Recent Advances in Non-Noble Bifunctional Oxygen Electro catalysts toward Large-Scale Production

Kai Zeng, Xiangjun Zheng, Cong Li, Jin Yan, Jing-Hua Tian,* Chao Jin,* Peter Strasser, and Ruizhi Yang*

The oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) are crucial reactions in energy conversion and storage systems including fuel cells, metal–air batteries, and electrolyzers. Developing low-cost, high-efficiency, and durable non-noble bifunctional oxygen electro catalysts is the key to the commercialization of these devices. Here, based on an in-depth understanding of ORR/OER reaction mechanisms, recent advances in the development of non-noble electro catalysts for ORR/OER are reviewed. In particular, rational design for enhancing the activity and stability and scalable synthesis toward the large-scale production of bifunctional electro catalysts are highlighted. Prospects and future challenges in the field of oxygen electro catalysis are presented.

1. Introduction

With the increasing of energy crisis and environment pollution, it is vital to develop efficient and ecofriendly energy conversion and storage systems. Among the numerous electrochemical devices, metal–air batteries, fuel cells, and water electrolyzers have received considerable attention due to their high energy conversion efficiency and environmental friendliness.[1] In the above energy conversion and storage devices, there are two key electrochemical reactions: oxygen reduction reaction (ORR) and oxygen evolution reaction (OER). Both of the two reactions require multielectrons transfer process associated with a complicated mechanism, resulting in slow kinetics and high overpotentials.[2] In the past several decades, great efforts have been focused on developing efficient electro catalysts for ORR/OER. It is well known that precious metal electro catalysts show the best performance. The Pt-based and Ru-/Ir-based materials are promising electro catalysts for the ORR and OER, respectively. However, Pt-based catalysts are unfavorable for OER since Pt could be easily oxidized to Pt oxides on the surface at a high potential.[3] Meanwhile RuO2 is extremely unstable at high potentials, forming RuO4 that can be dissolved in the electrolyte, leading to deactivation.[4] Furthermore, the high cost, limited reserves and low selectivity of Pt/Ru/Ir pose a great challenge to the large-scale commercialization of fuel cells, metal–air batteries, and water electrolyzers. Therefore, there is an urgent need to develop cost effective, earth abundant bifunctional electro catalysts for ORR and OER. In this regard, scale up of highly efficient and durable bifunctional electro catalysts for ORR and OER is highly demanded.

Considering the scale up of bifunctional electro catalysts for ORR and OER with a reduced environmental impact, carbon- and metal oxide-based catalysts are attractive due to their low cost, unique physicochemical structure, and easy functionalization.[5] As compared to metal oxides, carbon materials possess high electronic conductivity and more abundance. Carbon materials have been widely studied as promising electro catalysts for ORR. Some very good reviews of the recent research on carbon-based catalysts for ORR have been provided.[6] However, the activity and durability of carbon materials as bifunctional electro catalysts for ORR and OER still remain a great challenge, especially under the highly oxidative environment at high potentials during OER process. In contrast, metal oxides are more stable in alkaline solution under oxidative conditions, which are reported as effective catalysts for ORR and OER.[7] However, the poor electronic conductivity limits the catalytic activity of these materials. It is worth mentioning that the electrocatalytic activities of reported carbon- and transition metal oxide-based materials are still inferior to those of noble-metal-based catalysts, which requires rational design of material to address the challenges in the non-precious electro catalysts. With the help of advanced analytical and characterization techniques[8] and theoretical studies,[9] significant progress has been made on the identification of active sites and understanding the mechanisms of the ORR/OER.[10] Generally, the activity of a catalyst is the product of the catalytic site density and the intrinsic activity of a single site.[11] Meanwhile, the mass transport and charge transfer at solid–liquid–gas interface play crucial roles in the electrocatalytic activities.[12] Based on the accumulated in-depth knowledge, efficient design strategies of catalysts toward...
improving the catalytic activities and promoting interfacial mass transport and charge transfer have been explored.[31] As a result, various non-precious catalysts based on carbon- and transition metal-based materials have been developed. Therefore, a review with emphasis on the design and activity regulation toward the scale up of advanced non-precious bifunctional catalysts is of great significance, which will provide the guidance for the practical application of non-precious catalysts in energy conversion and storage devices.

In this view, recent advances on the design and development of non-precious bifunctional ORR/OER electrocatalysts toward the scale up are reviewed. First, the fundamentals of ORR/OER are explained in basic electrolyte. Based on in-depth understanding of the reaction mechanisms, we focus on design strategies of bifunctional ORR/OER catalysts with aiming to engineer active sites and to promote mass/charge transfer as well as scalable synthesis toward the large-scale production of efficient and durable electrocatalysts. Then the recent developments of carbon- and transition metal oxide-based electrocatalysts have been summarized. Finally, challenges and prospective in the large-scale production of highly effective bifunctional ORR and OER electrocatalysts are provided.

2. Fundamentals of ORR and OER

As is known, ORR and OER involve a series of electrochemical processes at multiple interfaces (solid, liquid, and gas phase), which involve oxygen diffusion, bond cleavage, reactant/intermediate adsorption, product desorption, and so forth.[14] In this section, the principles of ORR and OER in alkaline electrolytes are discussed.

2.1. Mechanism of ORR

The oxygen reduction reaction is dependent on catalysts and electrolytes. As illustrated in Figure 1a, a possible mechanism for the ORR on nitrogen-doped carbon materials was proposed, which involved two adsorption types on the surface of catalysts.[15] One is the bidentate O$_2$ molecule adsorption (two O atoms coordination to the catalysts), which corresponds to direct four-electron pathway to generate OH$^-$ in basic solution (Equation 1), respectively

$$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$$  \hspace{1cm} (1)

The other is end-on O$_2$ adsorption (one O atom coordination perpendicularly to the surface), which corresponds to indirect two-electron in two steps pathway. That is, the O$_2$ is first converted to HO$_2^-$ and further generates OH$^-$ in basic electrolytes (Equations (2)–(4)), respectively

$$\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{HO}_2^- + \text{OH}^-$$  \hspace{1cm} (2)

$$\text{HO}_2^- + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 3\text{OH}^-$$  \hspace{1cm} (3)

or

$$2\text{HO}_2^- \rightarrow 2\text{OH}^- + \text{O}_2$$  \hspace{1cm} (4)

Meanwhile, better understanding the mechanism of ORR has been obtained from the theoretical studies. Using density functional theory (DFT), Nørskov et al. studied the reaction mechanism of ORR through investigating the change of free energy of intermediates during the four-electron reaction.[16] For the efficient electrocatalysis, the ORR consists of four elementary reaction steps in alkaline medium:

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where * represents the active sites on the surface of catalysts, OOH*, O*, and OH* stands for the associated intermediates adsorbed on the active sites.

During the ORR process, the adsorption energy of oxygen-containing species on the active sites plays a crucial role in each step. Corresponding to Equations (5)–(8), the free energy for each elementary step of the four-electron ORR can be determined by the following equations

\[
\Delta G_1 = \Delta G_{\text{OOH}} - \Delta G_{\text{O}_2}
\]

\[
\Delta G_2 = \Delta G_{\text{O}} - \Delta G_{\text{OOH}}
\]

\[
\Delta G_3 = \Delta G_{\text{OH}} - \Delta G_{\text{O}}
\]

\[
\Delta G_4 = -\Delta G_{\text{OH}}
\]

Based on the scaling relationships, the adsorption energies of intermediates are correlated. The adsorption energies
of OOH* and OH* intermediates scaling relationship is \( \Delta G_{\text{OOH*}} = \Delta G_{\text{OH*}} + 3.2 \pm 0.2 \text{ eV} \), as found in some catalysts.\(^{[17]}\)

As shown in Figure 1b, 2-D volcano plot shows the “standard” scaling relationship for OOH* and OH*. Due to this unsatisfactory scaling relationship, the maximum lies well away from the scaling line for the materials are summarized. In other words, calculated catalysts need additional overpotentials at the top of the volcano map, which also limits the performance of a wide variety of different catalysts.\(^{[18]}\) In addition, the ORR activity is mainly restricted by the elementary reaction steps of \( \text{O}_2 \) reduction and \( \text{OH}^* \) reduction.\(^{[16,19]}\) It means that the above two steps need to be optimized by the rational design of catalysts to improve the catalytic activity.

2.2. Mechanism of OER

Similar to the ORR, typically, OER also involves four basic reaction steps in aqueous electrolyte.\(^{[20]}\) Figure 1c shows the OER mechanism under acid (blue line) and alkaline (red line) conditions.\(^{[23]}\)

In alkaline solutions:

\[ * + \text{OH}^- (aq) - e^- \rightarrow \text{OH}^* \]  \( (13) \)

\[ \text{OH}^* + \text{OH}^- (aq) - e^- \rightarrow \text{O}^* + \text{H}_2\text{O} (l) \]  \( (14) \)

\[ \text{O}^* + \text{OH}^- (aq) - e^- \rightarrow \text{OOH}^* \]  \( (15) \)

\[ \text{OOH}^* + \text{OH}^- (aq) - e^- \rightarrow \text{O}_2 (g) + \text{H}_2\text{O} (l) + * \]  \( (16) \)

Overall: \( 4\text{OH}^- (aq) - 4e^- \rightarrow \text{O}_2 (g) + 2\text{H}_2\text{O} (l) \)  \( (17) \)

where * represents the active sites of catalysts, intermediates \( \text{OH}^*\), \( \text{O}^*\), \( \text{OOH}^*\) are formed in each step, respectively. In addition, there exists another possible reaction path to produce \( \text{O}_2 \) (two \( \text{O}^*\) are coupled to form \( \text{O}_2 \)) as following:

\[ \text{O}^* + \text{O}^* \rightarrow \text{O}_2 (g) + 2* \]  \( (18) \)

