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Metal-Organic Frameworks Based Electrocatalysts for the Oxygen Reduction Reaction

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Abstract

In view of the clean and sustainable energy, metal-organic frameworks (MOFs) based materials, including pristine MOFs, MOF composites, and their derivatives are emerging as unique electrocatalysts towards oxygen reduction reaction (ORR). Thanks to their tunable compositions and diverse structures, efficient MOF-based materials provide new opportunities to accelerate the sluggish ORR at the cathode in fuel cells and metal-air batteries. This mini-Review first provides some introduction of ORR and MOFs, followed by the classification of MOF-based electrocatalysts towards ORR. Recent breakthroughs in engineering MOF-based ORR electrocatalysts are highlighted with an emphasis on synthesis strategy, component, morphology, structure, electrocatalytic performance, and reaction mechanism. Finally, some current challenges and future perspectives for MOF-based ORR electrocatalysts are also discussed.

Keywords: Metal-organic frameworks; derivatives; electrocatalysis; oxygen reduction reaction

1. Introduction

Today's society is facing growing concerns about the global energy and environmental challenges initiated by the consumption of limited fossil fuels.^[1-3] Among the next-generation energy technologies, fuel cells and metal-air batteries show great potential to meet our growing energy demands.^[1,4,5] However, their overall efficiency is severely limited by the sluggish oxygen reduction reaction (ORR), a key process in fuel cells and metal-air batteries.^[6,7] In the ORR, molecular oxygen is electrochemically reduced by a 4-electron pathway to H₂O (acidic media) or OH⁻ (alkaline media), or by a 2-electron pathway to H₂O₂ (acidic media) or HO₂⁻ (alkaline media) as the intermediate species (**Figure 1**).^[8-10] Usually, as a consequence of the higher reaction kinetics and efficiency, the 4-electron pathway is preferred. So far, platinum-based materials are regarded as ideal ORR electrocatalysts with a 4-electron pathway in practical applications. However, the scarcity, high cost, and inferior durability of Pt restrict the widespread application in these renewable energy technologies.^[10,11] Considering these limitations, developing earth-abundant alternatives with high activity and durability is a crucial yet challenging task.

As one new class of porous materials, metal-organic frameworks (MOFs) interconnected by the coordination bonds of metal ions/clusters and organic ligands possess high crystallinity and long-range order.^[12] In view of their intriguing features of high specific surface area, adjustable pore sizes and topologies, well-defined metal nodes, tunable chemical components, and surface functionality, MOF-based materials have been proved highly competitive to other porous materials as electrocatalysts towards ORR.^[13-15] According to the chemical nature, MOF-based ORR electrocatalysts are divided into three categories: pristine MOFs, MOF composites, and their derivatives (**Figure 2**). The combination of porous channels in MOFs with accessible sites possessing redox ability may enable a higher active site utilization than typical heterogeneous catalysts. However, insufficient electrical conductivity and low chemical stability seriously limit their electrocatalytic applications.^[16-18] Integrating MOFs with

advanced functional materials, including nanocarbons and inorganic nanoparticles (NPs), is an efficient method to obtain remarkable performance in electrocatalysis. Converting MOFs or MOF composites to inorganic composites by direct carbonization or indirect post-treatments is another simple and efficient approach. Owing to the structural and compositional advantages of MOFs, their derivatives usually display a high surface area, good electrical conductivity, and robust chemical stability.^[19-21] Under these guidelines, various MOF-based materials have been developed and well summarized in the past five years. However, these reviews mainly focus on MOFs and/or their derivatives for energy storage/conversion applications.^[16,19,20] Few reviews paid focused attention to the relationship of MOFs, MOF composites, and their derivatives towards ORR. Therefore, a timely and comprehensive review on the synthesis strategies, structure, composition, morphology, electrocatalytic performance, reaction mechanism, and practical application is noteworthy, which can provide constructive guidance and strong inspiration for the development of MOF-based ORR electrocatalysts and their applications in energy-related devices.

In this minireview, we outline the recent advances of MOFs, MOF composites and their derivatives as electrocatalysts towards ORR. Recent breakthroughs in engineering MOF-based ORR electrocatalysts are highlighted with an emphasis on synthesis strategy, component manipulation, morphology/structural control, and electrocatalytic performance evaluation. These MOF-based functional materials offer unprecedented opportunities in replacing precious-metal-based electrocatalysts towards ORR. Finally, this minireview is concluded with some major current challenges along with some solutions and potential development trends surrounding MOFs as advanced electrocatalysts towards ORR. We believe that this minireview will inspire extensive interest to further accelerate and explore the innovations of MOF-based materials in ORR-related energy technologies.

2. Classification of MOF-based ORR catalysts

MOFs being a relatively young but rapidly-growing family of porous materials have sparked enormous research interest in chemistry and materials science due to their attractive properties.^[22] So far, more than 20,000 MOFs have been reported, and the number of MOFs continues to grow exponentially assisted by the rapid development in synthetic methodologies, characterization techniques, and computational chemistry.^[12] The typical synthesis of MOFs involves solvothermal methods, where separate metal salt and ligand solutions are mixed together or a solvent is added to the mixture of solid salt and ligand in a reaction vial. Apart from solvothermal methods, other methods such as microwave-assisted synthesis, mechanochemical synthesis, electrochemical synthesis, and sonochemical synthesis have also been developed for synthesis of MOFs.^[23] Recently, MOF-based materials as electrocatalysts towards ORR have exhibited distinctive performance. Herein, using a classification of MOFs, MOF composites and their derivatives, we summarize their recent progresses in ORR and highlight some guiding works with an up-to-date appraisal.

2.1. Pristine MOFs

As a subclass of the broader coordination polymer family, MOFs have three important characteristics of crystallinity, porosity, and strong metal-ligand interactions, making them as a bridge between homogeneous and heterogeneous catalysts.^[24,25] The periodic structure allows MOFs to uniformly disperse the active sites throughout the porous framework, the well-defined characteristic of homogeneous catalysts, while the solid nature in nano/micro-scale endows MOFs as the promising heterogeneous catalysts.^[16,24-27] Therefore, the rational design of MOFs could meet the benefits of both heterogeneous and homogeneous catalysts in one system.

