for NiO/CoN PINWs and Ir/C (20%). (e) LSV of NiO/CoN PINWs, NiCo₂O₄ NWs, commercial Ir/C (20%), and Pt/C (20%) catalysts in O₂-saturated 0.1 mol L⁻¹ KOH solution. (f) The K-L plots of NiO/CoN PINWs, NiCo₂O₄ NWs, commercial Ir/C, and Pt/C. The inset in (f) shows kinetic current densities and the electron transferred numbers (on the top of the rectangular bars) for oxygen reduction on NiO/CoN PINWs, NiCo₂O₄ NWs, commercial Ir/C (20%), and Pt/C (20%) at 0.65 V vs RHE [68]. © 2017 American Chemical Society.

is an effective way to solve these problems. First, the graphitized carbon-based material has good electrical conductivity and can compensate for the low electrical conductivity of metal oxides. Secondly, metal oxides are loaded or wrapped by carbon-based materials in various forms, which can effectively avoid direct contact and thus reduce the possibility of agglomeration. Similarly, bimetallic oxides have disappointing electrical conductivity, and conductive substrates with large specific surface areas are beneficial for improving the electrical conductivity and accommodating more active bimetallic oxide catalysts in preparation of heterogeneous electrocatalysts [69].

Wei et al. [70] reported amorphous bimetallic oxide nanoparticles anchored on N-doped graphene oxide with simultaneous control of nanoparticle elemental composition, size, and crystallinity. Amorphous Fe_{0.5}Co_{0.5}O_x was obtained from Prussian blue analog nanocrystals. The prepared material shows excellent OER activity with a Tafel slope of 30.1 mV dec⁻¹ and an overpotential of 257 mV for 10 mA cm⁻² and superior ORR activity with a large limiting current density of -5.25 mA cm⁻² at 0.6 V. Zn-air batteries fabricated with these catalysts can achieve a specific capacity of 756 mA h g⁻¹ and a peak power density of 86 mW cm⁻² (Figure 7). In addition, the synergistic effect of transition metal oxides and carbon substrates will result in increased catalytic effects. Compared with pure spinel-Co₃O₄ and carbon materials, the synergistic coupling effect between Co₃O₄ and nitrogen doped graphene/carbon nanotubes contributes to the improvement of bifunctional catalytic performance and stability [71]. Li et al. [72] prepared a bifunc-

tional catalyst in which Co₃O₄ particles are encapsulated in a nitrogen-doped graphitized carbon structure. Excellent bifunctional catalytic activity is attributed to the following points: Co₃O₄ nanocrystal particles provide numerous active sites for electrocatalytic reactions, carbon substrates effectively improve conductivity and structural stability, the synergistic mechanism between the two components promotes the improvement of catalytic performance, and the pomegranate-like structure blocks the aggregation of metal oxides and provides a large number of mass transport routes. According to previous reports, nickel and cobalt oxides have remarkable ORR/OER catalytic activity [73,74]. Moreover, NiCo alloys can provide additional synergistic effect with the oxides. The difference in lattice strain between nickel and cobalt causes differences in oxidation-reduction potential and structural order. The Schottky barrier formed between NiCo alloys and transition metal oxides contributes to the separation of charges, so that the combination yields a promising electrocatalyst [75]. For example, Liu et al. [76] reported a bifunctional electrocatalyst composed of dominant NiCo alloy and a bit of Ni/Co oxides, and the composite was placed onto nitrogen-doped carbon nanotubes (recorded as NCNT/CoONiO-NiCo). The obtained material displayed superb performance as a bifunctional electrocatalyst for ORR and OER in Zn-air batteries owing to the fast charge-transfer rate and very likely synergistic effect between Co and Ni. NCNT/CoONiO-NiCo shows a significantly low overpotential (ca. 0.27 V) compared with the state-of-the-art IrO₂ (0.39 V) at a current density of 10 mA cm⁻² for OER, and an

Fig. 7. (a) Schematic illustration of the preparation of $\text{Fe}_{0.5}\text{Co}_{1-x}\text{O}_x/\text{NrGO}$ hybrids in a three-stage approach. (b) The overall polarization curves of $\text{Fe}_{0.5}\text{Co}_{0.5}\text{O}_x/\text{NrGO}$ and commercial Pt/C and IrO_2 catalysts for ORR and OER. (c, d) $\text{Fe}_{0.5}\text{Co}_{0.5}\text{O}_x/\text{NrGO}$ as a bifunctional air electrode for rechargeable Zn-air batteries in comparison with commercial Pt/C + IrO_2 catalysts. (c) Galvanodynamic charge/discharge profiles (left) and power density curves (right). (d) Galvanostatic discharge curves of primary Zn-air batteries [70]. © 2017 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

onset potential of 0.97 V with a half-wave potential of 0.83 V for ORR.

3.2.3. MOF-derived materials

MOFs are hybrid inorganic-organic microporous crystalline materials consisting of metal ions and organic linkers that form a three-dimensional structure through coordination bonds. MOF-derived materials have attracted huge interest because of the inherently high porosity, large surface area and tunable structure [77]. MOF-derived materials as bifunctional catalysts have the following advantages: the large surface area facilitates exposure of more active sites, the tunable hierarchical pore structure facilitates the transport of species, and metal centers/doped atoms have multiple selectivity [78].