However, this elementary step often requires higher thermodynamic barrier than \( \text{O}^* \) combining with \( \text{OH}^- \) to form \( \text{OOH}^* \) and release \( \text{O}_2 \).\(^{[22]}\) Therefore, this reaction step is more difficult to occur. The thermodynamic potential of OER is 1.23 V versus RHE. While an overpotential is often required to satisfy the reaction in the actual situation. As the OER proceeds in alkaline solution (Equations (13)–(16)), the reactivity of each step is also greatly dependent of the adsorption energy of oxygen-containing species. The free energy of each step of OER can be determined

\[ \Delta G_1 = \Delta G_{\text{OH}} \]  \( (19) \)

\[ \Delta G_2 = \Delta G_{\text{O}} - \Delta G_{\text{OH}} \]  \( (20) \)

\[ \Delta G_3 = \Delta G_{\text{OOH}} - \Delta G_{\text{O}} \]  \( (21) \)

\[ \Delta G_4 = \Delta G_{\text{O}_2} - \Delta G_{\text{OOH}} \]  \( (22) \)

These four steps are all thermodynamically uphill processes. Due to scaling relation, a correlation exists between the energy barriers of each step. Figure 1d shows the OER scaling relation of metal oxides with a volcano map.\(^{[23]}\) At the peak of the map, the two-step free energy is uniform, where \( \text{OH}^* \) converts to \( \text{O}^* \) and \( \text{O}^* \) converts to \( \text{OOH}^* \), resulting in the best performance. In addition, the rate-determining step (RDS) is the elementary step with the largest reaction free energy, which determines the catalytic properties of the material. The theoretical overpotential of the OER can be obtained by the following equations

\[ G_{\text{OER}} = \max \{ \Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4 \} \]  \( (23) \)

\[ \eta_{\text{OER}} = \frac{G_{\text{OER}}}{e} - 1.23 \text{ V} \]  \( (24) \)

In the four elementary steps of OER process, the rate-determining step (RDS) is often reported as the formation of \( \text{O}^* \) form \( \text{OH}^* \) or the evolution of \( \text{OOH}^* \) from \( \text{O}^* \).

3. Design Principle for the Bifunctional ORR/OER Electrocatalysts toward Scale Up

The electrocatalytic activity, durability, and scalable synthesis are crucial to the scale up of bifunctional electrocatalysts. The electrocatalytic activity of a catalyst is determined by the intrinsic activity of a single active site and number of active sites. Moreover, ORR/OER is an interfacial process, the mass transport and charge transfer at solid–liquid–gas interface are crucial in further enhancing electrocatalytic activity and durability. Scalable synthesis depends on the economic and facile synthetic methods.

3.1. Intrinsic Activity

To boost the intrinsic activity of electrocatalysts, electronic structure engineering is regarded as an important and highly effective strategy. It includes doping with heteroatom, anion, or cation and creating vacancy. The heteroatom, anion or cation doping facilitates the generation of subtle distortions in the arrangement of atoms and redistribute the electron or spin density,\(^{[6a,24]}\) which benefits the ORR and OER catalytic activity.

Vacancy, as one of defect types, is closely related to charge distribution and band structure.\(^{[1,24,25,60]}\) The presence of vacancies in the catalyst can significantly regulate the electron configuration to improve the electronic conductivity of material, and further enhancing the intrinsic activity of the electrocatalysts. Meanwhile, it is also regarded as a practical method to change the valence of the elements in the catalysts by creating vacancies. For the metal oxides and other types of transition metal compounds, oxygen vacancy and metal cation vacancy are the two most important vacancies. Compared with oxygen vacancy, metal cation vacancy have more fascinating and complex regulation change rule because of multiple electronic configurations and relative orbitals.\(^{[26]}\) In addition, metal cation vacancy may
also affect the surface electron structure around the active site of metal.[27]

3.2. Density of Active Sites

Morphology or/and structure control are critical to increase or expose active sites, thus affecting the catalytic activity of catalysts. Creating more edge sites with special morphology/structure possessing high surface area and porosity, such as nanowire,[28] nanosheet,[29] porous structure,[30] hollow structure,[31] and core–shell structure,[32,66] is considered as a good way to increase the active sites of the catalyst. Meanwhile, these special morphologies/structures are beneficial for the interfacial mass/charge transfer.

Moreover, it is known that atoms are arranged in different ways in different crystal facets. It is a promising approach to expose more active sites by rationally regulating the crystal facets. For example, more octahedral (Co$_3^{+}$oh) active sites were exposed in the {112} plane of Co$_3$O$_4$ nanopolyhedron,[33] which are beneficial for the ORR and OER activities.

3.3. Mass Transport and Charge Transfer

Mass transport and charge transfer are also important factors affecting the ORR/OER activity and durability. Structure control is also an effective approach to promote the diffusion of oxygen, mass transport of reactants and intermediates, and the penetration of the electrolyte where the ORR/OER takes place. In general, the specifically designed 0D (nanodot),[34] 1D (nanowire, nanotube),[28,35,77] 2D (nanosheet, graphene)[29,36] and 3D (sphere, hollow structure, core–shell structure and porous structure)[30–32,66] materials are beneficial for the interfacial mass transport and charge transfer.

3.4. Scalable Synthesis

Scalable synthesis of electrocatalysts depends on the facile synthetic methods, such as sol-gel,[30] template,[66] solvothermal/hydrothermal process,[36] based on the solution chemistry; electrodeposition,[71] plasma,[23] based on the surface chemistry; ball milling,[296] chemical vapor deposition,[37] microwave-assisted[38] approaches based on the solid-state chemistry. Cost-effective scalable synthesis with environmental benignity is critical to the scale up of electrocatalysts. Typical synthesis approaches for preparing carbon- and transition metal-based materials are compared in Table 1.

4. Bifunctional Electrocataysts for ORR/OER

In the past few decades, various highly efficient electrocatalysts based on non-precious metal materials have been developed and applied in bifunctional ORR/OER reactions. Among them carbon- and transition metal oxide-based materials have shown great potential in electrochemical applications.[35] Both of carbon- and transition metal oxide-based electrocatalysts are attractive due to abundant raw materials, low cost, and easy functionalization. Carbon-based materials own high surface area and excellent electrical conductivity, which are beneficial for improving the ORR/OER activity. However, the durability of most carbon-based electrocatalysts under the highly oxidative environment at high potentials of OER still remains a great challenge. In contrast, metal oxides are stable during OER process. However, the intrinsic large bandgap of metal oxides, which results poor electronic conductivity, limits their catalytic activity toward ORR/OER.

4.1. Carbon-Based Materials

4.1.1. Defective Carbon

In carbon materials, defects are critical to the intrinsic activity of electrocatalysis, such as topological defects, hole defects, edge defects and the like, the adsorption energy of intermediates of ORR/OER on which can be optimized by modulating the electronic configuration of the carbon via defects.[56] Mu et al. first adopted DFT calculation to illustrate that the inherent pentagon defects can induce the reconfiguration of local electrons and endow the carbon matrix greater charge density and better oxophile capacity.[72] The HOMO, LUMO, and local electronic redistributions of common hexagon (C6) and pentagon defect (C5) are shown in Figure 2a. C5 exhibited lower HOMO–LUMO energy gap and higher average charge density than C6, promoting the electron transfer in electrocatalytic reactions and rendering more carbon atoms as active sites. As a result, C5 presented a far stronger oxygen adsorption ability than C6 (Figure 2b). Moreover, Zhang and co-workers prepared graphene materials enriched with topological defects by carbonization of sticky rice and melamine via MgO templates, which showed remarkable electrocatalytic activity for ORR and OER.[58] The potential gap ($\Delta$E) between the half-wave potential ($E_{1/2}$) for ORR and the potential at 10 mA cm$^{-2}$ ($E_{10}$) for OER on this materials is only 0.90 V. The first-principles simulations revealed that the adjacent pentagon and heptagon defects (C5+C7) rather than N-doping sites contribute to the superb bifunctional activity for ORR and OER, rendering the lowest overpotential of 0.14 V for ORR and 0.21 V for OER (Figure 2c,d).

Moreover, defects in carbon can also lead to difference in electron spins, which affect the configuration of surface charge, promoting the catalytic activity in the electrochemical reaction.[59] Recently, Wang et al. investigated the defects and the defect-induced charge behavior by using HOPG as a model with help of scanning ion conductance microscopy and Kelvin probe force microscopy, bridging the surface charge of active sites to electrocatalytic activity.[60] The importance of topological defects on the electrocatalytic activities of carbon has been highlighted in several recent reviews.[56,63]

4.1.2. Heteroatom-Doped Carbon

In addition to defects, heteroatom-doping in carbon is another kind of significant approach to remarkably improve the activity...
of carbon catalysts. The introducing of heteroatoms (such as N, P, S, O, B, F, etc.) with different atomic size and electronegativity into carbon can effectively modulate the local electronic configuration of the doping sites and the charge distribution of adjacent carbon atoms, thereby enhancing the catalytic activity of carbon.\textsuperscript{12,63} As shown in Figure 2e, a volcano shape between the ORR/OER activity of p-block element in the periodic table doped carbon and the combined electronegativity and electron affinity of dopants (denoted as a descriptor of $\Phi$) has been established by Xia and co-workers.\textsuperscript{62} It is also found that ORR and OER catalytic active sites depend on the dopant types. For N-doping, two most active ORR and OER catalytic centers were created near the N dopant (Figure 2f). While for halogen elements-doping, ORR/OER centers were produced at the same spot (Figure 2g). Design principles for improving the catalytic activity of p-block element-doped carbon for both ORR and OER were provided.