Mao *et al.* pioneered in using pristine MOFs as electrocatalysts towards ORR with a Cu-based MOF (*i.e.*, Cu-bipy-BTC, bipy = 2,2'-bipyridine, BTC = 1,3,5-tricarboxylate).^[28] As shown in **Figure 3A**, the specific coordination mode of Cu^{II} centers renders the structural stability in neutral solution. The cyclic

voltammetry (CV) curves demonstrated the electrocatalytic activity towards ORR (Figure 3B). Subsequently, Kamiya *et al.* reported a hybrid ORR catalyst of copper-modified covalent triazine frameworks (CTFs) and carbon NPs.^[29] Although both works suggest the possibility of MOFs as electrocatalysts towards ORR, the development of pristine MOFs in ORR is still dawdling. Recent investigations indicate that homogenous molecular catalysts with ORR activity can be grafted into MOFs as active linkers to catalyze ORR.^[30] For instance, Lions *et al.* investigated the electrocatalytic ORR performance of Co-Al-PMOF with a molecular formula of $[\text{Al}_2(\text{OH})_2(\text{Co}(\text{tcpp}))]$ (tcpp = tetrakis(4-carboxyphenyl)porphyrin).^[31] As the porphyrin metalated analog of $[\text{Al}_2(\text{OH})_2(\text{H}_2\text{tcpp})]$ (H_2 -Al-PMOF) (Figure 3C), it exhibits remarkable stability in an acidic medium.^[32] Electrochemical characterization showed that the Co-Al-PMOF displayed an onset potential (E_{onset}) of 0.75 V versus reversible hydrogen electrode (vs RHE) and a diffusion limiting current density (j_L) of -0.6 mA cm^{-2} in an O_2 -saturated 0.1 M H_2SO_4 (Figure 3D). In the same year, Morris *et al.* reported a highly robust MOF named PCN-223-Fe by combining Zr_6 oxo clusters and Fe(III) porphyrin linkers, opening a new route to optimize MOFs as ORR electrocatalysts by selecting proton sources.^[33] These results exemplify that it is feasible to use ORR active complexes as the building blocks for preparing ORR-active MOFs. Unfortunately, most of these metalloporphyrin-based MOFs show poor performances due to the difficulties in maintaining and/or improving the ORR kinetics of the molecular complex in MOFs.

High conductivity is another desired important requirement for MOFs as electrocatalysts. However, MOFs are generally insulating due to the poor conduction of the redox-active sites surrounded by the typical organic linkers. Besides, the poor electronic interaction between metal nodes and organic linkers is another factor affecting the conductivity of MOFs.^[17] In the recent five years, a few approaches have been realized for the construction of conductive MOFs.^[17,34] In 2016, Miner *et al.* reported a two-dimensional (2D) MOF named $\text{Ni}_3(\text{hitp})_2$ (hitp = 2,3,6,7,10,11-hexaiminotriphenylene) with a high

electrical conductivity of 40 S cm^{-1} .^[35] As shown in Figure 3E, $\text{Ni}_3(\text{hitp})_2$ has a honeycomb-like layered structure and exhibits good electrocatalytic activity in an extensive range of pH value (4-13) (Figure 3F). Intensive research indicated that $\text{Ni}_3(\text{hitp})_2$ catalyzed oxygen reduction through a two-electron pathway by the ligands as active sites rather than metal centers (Figure 3G).^[36] This mechanism shows the importance of electron delocalization for accessing key intermediates and should be applicable for designing other conductive MOFs. Inspired by this work, Liu *et al.* designed two metal-catecholates with well-defined Ni-O₆ or Co-O₆ coordination sites.^[37] Unlike metal-nitrogen coordination sites in the above MOFs as active sites for ORR, the specific metal-O₆ sites in metal-catecholates can also function as active sites to reduce oxygen via a four-electron pathway.

Despite the successful demonstration of pristine MOFs as the emerging electrocatalysts towards ORR, their instability in electrochemical environment and poor electrical conductivity severely restrict their swift development in electrocatalysis. So far, one main strategy for improving the chemical stability of MOFs is to increase the bonding strength of metal-ligand coordination. In this case, some MOFs composed of high-oxidation metal ions and carboxylate ligands, or soft metal ions and basic azolate ligands have been developed.^[38,39] For the issue of poor electrical conductivity, some strategies have been developed, such as donor-acceptor interactions, redox-matching, and mixed valency.^[17,40] Recent investigations reported that *in-situ* growth of ultrathin MOF nanosheets on conducting substrates could also partly overcome the poor conductivity problem of pristine MOFs.^[41-43]

2.2. MOF composites

Integrating MOFs with various functional materials is an effective and viable strategy to improve ORR performance along with new functionality.^[22,44-47] To date, numerous MOF composites have been successfully obtained by assembling MOFs with functional materials, which can be divided into two categories based on the distribution of the main active sites.^[48-52] The first category is the combination

of MOFs and conductive carbon materials, where the MOFs are the main active species towards ORR while carbon materials serve as the vastly conductive network. For instance, Jahan *et al.* reported a hybrid of pyridine-functionalized graphene with iron-porphyrin MOF composite for ORR.^[48] As shown in **Figure 4A**, the composite (denoted as (G-dye-FeP)_n MOF) was formed by combination of G-dye and (Fe-P)_n MOF, where G-dye represents reduced graphene oxide (rGO) functionalized with donor- π -acceptor dye, and (Fe-P)_n MOF represents a MOF created by linking FeCl₃ and 5,10,15,20-tetrakis(4-carboxyl)-21*H*,23*H*-porphyrin (TCPP). By optimizing the structure-composition relationship, the composite with 50 wt% of G-dye manifested the best catalytic performance with an E_{onset} of 0.93 V vs RHE and a j_L of -6.3 mA cm⁻² (Figure 4B). In a most recent study by Zhong *et al.*, they reported a Cu-phthalocyanine-based 2D conjugated MOF (PcCu-O₈-Co) with square planar cobalt-bis(dihydroxy) complexes as linkages (Figure 4C).^[53] The introduction of carbon nanotubes (CNTs) into MOFs forms the composite of PcCu-O₈-Co/CNTs with the uniform mixture of layered MOFs and CNTs (Figure 4D). The high coverage of active sites and good conductivity as well as the porous structure jointly render the PcCu-O₈-Co/CNTs composite a 3.93-electron pathway for ORR in alkaline media. Both of the half-wave potential (E_{1/2}, 0.83 V vs RHE) and j_L (5.3 mA cm⁻²) are the record values reported for pristine MOF electrocatalysts (Figure 4E).

