REVIEW ARTICLE

Recent advances in vacancy engineering of metal-organic frameworks and their derivatives for electrocatalysis

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Abstract
The efficient electrocatalysis plays the key role in the development of electrochemical energy conversion technologies to alleviate energy crisis. Given their multiple active sites and large specific surface areas as electrocatalysts, metal-organic frameworks (MOFs) and their derivatives have attracted considerable interests in recent years. Specially, exploring the roles of the enhanced active sites in MOFs and their derivatives is significant for understanding and developing new effective electrocatalysts. Recently, the vital role of vacancies has been proven to promote electrocatalytic processes (such as H2 or O2 evolution reactions, O2 reduction reactions, and N2 reduction reactions). In order to in-depth exploring the effect of vacancies in electrocatalysts, the vacancies classification, synthetic strategy, and the recent development of various vacancies in MOFs and their derivatives for electrocatalysis are reviewed. Also, the perspectives on the challenges and opportunities of vacancies in MOFs and their derivatives for electrocatalysis are presented.

KEYWORDS
active sites, defect, derivatives, electrocatalysis, metal-organic frameworks, vacancy

1 INTRODUCTION

The pressure from the exhaustion of fossil fuels forces human beings to search new sustainable and more efficient energy resources to support rapid development of our society.1–8 Currently, many next-generation renewable energy devices have been discovered to replace fossil fuels in a clean way. Electrochemical energy conversion and storage technologies are considered as promising ways to become clean and sustainable energy devices.9–13 Hydrogen energy with high energy density and environmental benefits has been regarded as a potential alternative energy carrier. Electrocatalytic water splitting contains two reactions of oxygen evolution reaction (OER) and hydrogen evolution reaction (HER), which can produce hydrogen and oxygen simultaneously.14–17 In metal-air batteries, the oxygen reduction reaction (ORR) is utilized as reversible half reactions to convert chemical energy into electrical energy.18–21 In addition, electrochemical CO2 reduction reaction (CO2RR) and nitrogen reduction reaction (NRR) can transform electrical energy into chemical energy, which can be generated from abundant raw material of CO2 and N2 in atmosphere.22–27 However, the sluggish kinetics in electrochemical reactions hamper the efficiency of these renewable technologies and, therefore, demand a high overpotential to drive the reactions.28–31 To enhance the efficiency of these renewable technologies for commercialization, the catalysts based on noble...
metal-containing materials (ie, Pt/C, RuO₂, or IrO₂) have been employed to reach rapid reaction kinetics. However, the scarcity and cost-efficiency of these noble metal-based catalysts are of great limitation for their applications in renewable technologies. Consequently, it is vital to develop the alternative electrocatalysts with low cost, high properties, and durability for clean-energy technologies.

Considering the electrocatalysis of the gas-involving reactions, it is desirable to find electrocatalysts with the abilities of fast electron/mass transport and abundant triphase regions for interface reactions. In the past few decades, a large number of nanomaterials with superior electrocatalytic activity have been designed for electrochemical reactions, where, metal-organic frameworks (MOFs), a novel class of nanoporous materials, have acted as promising material platform with versatile applications such as catalysts, adsorbents of gas storage and separation, batteries, substrates for drug delivery and biosensors. Owing to their intrinsic aesthetic, such as large surface area, isolated active site, open crystalline structure, and exceptional porosity, MOFs have been considered as heterogeneous electrochemical catalysts for various electrocatalysis reactions. However, most MOFs display intrinsic poor electrocatalytic activity and electrical conductivity. Thus, huge efforts have been spent on overcoming the barrier through the strategies like metal node engineering, introduce defects, and carbonization. Among them, the introduction of defects has attracted considerable research attention because it can tune the electronic and surface properties, create open metal sites, and tune porosity. Thus, various MOFs and derivatives with defects have been investigated in recent years.

Among many various defects, vacancy could act as an important role in determining the physicochemical properties of catalysts and is commonly observed in many nanomaterials. With the harsh synthetic conditions (eg, temperature and/or pressure) of most crystals, vacancies can generate in crystalline materials by moving atoms into random positions or remove them from the crystal lattice. The creation of vacancy in crystalline materials generally give rise to the changes of performance or reactivity. In MOFs and derivatives, vacancies are controllable by modifying the structures of MOFs and tuning the conditions for the transformation of MOF derivatives, which can cause novel physical/chemical properties via the breaking and reforming of bonds, electronic compensation, lattice distortion, gap states at the Fermi level, and electron localization. In recent years, advanced synthesis technologies and characterization technologies have greatly accelerated the development of vacancies in MOFs and MOF-derivatives, such as plasma etching, reduction, and pyrolysis treatment, which could deeply explore the mechanism of electrocatalytic activity, improving the electroactivity. However, the roles of vacancy engineering in the development of MOFs and MOF-derivatives and energy-related applications have not been systematically discussed.