Zeolitic imidazolate frameworks (ZIFs) are the most representative kind of MOFs which are synthesized by coordinating transition metals (Zn^{2+} or Co^{2+}) with imidazole ligands. Pyrolysis of MOFs is one of the most common means of preparing such catalysts. With the combined carbonization-oxidation route of a cobalt-based MOF precursor, Guan et al. [79] reported a hierarchical catalyst consisting of irregular hollow Co_3O_4 nanospheres encapsulated in N-doped carbon nanowall arrays with efficient catalytic activity towards both OER and ORR. The hollow Co_3O_4 nanospheres with plenty of nanograins can provide sufficient active sites with short ion-diffusion length and the N-doped carbon coverage layer can enhance the electrical conductivity and stability. However, in the process of carbonization, the carbon framework is easy to self-aggregate to obstruct some pore structures and affect the contact between the electrolyte and the pores. One-dimensional (1D) nanomaterials can effectively prevent self-aggregation of carbon frameworks and have high electrical conductivity [80,81]. Chen et al. [82] prepared 1D $\text{MnO}_2/\text{ZIF-67}$ precursors with the assistance of MnO_2 hollow nanowires as templates. After subsequent pyrolysis, porous $\text{MnO}/\text{Co-N/C}$ nanomaterials were successfully

obtained, which exhibited outstanding bifunctional catalytic activity towards ORR and OER. Under the same experimental conditions, the stability and durability of the prepared material is even better than those of Pt/C. The exceptional bifunctional catalytic activity is attributed to synergistic effect of MnO and porous Co-N/C (Figure 8). Because of the coordinated environment and orderly arrangement, MOFs can effectively encapsulate metal ions. In order to prevent the collapse of the structure during pyrolysis at high temperature, and uncontrolled growth of metal particles, some strategies have been explored. Zhu et al. [83] developed a special method to obtain NiFe₂ alloy nanoparticles encapsulated in carbon cages with small core size, high dispersion and metal loading. At low temperatures, MOF-based NiFe-MILs (MIL-88b) are used to encapsulate metal ions. At high temperatures, melamine is employed as the N source and soft template after the disintegration of MOFs, which form graphitic carbon cages on transition metal surface to prevent further uncontrolled growth of metal particles. By optimizing the electronic modulation effect from appropriate metal cores, the NiFe@NCX catalyst shows high durability and activity with an onset potential of 1.03 V for ORR and overpotential of 0.23 V at 10 mA cm^{-2} for OER, obviously better than commercial Pt/C and IrO_2 catalysts (Figure 9).

4. Summary and outlook

Energy issues are becoming more and more intense, and searching for efficient energy storage and conversion devices is imminent. Zn-air batteries have attracted extensive attention due to their unique performances. The technical difficulty is to find efficient bifunctional cathode electrocatalysts to promote the ORR of the discharging process and the OER of the charging process. Based on this problem, much work has been conducted, and various electrocatalytic materials have been developed [84–91]. We have summarized the latest development of bi-

Fig. 8. (a, b) SEM and TEM images of MnO@Co-N/C. (c) LSV curves of the ORR and OER of different catalysts. (d) Discharge-charge cycling curves at 5 mA cm⁻² of a home-made Zn-air battery [82]. © 2018 The Royal Society of Chemistry.

Fig. 9. (a) Schematic illustration of the synthetic strategy of TMs@NCX composites. (b) ORR polarization curves for TMs@NCX samples in O₂-saturated 0.1 mol L⁻¹ KOH. (c) OER polarization curves of TMs@NCX samples and commercial IrO₂ and Pt/C catalysts [83]. © 2016 American Chemical Society.

functional catalysts without precious metals and divided them into two major categories, metal-free and metal-based catalysts. For metal-free bifunctional catalysts, heteroatom-doped carbon materials are the focus of research because of the efficient catalytic activity, stability and cost-effective characters. For metal-based bifunctional catalysts, we divided them into three categories according to their composition and preparation, namely metal and carbon/nitrogen hybrid materials, metal oxides and carbon hybrid materials and MOF-derived materials. Among them, the composites of transition metal oxides and carbon materials have become the most promising substitutes for precious metal catalysts due to their unique proper-

ties and their synergistic effects.

Different types of electrocatalysts have their own advantages and disadvantages. Carbon materials are considered to be candidates for metal-free catalysts due to their catalytic activity, stability and cost-effective characters. Moreover, the catalytic activity can be improved by heteroatom (N, S, P, or B) doping or structural engineering adjustment. But carbon-based materials are usually used as ORR electrocatalysts, the bifunctional catalytic performance is rarely reported, mainly because of their fairly low OER catalytic activity and the inevitable carbon corrosion under the high oxidation potentials of the OER, which could result in catalyst agglomeration and cover the ac-

tive surface with carbonates. This problem can lead to deactivation of the electrocatalysts. Transition metals are considered to be effective alternatives to precious metal catalysts because of their abundant reserves, low cost, easy preparation, environmental friendliness and chemical reactivity in alkaline electrolytes. Due to the multiple valence states, transition metals can form various oxides with different crystal structures, which impart active electrochemical reaction characteristics to transition metal oxides. The use of transition metals as bifunctional catalysts has undergone a lot of research and development; however, the catalytic activity and stability are still limited by low conductivity and agglomeration of metal oxide nanoparticles. These shortcomings limit the catalytic performance and service life of the electrocatalyst.