As a p-block element in the periodic table, N is the most extensively studied dopant. Recently, Qu and co-workers summarized the advances in metal-free N-doped carbon nanomaterials and perspectives on the preparation of more efficient and sustainable carbon electrocatalysts were presented.\textsuperscript{64} As an example, Li et al. reported an N-enriched hierarchically porous carbon electrocatalyst (Figure 3a) prepared by ball milling method, exhibiting remarkable performance for ORR and OER. For overall oxygen electrocatalysis, the potential gap between the half-wave potential ($E_{1/2}$) for ORR and the potential at $10 \text{mA cm}^{-2}$ ($E_{10}$) was only 0.73 V in 0.1 M KOH (Figure 3b). The superior activity is attributed to the abundant N doping active sites and hierarchically porous architecture.\textsuperscript{65} Zheng and co-workers prepared a hollow cubic N-doped carbon material via a low-cost and facile NaCl template process. Benefiting from the peculiar hollow cube with hierarchical porous structure, high specific surface area, and uniform N-doping, the catalyst showed a high ORR activity with a negative shift of only 61 mV in the $E_{1/2}$ with respect to the Pt/C (20 wt%) and a OER activity higher than that of RuO$_2$/C.\textsuperscript{66} Based on the doping principles suggested by Xia et al. as mentioned above, P is another popular dopant and is also widely studied. For instance, Chen et al. prepared 2D P-doped carbon nanosheets (2D-PPCN) via a templating method by using glucose as carbon precursor and P$_2$O$_5$ as phosphorous source (Figure 3c). As shown in Figure 3d, 2D-PPCN-2/6 produced by optimizing the molar ratio of carbon to phosphorous showed the best ORR/OER activity. It delivered a same half wave potential of ORR as that of Pt/C (0.85 V), a smaller overpotential of OER (365 mV) than IrO$_2$, and the lowest potential gap of 0.74 V (between 2 mA cm$^{-2}$ for ORR and 10 mA cm$^{-2}$ for OER).\textsuperscript{66} In addition to N and P, other heteroatom-doped carbon has also been studied. Narayanan et al. first reported B-doped graphene derived from rhombohedral B$_6$C as an effective bifunctional catalyst for ORR/OER in 2015.\textsuperscript{68}

In addition to single type of doping, some of binary or ternary heteroatom doping, such as N and P, N and O, N, P and S codoping, etc. can yield optimal electronic and geometric structures favorable for ORR and OER.\textsuperscript{56,60} Recently, Dai and co-workers synthesized N and P dual doped porous carbon spheres (NPCS) electrocatalyst by an in situ interfacial polymerization of phytic acid and aniline followed a pyrolysis process (Figure 3d). As shown in Figure 3e, the resultant NPCs-900 by optimizing carbonization temperatures exhibited the greatest bifunctional catalytic performance, with the highest half-wave potential of 0.83 V for ORR and the smaller overpotential of 0.42 V for OER. Density functional theory (DFT) calculations and volcano plots (Figure 3f) demonstrated that the edge doping of N and P was more effective than the inner doping to improve catalytic performance.\textsuperscript{70} Moreover, Ma et al. reported N, F, B ternary doped\textsuperscript{71} and N, P ternary doped porous carbon fibers\textsuperscript{72} as a bifunctional electrocatalyst for ORR/OER and Zn–air battery.

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**Table 1.** Comparison of typical synthesis approaches for preparing carbon- and transition metal-based catalysts.

<table>
<thead>
<tr>
<th>Methods</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>Representative samples</th>
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<tr>
<td></td>
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<td>MnCo$_2$O$_4$ nanoparticles Anhcoated on NCNTs\textsuperscript{43}</td>
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<tr>
<td></td>
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<td></td>
<td>N, P codoped graphene frameworks\textsuperscript{36} Multishell mixed metal oxygen-phosphide particles\textsuperscript{46}</td>
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<td></td>
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<td></td>
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<td></td>
<td>porous Mn$_2$O$_3$ nanoballs\textsuperscript{53}</td>
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<td></td>
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<td></td>
<td>La$_6$Sr$_5$Co$_2$O$_9$/C particles\textsuperscript{54}</td>
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Figure 2. a) HOMO and LUMO distribution and local electronic redistributions. b) Oxygen adsorption energies of C6 and C5. Reproduced with permission.[57] Copyright 2019, Wiley-VCH. c) Schematic illustration of graphene nanoribbon with different N-doping species or topological defects. d) Volcano plots of ORR and OER overpotential with respect to adsorption energy of OH$. Reproduced with permission.[58] Copyright 2016, Wiley-VCH. e) Minimum overpotential of ORR/OER versus the descriptor $\Phi$ for graphene doped with different elements. Differential charge density distributions of f) nitrogen and g) fluorine-doped graphene sheets. Reproduced with permission.[62] Copyright 2015, Wiley-VCH.
It should be noted that some codoped carbon catalysts may show a worse activity than that of separated element doped carbon. For example, the separated B and N doping can turn inert CNTs into ORR electrocatalysts, while B and N codoping cannot improve ORR activity,\[73\] which is due to the neutralization occurring between N and B in the codoping case. These facts indicate that the doping microstructure plays an important role in the ORR performance, which is important in designing the carbon catalysts by multidoping.

The electrocatalytic activity of heteroatom-doped carbon depends on the dopant types and the combination of different dopants. Along with nonmetallic heteroatom-doped carbon, metallic and nonmetallic heteroatoms codoped carbon is another largest group of carbon catalysts. The metal–nitrogen–carbon (M–N–C) structures in carbon catalysts have attracted much attention due to the significant improvement in the catalytic activity and stability for ORR and OER under alkaline and acidic conditions. Generally, the M–N–C catalysts are prepared by pyrolysis of transition metal salt, nitrogen-containing compounds and carbon precursors under high temperature.\[55a,74\]

In addition, a series of metal macrocyclic compounds with M-N₄ structure can also be used to synthesize M–N–C catalysts. The catalytic activities of M–N–C materials are greatly dependent
on the precursors, metal choice, pyrolysis temperature and synthesis methods.[74] Li et al. synthesized the bifunctional ORR/OER electrocatalyst of 3D Fe–N codoped hierarchical mesoporous graphene (Fe–N HPC) by pyrolysis of polyacrylamide and Fe salt. The best-performing sample showed a good overall oxygen electrocatalytic activity and durability, the potential gap of 0.771 V between half-wave potential for ORR and the potential at 10 mA cm$^{-2}$ for OER was obtained. The high activity is attributed to the high density of active Fe–N sites and mesoporous structure.[75] Mu and co-workers prepared Co–N,C nanorod array electrocatalysts by using zeolitic-imidazolate frameworks (ZIFs) as precursors. The resulting Co–N,C presented superior electrocatalytic activity and stability for ORR and OER, a potential gap between $E_{1/2}$ for ORR and $E_{10}$ for OER was only 0.65 V.[76] Fransaer et al. synthesized a series of benzene-1,3,5-tricarboxylate (BTC)-based MOFs by electrodeposition technology, including Ni-BTC-DMF, Ni-BTC-body and Co-BTC-body. On the basis of above MOFs, the corresponding M–N–C catalysts were obtained after pyrolysis with different temperatures. Benefiting from the maximum electrochemical surface area and highest N content, Co-BTC-body-700 exhibited the best ORR (the smallest half-wave potential, lowest Tafel slope and a typical for the 4-electron process) and OER (the potential of 1.63 V at 10 mA cm$^{-2}$ better than IrO$_2$) activity. DFT calculations revealed that not only the metal choice (Co or Ni) but also N dopant species (pyridinic N or pyrrolic N) and coordination number of N greatly affect the activity of M–N–C. The Co–N$_{pyrid3}$–C, Co–N$_{pyrid4}$–C and Co–N$_{pyrro2}$–C were demonstrated to be the primary catalytically active sites in the Co–N–C structure.[77]

In recent years, catalysts with atomically dispersed metal on support, which is so called single-atom catalysts (SACs), have been emerged as a new kind of catalyst due to the maximum atom-utilization efficiency of metal atoms and excellent electrocatalytic performance.[25,78] Most of the reported single transition metal atom catalysts are supported on carbon materials, usually accompanied by the introduction of the nitrogen atoms, which is beneficial for the anchoring of metal atoms on the carbon matrix.[79] Wu and co-workers explored the atomically dispersed Fe–N$_x$ species on N and S codoped hierarchical carbon layers (S,N-Fe/N/C-CNT) as bifunctional ORR/OER electrocatalysts. Owing to the highly active Fe–N$_x$ species with atomically dispersed, increased accessible active sites by the porous structure and an improved electrical conductivity originating from the doping of N and S, the as-prepared S,N-Fe/N/C-CNT displayed a high ORR/OER activity with a potential gap of 0.75 V.[80] Han and co-workers reported the synthesis of Co single atoms on N-doped carbon with hierarchical urchin-like nanotube structure (UNT Co SAs/N-C) as a highly efficient bifunctional ORR/OER catalyst by using the UNT ZIF-67 as a precursor.[81] As revealed by HAADF-STEM, XANES and EXAFS in (Figure 4a–c), the single Co atom existed as CoN$_4$ local structure in UNT SAs/N-C. As a result, the UNT SAs/N-C exhibited excellent bifunctional activity for ORR and OER (Figure 4d,e). For overall oxygen electrocatalysis, a quite lower potential gap of 0.72 V, better than that of Pt/C and IrO$_2$ combination, was obtained. DFT calculations reveal that CoN$_4$ active sites play an important role in the oxygen electrocatalytic activity (Figure 4f).

Figure 4. a) HAADF-STEM image of hierarchical UNT Co SAs/N-C catalysts. b) Co K-edge XANES spectra. c) EXAFS spectrum with k$^3$-weight in R-space of UNT Co SAs/N-C, UNT Co S-NPs/N-C, UNT Co NPs/N-C, Co foil, and CoO reference. d) ORR LSV curves. e) OER LSV curves of samples. f) Free-energy diagrams for ORR/OER pathways on CoN$_x$ (x = 1–4) active sites in an alkaline media. Reproduced with permission.[81] Copyright 2019, Elsevier Ltd.
More recently, Hu and co-workers\textsuperscript{[82]} reported the synthesis of dual metal single-atom catalysts with bimetallic Co–Ni atoms supported on N-doped hollow carbon nanocube (CoNi-SAs/NC) as a bifunctional electrocatalyst for ORR and OER. The rechargeable Zn–air battery assembled with the CoNi-SAs/NC as the cathode catalyst delivered the electrochemical performance superior to that of the Pt/C-IrO\textsubscript{2} counterpart. Experimental and theoretical studies reveal that the homogeneously isolated single atoms of Co and Ni and the synergistic effect of diatomic Co–Ni active sites contribute to the fast ORR/OER kinetics. Zhou and co-workers\textsuperscript{[83]} designed a bifunctional Fe/Co single atom codoped graphite nanoarrays coupled with carbon microspheres (FeCo(a)-ACM). The as-prepared FeCo(a)-ACM also exhibited excellent ORR ($E_{1/2} = 0.9$ V) and OER ($E_{10} = 1.60$ V) activity because of the special structure and doping of Fe/Co single atoms.\textsuperscript{[83]}