In this review, the categories of vacancy defects in MOFs and derivatives for electrocatalysis have been summarized (Scheme 1). We start with an introduction of the development of vacancy defects and their effectivity in MOFs and derivatives for electrocatalysis. Afterwards, we summarize the design principles of vacancies in MOF-based electrocatalysts according to vacancy types and synthetic strategies. Meanwhile, recent remarkable findings about electrocatalysts with vacancies on electrocatalysis are summarized to understand the relationship between vacancy defects and electrochemical performance. Though various MOFs and derivatives with vacancy defects have been reported, the significance of the vacancies in the electrocatalytic process should be emphasized and reviewed to guide the design of desirable electrocatalysts. Finally, we propose the challenges and opportunities in vacancy engineering, which could give some guidelines in the future exploration on vacancy electrocatalysts.

2 TYPES OF VACANCIES IN MOFS AND DERIVATIVES

Various types of vacancies (ie, coordinatively unsaturated metal sites [CUMs], link missing, anion/cation...
vacancies\textsuperscript{106–108} have been demonstrated to show the potential of activities for triggering functionalities in electrocatalysts.\textsuperscript{109} Vacancies introduced in catalysts have risen as a new method to enhance electrochemical reactions. The vacancy engineering method can optimize the ability to adjust the band structure, capture electrons, and change the reaction pathway.\textsuperscript{110–113} In this part, we mainly focus on the type of vacancies as the active sites in MOFs and their derivatives.

### 2.1 Coordinatively unsaturated metal sites

MOFs have been considered as promising electrocatalytic materials due to their modifiable coordination bonds between metal ions and organic ligands. The rich metal centers in MOFs can offer potential active sites, which is conducive to the transport of mass and electronics. However, there is no available adsorption sites for the fully coordinated metal ions, which results in the poor activity of intrinsic MOFs for electrocatalysis. In recent years, the introduction of CUMGs has been applied as highly active catalytic sites for catalysis, separation, and sensing.\textsuperscript{101,114} The CUMs can expose more active sites and act as catalytic centers, which can be beneficial to the adsorption of reactants to enhance electrocatalysis.

For example, Tao and coworkers created CUMGs in ZIF-67 (CUMGs-ZIF-67) as accessible sites for electrocatalysis via dielectric barrier discharge (DBD) plasma etching (Figure 1).\textsuperscript{101} The density-functional theory (DFT) calculations demonstrated that CUMGs acted as excellent catalytic centers and the OER performance of CUMGs-ZIF-67 was improved significantly. With the deduction of one ligand, the charge on metal sites remained a highly positive charge, which facilitated the adsorption of O\textsubscript{2} and intermediates and the formation of active centers. Moreover, the OER activity of the CUMGs was reversible since supplementing the missing ligands while CUMGs were regarded as the catalytic centers.

Recently, the Zhuang group reported a facile fabrication of ultrathin MOF-74 nanosheets (NSs) with rich CUMs (FeCo-MNS-1.0) through 2D oxide sacrifice approach (2dOSA).\textsuperscript{114} The CUMs played an active role for OER, which maximized the exposure of metal active center. The ex situ extended X-ray absorption fine structure (EXAFS) showed that the coordination numbers (C.N.) for Co-site and Fe-specie in FeCo-MNS-1.0 were reduced comparing to the bulk FeCo MOF-74, which was attributed to the generation of extra CUMs. According to DFT calculations, the adsorption energy of OH\textsuperscript{*} on FeCo-MNS-1.0 was higher than that on FeCo-MB, suggesting that the CUMs were conducive to adsorb OH\textsuperscript{*} and intermedia during OER progress. Thus, the FeCo-MNS-1.0 showed an outstanding OER performance with a low overpotential of 298 mV@10 mA/cm\textsuperscript{2} and a small Tafel slope of 21.6 mV/dec in an O\textsubscript{2}-saturated 0.1 M KOH solution.

Zhao and coworkers reported the excellent OER activities of NiCo bimetal-organic framework NSs (NiCo-UMOFNs) with coordinatively unsaturated metal atoms, synthesized from self-assembly of Ni\textsuperscript{2+}, Co\textsuperscript{2+}, and benzenedicarboxylic acid (BDC).\textsuperscript{102} The nanometer thickness extremely exposed the catalytic active surfaces and the CUMs ensured a high catalytic activity. The as-prepared NiCo-UMOFNs loaded on copper foam required a low onset potential of 1.39 V and an overpotential of 189 mV@10 mA/cm\textsuperscript{2} in alkaline conditions. They proposed that the coordinatively unsaturated atoms on the surface possessed open sites for adsorption, which was evidenced through a suite of measurements. The EXAFS data in Figure 2A show that the obvious and
identical decrease for the average coordination number of the M-O or M-C shell in all UMOFNs. As shown in Figure 2B, the exposed metal atoms of UMOFNs located at site S1 were coordinatively unsaturated while the surface metal atoms at the crystallographic distinct site S2 were octahedrally coordinated, suggested by X-ray absorption near-edge structure (XANES). The DFT calculation in Figure 2C shows that the formation energy on metal site S2 (−1.28 eV/atom) was lower than that on site S1 (−0.98 eV/atom), which is more favorable for the oxygen absorption. The combination of XANES and DFT demonstrated that the coordinatively unsaturated metal atoms were the dominating active centers of NiCo UMOFNs.