The second category is the combination of MOFs with metal or metallic compounds, where the metal or metallic compounds are the active species and MOFs function as support or reaction chamber.^[45,54] He *et al.* reported a bifunctional electrocatalyst based on MIL-101-Cr (MIL= Material from Institut Lavoisier) and cobalt.^[55] The as-prepared Co/MIL-100-Cr with higher Co^{II} contents showed better ORR activity. Cho *et al.* used thioacetamide to partially vulcanize a MOF of HKUST-1 [Cu₃(BTC)₂·(H₂O)₃] to prepare a series of nano-CuS (x wt%)@HKUST-1 (x stands for the amount of nano-CuS) composites (Figure 4F).^[52] Interestingly, the increasement of electrically conducting nano-

CuS NPs in the composite resulted in a decrease in porosity but an increase in electrical conductivity. The optimized composite with 20 wt% CuS NPs exhibited an E_{onset} of 0.91 V vs RHE in an alkaline solution (Figure 4G). This work revealed the importance of both porosity and electrical conductivity to the electrocatalytic performance. The uniform and adjustable pores in MOFs can not only act as reaction chambers to confine noble metallic NPs but also more importantly limit the immersion of other bigger molecules such as methanol, thus providing a good model for designing efficient and selective electrocatalysts towards ORR.^[56]

Benefiting from the functional materials and sophisticated architectures, these MOF composites possess not only enhanced electrical conductivity but also robust chemical stability. More notably, the synergistic effect from the interaction of component and structure enables these composites to possess new physical and chemical properties that are not present in the individual components, resulting in great activity and stability. Moreover, the abundance of MOFs and functional materials together with the development of new synthesis methods will create more advanced MOF composites with high electrocatalytic activity and stability.

2.3. MOF derivatives

In comparison to the attempts to adapt MOFs and MOF composites for ORR, much more efforts have been devoted to converting them into inorganic functional materials with controllable size, morphology, and composition.^[19,57] On the one hand, the diversity of metal ions and ligands in MOFs renders them ideal precursors for preparing functional inorganic materials with various components. On the other hand, the flexible topology and size of MOFs also make them interesting precursors/templates to obtain the derived materials with desired morphology, structure and size. As described below, these MOF-derived materials often possess some unique advantages over the traditional porous materials. (1) The size, morphology, structure and other features inherited from the MOFs can be effectively preserved, enriching

the database of structure and composition for porous materials.^[21,58] (2) The carbon matrix pyrolyzed from the organic ligands possesses high conductivity and specific area, promoting the charge transfer and mass transport.^[59] (3) Various heteroatoms can be directly doped into the carbon matrix through the organic ligands, which can not only induce the charge redistribution in the carbon matrix, but also interact with other functional components, producing more active sites.^[60] (4) The metal atoms can evolve into ultrafine metal and metal compound NPs confined in the carbon network, preventing them from further agglomeration and sintering.^[15,61] On the basis of chemical composition, we divided these derivatives into the following three categories to summarize their recent progresses as electrocatalysts towards ORR. Herein, we highlight recent works that have guiding significance in the synthesis strategy, morphology/structure control, component manipulation, and practical application in fuel cells and metal-air batteries.

2.3.1. Metallic compounds

Due to the natural advantages of abundant metal species, MOFs can be easily transformed into metallic composites, which are promising alternatives to Pt-based catalysts in ORR. However, their intrinsically poor electrical conductivity and low specific area lead to insufficient activity.^[62,63] Extensive efforts have been devoted to improving their catalytic activities by nanostructure engineering or compounding with highly conductive materials.^[62,64] With various topographical dimensions and tunable sizes, MOFs are often used as desirable templates and/or precursors to obtain wanted nanostructures. When the organic ligands in MOFs are consumed by calcination in air or chemical etching, metallic compounds without carbon will be obtained as the first category of MOF derivatives.^[65-68] More importantly, the consumption of organic ligands in MOFs will generally create high specific area and porosity at the same time, which are critical to expose more active sites.

Metal oxides are the most widely studied class of compounds for ORR in view of their easy preparation and considerable stability in an oxidative or alkaline environment. Recently, Prussian blue analogues (PBAs) have been recognized as promising precursors for the synthesis of porous metal oxides.^[69,70] Nai *et al.* explored the mechanism of assembling anisotropic PBA NPs into open frame-like superstructures and prepared two typical nanocuboids-assembled frame-like superstructure (NAFS) of Co-Fe mixed oxides by thermal treatment of Co-Fe PBA NAFSs in air.^[71] The formation process and mechanism of the KCoFe-1 NAFSs (a PAB with K/Co/Fe = 0.67:1:0.71) and KCoFe-2 (a PAB with K/Co/Fe = 0.07:1:0.67) NAFSs were well investigated by time-dependent experiments, which shows the structural evolution process from NPs to NAFSs (**Figure 5A,B**). While annealing KCoFe-1 and KCoFe-2 NAFSs in the air, they obtained the Co-Fe oxides with the uniform 3D cubic frame-like structures (**Figure 5C-H**). Subsequently, they also developed a self-templated epitaxial growth strategy for the construction of single-crystalline hollow nanostructured PBAs.^[72] Due to the tunable growth kinetics and topological complexity, this strategy enables a controllable synthesis of Co-Fe PBA cages, frames, and boxes with diverse geometries. By simple annealing these PBAs with tailorable topologies in air, they obtained the corresponding Co-Fe mixed oxides (Co-Fe-O) with nanostructures of frames, cages, and boxes (**Figure 5I-N**).

Although these porous oxides can be further evolved into other slightly more conductive compounds (*e.g.*, carbides, nitrides, phosphides, and selenides),^[67,73] their conductivity is still insufficient to meet the needs of electrocatalysis, especially compared to carbon-based materials. In fact, in order to obtain more efficient and stable electrocatalysts, the organic ligands in these MOFs are mostly retained in the form of inorganic carbon-based materials.

2.3.2. Carbon materials

In view of the great diversity of MOFs, pyrolysis of MOFs has been demonstrated to be a promising method for preparing novel carbon-based materials with controllable size, shape, and composition by choosing MOF precursors and calcination conditions.^[59] MOF-derived carbon-based ORR electrocatalysts can be divided further into two categories: pristine carbon materials with defects and heteroatom-doped carbon materials. Before recognizing the function of defects in the ORR, it is generally believed that the pristine carbons show little electrocatalytic activity towards ORR due to the sp^2 -bonded carbon atoms without polarization, which cannot accommodate the chemical adsorption of reactants and electronic attack of intermediates.^[74,75] However, recent studies revealed that some carbons without heteroatom dopants still exhibit excellent ORR activity, in which the topological defects can break the sp^2 orbitals of pristine carbon and generate charged sites as potential active sites for ORR.^[76,77] Even though significant advances have been achieved by introducing defects in pristine carbons to boost the ORR activity, their activity is still relatively low and some critical issues remain to be addressed: 1) the identification of the most active defects towards ORR; 2) the precise control of the local structure of defects.