4.1.3. Carbon-Based Composites

By creating defects or doping heteroatom in carbon, the ORR/OER activities of carbon can be greatly enhanced. However, the durability of carbon toward OER still remains a great challenge due to the highly oxidative environment at high potentials. It is known that some electrocatalysts, including carbon materials, sulfides and phosphides, are easily oxidized at high potential, resulting in changes in morphology, structure and composition, which in turn irreversibly affects the ORR activity of the catalysts. The standard Nernstian potential for the OER is 1.229 V versus RHE. The oxidation of carbon occurs above a thermodynamically potential of 0.207 V versus RHE (C + 4OH$^-$ $\rightarrow$ CO\textsubscript{2} + 2H\textsubscript{2}O + 4e$^-$) and becomes significant above 1.0 V versus RHE.\textsuperscript{[1a]} To address this challenge, selection of material with high stability under oxidative environment of OER process is important, for example, metal oxides and highly graphitic carbon are usually stable during OER. Moreover, by taking advantage of high ORR activity of some relative nonstable catalysts during OER (such as low graphitic carbon), coating or decorating with stable active materials on the surface of these catalysts is also a very promising approach to improve the stability of catalysts during OER. For example, Yang and co-workers reported an excellent bifunctional ORR/OER electrocatalyst of N-doped carbon nanofibers decorated with NiCo alloy nanoparticles using a facile electrospinning method (Figure 5a,b).\textsuperscript{[84]} The best performing sample displayed high ORR activity which was superior to that of commercial Pt/C catalyst, and OER activity comparable to that of RuO\textsubscript{2}. More importantly, the current of the sample still retained up to 79.5% after continuous operation at 1.71 V (vs RHE) for 7 h. Wu and co-workers\textsuperscript{[85]} reported the fabrication of FeCoNi alloy particles decorated on ultralarge sized N-doped graphene tubes as a new class of bifunctional oxygen electrocatalyst (Figure 5c,d). By using dicyandiamide as the precursor and water as the solvent, no additional template or carbon was used, the synthesis of graphene tube catalysts is scalable as well. The FeCoNi-derived N-GT catalyst demonstrates excellent ORR/OER activity and sufficient electrochemical durability in a wide range of potential (0–1.9 V) in alkaline solution. The high graphitization degree of tubes, presence of FeCoNi alloy particles along with nitrogen doping have accounted for the excellent ORR/OER performance. Cho and co-workers\textsuperscript{[86]} presented a homogeneous ternary Ni\textsubscript{46}Co\textsubscript{40}Fe\textsubscript{14} with a size distribution between 30 and 60 nm dispersed in carbon (C@NCF-900) as a highly efficient bifunctional electrocatalyst for ORR/OER. The as-prepared C@NCF-900 exhibited the highest ORR performance with $E_{1/2}$ of 0.93 V (vs RHE), and a low potential of 1.66 V (vs RHE) at 10 mA cm$^{-2}$ in 0.1 m KOH. Moreover, C@NCF-900 exhibited long-term stability over 10 000 voltage cycles.

![Figure 5. a) SEM images and b) TEM images and HRTEM in the inset of NiCo@N-C. 2. Reproduced with permission.\textsuperscript{[84]} Copyright 2018, Wiley-VCH. c) SEM images and d) TEM images of N-doped graphene tubes decorated with FeCoNi alloy particles. Reproduced with permission.\textsuperscript{[85]} Copyright 2016, Wiley-VCH. e) Schematic of the synthesis of MoO\textsubscript{3}-coated CNT and TEM images of pristine CNT, MoO\textsubscript{3}/CNT. Reproduced with permission.\textsuperscript{[83]} Copyright 2019, Elsevier Ltd.](image-url)
cycles with very little activity decay (minor potential reduction of only 0.006 V).

In addition to metal alloy nanoparticles, catalytic active metal oxides were also reported to be supported on the surface of carbon to produce efficient and stable bifunctional electrocatalysts for ORR and OER. In this case, the advantages of high electrical conductivity of carbon and high activity of metal oxides are their distinguished representative.

Transition-metal oxides (TMOs) are one of important and enormous family of bifunctional oxygen electrocatalysts for both ORR and OER, spinel oxide, perovskite oxide, and rutile-type oxide are their distinguished representative.

Despite some of them are instability in acidic electrolytes, most of them generally are sufficiently stable in alkaline media, making that these TMOs could be applied as bifunctional oxygen electrocatalysts in fuel cells and metal–air batteries in practice. In this section, the electrocatalytic properties, influence factors and designing strategies of various spinel oxides, perovskite oxides and rutile-type oxides will be systematically reviewed, respectively.

### 4.2. Transition-Metal Oxides

Transition-metal oxides (TMOs) are one of important and enormous family of bifunctional oxygen electrocatalysts for both ORR and OER. In this section, bifunctional oxygen electrocatalysts in fuel cells and metal–air batteries in practice. In this section, bifunctional oxygen electrocatalysts in fuel cells and metal–air batteries in practice.

#### 4.2.1. Spinel Oxides

Spinel oxides are undergoing much attention as bifunctional ORR/OER electrocatalysts. Typical spinel oxides can be described group oxides with the formula $\text{AB}_2\text{O}_4$, where $A$ is a...
divalent metal ion (such as Zn, Cu, Mg, Fe, Co, Ni, Mn) and B is a trivalent metal ion (such as Al, Fe, Co, Cr, or Mn). Usually, A\(^{2+}\) occupies part or all of the center of tetrahedral sites, B\(^{3+}\) occupies part or all of the center of octahedral position, and O\(^{2-}\) sits at the polyhedral vertexes.\(^{[101]}\) Actually, the distribute of A\(^{2+}\) and B\(^{3+}\) is complicated. According to their different dispersion ratios in the octahedral and tetrahedral interstices, spinel oxides can be divided into three types: normal, inverse, and complex spinels, as shown in Figure 6a. There are three main factors that affect the distribution of A\(^{2+}\) and B\(^{3+}\), including radius of cations, coulomb interaction between cations, and crystal field effects of the octahedral site preference energy of cations.\(^{[102]}\)

In addition, some external factors can also lead to the structural changes, such as Co\(_3\)Mn\(_{1-x}\)O\(_4\) can undergo a reversible structural transition of normal-inverse due to Co\(^{3+}\) and Mn\(^{4+}\) redistribution at elevated temperatures or pressures.\(^{[103]}\) As for spinel oxides, the controllable structure, accurate composition, desired morphology (micro/nano structure) are some alternative strategies to optimize their ORR/OER bifunctional electrocatalytic activities.

Chen’s group has done lots of works on Co–Mn–O spinel system. For example, they successfully synthesized both cubic and tetragonal phase of CoMnO\(_4\) spinels via an oxidation-precipitation process at 180 °C, as shown in Figure 6b, and found that the cubic phase Co–Mn–O spinel has higher intrinsic ORR activity but worse OER activity as compared to the tetragonal phase because of a stronger oxygen binding ability.\(^{[104]}\) Fe-doping has also been reported to adjust phase transformation of Co\(_3\)O\(_4\) spinel, it is found that a normal Co\(_3\)O\(_4\) spinel can be tuned to its inverse phase and then back to normal phase through controlling Fe-doped contents, and the inverse phase with a formal of (Co)[FeCo]O\(_4\) demonstrated the highest ORR activity due to the elongated O=O bonds and the modulated oxygen adsorption energy.\(^{[105]}\) Ge prepared a dual-phase MnCo\(_2\)O\(_4\) (dp-MCO) with both cubic and tetragonal spinels by a facile hydrothermal reaction and a freeze-drying posttreatment. Because of optimized Mn\(^{4+}/\)Mn\(^{3+}\) redox couples (ORR active sites) and increased surface Co\(^{3+}\) cations (OER active sites), the as-prepared dp-MCO demonstrated superior ORR/OER bifunctional activities compared to commercial Pt/C (30 wt% Pt) electrocatalysts, which makes a rechargeable zinc–air battery successfully be discharged–charged for 64 cycles (≈768 h).\(^{[106]}\)

Insights into the relationship between the crystal planes of spinel oxides and the catalytic activity play a crucial role in designing highly efficient bifunctional oxygen electrocatalysts. With a simple template-free hydrothermal strategy, Han controllably synthesized Co\(_3\)O\(_4\) nanocube, nanotruncated octahedron and nanopolyhedron with exposed crystal planes of...
(001), [010] + [111], and [112], respectively. Their study indicates that there are abundant octahedrally coordinated Co\(^{3+}\) sites on the [112] plane, where the adsorption, activation, and desorption of oxygen-containing species are optimized, and benefits ORR/ORR activities as well as Zn–air battery performances.\(^{[13]}\) Liu et al. have done a similar work with exposed planes of [100], [110] and [111], respectively. They consider that the surface Co\(^{3+}\) cations favor higher ORR performance, while the surface Co\(^{2+}\) cations present better ORR activity.\(^{[107]}\)

Elements doping is an effective way to tune electrical structures, change the chemical composition and the valence state of spinel oxides, and then enhance their electrocatalytic properties.\(^{[108]}\) Alkali metal, transition metal, rare-earth metal and even nonmetallic element can be selected as doping elements.\(^{[109]}\) Liu et al. reported Li-doped Co\(_3\)O\(_4\) solid solution nanocrystals as ORR/ORR electrocatalysts. They found that Li-doped Co\(_3\)O\(_4\) with 5% Li doped contents exhibits the best activity, Li-doping not only contributes to dramatically increasing content of valent O=C–O=Co\(^{3+}\)=O bonds to promote the oxidation of Co\(^{3+}\) into Co\(^{4+}\), but also significantly benefits facilitating the surface hydroxide substitution.\(^{[110]}\) Schechter et al. discussed effects of Ni-doping on bifunctional ORR/ORR activities of MnCo\(_2\)O\(_4\). Their studies indicate that the optimized Ni\(_{1.5}\)Co\(_{0.75}\)Mn\(_{0.5}\)Co\(_{0.5}\)O\(_4\) catalyst displays the best OER/ORR activity with an overpotential gap (\(\Delta E = E_{\text{ORR}} - E_{\text{OER}}\)) of 0.79 V versus RHE between two reactions in alkaline solution, nickel substitution leads to the in situ formation of ternary phases in the catalyst which is the key factor for improved activity and durability.\(^{[111]}\) Iron incorporation into cobalt vanadate (Co\(_3\)VO\(_4\)) has also been reported, Fe-doping makes Co\(_3\)V\(_2\)O\(_7\) from a normal to an inverse FeCo\(_2\)O\(_4\) spinel, Co\(_{1.3}\)Fe\(_{0.7}\)O\(_4\) exhibits a small \(\Delta E\) of 0.83 V versus RHE in 1.0 M KOH solution.\(^{[112]}\) Huang et al. recently found that Zr-doping into CoFe\(_2\)O\(_4\) can tune the local electronic environment of spinel and then induce charge transfer between Fe and Co ions, simultaneously, oxygen adsorption properties on the surface of oxides can also be optimized (Figure 6c). As a result, the as-prepared 3D CoFeZr oxide nanosheets demonstrate a superior OER activity with a low overpotential of 248 mV at 10 mA cm\(^{-2}\) in 1.0 M KOH.\(^{[113]}\) Coming from the same group, Yan et al. reported C-doped Co\(_3\)O\(_4\) by CH\(_4\) plasma treatment, and found that vast oxygen vacancies and novel Co–C bond (C-doping) can be achieved, which will modulate Co valence distribution in Co\(_3\)O\(_4\) and improve its oxygen electrocatalytic activities.\(^{[114]}\)