2.2 | Missing linker

Optimizing the electronic structure of catalytic centers is one of the most efficient methods to improve the electrocatalytic performance of solid materials, which can change the intrinsic properties (i.e., electronic conductivity and the reaction energy barrier) of catalysts. The intrinsic properties of MOFs are mainly reflected by topological structure and coordination environment. Therefore, the controllably missing linkers can be introduced into MOFs base on the high design flexibility of MOFs, which can change their electronic structure without the loss of crystallinity and the porosity of materials.

Xue and coworkers reported that the incorporation of missing linkers into MOFs could enhance electrocatalytic properties. The theoretical calculations demonstrated that the introduction of missing linkers could regulate the electronic structure of MOFs, which significantly improved the OER performance. As shown in Figure 3A, the missing linker, such as carboxyferrocene (Fc), present in CoBDC could alter the band gap and charge distribution, which was favorable for the adsorption of the reaction intermediates. As shown in Figure 3B, DFT calculations revealed that the missing linker of Fc could replace the terephthalic acid in CoBDC and form a new stable MOF (CoBDC-Fc). New electronic states generated near the Fermi level after introducing missing linkers, which demonstrated a more conductive electronic structure of CoBDC-Fc (Figure 3C). The obtained self-supported MOF nanoarrays with missing linkers displayed excellent OER performance with the overpotential of 241 mV@100 mA/cm².

Recently, Yu and coworkers proposed a new type of vacancies, as shown in Figure 4A. The unusual carbon-nitrogen vacancy (V_{CN}) was presented in Prussian blue analogues (PBA) through a nitrogen plasma bombardment, which endowed the electrocatalyst with a low overpotential of 283 mV@10 mA/cm² for OER. The calculation demonstrated that the positrons were mainly concentrated in the center of V_{CN} (Figure 4B). The V_{CN} was greatly different from other vacancies, on the one hand, they can adjust the electronic structure and coordination environment around Ni-Fe sites to enhance the OER performance. On the other hand, V_{CN} can prevent the release of Fe element during reaction process, which favors the growth of high-performance Ni-Fe oxyhydroxide from PBA precatalyst during OER.

2.3 | Anion vacancy

Anion vacancies in catalysts can induce abundant unsaturated coordination sites and high-energy dangling bonds to further optimize the electronic environment and local electronic structure. Given the low formation energy of oxygen vacancies, they are widely concerned to promote electrochemical reactions. With the presence of oxygen vacancies, the physicochemical properties of metal oxides may be changed.

Gao and coworkers reported an ideal model of oxygen vacancies confined in oxide-based atomic layer, which could reveal the atomic-level effect between oxygen vacancies and CO₂ reduction. As shown in Figure 5A, the
Vo-rich and Vo-poor Co₃O₄ single-unit cell layers were prepared through annealing the lamellar inorganic–organic hybrid intermediate at different atmosphere. The X-ray photoelectron spectroscopy (XPS) and synchrotron radiation X-ray absorption fine structure (XAFS) revealed the distinct local atomic arrangement of Vo-rich Co₃O₄ and Vo-poor Co₃O₄ single-unit-cell layers (Figure 5B-D). The DFT calculations suggested that the oxygen vacancy was the main defect, while the distinct oxygen vacancy concentrations were confirmed by X-ray absorption fine structure spectroscopy. Moreover, the energy calculations demonstrated that the oxygen vacancies in Co₃O₄ single-unit cell layers helped to lower the rate-limiting activation barrier from 0.51 to 0.40 eV by stabilizing the formate anion radical intermediates, which was favorable to lower the onset potential from 0.81 to 0.78 V and could decrease the Tafel slope from 48 to 37 mV/dec. In addition, Vo-rich Co₃O₄ single-unit cell layers showed the current densities of 2.7 mA/cm² with ca. 85% formate selectivity after 40 h tests.

Recently, Wang and coworkers presented a nitrogen-doped Co₃O₄ nanoparticles/nitrogen-doped carbon framework (N-Co₃O₄@NC) coupled porous nanocubes derived from ZIF-67 through a controllable N-doping method. The defect-engineered N-Co₃O₄@NC with oxygen vacancies achieved remarkable OER catalysis with superior catalytic stability, which displayed a low overpotential of only 266 mV@10 mA/cm² and a low Tafel slope of 54.9 mV/dec. As shown in Figure 6, N-doping could cause the formation of oxygen vacancies indicated by XAFS, XPS, and the stronger electron spin resonance (ESR). Remarkably, the oxygen vacancies showed high intensity as the N-doping temperature increased, which could enhance electronic conductivity by creating new defect states around the band gap and exciting the conduction band more easily. In addition to the oxygen vacancies, other anion vacancies, such as sulfur vacancies, also have been investigated as a new active center in catalysts. For example, Wang and coworkers reported hierarchically porous carbon nanohybrids with rich sulfur vacancies.
derived from MOF precursors for electrocatalysis.\textsuperscript{127} The porous carbon nanohybrids showed excellent electrocatalytic performance with a low overpotential of 116 mV@10 mA/cm\textsuperscript{2} for OER in alkaline solutions. The formation of sulfur vacancies played an important role in reaction process, which can be occupied by hydrogen atoms to maintain the long-term efficiency of activity sites.