In contrast, the doping of heteroatoms is an appealing strategy, which can not only create defects but also easily cause changes in the electronic structure of surrounding carbon materials, thus introducing more active sites.^[60,78,79] Since the first report by Dai and coworkers that N-doped carbon nanotubes possess superior ORR activity and stability compared to platinum,^[79] various heteroatom-doped carbon-based electrocatalysts were reported. These heteroatoms include non-metallic elements (*e.g.*, nitrogen, boron, sulfur, phosphorus, iodine) and metallic elements. Among the metal-free doped carbons, N-doped porous carbon was the first reported MOF-derived non-metallic atom-doped ORR electrocatalyst.^[80] Nanostructure engineering is an effective strategy to enhance the electrocatalytic performance by exposing more active sites and accelerating electron/mass transfer. In this context, Yu and coworkers

reported N-doped carbon nanofibers by calcinating 1D ZIF-8 nanofibers, which are prepared by using Te nanowires as the template (**Figure 6A**).^[81] These novel porous carbon nanofibers possess a complex network structure with hierarchical pores and high surface area (Figure 6B). Coincidentally, a bottom-up method was proposed by Chai *et al.* for synthesizing hollow N-doped carbon spheres (HNCSs) by using Zn-BTC microspheres as precursors (Figure 6C).^[82] The scanning electron microscope (SEM) and TEM images (Figure 6D) showed the unique hollow architecture with numerous mesopores, which facilitates the diffusion and access of electrolyte and oxygen molecules, also exposing more active sites for ORR. Although many studies have been conducted on the carbonization of MOFs, few of them have examined the influence of annealing atmosphere on the structure of derivatives. In 2015, Xia *et al.* prepared N-doped carbon nanotube frameworks (NCNTFs) by direct pyrolysis of ZIF-67 particles under an Ar/H₂ atmosphere (Figure 6E).^[83] Benefiting from the features of composition and structure, the optimized NCNTFs could catalyze the reduction of oxygen molecules by a nearly 4-electron pathway with higher electrocatalytic activity than that of commercial Pt/C in alkaline solution. The success of N doping has triggered the study of other dopants, such as B, P, S and I. Moreover, simultaneous doping of two or more elements with anti-electronegativity into the resultant carbon matrix can induce unique electron-donor properties, creating more defects and active sites for ORR.^[78,84,85] Remarkably, a controllable multi-heteroatoms (B, N, P, S) doped porous carbon nanofibrous network was prepared by Huang *et al.* using a 3D network of ZIF-8/polymeric nanofiber as the template (Figure 6F).^[86] By controlling the absorption amount of B₄O₇²⁻, HPO₄²⁻, and SO₄²⁻, single, dual, ternary, and quaternary heteroatoms doped carbons were obtained, suggesting high degree of doping capability.

Compared to the development of metal-free carbon materials in ORR, metal-doped carbon materials have received even more attention, in which the metal atoms can be well dispersed in the resultant porous carbon, leading to an improved density of active sites.^[87,88] It has been recognized that the M-N_x moieties

in M-N-C (also known as single-atom catalysts, SACs) are the real active sites for ORR.^[89,90] The interaction between oxygen molecules and the 3d orbital of metals plays a critical role in boosting ORR activity, which can facilitate the charge transfer from metal to O₂ π^* orbitals and activate the oxygen molecules to promote the subsequent reduction of oxygen.^[91] In 2011, Ma *et al.* firstly reported the MOF-derived M-N-C for ORR by thermal activation of a cobalt imidazolate framework.^[92] Thereafter, various M-N-C materials have been developed for ORR. From the literature, the current synthesis strategy based on MOFs for M-N-C mainly includes: 1) direct pyrolysis of pristine MOFs;^[93,94] 2) pyrolysis of MOFs with space-confined metal-containing molecules;^[95] 3) pyrolysis followed with an acidic wash;^[96] 4) top-down synthesis from bulk metals.^[97,98] The detailed discussion about these four strategies has been well done by Han *et al.*, who summarized the recent advances on MOF-derived carbon-supported SACs.^[99] Recently, Chen and coworkers developed an Ir-N-C SAC (Ir-SAC) by pyrolysis of a ZIF-8 encapsulated with Ir acetylacetonate under an H₂/Ar atmosphere (**Figure 7A**).^[95] The elemental mapping result revealed the well-retained nanostructure and absence of any observable Ir NPs/nanoclusters (Figure 7B). Extended X-ray absorption fine structure (EXAFS) and X-ray absorption energy near edge structure (XANES) spectroscopy further confirmed that these Ir atoms were doped into NC with a coordination form of Ir-N₄ (Figure 7C-E). Electrochemical evaluations showed that the prepared Ir-SAC exhibits orders of magnitude higher ORR activity than Ir NPs in acidic electrolyte with a record-high turnover frequency (TOF) of 24.3 e⁻ site⁻¹ s⁻¹ at 0.85 V vs RHE, impressive mass activity of 12.2 A mg⁻¹_{Ir}, and superior stability (Figure 7F,G). Density functional theory (DFT) calculations revealed that active sites in Ir-SAC are the mononuclear Ir coordinated with four N atoms, which possess the moderate adsorption energy of the ORR intermediates (Figure 7H), resulting in a mechanism of 4-electron pathway (Figure 7I). These findings provide an in-depth understanding and important guidance for the future development of high-performance SACs for ORR in acidic media.

2.3.3. Metallic compound/carbon hybrids

When the metal in the above-mentioned metal-doped carbons grows from the atomic scale to the molecular scale, the third category of MOF-derived materials is produced, that is, metal or metallic compound/carbon hybrids. Due to the reductive atmosphere created by the pyrolytic carbon from MOFs, abundant metal atoms can be reduced into metallic NPs via calcination in inert atmosphere under high temperature.^[100-102] The derived carbon matrix (especially heteroatom-doped carbons) works as a support for metallic NPs and prevents their aggregation.^[101] At the same time, the strong interaction between metallic NPs and the carbon support can tune the electronic structure and enhance the electrocatalytic activity.^[103] In turn, metallic NPs can also increase the degree of graphitization of the carbon matrix, improve the protection of carbon on metallic NPs, and avoid their dissolution during electrocatalysis.^[82] For example, Guan *et al.* developed a MOF composite-assisted strategy for the synthesis of single-holed cobalt/N-doped carbon (Co/NC) hollow particles by controlled pyrolysis of yolk-shelled polystyrene@ZIF-67 (PS@ZIF-67) composites (**Figure 8A**).^[101] The samples retained their spherical morphology after carbonization with a single large hole on each shell, in which Co nanocrystals were uniformly distributed (Figure 8B,C).