With the significant progress of nanotechnology, synthetic chemistry and advanced characterization, in the past few decades, people are more and more aware of the importance of intrinsic defects to catalytic properties.\(^{[115]}\) Oxygen vacancies are the most popular anion defects, many researchers believe that oxygen vacancy can tailor the surface electronic properties and gap states of spinel oxides, which benefits the improvement of oxygen catalytic activities. For example, Sun and co-workers introduced oxygen vacancy into CoFe\(_2\)O\(_4\) spinel using ionic liquid as a dopant, which demonstrate the best OER activity with an overpotential of 250 mV and a small Tafel slope of 41 mV dec\(^{-1}\), based on spinel electrocatalysts so far.\(^{[116]}\) Peng et al. developed a novel “adsorption-calcination-reduction” strategy to prepare series spinel oxides (NiCo\(_2\)O\(_4\), CoMn\(_2\)O\(_4\), NiMn\(_2\)O\(_4\)) with a unique yolk–shell structure and rich oxygen vacancies, the as-prepared spinel oxides offer superior OER activities.\(^{[117]}\) Qiu et al. prepared typical FeCo\(_2\)O\(_4\) spinel nanoparticles with abundant oxygen vacancies by the laser fragmentation method, which exhibit an excellent bifunctional oxygen electrocatalytic performance with lower half-wave potential of 0.82 V for ORR and smaller overpotential of 276 mV for OER to sustain a current density of 10 mA cm\(^{-2}\). As illustrated in Figure 6d, DFT calculations show the oxygen vacancies can effectively lower the thermodynamic energy barriers and accelerate the electron transfer.\(^{[118]}\) Plasma technique has also been utilized to create oxygen vacancy. Wang and co-workers reported that Co\(_3\)O\(_4\) nanosheets only needed an OER potential of 1.53 V versus RHE to reach a current density of 10 mA cm\(^{-2}\) after Ar-plasma etching, reduced 240 mV than that of the pristine Co\(_3\)O\(_4\) nanosheets. Abundant oxygen vacancies and increased surface area result in the enhanced OER performances.\(^{[119]}\)

As for spinel bifunctional oxygen electrocatalysts, there are plenty of works focusing on designing micro/nanostructures with various morphologies, including quantum dots,\(^{[119]}\) nanoparticles,\(^{[120]}\) nanorods,\(^{[121]}\) nanowires,\(^{[122]}\) nanotubes,\(^{[123]}\) nanofibers, nanosheets,\(^{[125]}\) nanocubes,\(^{[126]}\) nanoflowers,\(^{[127]}\) hollow microspheres,\(^{[128]}\) and nanowires arrays\(^{[129]}\) to enhance active sites and enhance catalytic activity (Figure 6e–h). CoMn\(_2\)O\(_4\) quantum dots (CMO QDs) have been prepared by a combined hot-injection and heat-up method. CMO QDs with average size of 3.9 nm owns a lower band gap energy, a moderate surface oxygen adsorbed energy, and a larger charge carrier concentration, and presents the highest OER/ORR activities among all investigated materials.\(^{[130]}\) CuCo\(_2\)O\(_4\) QD NiFe\(_2\)O\(_4\) QD and CoMn\(_2\)O\(_4\) nanodots have also been reported with desirable OER/ORR performances due to facile charge transfer and high fraction of active edge sites resulting from strong coupling.\(^{[131]}\) Recently, Jung et al. fabricated 1D MnCo\(_3\)O\(_4\) and CoMn\(_2\)O\(_4\) nanofibers as ORR/OER bifunctional electrocatalysts for rechargeable Zn–air battery via an electrospinning technique, a reduced discharge–charge voltage gaps could be achieved.\(^{[132]}\) A mesoporous thin-walled CuCo\(_2\)O\(_4\)@C hollow has been prepared through the same electrospinning process, which significantly lowered charge–discharge voltage gap (0.79 V at 10 mA cm\(^{-2}\)) and extended a long cycling life (up to 160 cycles for 80 h of Zn–air batteries).\(^{[133]}\) Nanoengineered hierarchical core–shell NiCo\(_2\)O\(_4\) chestnut-like structures was reported with a small OER/ORR potential difference of 0.90 V in 0.1 M KOH solution.\(^{[134]}\) Jin and co-workers developed a facile template-free coprecipitation route to fabricate well-ordered NiCo\(_2\)O\(_4\) (NCO) spinel nanowire arrays, which avoids the collapse during the fabricating process, possesses a specific surface area as high as of 124 m\(^2\) g\(^{-1}\), and delivers an ORR/OER bifunctional activities close to that of commercial Pt/C and IrO\(_2\) electrocatalysts.\(^{[136]}\) With PS colloidal microspheres and KIT-6 mesoporous silica as hard templates, three-dimensionally ordered macroporous (3DOM) CoFe\(_2\)O\(_4\) and CuCo\(_2\)O\(_4\) were prepared as bifunctional oxygen electrocatalysts for rechargeable Li–O\(_2\) batteries, they represent substantially enhanced specific capacity of 11 658 mAh g\(^{-1}\) and 7456 mAh g\(^{-1}\), respectively.\(^{[133]}\)

Considering relatively low electrical conductivity of spinel oxides, modifications with high-electronic-conductivity materials have been carried out. Cao and co-workers fabricated conducting polypyrrole modified MnCo\(_2\)O\(_4\) spinel as ORR/OER electrocatalysts.\(^{[136]}\) Carbon-coated MnCo\(_2\)O\(_4\) (MCO) nanowire has also been reported as bifunctional oxygen catalysts...
for rechargeable Zn–air batteries. The surface carbon shell not only provides conductive network to promote electron transfer, but also limits the growth of MCO nanoparticles during the discharge–charge process.[138] Moreover, Han and co-workers in situ constructed a conductive Mn−Co−P shell on the surface of MCO spinel through a facile phosphating, which only requires an OER overpotential of 269 mV to drive a current density of 10 mA cm\(^{-2}\) in 1.0 M KOH, and exhibits a strong long-term catalytic durability.[137] Moreover, Yang’s group reported a bifunctional electrocatalyst of MnCo_2O_4 modified with highly conductive Ti_4O_7, which was synthesized by a facile solvothermal method. The MnCo_2O_4/Ti_4O_7 was employed as a cathode catalyst for Li−air batteries. The synergistic effect between Ti_4O_7 and MnCo_2O_4 improved the ORR/OER kinetics, resulting in a high specific capacity of 5400 mAh g\(^{-1}\) @ 100 mA g\(^{-1}\) and long cycling stability of 100 cycles @200 mA g\(^{-1}\).[138]

There are some other potential factors that will affect the ORR/OER performances of spinel. For instance, Cao and co-workers reported that calcination temperature will affect the size and porosity of MnCo_2O_4, and then make a nonignorable influence on its bifunctional catalytic activities.[140] In addition, Zhao et al. developed a strategy to engineer the active sites for improved ORR/OER activities of NiCo_2O_4 (NCO) spinel via a simple tuning annealing temperature. They found that NCO-250 (250 °C) shows superior bifunctional oxygen electrocatalytic performances due to the highest value of Ni^{3+}/Ni^{2+} sites and the lowest value of Co^{3+}/Co^{2+} sites.[140]

The ORR/OER bifunctional performances based on spinel oxides mentioned above as well as other recent related reports have been summarized in Table 3.