\section*{2.4 Cation vacancy}

Apart from anion vacancies, the introduction of cation vacancies also has a crucial impact on the properties of the catalysts. Metal vacancies possess surprising properties due to their multifarious electron and orbital distributions.\textsuperscript{128-130} With the existence of metal vacancies, the surface electronic structure can be tuned and the valence state of nearby metal centers can be increased, which greatly enhance the electrocatalytic activity.\textsuperscript{131-134} However, it is a challenge to overcome the large formation energy of metal vacancies to investigate the effect of metal vacancies on the electrochemistry performance. Various MOF-based materials with metal-cation vacancies have been developed to investigate the real effect of cation vacancies on the electrocatalysis. For example, the Jiao group reported an efficient and novel fabrication to prepare an electrocatalyst (Ni/NiO nanoparticles) with electrochemically active sites derived from Ni-based MOF.\textsuperscript{135} The incorporation of Ni\textsuperscript{3+} into the lattice of Ni/NiO nanoparticles provided abundant active sites caused by a subtle atomic rearrangement. Note that the Nickel vacancies in Ni/NiO nanostructures would cause a Jahn–Teller distortion mismatch between the Ni\textsuperscript{2+} (t\textsubscript{2g}\textsuperscript{6}e\textsubscript{g}\textsuperscript{2} without Jahn–Teller effect) and Ni\textsuperscript{3+} (t\textsubscript{2g}\textsuperscript{6}e\textsubscript{g}\textsuperscript{1} significant Jahn–Teller effect) coordination octahedral, leading to the formation of subtle lattice distortion in Ni/NiO to provide active sites (Figure 7A).\textsuperscript{136} The lattice distortion was a key to promote Faradaic reaction and HER activity. Furthermore, the DFT calculations in Figure 7B-E showed that the introduction of Ni\textsuperscript{3+} decreased the Gibbs free energy of atomic hydrogen absorption, which was beneficial for HER. The Ni/NiO, calcined at 400°C, displayed
an overpotential as low as 41 mV@10 Ma/cm² with a low Tafel slope of 59 mV/dec for HER.

Recently, Chen and coworkers reported a low-temperature pyrolysis synthesis of reduced graphene oxide hybrid composites (Ni QD@NC@rGO) anchored with defective nickel quantum dots (Ni QD), which were encapsulated in N-doped carbon (NC) derived from nickel zeolite imidazolate framework. The Ni QD@NC@rGO exhibited superior electrocatalysis performance, which only required the overpotential of 265 and 133 mV@10 mA/cm² for OER and HER in 1.0 M KOH, respectively. Importantly, the existence of Ni vacancies created more active sites and facilitated the adsorption of H* and/or OH−* intermediates. The formation of rich vacancies in Ni QDs could attribute to the dual carbon confinement toward Ni crystals during pyrolysis or the intrinsically coordinated unsaturated Ni sites in Ni-ZIF. According to the DFT calculations (Figure 8), the introduction of vacancy in Ni could give rise to the strain or ligand effects, which promoted charge transfer from Ni core to C layer.

3 | SYNTHETIC STRATEGIES OF VACANCIES IN MOFS AND THEIR DERIVATIVES

In view of excellent properties of vacancies in electrocatalysis, abundant MOFs and derivatives with vacancies have been developed with remarkable results. However, the stability of vacancy remains an obstacle to its applications in electrocatalysis. In the past few years, lots of effort have been spent on searching for simple and environmental friendly preparation methods to improve the stability of vacancy. In the following section, we will summarize and discuss these diverse fabrication strategies, which have been experimentally developed to prepare various vacancies in MOF and derivatives.

3.1 | Plasma etching

Plasma is generated through activating the gas with sufficient energy. The electrons in plasma are free and can move freely with high energy, which can break the covalent bonds to produce vacancies by ejecting the surface atoms. The plasma etching is a suitable alternative to modify the surface of materials. Nowadays, the plasma technology with high electron temperature and low gas temperature has been considered as an efficient and low-energy consumption method for the preparation or modification of materials without chemical waste. Importantly, it could also act as an emerging environmental friendly technology to modify solid materials without changing their intrinsic properties. Recently, the plasma technology is used to create the vacancies on the surface of electrocatalysts due to its strong etching effect. For instance, MOFs with abundant vacancies were
The Jiang group reported a novel fabrication of microwave-induced plasma engraving to endow Co-MOF-74 with abundant missing linkers under controlled conditions. As shown in Figure 9, the engraved CUMSs generated on the surface of Co-MOF-74 by plasma engraving. The high-density electrons bombardment of plasma can break the coordinated bonds between metal cluster and organic ligand to introduce the CUMSs without the destruction of its phase integrity. Moreover, the carrier gas species can affect the formation of CUMSs, and the hydrogen plasma engraved CUMSs can boost the cobalt intrinsic activity of Co-MOF-74 for enhanced OER performance.

Recently, Chen and coworkers reported a unique triangular-shaped “cheese-like” Fe/Co–carbon NSs derived from plasma-enabled Fe doping of Co-based 2D MOF NSs through plasma technology, which possessed mesoporous structure, complete framework structure, and densely distributed reactive centers. The O$_2$–Ar radio frequency (RF) plasma resulted in the generation of oxygen vacancies and the oxidation states of active metals were modified (Figure 10). The optimized Fe$_x$Co$_{1-x}$/V$_{O}$-800 displayed an outstanding OER performance with an overpotential of 260 mV@10 mA/cm$^2$ and a small Tafel slope of 53 mV/dec.