Compared to the single metals, metal alloys exhibit superior electrocatalytic activity due to the intrinsic polarity between different metals which can promote catalytic reactions.^[104,105] One typical example is the preparation of ultra-low-loading precious-metal-based alloys/carbon composites from MOFs precursors for proton-exchange membrane fuel cells (PEMFC). Recently, Liu and coworkers used ZIF-67 or ZIF-8@ZIF-67 as precursors to obtain uniformly dispersed PtCo alloy NPs over a substrate of dense Co-N_x-C_y sites and onion-like graphitic layers encapsulated Co nanocrystals (Figure 8D).^[106] High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images show that the PtCo alloy NPs are surrounded by individual Co atoms and a trace amount of Pt atoms (Figure 8E,F).

High-resolution transmission electron microscopy (HRTEM) reveals the PtCo core and Pt shell in alloy NPs (Figure 8G). The LSV curves show the increased ORR activity of PF-2 (PF: platinum-group metal (PGM)-free) < Pt₃Co/ZC (ZC: ZIF-8-derived carbon) ≤ commercial Pt/C < LP@PF-1 (LP@PF: PtCo alloy NPs with an ultralow concentration of Pt supported over PGM-free materials) < LP@PF-2, and the electron transfer number for both ORR of LP@PF-1 and LP@PF-2 is 3.99 (Figure 8H). When LP@PF-1 and LP@PF-2 were incorporated in the cathode of the membrane electrode assembly (MEA), both displayed higher catalytic activities than the comparative MEAs within the high-voltage regions in a H₂-O₂ cell (Figure 8I). Moreover, these two MEAs both showed higher mass activities (MAs) than those of comparative MEAs, and LP@PF-1 MEA possessed the highest durability after 30000 cycles (Figure 8J). Computational modeling studies revealed that the interaction between PtCo alloy NPs and Co-N_x-C_y sites contributed to the satisfactory ORR activity and durability in the fuel cell.

Moreover, the carbonization temperature has a significant influence on the phase of MOF derivatives, particularly the Fe-based MOF derivatives.^[107-109] During pyrolysis, iron ions are reduced to Fe NPs, as the temperature increases, carbon atoms from the surrounding shells diffuse into the Fe cores, forming Fe_xC NPs. Noteworthily, Guan *et al.* prepared Fe₃C NP-embedded N-doped carbon nanotube assemblies supported by a porous N-doped carbon matrix (Fe₃C@N-CNT assemblies) using a dual-MOF confined-pyrolysis strategy (**Figure 9A**).^[110] The introduction of a second MOF (MIL-88B nanorod) into a MOF host (ZIF-8 polyhedron) guaranteed a confined-pyrolysis process for the synthesis of uniform Fe₃C@N-CNT assemblies without aggregation of Fe₃C NPs and metal Fe impurity (Figures 9B-D). The unique structure and composition lead to the remarkable ORR performance including electrocatalytic activity, durability, and methanol tolerance capability (Figure 9E-G). Furthermore, this dual-MOF precursor strategy can be used in the design and synthesis of many other hybrid functional materials,

providing a new approach to the development of highly active MOF-derived porous materials for future energy storage and conversion technologies.

Besides the carbonization temperature, the detailed conversion conditions also have important influence on the composition of MOF derivatives, resulting in metal oxides, chalcogenides, phosphides, and nitrides. Recently, numerous MOF-derived metal oxide/carbon composites with desired nanostructure and composition have been prepared by the pyrolysis strategy under an inert atmosphere followed with an oxidation in air, such as Co₃O₄-carbon porous nanowire arrays,^[64] Co@Co₃O₄@C core@birefringent NPs,^[111] Co@Co₃O₄ encapsulated in CNT-grafted N-doped carbon polyhedra,^[112] and Co-Co₃O₄-based multi-level nanoarchitectures embedded in hollow N-doped carbon polyhedral.^[113] Apart from cobalt oxides, manganese oxides have also drawn considerable interest for ORR because of their multiple 3d electron configurations and various morphologies and phases.^[114-116] Most recently, Lu *et al.* engineered abundant MnO/Co heterointerfaces in porous graphitic carbon (MnO/Co/PGC) polyhedrons via one-step pyrolysis of a bimetal-organic framework (Figure 9H).^[117] After calcination, the MnO/Co/PGC polyhedrons possess a rough surface with a distinct graininess (Figure 9I). The *in-situ* generated Co nanocrystals are uniformly distributed within porous graphitic carbon polyhedrons (Figure 9J), creating well-defined heterointerfaces. Owing to the desired composition and formation of the heterostructures, the resulting MnO/Co/PGC exhibits superior activity and stability towards ORR (Figure 9K). More importantly, the MnO/Co/PGC also shows high activity towards oxygen evolution reaction (OER), thus making it an efficient air cathode for the rechargeable Zn-air battery (ZAB). The homemade ZAB was able to deliver excellent performance including a peak power density of 172 mW cm⁻² and a specific capacity of 872 mAh g⁻¹ (Figure 9L), as well as excellent cycling stability (350 cycles), outperforming the mixed commercial Pt/C||RuO₂ catalysts (Figure 9M). A light-emitting diode screen can be powered by two ZABs connected in series (inset in Figure 9M), suggesting its promising

application in energy storage. This work highlights the synergy from heterointerfaces in oxygen electrocatalysis, more importantly provides a simple and effective approach for preparing durable, cost-effective and highly active bifunctional electrocatalysts for electrochemical energy storage and conversion.

Metal chalcogenides are usually formed by the interaction between the central metal (*e.g.*, Co, Ni, Fe, Ir, Ru) and chalcogen atoms (*e.g.*, S, Se, Te), resulting in a unique cluster-like crystal structure. These clusters can provide a good reservoir for electron transfer from catalysts to adsorb oxygen during ORR. Meanwhile, the chalcogenization can also lead to changes in the surface chemistry of the metals and prevent oxidation poisoning of the prepared electrocatalyst in an alkaline solution as well as dissolution in an acidic medium.^[10,52] Metal sulfides are well studied due to the variety of sulfur sources and the simplicity of the vulcanization.^[118,119] In 2015, Chen *et al.* reported the preparation of $\text{Co}_x\text{S}_y@\text{C}$ from ZIF-67.^[120] Subsequently, Hu *et al.* adopted ZIF-67 as the templating precursor and thioacetamide as the sulfur source to construct novel Co NP-embedded carbon@ Co_9S_8 double-shelled nanocages (Co-C@ Co_9S_8 DSNCs) as electrocatalysts for ORR, where numerous particles were uniformly dispersed without aggregation (Figure 9N-P).^[121] The unique architecture not only possesses uniformly distributed high-density active sites but also significantly shorten the diffusion pathway of the electrolyte and improve mass transport of the gas and electrolyte, thereby rendering them high catalytic activity and superior long-term stability for ORR. The introduction of a phosphorus or nitrogen source prior to MOF carbonization produces a highly conductive and stable phosphide or nitride, which also displays superior electrocatalytic activity and stability towards ORR. These phosphorus or nitrogen sources can be obtained by regulating organic ligands or introducing additional inorganic sources (*e.g.*, $\text{Na}_2\text{H}_2\text{PO}_2$, red phosphorus, phytic acid, NH_3 , and urea).^[58,66,122-125] Recently, Sun *et al.* prepared a hybrid nanostructure comprising Ni_2P nanoparticles anchored on MOF-derived Co, N-codoped porous carbon polyhedrons,