### Table 3. ORR/OER performance of typical reported bifunctional spinel oxide catalysts.

<table>
<thead>
<tr>
<th>Active material</th>
<th>(E_{1/2}) (V)</th>
<th>(\eta_0) (V)</th>
<th>(E_g-E_{1/2}) (V)</th>
<th>Electrolyte</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mesoporous MnCo_2O_4[141]</td>
<td>0.83 V</td>
<td>0.42 V</td>
<td>0.85 V</td>
<td>0.1 M KOH</td>
</tr>
<tr>
<td>Hierarchical core–shell NiCo_2O_4 chestnut-like structures[154]</td>
<td>0.73 V</td>
<td>0.4 V</td>
<td>0.9 V</td>
<td>0.1 M KOH</td>
</tr>
<tr>
<td>CoMn_2O_4 porous microspheres[142]</td>
<td>0.75 V</td>
<td>0.6 V</td>
<td>1.08 V</td>
<td>0.1 M KOH</td>
</tr>
<tr>
<td>Core–shell Co@Co_2O_4 nanoparticles[143]</td>
<td>0.78 V</td>
<td>0.41 V</td>
<td>0.87 V</td>
<td>0.1 M KOH</td>
</tr>
<tr>
<td>Flower-like nanoneedle assembly NiCo_2O_4[144]</td>
<td>0.82 V</td>
<td>0.35 V</td>
<td>0.76 V</td>
<td>1 M NaOH</td>
</tr>
<tr>
<td>CuCo_2O_4 quantum dots decorated on N-doped CNTs[152]</td>
<td>0.8 V</td>
<td>0.47 V</td>
<td>0.9 V</td>
<td>0.1 M KOH</td>
</tr>
<tr>
<td>ZnCo_2O_4 quantum dots dispersed on NCNTs[156]</td>
<td>0.8 V</td>
<td>0.42 V</td>
<td>0.85 V</td>
<td>0.1 M KOH</td>
</tr>
<tr>
<td>NiCoO_2 nanowire arrays[18]</td>
<td>0.65 V</td>
<td>0.41 V</td>
<td>0.99 V</td>
<td>0.1 M KOH</td>
</tr>
<tr>
<td>Fe-doped Co_2O_4[112]</td>
<td>0.66 V</td>
<td>0.3 V</td>
<td>0.83 V</td>
<td>1 M KOH</td>
</tr>
<tr>
<td>5% Ni-doped Co_2O_4[145]</td>
<td>0.83 V</td>
<td>0.38 V</td>
<td>0.78 V</td>
<td>0.1 M KOH</td>
</tr>
<tr>
<td>N-doped NiCo_2O_4 Microsphere[146]</td>
<td>0.63 V</td>
<td>0.42 V</td>
<td>1.02 V</td>
<td>0.1 M KOH</td>
</tr>
<tr>
<td>Co_3O_4 nanoparticles with abundant oxygen vacancies[147]</td>
<td>0.88 V</td>
<td>0.27 V</td>
<td>0.62 V</td>
<td>1 M KOH</td>
</tr>
<tr>
<td>NiCoO_2 ultrathin nanosheets with oxygen vacancies[148]</td>
<td>0.74 V</td>
<td>0.44 V</td>
<td>0.93 V</td>
<td>0.1 M KOH</td>
</tr>
<tr>
<td>FeCo_2O_4 with oxygen vacancies[113]</td>
<td>0.82 V</td>
<td>0.28 V</td>
<td>0.69 V</td>
<td>0.1 M KOH</td>
</tr>
<tr>
<td>Co_3O_4 with oxygen vacancies on the carbon black surface[149]</td>
<td>0.87 V</td>
<td>0.42 V</td>
<td>0.78 V</td>
<td>1 M NaOH</td>
</tr>
<tr>
<td>Surface modification of MnCo_2O_4 with conducting PPy[114]</td>
<td>0.72 V</td>
<td>0.51 V</td>
<td>1.02 V</td>
<td>0.1 M KOH</td>
</tr>
<tr>
<td>Co_3O_4 with different exposed crystal facets on N-doped rGO[153]</td>
<td>0.76 V</td>
<td>0.38 V</td>
<td>0.85 V</td>
<td>0.1 M KOH</td>
</tr>
<tr>
<td>NiMnO_4/AlNiMnO_3 heterojunction[155]</td>
<td>0.75 V</td>
<td>0.38 V</td>
<td>0.86 V</td>
<td>0.1 M KOH</td>
</tr>
<tr>
<td>Carbon-coated MnCoO_2 nanowire[24]</td>
<td>0.77 V</td>
<td>0.43 V</td>
<td>0.89 V</td>
<td>0.1 M KOH</td>
</tr>
</tbody>
</table>

#### 4.2.2. Perovskite Oxides

Perovskite oxides are promising functional materials of non-stoichiometric oxides, which can be described with a general formula ABO_3−δ (Figure 7a), where A is a rare earth and/or alkaline-earth element (La, Pr, Sr, Ca, Ba), and B is transition-metal element (Fe, Co, Ni, Mn, Cr, Cu).[151] Because of possessing vast oxygen vacancies and versatile valences of B elements, most ABO_3−δ perovskite oxides are ionic-electronic mixed conductors, which endows them outstanding oxygen electrocatalytic activities.[152] The application of nonstoichiometric perovskite oxides as ORR/OER bifunctional electrocatalysts in metal–air batteries and fuel cells has been already demonstrated in practical systems. In this section, we will make a brief review on feasible strategies to optimize their catalytic activities and stabilities of perovskite oxides.

The electrocatalytic properties of perovskite oxides can vary dramatically with different A- or B-site cations. Generally, A-site substitution with alkaline-earth element will mainly affect the ability of adsorbed oxygen and benefit creating oxygen vacancy, while B-site doping with transition-metal element will influence the activity of the adsorbed oxygen and help to adjust electronic conductivity.[153] For example, Zhao and co-workers[154] discussed effects of Sr-doping on bifunctional oxygen catalytic activities of LaMnO_3 electrocatalysts. They found that La_{0.4}Sr_{0.6}MnO_3 not only exhibits the higher content of surface adsorption oxygen and larger specific surface area, but also increases the content ratio of Mn^{4+}/Mn^{3+}, finally, the smallest discharge–charge potential gap of 0.971 V was obtained for rechargeable Li−O_2 batteries. Sr-doped PrBa_{1−x}Sr_{x}Co_{2}O_{5−δ} (x = 0−1.0) double perovskite oxides has been reported, here, on the one hand, Sr substitution increases the covalency between

...
Co 3d and O 2p orbitals due to the lattice contraction, on the other hand, Sr-doping destroys the ordering of Pr–O and Ba(Sr)–O layers, increases the concentration of Co⁴⁺ (σ sama = 1) and promotes the formation and deprotonation of the OOH species, and the adsorption of O₂. These factors contribute to its superior ORR/OER electrocatalytic behaviors. As for Laₓ₋ₓSrₓCoO₃(M = Ca, Sr), Ca doped material shows slightly better ORR performance, whereas Sr-substituted material exhibits better OER activity. The Fe substitution into La₀.₆Ca₀.₄CoO₃₋δ were also discussed, it was suggested that the oxidation of Fe²⁺ to Fe³⁺ and partial reduction of Co³⁺ to Co²⁺ may be responsible for the enhanced ORR/OER activities. Moreover, nonmetal elements doping can represent positive influence on the bifunctional oxygen catalytic activities of perovskite oxides, including P-, S-, F-doping. For instance, Peng et al. controllable large-scale prepared sulfur-doped CaMnO₃ nanotubes as ORR/OER electrocatalysts for Zn–air batteries via an electrospinning technique. It is proved that the S-doping...
engineering increases the electric conductivity and adds surface vacancies defect, resulting in enhanced O_2_ adsorption capability and promising performance of Zn–air batteries.\[158b\]

Similar to Pt, IrO_2, and RuO_2 electrocatalysts, the crystallographic orientations of perovskite oxides have also demonstrated a significant influence on the bifunctional oxygen catalytic activities. For example, the (001) orientation of La_0.6Ca_0.4CoO_3 showed higher ORR/OER performances than (110) orientation.\[159\] It was found that the (001) oriented LaMnO_3 single-crystalline thin films show intrinsic ORR activities comparable to those of LaMnO_3 polycrystalline with high surface area, more oxygen vacancies and Mn^3+ active sites for ORR.\[160\] Furthermore, different planes of SrRuO_3 exhibited different ORR activities, following a decreasing order, i.e., SrRuO_3 (111) > SrRuO_3 (110) > SrRuO_3 (001), the density of surface defects controlled their OER performances.\[161\]

O_2 band center relative to Fermi-level, which measures the strength of the ionic bond of perovskites with intermediates, and the occupancy of \( \varepsilon_g \) orbitals, which measures the strength of the covalent bond, are two good descriptors for ORR and OER on various perovskite catalysts.\[162\] Ciucci and co-workers believed that the optimized \( \varepsilon_g \)-centered band gap between perovskites with enhanced bifunctional activities compared with disordered Nd_0.3Ba_0.7MnO_3 as well as NdBaMnO_3.5 and NdBaMnO_3.5δ (\( \delta < 0.5 \)), as shown in Figure 7b.\[163\] According to the molecular orbital principle and \( \varepsilon_g \) orbital filling of B ions, Suntivich et al. found that the intrinsic ORR and OER activities of perovskite oxide demonstrate a volcano-like trend, respectively. With \( \varepsilon_g \) orbital filling close to 1.0, LaMnO_3δ4+ exhibits the best intrinsic ORR activity, whereas, as exhibited in Figure 7c, Ba_0.5Sr_0.5Co_0.8Fe_0.2O_3 (BSCF) demonstrates the highest intrinsic OER activity, which are comparable to state-of-the-art Pt/C electrocatalysts for ORR and IrO_2 electrocatalysts for OER.\[164\] However, there are some drawbacks for these two perovskite oxides. As for LaMnO_3,\[\delta\] theoretic calculation and experimental results show that it is not an optical OER catalyst, although it presents the highest intrinsic ORR activity. Lu and co-worker coated a high OER active nano-layer (NiCo_2O_4 shell) on the surface of La_0.9Sr_0.1MnO_3 (LSM) nanorods to obtain a core–shell NCO@LSM heterojunction as ORR/OER electrocatalysts for rechargeable Li_2O_2 batteries, as displayed in Figure 7d.\[165\] Low electronic conductivity and large OER potential are big shortcomings for BSCF, which limits its low temperature application.\[166\] Adding conductive carbon to make BSCF composite electrocatalysts is a useful method to adjust its ORR/OER performances.\[167\] Jin et al. suggested that the electronic interaction between carbon and BSCF was the driver of enhanced activities.\[168\] Jung and co-workers synthesized \( \text{Li}_x\text{Ba}_2\text{Sr}_{3-x}\text{Co}_3\text{O}_7\text{Fe}_{0.1}\text{O}_{3-\delta} \) as ORR/OER bifunctional catalysts. Surprisingly, a novel structure with rhombohedral LaCoO_3 nanoparticles (=10 nm) dispersed on cubic BSCF surface was found, which features an optimized ORR/OER activities comparable to/better than those of the state-of-the-art RuO_2 and IrO_2 catalysts.\[169\] In addition, a BSCF-decorated (001)-oriented LSM thin film electrode as bifunctional catalysts was reported, which exhibited ORR/OER activities suppressing those of single LSM and BSCF.\[161\]