### 3.2 Reduction method

Chemical reduction can lead to the reaction happening between electrons and the atoms in the lattices, therefore, forming the corresponding vacancies in the matrix. Two methods have been used to create vacancies: one is pyrolysis under the high temperature in reductive atmosphere. The reductive gas that is adsorbed on the MOFs materials can transfer electrons to the lattice atoms, leading to the reduction of the precursors and the generation of the vacancies. Another route is aqueous reduction at room temperature by using reducing agents, such as sodium borohydride (NaBH$_4$), which can possess a strong reductive capacity by releasing H$_2$.

Wang et al. presented an effective strategy to introduce oxygen vacancies on Co$_3$O$_4$ ultrathin NSs to enhance OER performance. The Fe-Co-O NSs with oxygen vacancies exhibited a low overpotential of 260 mV@10 mA/cm$^2$ and a Tafel slope of 53 mV/dec. As shown in Figure 11, the Fe-C≡N-Co planar units of the cyanogel were constructed through the coordination reaction between FeCl$_3$ and K$_3$Co(CN)$_6$, and the Fe-Co-O NSs were obtained after adding the NaBH$_4$ solution, which could reduce partial O atoms to form oxygen vacancies. The effective reduction method favored the formation of oxygen vacancies in 2D ultrathin NSs. Dai et al. reported a chemical reduction using NaBH$_4$ to engineer the interface of Co-MOFs-derived Co$_3$O$_4$ nanoarrays. The chemical reduction method of Co$_3$O$_4$ NAs was an efficient way to form oxygen vacancies on the surface, which was beneficial for the enhancement of electric conductivity. The hydrolysis of NaBH$_4$ was triggered to release hydrogen, which was favorable to the chemical reduction of Co$_3$O$_4$ in a mild environment.

### 3.3 Pyrolysis treatment

Pyrolysis at elevated temperatures will cause the loss of oxygen atoms, which promotes the formation of oxygen vacancies. The pyrolysis treatment was generally carried out at a specific heating ramp rate and temperature in a vacuum system under carrier gas (eg, Ar, N$_2$, and O$_2$). With the constant flow rate and a desire pressure, the
vacancies are formed under a constant reaction temperature and pressure for a certain period.

Ding and coworkers proposed a two-step pyrolysis-oxidation strategy to fabricate bifunctional electrocatalysts with a Co-based MOF (ZIF-67) as the precursor.\textsuperscript{153} Figure 12 illustrates the synthesis progress of Co-Co$_3$O$_4$-containing hybrid materials based on a two-step pyrolysis-oxidation method. The strategy could control the oxidation process of Co nanoparticles accurately and effectively, and a series of Co-Co$_3$O$_4$-based unique nanostructures with abundant oxygen vacancies and tetrahedral Co$^{2+}$ (Co$^{2+}_{Td}$) were synthesized. The oxygen vacancies served as the H$_2$O or oxygen ion adsorption sites. The optimal yolk@shell Co$_3$O$_4$/HNCP-40 exhibited excellent catalytic activity for OER with a low overpotential of 333 mV@10 mA/cm$^2$ and a small Tafel slope of 69 mV/dec. Besides, it also displayed high ORR activity with a half-wave potential of 0.834 V. Xu and coworkers reported a fabrication of porous microrod arrays (MRAs) anchored with NiCo@NiCoO$_2$ core@shell nanoparticles (NiCo@NiCoO$_2$/C PMRAs) derived from bimetallic (Ni, Co) MOF MRAs through carbonization and controlled oxidative calcination.\textsuperscript{154} The controllable
FIGURE 9  Schematic diagram of the preparation of catalysts by plasma engraving. Reproduced with permission from Ref. [146]. Copyright 2019, American Chemical Society

FIGURE 10  Schematic diagram of the preparation process for porous Fe/Co-carbon with a microstructure inspired by triangular-shaped cheese. Reproduced with permission from Ref. [141]. Copyright 2019, The Royal Society of Chemistry

FIGURE 11  Scheme of the synthetic route to Fe-Co-O ultrathin NSs. Reproduced with permission from Ref. [149]. Copyright 2020, Wiley-VCH
oxidative calcination resulted in the domination of oxygen vacancy in oxygen species of NiCo@NiCoO₂/C PMRAs. The oxygen vacancy significantly improved the conductivity of NiCoO₂ and boosted the kinetics of oxidation reactions, which enhanced the OER performance of NiCo@NiCoO₂/C PMRAs accordingly.

4 ELECTROCATALYTIC APPLICATIONS WITH VACANCY

Electrocatalysis is an effective way in energy conversion systems such as OER, ORR, HER, and NRR. Generally, the electrocatalytic reactions are carried out in a three-electrode system under different conditions (e.g., acidic, alkaline, and neutral). To enhance the electroactivity of the catalysts under various environments, lots of effort have been input on the design and optimization of electrocatalysts. Recently, MOFs and MOF-derivatives with defects show high surface areas, clear active sites, and unique structures, which are beneficial to investigate the mechanism for energy-related MOF-based electrocatalysts. In following section, the advanced MOFs and MOF-derivatives with vacancies for the application of electrocatalysis will be summarized.