demonstrating excellent trifunctional electrocatalytic performances for hydrogen evolution reaction (HER), OER and ORR.^[122] Unlike this work using NaH_2PO_2 as the phosphorus source, Wang *et al.* selected a Cu-based MOF containing phosphorus atoms and nitrogen atoms in the ligands as the single precursor and template to prepare novel Cu_3P NPs coated by a N, P-codoped carbon shell.^[126] Recently, Guan *et al.* synthesized unique hybrid cobalt/cobalt nitride NPs well-integrated with N-doped carbon (NC-Co/ CoN_x) nanoarrays through nitridation of 2D layer-structured Co-ZIF-derived Co NP-decorated NC nanoarrays.^[124] The well-integrated NC-Co/ CoN_x electrode combined the merits of every single component and delivered remarkable bifunctional activity towards both OER and ORR in alkaline media, thus rendering it a promising air cathode for ZABs.

For the synthesis of most MOF derivatives, two basic strategies are often employed to control the chemical composition: 1) tuning the composition of MOF precursors; 2) manipulating the conversion conditions. Certainly, these two strategies are adapted simultaneously in many cases to achieve superior electrocatalytic activity and stability. Thanks to the great diversity in MOFs and the conversion processes, these MOF derivatives usually possess multiple components and thus multi-functional electrocatalytic capability. Even so, the development of MOF derivatives is perhaps still in the infancy, and their electrocatalytic performance needs to be further improved. Therefore, the relation of material physicochemical properties with their electrocatalytic performance should be reflected while designing and constructing these MOF derivatives as electrocatalysts towards ORR. First, the component properties determine the intrinsic activity and conductivity. Second, modification of the materials' morphology/structure can expose a greater number of active sites. Third, favorable structures can prevent catalysts from agglomeration and promote mass transfer, thus enabling high electrocatalytic activity and stability. With these points in mind, more efforts should be dedicated to exploring MOF derivatives for highly efficient ORR.

3. Conclusions and Perspectives

In summary, this minireview provides an overview of the recent developments of MOF-based materials as highly efficient electrocatalysts towards ORR, which is one important reaction in fuel cells and metal-air batteries. An ideal electrocatalyst should possess several important features including high intrinsic catalytic activity (*i.e.*, TOF), abundant exposed active sites (*i.e.*, electrochemically active surface area (ECSA)), decent electron transfer and mass transport capabilities (*i.e.*, Tafel slope), and durable stability.^[127-129] As a class of newly emerging versatile materials, MOF-based materials provide great opportunities for obtaining various advanced electrocatalysts with desired morphologies, structures, compositions, and properties. Regarding their inherent characteristics, a variety of synthetic strategies have been developed to obtain highly efficient electrocatalysts for ORR, which can be generally summarized in the following aspects.

First, the ordered porous structure and solid character of pristine MOFs render them as a bridge between homogeneous and heterogeneous electrocatalysts. This provides an opportunity for studying the catalytic mechanism at the molecular level. In the context of electrocatalytic ORR, MOFs with a high degree of stability in aqueous solution and particularly with tolerance to varying pH conditions are desirable. For example, the bonding strength of metal-ligand coordination in some MOFs can be often enhanced with carboxylate-terminated linkers, tetra-carboxylate ligands and 4-connected $\text{Al}(\text{OH})(\text{RCOO})_2$ chains and Fe(III) porphyrin linkers, which in turn leads to better chemical stability. High electrical conductivity is another important factor for improving the electrocatalytic activity and electron transfer number. Inspired by the high activity of the conductive 2D MOF, $\text{Ni}_3(\text{hitp})_2$, more and more strategies, including redox-matching, donor-acceptor interactions and mixed valency as well as growing ultrathin 2D MOFs directly on conducting substrate, have been used to improve the electrical conductivity thus leading to higher catalytic efficiency.

Second, MOF composites integrated with many inorganic functional materials have been explored and efficiently utilized as electrocatalysts towards ORR. These functional materials usually possess higher electrical conductivity or electrocatalytic activity and stability, such as carbon materials (*e.g.*, heteroatoms doped or undoped CNTs and graphene, as well as their composites), metallic NPs, metal oxides and sulfides. Each component in the MOF composites possesses a unique function. As a result, MOF composites can often overcome the drawbacks of the individual counterparts and generate synergistic effects for enhanced electrocatalytic performance. Moreover, the pores in the MOFs can act as gates to effectively regulate the contact of reactants and electrolytes with the catalyst, providing a good model for designing electrocatalysts with selective function.

Third, inheriting the remarkable features of MOFs to a great extent, the MOF derivatives have unique advantages in comparison to the traditional porous materials, such as simple and efficient preparation procedure, large specific surface area and porosity inherited from MOFs, facile doping of highly dispersed heteroatoms, and controllable size/morphology/component by pre-designing MOFs and MOF composites. Therefore, the derivation of MOFs and MOF composites opens a promising avenue to prepare diversified highly efficient electrocatalysts towards ORR. On the one hand, the organic ligands can be pyrolyzed to highly conductive porous carbon matrix with/without doping of heteroatoms, which can not only function as catalysts or catalyst supports for loading other active species but also guarantee the fast charge transfer/mass transport and the exposure of active sites. On the other hand, the metal elements at the nodes can be converted to various inorganic substances through direct calcination or post-treatment, such as single atoms, metal or metal alloys, metal carbides, oxides, sulfides, phosphides and nitrides. Moreover, compared to carbon materials, these single metal atoms, metal/alloy NPs and metallic compounds can be well dispersed in the resultant porous carbon, therefore improving the density of active sites. In addition, unique morphologies and structures are also generated in the micrometer/nanometer

scale. These derivatives possess a large number of robust and highly active catalytic sites as a result of desired structure and component, where the adsorption mode of O₂ molecules, cleavage style of O-O bonds and bonding strength of intermediates can be well optimized, leading to high electrocatalytic ORR activity and stability.

Overall, though incredible advances have been achieved, the development of MOF-based electrocatalysts towards ORR is perhaps still in the infancy and there are still many challenges for further investigations of more efficient MOF-based electrocatalysts towards ORR, some of which are listed below.