The development of bifunctional oxygen electrocatalysts has a long way to go, and there is still severe difficulty to overcome. For different materials, the catalytic active sites of ORR and OER may be the same or different. The calculation is an important mean to design a high-efficiency bifunctional electrocatalyst. By calculations, the chemical environment required for ORR and OER, and effective catalytic site of the catalyst can be obtained, and then the number of catalytic sites can be increased and the position of the catalytic sites can be exposed by experimental means. For the rational design of catalysts, we propose the following points of view. First, for carbon-based materials, hierarchical structure and defects/dopants are two important factors. The hierarchical structure includes a large number of pores in which mesopores provide large specific surface area and thus can expose more catalytically active sites, while macropores provide the pathway for the transport of reactants and products. Heteroatom doping and the fabrication of defects can modify the electronic structure to create more active sites. Adjusting one or more of these properties is significant to the preparation of high performance carbon based bifunctional catalysts. Metal-based bifunctional catalysts, mainly including transition metals and their oxides, exhibit high activity and stability, but the mass specific activity when

compared with noble-metal based materials is still low. In order to achieve higher catalytic activity, larger loading may result in agglomeration of metals or their oxides which in turn produces higher electrical resistance. Therefore, it is important to increase the catalytic activity of catalysts based on a limited mass or volume loading. Reducing the size of metal or metal oxide particles to expose more active sites and relieving metal agglomeration could provide effective catalytic activity with limited loading. In addition, modifying the morphology, structure, crystalline phase and valence state of the metal catalyst is also an effective mean for preparing high-efficiency metal-based catalysts. The durability of the catalyst is also a very critical issue, because it involves the actual service life of Zn-air batteries, but there are few studies on the durability of the catalyst. In the future, the stability and durability of bifunctional oxygen electrocatalysts should be investigated extensively.

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Graphical Abstract

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Bifunctional electrocatalysts for rechargeable Zn-air batteries

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This review summarizes bifunctional oxygen electrocatalysts for Zn-air batteries, including heteroatom-doped carbon and carbon nitride materials, metal and carbon/nitrogen hybrid materials, metal oxides and carbon hybrid materials, and metal-organic frameworks MOF-derived materials.

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可充电锌空气电池的双功能电催化剂

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摘要: 随着人类社会的发展, 对能源的需求急剧增长, 能源的过度消耗已经给人类敲响了警钟, 可持续发展进入人们的视野, 并迅速成为现代社会关注的焦点。众多的研究在绿色和可持续能源开发方面作出了巨大努力, 极大地推动了电化学储能和转换技术的进步。目前, 锂离子电池正在引领着能量存储领域。然而, 可充电锂离子电池的能量密度不足, 限制了它们进一步的应用和发展。金属空气电池的理论能量密度是最先进锂离子电池的几倍, 使其成为锂离子电池良好的替代品。根据负极金属的种类, 金属空气电池可分为几种不同类型, 其中锂空气电池和锌空气电池是最具有潜力的金属空气电池。但是, 锂空气电池存在一些缺点和潜在的危险, 例如锂金属成本相对较高且化学性质十分活泼, 有机电解质十分易燃。这些问题阻碍了未来锂空气电池的商业化进程和大规模应用。

锌空气电池因具有能量密度高、安全性好、成本低和环保等特性而备受关注。但是, 由于锌空气电池的可充电性能较差, 实现其实际应用仍然是一个巨大的挑战。阻碍其发展的最大障碍是空气正极上固有的缓慢的反应动力学过程, 包括放电过程中的氧还原反应和充电过程中的氧析出反应。寻找廉价高效的双功能氧电催化剂来取代传统的单功能贵金属催化剂是解决这些问题的关键。

在这篇综述中, 首先简要介绍了锌空气电池的结构和空气电极上基本的电化学反应。然后, 详细介绍了最新的用于锌空气电池的双功能氧电催化剂, 并将其分为无金属催化剂和金属催化剂两大类。对于不含金属的双功能催化剂, 杂原子掺杂碳材料是研究重点, 这是由于它们具有较高的催化活性、稳定性和低成本等特点。对于金属基双功能催化剂, 根据其组成和制备分为三类: 金属和碳/氮杂化材料; 金属氧化物和碳杂化材料; MOF衍生材料。其中, 过渡金属氧化物和碳的复合材料由于其独特的性质和协同效应而成为贵金属催化剂最有潜力的替代品。最后, 本文对双功能氧电催化剂的设计方法和未来研究进行了展望。

关键词: 双功能电催化剂; 氧还原反应; 氧析出反应; 锌空气电池; 杂化材料

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