4.1 Oxygen evolution reaction

The electrocatalyst for OER is the reaction center to realize energy conversion. However, the large overpotential of electrocatalysts seriously reduce the energy conversion efficiency and obstruct the practical application. Given the low cost, high activity and stability, transition metal-based catalytic materials have been extensively studied to replace expensive noble metal catalysts (RuO₂ and IrO₂). In recent years, MOF-based electrocatalysts have been considered as promising materials for OER due to their structural characteristics and inherent advantages. Various MOF-based electrocatalysts with abundant vacancies have been fabricated.

Owing to the low cost and relevant stability under alkaline conditions, Co-based materials have shown promising potential for OER. Among them, Co₃O₄ with various nanostructures have been extensively demonstrated as ideal electrocatalysts for OER owing to their catalytic activity and high corrosion stability. MOFs are desirable sacrificial templates for the fabrication of porous electroactive Co₃O₄ with various structures under controllable condition. For example, ultrathin Co₃O₄ nanomeshes with abundant oxygen vacancies were fabricated by employing ZIF-67 NSs as sacrificial...
templates proposed by Wei and coworkers (Figure 13A).\textsuperscript{167} The Co\textsubscript{3}O\textsubscript{4} nanomeshes presented high activities for OER with a small onset potential and a small Tafel slope of 74 mV/dec and remarkable stability. Note that the oxygen vacancy and Co\textsuperscript{2+}/Co\textsuperscript{3+} could maintain the electrical neutrality during the annealing process. According to the theoretical calculations, the oxygen vacancy generated through the reduction of Co\textsuperscript{3+} could cause new defect in the band gap of Co\textsubscript{3}O\textsubscript{4}, where two electrons could be excited to enhance the conductivity. Furthermore, the oxygen vacancies and lattices could accelerate ion transport to improve the electrochemical performance.

Li et al. presented oxygen-defect-rich Co\textsubscript{3}O\textsubscript{4} flakes derived from Co-MOFs array vertically grown on nickel foam substrates as shown in Figure 14A.\textsuperscript{168} The Co\textsubscript{3}O\textsubscript{4} arrays possessed a hierarchical interconnected porous flake network structure with excellent OER performance in alkaline media with an ultralow overpotential of 205 mV@10 mA/cm\textsuperscript{2} and a small Tafel slope of 65.3 mV/dec as shown in Figure 14B and C. The Co\textsubscript{3}O\textsubscript{4} arrays with tunable oxygen vacancies could significantly improve electrical conductivity. The DFT calculations exhibited that oxygen-defective Co\textsubscript{3}O\textsubscript{4} catalyst required a lower overall reaction barrier for OER than that of the pristine Co\textsubscript{3}O\textsubscript{4} catalyst, suggesting that the Co\textsubscript{3}O\textsubscript{4} with oxygen vacancies showed a high OER activity.

Two-dimensional (2D) MOFs have been reported to increase the porosity, conductivity, and catalytic centers. Duan and coworkers developed a generic strategy to fabricate ultrathin NSs array of MOFs on various substrates via dissolution–crystallization mechanism.\textsuperscript{14} The obtained nickel-iron-based MOF array showed superior electrocatalytic performance for OER with a low overpotential of 240 mV@10 mA/cm\textsuperscript{2}, and the turnover frequency of the electrode is 3.8 s\textsuperscript{-1} at an overpotential of 400 mV. The same group proposed that some incorporation of Fe could cause the introduction of additional structural vacancies and enhance the activity of Ni-based catalysts. Furthermore, 2D nanostructure could give rise to vacancy engineering inside the material, which could increase the carrier concentration of NiFeO\textsubscript{6} in the MOF to enhance the conductivity of materials. Based on the excellent properties of MOFs NSs, Wang and coworkers reported a preparation of amorphous porous nickel iron hydroxide nanolayers with rich oxygen vacancies supported on carbon paper (NiFe(OH)\textsubscript{x}/CP) via electrochemical deposition of Prussian blue (PB) and alkaline etching process for growing Ni(OH)\textsubscript{x} layer.\textsuperscript{169} The optimized NiFe(OH)\textsubscript{x}/CP showed excellent OER performance with a low overpotential of 303 mV@100 mA/cm\textsuperscript{2} and small Tafel slope of 33.8 mV/dec in alkaline environment. The amorphous and distorted structures caused massive oxygen vacancies, which resulted in superior electrocatalytic OER activity.

Recently, the Gao group reported a facile fabrication of trimetallic MOF-derived hierarchical nanoflower electrocatalysts stacked by porous oriented NSs through tuning the ratio of metal ions (Figure 15).\textsuperscript{170} They found that the strong synergistic effect in trimetallic components would induce oxygen vacancies, leading to high activities for catalytic properties. Thus, the optimized Co0.2Fe0.8Ni-OCNF showed an excellent activity that required a low overpotential of 291 mV@10 mA/cm\textsuperscript{2} with a very small Tafel slope.
of 36.1 mV/dec. Meanwhile, high degree graphitization of Co0.2Fe0.8Ni-OCNF could enhance the electron transfer and protect the catalytic sites, resulting a high durability for OER.