(1) Limited availability of MOFs for special uses, such as, highly conductive and stable MOFs as pristine electrocatalysts, and MOF precursors or templates for metal-free carbon-based derivatives.

(2) Large-scale synthesis of MOFs. The high price of ligands, harsh synthetic conditions for some MOFs, and limited number of synthesis methods severely hamper the development process from basic research to practical industrialization.

(3) Mechanistic studies are needed for the so-called synergistic effects in promoting catalytic activity enhancement in MOF composites and derived inorganic composites.

(4) Although there are some recent reports indicating that some pristine MOFs can be directly used for electrocatalysis, the surface of MOFs may undergo an irreversible phase change during the ORR process. Therefore, the real active sites should be identified by more advanced characterizations.

(5) Difficulty in preparing pure carbon materials derived from MOFs. Traces of metal often remain in MOF-derived metal-free carbon materials even after an acidic wash.

(6) Precise control over the active sites, especially in MOF derivatives. These derivatives usually contain multiple phases due to the complex variability during carbonization and/or post-treatment processes.

(7) Accurate control and regulation of pore structure in MOF derivatives. The pyrolysis usually requires high temperature, which puts an obstacle in rationally controlled synthesis of derivatives with desired porous characteristics.

(8) Lack of understanding of the transformation process from MOFs to their derivatives.

(9) The electrocatalytic activity and stability of MOF-based materials need to be further improved, especially in acidic media.

(10) Efficient and stable electrocatalysts with special requirements are highly desired for the practical applications of MOF-based materials in energy storage and conversion. For example, strong tolerance to contaminants (*e.g.*, methanol, CO_x, halide ions, sulfur oxides, nitrogen oxides) for fuel cells, and robustness and bifunctionality for rechargeable metal-air batteries.

To overcome the above challenges, some solutions and potential development trends might be noted as follows.

(i) The synthesis of MOFs possessing strong metal-ligand coordination bond, redox activity, donor-acceptor interactions, and mixed valency, is of great necessity. The coordination between the metal centers and organic ligands determines largely the stability, while other factors determine the conductivity.^[30,38,39,130,131] Along this line, some MOFs such as porphyrin MOFs, phthalocyanine-based conjugated MOFs and UiO family (UiO = Universitetet i Oslo) show great promise as pristine electrocatalysts towards ORR.

(ii) Covalent organic frameworks, with complete organic skeletons, provide great opportunities to facilely construct porous pure carbon materials with the precise control over heteroatom doping.^[132-134]

(iii) More facile approaches for the synthesis of MOF-based materials should be developed. For example, post-synthetic modifications of metal nodes and ligands of MOFs, such as multi-metal coordination and solvent-assisted ligand incorporation, should be used to enrich the types of MOFs.^[131,135]

Constructing more MOF composites (MOFs with metal clusters, polyoxometallates, NPs, semiconductor, and polymer) and postprocessing of derivatives are the other two popular ways.^[19,47,57]

(iv) *In-situ* characterization techniques would be very helpful to understand the evolution of the electrocatalyst and the mechanism of the electrocatalytic reaction. Operando *in-situ* monitoring the growth of MOFs and the transformation process to derivatives is essential for developing new electrocatalysts. Advanced testing techniques combining electrochemical measurements with *in-situ* spectroscopy (FT-IR, Raman, XPS, and EXAFS) or *in-situ* scanning probe microscopy can be helpful in the real-time analysis of the dynamic reaction mechanism of ORR.^[136-138]

(v) With the advances of computer science and quantum chemistry, the combination of experimental and theoretical studies will give new insights into the synergetic effects and create many new opportunities for discovery and breakthroughs in advanced electrocatalysts.^[87,139]

(vi) System-level studies would be appreciated for the design and synthesis of highly efficient electrocatalysts. Other than highly active sites, the density and utilization rate of active sites, charge transfer, interface properties between different components, electrocatalysts and electrolyte, *etc.*, are all important factors for improving the overall electrocatalytic performance.^[140,141]

(vii) Highly efficient and stable electrocatalysts in acidic media can be realized by incorporation of M-N-C moieties^[90,95,99,142,143] or Pt-based alloys into MOFs, MOF composites, and MOF derivatives.^[56,106,144]

(viii) The specific requirements of electrocatalysts for practical applications can sometimes be satisfied with the design of catalysts. For example, uniformly tunable pores in MOFs and mesoporous carbon wall in MOF derivatives can provide effective selectivity towards oxygen molecules but largely prevent crossover by contaminants.^[56,106] For long-life rechargeable metal-air batteries, robust and bifunctional electrocatalysts should be aimed, which can be prepared by integrating the OER active sites

and the ORR active sites in a single catalyst.^[117,124,145] Equally important, considerable efforts should be devoted to the fabrication of devices with different electrolytes for practical applications in the future.^[5,145,146]

In conclusion, MOFs will undoubtedly continue to spark more research on electrocatalysts for ORR and other reactions. From a practical point of view, MOF-based materials with earth-abundant elements should be employed to fully address the pressing challenges faced by our society in energy and environment. With persistent research efforts, we should have a good chance to witness a revolution of new technologies in renewable energy and environmental science in the near future.

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Conflict of Interest

The authors declare no conflict of interest.

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Figures and Captions

Figure 1. Illustration of the reaction pathway for ORR and the resulting intermediates on the surface of a catalyst. The blue arrows show the proton/electron transfer. The yellow arrows indicate the O-O bond cleavage.

Figure 2. The classification and operation of metal-organic frameworks (MOFs) towards ORR: pristine MOFs, MOF composites and their derivatives.

Figure 3. (A) Coordination geometry of Cu atoms in Cu-bipy-BTC and (B) its CVs in 0.10 M phosphate buffer saturated with N₂ (dotted curve) and O₂ (solid curve).^[28] Copyright 2012, Elsevier. (C) The framework structure of Co-Al-PMOF, and (D) LSV curves for different samples in O₂-saturated 0.1 M H₂SO₄.^[31] Copyright 2017, Royal Society of Chemistry. (E) Perspective view of the 2D layered Ni₃(hitp)₂.^[35] Copyright 2016, Nature Publishing Group. (F) Cyclic voltammograms under O₂ atmosphere in pH 13, pH 8, and pH 4, and (G) reaction mechanism of 2-electron transfer pathway for Ni₃(hitp)₂ towards ORR.^[36] Copyright 2017, American Chemical Society.