Although most perovskite oxides show relatively high intrinsic ORR and/or OER activities (specific surface area activity), the high temperature (>800 °C) calcination and long annealing process must be needed to synthesize crystalline perovskite oxides, which results in low specific surface area and mass activity. Thereby, it is urgent and necessary to develop new synthetic methods to prepare nanostructured materials with various morphologies, including nanoparticles, hollow sphere, urchin-like microsphere, hollow nanotubes, hollow nanofibers, yolk–shell structured microspheres, and etc.\[170\] For example, porous LaNiO_3 nanocubes show excellent Li–air batteries’ performances with an enhanced discharge capacity (3407 mAh g\(^{-1}\)) and good cycling stability (75 cycles).\[171\] Jin and co-workers reported serial nanostructured \( \text{La_0.8Sr_0.2MnO_3-\delta} \) (LSM) as ORR/OER catalysts, such as urchin-like, hollow spherical, nanorods with vast micropores.\[172\] It’s found that nanostructure can improve specific surface area and OER activity of LSM. Bie et al. prepared yolk–shell structured \( \text{La_0.9Sr_0.1CoO_3-\delta} \) perovskite microspheres through a one-pot hydrothermal method, as shown in Figure 7e, the shell number could be controlled by using different solvents. The large specific surface area of 23.82 m\(^2\) g\(^{-1}\) and improved ORR/OER activities and durability are obtained.\[173\] The 3D ordered macroporous LaFeO_3 (3DOM-LaFeO_3) was synthesized by a facile colloidal crystal template method and used as bifunctional oxygen catalysts for rechargeable Li–air battery. Compared with LaFeO_3 nanoparticles, 3DOM-LaFeO_3 exhibited high specific capacity, low discharge–charge potential gap, good rate capacity, and stability (Figure 7f).\[174\] Hollow porous \( \text{La}_{0.75}\text{Sr}_{0.25}\text{MnO}_3 \) nanotube (Figure 7g) fabricated by electro-spinning method has been reported as ORR/OER catalysts for Li–O_2 battery. High specific surface area helps to provide more active sites, unique hollow channel structure of the porous \( \text{La}_{0.75}\text{Sr}_{0.25}\text{MnO}_3 \) nanotube benefits the formation/decomposition of discharge products. As a result, the as-prepared Li–O_2 battery displayed stable capacities of >11 000 mAh g\(^{-1}\) after five full discharge–charge cycles.\[175\]

Other than ABO_3 type cubic perovskite oxides, there are some \( \text{A}_2\text{BO}_4 \) layered type and AA’B_2O_6 double type perovskite oxides have been reported as ORR/OER bifunctional electrocatalysts.\[176\] Jung et al. systematic studied effects of Sr\(^2+\) or Ca\(^2+\) doping on the ORR/OER performances of \( \text{La}_2\text{NiO}_4 \). The ORR onset and half-wave potentials and the OER activities show the same trend in increasing order, i.e., \( \text{La}_2\text{NiO}_4 < \text{La}_{1.5}\text{Ca}_0\text{NiO}_2 < \text{La}_{1.5}\text{Sr}_0\text{NiO}_2 < \text{La}_2\text{Sr}_0\text{NiO}_4 \). In order to overcome intrinsically low electronic conductivity of \( \text{La}_2\text{Sr}_0\text{MnO}_4 \), Wang et al. fabricated a carbon-coating layer with thickness <5 nm on the surface of \( \text{La}_0.8\text{Sr}_0.2\text{MnO}_{4+\delta} \) by a bottom-up strategy, and improved its ORR activity and stability.\[177\] PrBa_0.5Sr_0.5Co_3Fe_0.1O_7 (PBSCF) double perovskite were reported as ORR/OER bifunctional electrocatalysts, and porous PBSCF nanofibers fabricated by electrospinning method demonstrated a 20 times of mass activity and >1.6 of times intrinsic activity with respect to that of bulk PBSCF.\[178\] Bu and co-workers also fabricated mesoporous \( \text{PrBa}_0.5\text{Sr}_0.5\text{Co}_3\text{Fe}_{0.1}\text{O}_{7+\delta} (x = 0, 0.5, 1, 1.5, \text{ and } 2) \) perovskites nanofibers by an electrospinning method, as shown in Figure 7h, which demonstrates well B-site cation-ordered structure and large surface area (~20 m\(^2\) g\(^{-1}\)), finally leading to excellent electrochemical performances of Zn–air batteries.\[176\] Transition-metal oxides (Fe\(^{3+}\), Ni\(^{2+}\), Cu\(^{2+}\), and Mn\(^{3+}\)) doped \( \text{NdBa}_0.85\text{Ca}_0.15\text{Co}_3\text{O}_{4+\delta} \) double perovskite catalysts, among
them, Fe-doping oxides exhibited the best $\Delta E$ (ORR and OER overpotential at selected current density) value of 0.948 V, as displayed in Figure 7i.[180] $\text{Sr}_2\left(\text{La}_{0.5}\text{Sr}_{0.5}\right)_2\text{CoO}_3$ ($x = 0, 0.25, 0.5, 1.0$) and Co doped $\text{Sr}_2\text{FeMoO}_6$ were studied as bifunctional oxygen catalysts. High electrical conductivity contributes to high electrocatalytic activity for both ORR and OER.[181] In addition, some novel perovskite oxides have also been studied. For instance, $\text{Ba}_{0.9}\text{Co}_{0.5}\text{Fe}_{0.4}\text{Nb}_{0.1}\text{O}_3$ demonstrates excellent bifunctional activities for the formation and decomposition of $\text{Li}_2\text{O}_2$.[182] $\text{CaMnO}_3$ perovskite with open tunnels and multivalences demonstrated excellent ORR/OER activities. As a catalyst for rechargeable lithium–air batteries, a lower discharge–recharge overpotential of 0.98 V, improved rate capability and cycling stability (>80 cycles) were obtained.[183]

Very recently, there appear some new strategies to optimize ORR/OER bifunctional electrocatalytic activities. According to the exsolution phenomenon of B cations from $\text{ABO}_3$ perovskite oxides in reducing atmosphere to form well-dispersed metal and/or alloy nanoparticles (NPs) on the parent perovskite surface, Wang et al. prepared $\text{La}_2\text{O}_3$-NCNTs hybrids in situ derived from $\text{LaNi}_x\text{Fe}_y\text{O}_3$ perovskite oxides as novel robust bifunctional oxygen electrocatalysts, typical morphology of N-doped carbon nanotubes, coupling effect between NCNTs and $\text{La}_2\text{O}_3$ coming from the formation of active $\text{La}^{4+}$ and $\text{C}–\text{O}$ bonds attribute to the excellent bifunctional activities.[184] However, $\text{LaNi}_x\text{Fe}_y\text{O}_3$ was decomposed in this work. In further work, Wang et al. selected $\text{La}_0.5\text{Sr}_0.5\text{Co}_{1-x}\text{Fe}_x\text{O}_3$ ($0 \leq x \leq 0.5$) as parent perovskite, and obtained a LSCN/Ni$_2$P heterogeneous structure bifunctional catalyst by a facile reducing and in situ phosphating process. Island-like Ni$_2$P nanoparticles well embedded into the surface of LSCN skeleton. Benefitting from the unique LSCN/Ni$_2$P interface, excellent OH$^-$ adsorbability, enhanced conductivity and optimized band center location of $\text{O}_2\text{P}$, the OER activity is improved by ~6.2 times and mass activity by ~10.2 times.[162c] Similarly, an ORR/OER bifunctional electrocatalyst featuring CoP socketed on an oxygen deficient $\text{PrBa}_{0.85}\text{Ca}_{0.15}\text{MnFeO}_5$ nanofiber[159b] exhibits the lowest ORR/OER overvoltage gap of 1.009 V versus RHE. The synergistic interaction and the interfaces between $\text{LaCoO}_3$ and $\text{CeMoO}_6$ ($x = 0, 0.25, 0.5, 1.0$) is prepared via an in situ redox reaction, Zhu et al. prepared MnO$_x$ decorated CeO$_2$ nanorods as efficient ORR/OER electrocatalysts for lithium–air batteries with a high discharge capacity (2617 mAh g$^{-1}$) and good rate capability (up to 400 mA g$^{-1}$).[196] Sun and co-workers reported a $\text{FeCoO}_3$/$\text{CeO}_2$ heterostructure as ORR/OER bifunctional electrocatalyst in 0.1 M KOH, which exhibits the lowest ORR/OER overpotential gap of 1.009 V versus RHE. The synergistic interaction and the interfaces between $\text{FeCoO}_3$ and $\text{CeO}_2$ contribute to the outstanding bifunctional activities.[24]

Due to their various structures and variable valences, manganese oxides have attracted much attentions as bifunctional batteries, and exhibits a competitive overpotential (0.440 V) in overall water splitting.[185]

Table 4 summarized some ORR/OER bifunctional electrocatalytic parameters of related perovskite oxides for comparisons.

### 4.2.3. Other Typical Transition Metal Oxides

In this section, the recent process of other typical transition metal oxides based ORR/OER bifunctional electrocatalysts, e. g., CeO$_2$-related, MnO$_x$, NiO$_x$-based and others oxides is briefly summarized.