### 4.2 Hydrogen Evolution Reaction

Electrocatalytic water splitting is considered as a sustainable strategy to produce H₂ for renewable energy storage and transportation. The efficient and stable electrocatalysts for HER is of great significance in practical application. It is known that Pt-based catalysts are the benchmark HER catalysts. To pursue a higher cost efficiency, various non-noble metal-based electrocatalysts have been widely explored as promising alternative catalysts. In recent years, MOFs derivatives have been extensively applied in electrochemical reactions due to their abundant defects, diverse structures, and outstanding conversion efficiency.

For example, the Gan group proposed a surface engineering strategy to fabricate MOF-derived hierarchical nickel-copper nitride electrode with Ni and oxygen vacancies for achieving HER activity. The optimized nickel-copper nitride electrode exhibited a remarkable HER performance with a low overpotential of 58 mV@10 mA/cm² and outstanding stability without the change of morphologies and potential after uninterrupted testing. Owing to a higher $E^\ddagger$ of Cu$^{2+}$/Cu than $E^\ddagger$ of Ni$^{2+}$/Ni, they found that part of Cu$^{2+}$ was reduced to Cu with a release of Nickel ions, therefore, generating Ni and oxygen vacancies. The introduction of defect maximized the exposure of active sites and minimized the resistance of charge transfer for HER.

Chen and coworkers proposed an efficient fabrication of ultrathin Co–Fe bimetallic PBA NSs arrays with open bimetal centers. The ultrathin NSs exposed abundant active sites and promoted the mass transfer. Remarkably, the CoFe-PBA with unsaturated metal centers (U-CoFe-PBA) showed a smaller adsorption energy of OH$^-$ than that of CoFe-PBA with coordinatively saturated metal centers (S-CoFe-PBA), suggesting that the existence of open metal centers was beneficial for adsorbing OH$^-$ to promote the following phase transformation. The charge redistributions systems revealed that unsaturated metal centers would cause the charge polarization and accumulation, strengthening the interaction between active Fe/Co sites and OH$^-$ and shortening their bonding lengths. Therefore, the optimized PBA NSs arrays presented outstanding HER performance with the overpotential of 48 mV and a small Tafel slope of 66 mV/dec in 1.0 M KOH. Chen and coworkers proposed an efficient fabrication of ultrathin Co–Fe bimetallic PBA NSs arrays with open bimetal centers. The ultrathin NSs exposed abundant active sites and promoted the mass transfer. Remarkably, the CoFe-PBA with unsaturated metal centers (U-CoFe-PBA) showed a smaller adsorption energy of OH$^-$ than
that of CoFe-PBA with coordinately saturated metal centers (S-CoFe-PBA), suggesting that the existence of open metal centers was beneficial for adsorbing OH\(^-\) to promote the following phase transformation. The charge redistribution systems revealed that unsaturated metal centers would cause the charge polarization and accumulation, strengthening the interaction between active Fe/Co sites and OH\(^-\), and shortening their bonding lengths. Therefore, the optimized PBA NSs arrays presented outstanding HER performance with the overpotential of 48 mV and a small Tafel slope of 66 mV/dec in 1.0 M KOH.

4.3 | Oxygen reduction reaction

The ORR on the cathode is a key process to determine the energy conversion efficiency of fuel cells and metal-air batteries. Owing to the low rate of ORR, it relies severely on Pt-based electrocatalysts.\(^{15,180}\) However, the high cost and scarcity of Pt as well as the stability greatly hinder their commercial application. In order to break the bottlenecks, rational design and synthesis of nonprecious metals catalysts have been widely investigated to replace commercial Pt/C.\(^{181-183}\) MOFs as a series of novel porous materials possess some specific advantages for ORR such as the structural diversity, easily functionalized, and good designability.\(^{184-186}\)

In recent years, CeO\(_2\) has been considered as a potential matrix in electrocatalytic applications due to its outstanding oxygen storage capacity and conductivity of electron/ion.\(^{187,188}\) Owing to the abundant oxygen vacancies and swift transition between Ce\(^{3+}\) and Ce\(^{4+}\), CeO\(_2\) can act as a reaction site to promote the activation of the reactants.\(^{189}\) Thus, various MOF-derived catalysts containing CeO\(_2\) with oxygen vacancies have been investigated for electrochemistry. Zhang and coworkers presented a series of Ce/La dual lanthanide MOF derived Fe/N-doped porous carbons catalysts with La-embedded CeO\(_2\) for ORR through a simple coprecipitation method.\(^{182}\) The preparation is shown in Figure 16. La\(^{3+}\) embedded into the lattice
of CeO$_2$ created abundant oxygen vacancies and effectively bound the oxygen molecules. Massive oxygen vacancies in La-embedded CeO$_2$ nanoparticles endowed the catalyst with excellent ORR performance with a half-wave potential of 0.870 V and a current density of 5.43 mA/cm$^2$. The synergies between bimetallic oxides show the high catalytic activity for OER and ORR. Thanks to the compatible Ce$^{3+}$/Ce$^{4+}$ redox couple, the Li group reported ZIF-67-derived porous Co$_3$O$_4$@Z67-NT (T-temperature, 500–900$^\circ$C) cores coated with CeO$_2$ shells (Co$_3$O$_4$@Z67-N700@CeO$_2$) through a facile hydrothermal method. The oxygen storage capability, redox properties, and tunable vacancies of CeO$_2$ shell combined with Z67-NT shell can effectively protect the active sites of Co$_3$O$_4$ (core) to enhance the ORR performance. Thus, Co$_3$O$_4$@Z67-N700@CeO$_2$ displayed an outstanding catalytic activity with a $\Delta E [E_j = 10^{(OER)} - E_{1/2}(ORR)]$ of 0.70 V since the half-wave potential of 0.88 V (vs. RHE) for ORR. The oxygen vacancies on CeO$_2$ can improve the ORR activity through the enhancement of O$_2$ adsorption on the interfaces, which is favorable to the activation of adsorbed O$_2$ to O$_2^-$ and the alleviate O$_2$ deficiency during the reaction.