Figure 4. (A) Schematic of the chemical structures of (G-dye-FeP)_n MOF and its magnified view of layers inside the framework; (B) LSV curves of different samples in O₂-saturated 0.1 M KOH.^[48] Copyright 2012, American Chemical Society. (C) Schematic structure of PcCu-O₈-M (Red: O, blue: C, white: H, brown: Cu, green: metal atoms, M= Co, Fe, Ni, Cu); (D) TEM image of PcCu-O₈-Co/CNTs; (E) LSV curves of PcCu-O₈-Co/CNTs in O₂-saturated 0.1 M KOH.^[53] Copyright 2019, WILEY-VCH. (F) Schematic illustration of the synthesis and structure of CuS(x wt%)@HKUST-1; (G) LSV curves of HKUST-1 (line I), CuS(x wt%)@HKUST-1 (line II: 1.4 wt%, line III: 5.3 wt%, line IV: 8.8 wt%, line V: 28 wt%, line VI: 56 wt%), nano-CuS (line VII), and commercial Pt/C (line VIII) in O₂-saturated 0.1 M KOH.^[52] Copyright 2016, WILEY-VCH.

Figure 5. (A) FESEM images of the samples obtained at 5 s and 2, 6, 9, 18, and 36 hours of the reaction process, showing the morphological change from NCs to NAFSs; (B) schematic illustration of the formation mechanism of a NAFS, in which four stages were involved: I, site-selected deposition; II, the formation of the new KCoFe-1 phase; III, epitaxial growth of the NCBs; IV, core@satellite superstructure transform to NAFS; FESEM (C) and TEM (D,E) images of Co-Fe mixed oxides derived from KCoFe-1 NAFS s; FESEM (F) and TEM (G,H) images of Co-Fe mixed oxides derived from KCoFe-3 NFs .^[71] Copyright 2017, American Association for the Advancement of Science. FESEM (I) and TEM (J) images of Co-Fe-O cages; FESEM (K) and TEM (L) images of Co-Fe-O frames; FESEM (M) and TEM (N) images of Co-Fe-O boxes.^[72] Copyright 2018, Elsevier.

Figure 6. (A) Schematic illustration of porous N-doped carbon nanofibers, and (B) their TEM image.^[81] Copyright 2014, American Chemical Society. (C) Schematic illustration of hollow N-doped carbon spheres (HNCSs), and (D) their SEM image (Inset is the TEM image, scale bar: 500 nm).^[82] Copyright 2019, Elsevier. (E) FESEM image of N-doped carbon nanotube frameworks (NCNTFs) obtained at 700 °C in the presence of H₂.^[83] Copyright 2016, Nature Publishing Group. (F) Schematic illustration of controllable multi-heteroatom (N, B, P, S)-doped porous carbon nanofibrous network.^[86] Copyright 2017, American Chemical Society.

Figure 7. (A) Scheme showing a host-guest strategy for the fabrication of iridium single-atom catalyst (Ir-SAC); (B) elemental mappings for the Ir-SAC; (C) Fourier transforms of κ^3 -weighted Ir L₃-edge EXAFS data; (D) XANES of Ir L₃-edge, where the white line intensity shows the valence state of Ir in Ir-SAC is between 0 and 4⁺; (E) Ir L₃-edge EXAFS of Ir-SAC in R spaces, where curves from top to bottom are the Ir-N, Ir-O and Ir-C two-body backscattering signals (χ_2) included in the fit and the total signal (red line) is superimposed on the experimental signal (black line); (F) ORR polarization curves with a scanning rate of 5 mV s⁻¹ at rotating speed of 900 rpm for the synthesized catalysts in 0.1 M HClO₄ solution; (G) stability test of Ir-SAC in 0.1 M HClO₄ solution (inset is the mass activity comparison between Ir-SAC and Pt/C); (H) Gibbs free energy diagram for ORR on IrN₄; (I) the proposed ORR mechanism on the IrN₄ site.^[95] Copyright 2019, WILEY-VCH.

Figure 8. (A) Schematic illustration of the formation process, (B) FESEM and (C) TEM images of single-holed cobalt/N-doped carbon (Co/NC) hollow particles.^[101] Copyright 2017, WILEY-VCH. (D) Schematics of LP@PF catalysts, showing coexistence of Pt-Co NPs, Co@graphene, and Co-N_x-C_y PGM-free active sites; (E) A HAADF-STEM image of Pt-Co NPs in LP@PF-1 situated over (F) PGM-free support containing atomically dispersed Co (circled in red) and trace Pt (circled in blue); (G) HRTEM image of a representative PtCo alloy NP with Pt₃Co superlattice core and Pt skin partially covered by CoN and CoC terraces; (H) LSVs of different catalysts recorded in O₂-saturated 0.1 M HClO₄ (Bottom) and corresponding electron transfer number (Top); (I) H₂-O₂ fuel cell i-V polarization (solid symbols and lines) and power density (hollow symbols and dashed lines) plots of different catalysts recorded under 1 bar of O₂ pressure (LP@PF-1: black stars, LP@PF-2: red diamonds, PF-2: green triangles, 3% Pt₃Co/ZC: blue spheres, commercial 47% Pt/C: magenta squares); (J) Fuel cell MAs at 0.9 V_{iR-free} before and after 30000 voltage cycles.^[106] Copyright 2018, American Association for the Advancement of Science.

Figure 9. (A) Schematic illustration of the formation process, (B) FESEM, and (C) TEM images of the iron carbide nanoparticle-embedded N-doped carbon nanotubes (Fe₃C@N-CNTs) assembly; (D) XRD patterns of Fe₃C@N-CNTs assemblies and Fe₃C-Fe/N-CNT mixture; (E) LSV curves of different samples; (F) Durability and (G) methanol tolerance test of Fe₃C@N-CNTs and Pt/C towards ORR in O₂-saturated 0.1 M KOH solution.^[110] Copyright 2016, The Royal Society of Chemistry. (H) Schematic illustration of the formation process, (I) FESEM, and (J) TEM images of MnO/Co/PGC; (K) LSV curves for ORR of different samples recorded in O₂-saturated 0.1 M KOH solution; (L) Discharge polarization and power density curves and (M) long-term cycling performance of home-made Zn-air battery (Inset is the photograph of a blue LED screen powered by two Zn-air batteries in series with MnO/Co/PGC as the air-cathode).^[117] Copyright 2019, WILEY-VCH. (N) Schematic illustration of the formation process, (O) FESEM, and (P) TEM images of Co-C@Co₉S₈ double-shelled nanocages (DSNCs).^[121] Copyright 2016, The Royal Society of Chemistry.

For Table of Contents Entry

This mini-Review summaries some major recent research efforts and advances on metal-organic frameworks (MOFs) based electrocatalysts towards the oxygen reduction reaction. Despite the rapid developments in the past decade, many great challenges in this field still remain for the practical use of MOF-based electrocatalysts. Some promising directions and strategies are also discussed.