Fluorite cubic structured CeO$_2$ is an important functional ceramic family. Ce$^{4+}$/Ce$^{3+}$ redox couple, Ce$^{3+}$, and the abundant surface oxygen vacancies, are useful active sites for ORR/OER.[193] There are lots of literatures about CeO$_2$ as carrier material to disperse Pt nanoparticles.[194] CeO$_2$ cannot only suppress Pt oxidation due to the oxidation of Ce$^{3+}$ to Ce$^{4+}$, but prevent the growth of Pt nanoparticles, finally resulting in enhanced ORR activities and stabilities. Jin and co-workers synthesized Au nanoparticle-decorated Gd$_0.5$Ce$_0.5$O$_2$ nanotubes via a facile selfetching method, an improved ORR performances has been achieved.[195] Doped CeO$_2$ have also been reported as bifunctional oxygen catalysts for metal-air batteries.[190] For example, Kalubarme et al. showed that a promising discharge capacity of 8435 mAh g$^{-1}$ and a lower discharge–charge potential gap could be obtained through utilizing the Zr-doped CeO$_2$ as electrocatalysts.[197] Through an in situ redox reaction, Zhu et al. prepared MnO$_x$ decorated CeO$_2$ nanorods as efficient ORR/OER electrocatalysts for lithium–air batteries with a high discharge capacity (2617 mAh g$^{-1}$) and good rate capability (up to 400 mA g$^{-1}$).[196] Sun and co-workers reported a $\text{FeCoO}_3$/$\text{CeO}_2$ heterostructure as ORR/OER bifunctional electrocatalyst in 0.1 M KOH, which exhibits the lowest ORR/OER overpotential gap of 1.009 V versus RHE. The synergistic interaction and the interfaces between $\text{FeCoO}_3$ and $\text{CeO}_2$ contribute to the outstanding bifunctional activities.[24]

<table>
<thead>
<tr>
<th>Active material</th>
<th>$E_{1/2}$</th>
<th>$\eta_{0}$</th>
<th>$E_{1/2} - E_{0}$</th>
<th>Electrolyte</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yolk–shell $\text{La}<em>{0.5}\text{Sr}</em>{0.5}\text{CoO}_3$ microspheres[131]</td>
<td>0.68 V</td>
<td>=0.52 V</td>
<td>1.07 V</td>
<td>0.1 M KOH</td>
</tr>
<tr>
<td>Mesoporous $\text{PrBa}<em>{0.5}\text{Sr}</em>{0.5}\text{CoO}_3$–$\text{FeO}_3$ nanofibers[136]</td>
<td>=0.69 V</td>
<td>0.3 V</td>
<td>0.84 V</td>
<td>0.1 M KOH</td>
</tr>
<tr>
<td>Hierarchical mesoporous $\text{La}<em>{0.5}\text{Sr}</em>{0.5}\text{CoO}_3$ nanowires[187]</td>
<td>=0.76 V</td>
<td>=0.6 V</td>
<td>1.07 V</td>
<td>0.1 M KOH</td>
</tr>
<tr>
<td>$\text{La}<em>2(\text{Ba}</em>{0.5}\text{Sr}_{0.5})_2\text{CoO}_3$–$\text{FeO}_3$ nanowires[188]</td>
<td>=0.66 V</td>
<td>0.37 V</td>
<td>0.94 V</td>
<td>0.1 M KOH</td>
</tr>
<tr>
<td>Hierarchical mesoporous/macroporous $\text{La}<em>{0.5}\text{Sr}</em>{0.5}\text{CoO}_3$ nanotubes[176b]</td>
<td>=0.66 V</td>
<td>=0.4 V</td>
<td>0.97 V</td>
<td>0.1 M KOH</td>
</tr>
<tr>
<td>N-doped $\text{LaNiO}_3$[179]</td>
<td>0.67 V</td>
<td>=0.5 V</td>
<td>1.09 V</td>
<td>0.1 M KOH</td>
</tr>
<tr>
<td>P-doped $\text{SrCoO}_3$–$\text{MnO}_2$[184]</td>
<td>0.75 V</td>
<td>0.45 V</td>
<td>0.93 V</td>
<td>0.1 M KOH</td>
</tr>
<tr>
<td>S-doped $\text{CaMnO}_3$[178]</td>
<td>0.76 V</td>
<td>0.47 V</td>
<td>0.94 V</td>
<td>0.1 M KOH</td>
</tr>
<tr>
<td>Sr-doped double perovskite oxides $\text{PrBa}<em>{0.5}\text{Sr}</em>{0.5}\text{CoO}_3$[153]</td>
<td>=0.7 V</td>
<td>0.42 V</td>
<td>0.95 V</td>
<td>0.1 M KOH</td>
</tr>
<tr>
<td>$\text{La}_2\text{Sr}_2\text{CoO}_3$–$\text{NiO}_3$ layered perovskite[190]</td>
<td>0.57 V</td>
<td>0.59 V</td>
<td>1.25 V</td>
<td>0.1 M KOH</td>
</tr>
<tr>
<td>$\text{PrBa}<em>{0.5}\text{Ca}</em>{0.5}\text{MnFeO}_3$–$\text{O}_3$[191]</td>
<td>0.77 V</td>
<td>0.4 V</td>
<td>0.86 V</td>
<td>0.1 M KOH</td>
</tr>
<tr>
<td>$\text{Ba}_2\text{Sr}_2\text{CoO}_3$–$\text{FeO}_3$ supported on N-doped mesoporous carbon[192]</td>
<td>0.77 V</td>
<td>0.35 V</td>
<td>0.81 V</td>
<td>0.1 M KOH</td>
</tr>
</tbody>
</table>
electrocatalysts for oxygen electrochemistry. Crystallographic structure plays an important role on catalytic activities of MnO₂, following an order of α- > β- > γ-MnO₂. Ohsaka and co-workers considered that the chemical composition is also a key factor to influence the electrocatalytic performances of MnOₓ, following a trend of MnOOH > Mn₂O₃ > Mn₃O₄ > Mn₄O₆. Doping with low-valent metal elements (Ni, Mg, Ca, etc.) have been carried out to promote the transfer of O₂ads to O₂astabilize the Mn²⁺/Mn⁴⁺ redox couple in the MnOₓ materials, and consequently improve the ORR/OER activities. The ORR/OER performances of MnOₓ are also dependent on their morphology and surface area. Liu and co-workers fabricated amorphous MnOₓ nanowires on conductive KB carbon skeleton, as for electrocatalysts for rechargeable Zn–air battery, which delivered a maximum power density of ≈ 190 mW cm⁻². Theoretically, NiO₂ is considered to be intrinsically inactive because of its too strong or too weak Ni–O bonding strength. Fe and/or Co doping can be used to optimize its ORR/OER activities to some extent. NiₓFe₁₋ₓO₂ have been extensively studied as bifunctional oxygen catalysts, and NiₓOₓFeₓO₂ exhibited similar ORR activity to that of BSCF. The formation of NiₓOₓFeₓO OH layered double hydroxide structure and a partial-charge transfer activation effect on Ni after Fe-doping may be contribute to the enhanced performances. In addition, Co-doped NiO₂ have also been reported as oxygen electrocatalysts, but its function in NiO₂ was not fully understood.

Considering the commercial utilization of metal–air batteries and fuel cells in the future, how to mass prepare these bifunctional electrocatalysts based on transition metal oxides is a big challenge. Wang et al. prepared mesoporous MnCo₂O₄ spinel ORR/OER bifunctional electrocatalysts in large scale, which exhibits an ORR/OER overpotential as low as 0.83 V due to the preferred Mn⁴⁺ and Co³⁺-rich surface. Micro-wave-assisted route has been reported to mass synthesize Cu doped Mn₃O₄ nanoballs as bifunctional electrocatalysts for alkaline fuel cells. Da et al. successfully fabricated single-crystal CoO nanorods in large-scale as efficient bifunctional electrocatalysts for the all-solid-state Zn–air batteries, resulting from oxygen vacancies and highly active facets on an electronic conductive substrate, excellent electrochemical performance with low charge/discharge overpotentials, high energy density together with stable long-term cycling have been obtained. Recently, amorphous NiFeMo oxides have been large-scale synthesized by a simple supersaturated coprecipitation method (up to 515 g one batch), the as-prepared amorphous NiFeMo oxides exhibited homogeneous elemental distribution and superior OER activity with an overpotential of 280 mV at 10 mA cm⁻² in 0.1 M KOH.

In summary, various approaches for effectively regulating the ORR/OER activities of different metal oxides have proved successful. The synthetic methods based on facile, scalable strategies as reported in the above examples are expected to be beneficial for the scale up of electrocatalysts. As compared to carbon, metal oxides are less abundance in resources. From the economic point of view, reducing the cost of raw materials for producing the metal oxides, especially in the perovskite oxides, is more meaningful for this end.

5. Challenges and Perspectives

The ORR and OER are the key reactions in the electrochemical energy conversion and storage devices. The multistep proton-coupled electron transfer in ORR/OER with slow kinetics limits the energy conversion efficiency. The large-scale production of efficient and durable bifunctional electrocatalysts is crucial to the commercialization of these energy conversion and storage devices. The challenges in the large-scale production of bifunctional electrocatalysts are as following:

1. Catalytic activity of the electrocatalysts: In the past decade, carbon- and transition metal-based catalysts have been reported to be the promising electrocatalysts for ORR and OER. However, according to the scaling relationships of oxygen-containing intermediates in the four-electron steps process of ORR/OER, it is difficult for catalysts to possess both ORR and OER activity simultaneously. Although great efforts have been made on enhancing the bifunctional electrocatalytic activity of carbon- and transition metal-based catalysts, their activities are still inferior to those of state-of-art Pt- and RuO₂/IrO₂-based catalysts. Rational design of electrocatalysts for improving the bifunctional catalytic activity is highly required.

2. Durability of the electrocatalysts: The OER proceeds under highly oxidation conditions (>1.2 V vs RHE). This is more challenging for carbon-based catalysts because carbon would corrode at this high potential range. This situation holds true for the carbon support for metal oxide electrocatalysts. High graphitization of carbon can alleviate this problem to some extent. Protection of carbon with other approaches still remains a great challenge. In the case of carbon support, more potentials remain to be explored to replace carbon with other corrosive-resistant highly conductive support.

3. Scalable synthesis of electrocatalysts and the abundance of resources: The physicochemical properties and catalytic activity of the electrocatalysts depend strongly on the synthesis method. While the preparation of materials by economical ways is essential to the large-scale production of electrocatalysts and is still challenging. The optimization of synthetic methods is requested for this end. In view of high cost and scarcity of Pt- and RuO₂/IrO₂-based catalysts, earth abundant resources are also critical for reducing the cost and beneficial for the scale up of electrocatalysts.

4. Guide the design of electrocatalysts: Rational design and development of efficient and stable bifunctional oxygen electrocatalysts in a wide pH range benefits to the application of catalysts in different electrocatalytic systems and energy storage devices, such as fuel cells, metal–air batteries and water electrolyzers. Although numerous efforts have been made in understanding the catalytic activity of electrocatalysts by using modeling and/or simulation methods, understanding of the degradation mechanism of electrocatalysts during ORR especially OER process is still far falling behind. Combined computational modeling and in situ characterization techniques (such as in situ X-ray absorption spectroscopy, in situ Raman spectroscopy and in situ X-ray diffraction,
et al.) play a critical role in guiding the design of efficient and durable electrocatalysts toward large-scale production.

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Conflict of Interest
The authors declare no conflict of interest.

Keywords
bifunctional electrocatalysts, large-scale production, oxygen evolution reaction, oxygen reduction reaction, rational design

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