4.4 Nitrogen reduction reaction

Ammonia, as a clean energy carrier, has been widely applied in industry and agriculture due to their high energy density, abundant N$_2$ raw material in atmosphere, and environmental friendly fuel products combustion products. However, the high bond energy of N≡N requests thermodynamically strong energy barrier. Therefore, NRR has achieved great progress in the preparation of ammonia with low pollution and low energy consumption. In the past few years, a large number of electrocatalysts have been successively analyzed and optimized with good NRR properties. Generally, electrocatalysts with rich active sites promote the adsorption and activation of N$_2$, which was exposed at the interface between materials and electrolyte. However, the electrolyte is a natural source of protons and exhibits lower activation energy than that of N$_2$, which facilitates to occupy active sites. To enhance NRR performance, the tactic of various synthetic defects is an efficient way to tune the intrinsic properties of the electrocatalysts. In recent years, the oxygen vacancies have been proven as an active role for NRR, which can achieve the electron acceptance-giving process, effectively capture metastable electron, and inject them into the antibonds of N$_2$. For example, Luo and coworkers presented a MOF-derived carbon/Y stabilized ZrO$_2$ nanocomposite (C@YSZ) with oxygen vacancies for electrochemical NRR. The obtained C@YSZ showed a large NH$_3$ yield of 24.6 mg/h/mgcat and a high Faradaic efficiency (FE) of 8.2% at -0.5 V versus RHE. The oxygen vacancies are the dominant active sites for NRR and the introduction of Y$^{3+}$ significantly increased and stabilized...
the oxygen vacancies. Meanwhile, the C@YSZ exhibited a long-term stability of 7 days without change.

Recently, the Luo group reported an efficient electrocatalyst of nitrogen-doped carbon/Co3O4 nanocomposites (Co3O4@NCS) with core-shell structure derived from ZIF-67 for the artificial nitrogen fixation in 0.05 M H2SO4 under atmospheric pressure.205 The Co3O4@NCS was inherited the framework of ZIF-67 with high specific surface and possessed a remarkable stability of the structure. Moreover, the ESR signal trapped the electrons on oxygen vacancies, which proved the high concentrate of oxygen vacancies consistent with XPS results. In view of the effect of oxygen vacancy for adsorption and activation of N2, the optimized Co3O4@NCS exhibited a high NH3 production of 42.58 μg/h/mgcat. and a FE of 8.5% at -0.2 V versus RHE.

5 | CONCLUSIONS AND PERSPECTIVES

MOFs and their derivatives with rich vacancies possess great properties as promising electrocatalysts for OER, HER, ORR, NRR, and CO2RR, and they largely promote the development of energy conversion technologies. The information of various vacancies is more accurate through advanced characterization methods to insight into the effect of vacancies, which could further explain the relationship between vacancies and efficiency. As summarized in this review, the vacancies presented in MOFs and their derivatives play a crucial role in the change and the redistribution of the electron density for improving specific electrochemical reactions. Meanwhile, the vacancies can enhance the electrocatalytic kinetics through promoting the mass transport on the interface area. In addition, the in-situ and ex-situ synthetic strategies of vacancies can further enrich the principles for the design of MOFs and their derivative electrocatalysts. Although numerous research progresses in preparing different vacancies have been made, continuous attention on the effect of various vacancies should be explored on electrocatalysts as following:

(i) Controllable methods to generate vacancies: In view of distinct energy barriers in the possess of various electrochemical reactions, the vacancy defects as active sites are promising to the preparation of ideal electrocatalysts. To maximize the catalytic efficiency, it is urgent to explore the novel controllable strategies on vacancy engineering to better clarify the basic relationship between vacancy and activity.

(ii) Advanced characterization methods: In order to study the impact of vacancies on the electrochemical performance systematically, it is necessary to explore and develop more accurate and advanced methods (such as in situ measurements) that could help us to investigate the effect of vacancies dynamically and clearly during the real-time electrocatalytic process.

(iii) Stability of vacancies: Although the electrocatalysts with various vacancies could show desirable stability in electrocatalysis progress, the long-term stability of vacancies is still an important parameter for practical applications. Thus, more attention should be paid to whether the vacancies are changed or reconstructed during the electrochemical reactions. To establish the correct design concept of electrocatalysts, some in-situ testing technologies should be developed and the evolution of vacancies during the reaction should be tracked.

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