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Chapter 6

Metal-Organic Frameworks and their Applications in Hydrogen and Oxygen Evolution Reactions

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Additional information is available at the end of the chapter

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Abstract

The hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) play a vital role in many energy storage and conversion systems, including water splitting, rechargeable metal-air batteries, and the unitized regenerative fuel cells. The noble-metal catalysts based on Pt, Ir, and Au are the best electrocatalysts for the HER/OER, but they suffer from high price and scarcity problems. Therefore, it is urgently necessary to develop efficient, low-cost, and environment-friendly non-noble metal electrocatalysts. Metal-organic frameworks (MOFs) are crystalline materials with porous network structure. MOFs possess various compositions, large specific surface area, tunable pore structures, and they are easily functionalized. MOFs have been widely studied and applied in many fields, such as gas adsorption/separation, drug delivery, catalysis, magnetism, and optoelectronics. Recently, MOFs-based electrocatalysts for HER/OER have been rapidly developed. These MOFs-based catalysts exhibit excellent catalytic performance for HER/OER, demonstrating a promising application prospect in HER/OER. In this chapter, the concept, structure, category, and synthesis of MOFs will be first introduced briefly. Then, the applications of the MOFs-based catalysts for HER/OER in recent years will be discussed in details. Specially, the synthesis, structure, and catalytic performance for HER/OER of the MOFs-based catalysts will be emphatically discussed.

Keywords: metal-organic frameworks, electrocatalytic water splitting, hydrogen evolution reaction, oxygen evolution reaction, electrocatalysts

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1. Introduction

Electrocatalytic hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) are the key reactions for many energy storage and conversion systems, including water splitting, rechargeable metal-air batteries, and the unitized regenerative fuel cells [1–3]. However, the two reactions are kinetically sluggish, which leads to large overpotentials in the electrodes, decreases the performance of these systems, and makes them difficult to meet the requirements for commercialization at present. It has been reported that suitable electrocatalysts can effectively accelerate the HER/OER and reduce their overpotentials in the electrodes. At present, noble metal catalysts show the best catalytic performance for HER and OER. For example, carbon-supported Pt catalysts exhibit the best catalytic performance for HER [4], while IrO_2 and RuO_2 are very effective for OER [5]. However, the reserves of these noble metals are extremely limited in nature resulting in a high price of these noble metal catalysts, which restricts their practical applications. Therefore, the development of highly efficient electrocatalysts with low cost for HER/OER is indispensable. In recent years, a large amount of non-noble metal catalysts have been synthesized for HER/OER. The non-noble metal catalysts for HER mainly include transition metal phosphides [6–8], such as CoP, NiP, transition metal sulfides [9–11], such as MoS_2, CoS, Ni-S, and their alloys [12, 13] such as Ni-Mo, Ni-Cu. As for OER, the non-noble metal catalysts mainly focus on metal oxides [14–16] such as Co_3O_4, MnO_x, $Ni_xCo_{3-x}O_4$, and metal sulfides [17, 18] such as Ni_3S_2, $NiCo_2S_4$. Although these non-noble metal catalysts have shown excellent catalytic performance for HER and/or OER, to date, there is no one catalyst that can fully meet the demands of the practical applications. It is necessary to develop more economically viable electrocatalysts with higher catalytic performance for HER and/or OER, and further accelerate the commercial applications of these energy storage and conversion systems.

Metal-organic frameworks (MOFs) are porous crystalline materials with topological structures. MOFs are formed by assembling metal nodes and organic ligands. The metal node precursors mainly come from metal nitrates or chlorides, while the organic ligands mainly include benzimidazolate, dicarboxylic acid, and others. MOFs can be synthesized by some simple methods under mild conditions such as solvothermal, diffusion, microwave, and ionothermal methods [19–22]. MOFs possess unique structural characterizations such as high porosity, ultrahigh specific surface area (~6240 $m^2\ g^{-1}$) and tunable pore structure and easy functionalization [23], and they have been widely investigated and applied in gas adsorption/separation [24], magnetism [25], optoelectronics [26], and catalysis [27]. In recent years, MOFs have attracted great attention for use in energy conversion and storage systems such as water splitting, fuel cells, metal-air batteries, and supercapacitors. More recently, the applications of MOFs have been expanded to the HER and OER catalysis. To date, some novel MOFs-based catalysts for HER and OER have been synthesized. On the one hand, the active species can be introduced into the structures of MOFs, directly acting as effective catalysts for HER and/or OER; on the other hand, MOFs also can be used as supports to disperse the active species for HER and/or OER due to their porosity. In addition, the highly porous MOFs can be transformed to the derived catalysts by self-sacrifice methods. These MOFs-derived catalysts usually possess improved electronic conductivity and remarkable HER and/or OER

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catalytic performance. This chapter reviews recent progress of MOFs and MOFs-derived electrocatalysts for HER and/or OER. The MOFs are first introduced briefly. The applications of MOFs-based catalysts for HER and/or OER are the main contents and involve details. This work provides a helpful reference for researchers who are studying the MOFs-based electrocatalysts for HER and/or OER.

2. Overview of metal-organic frameworks

As a class of the coordination polymers, MOFs are crystalline porous materials. MOFs are formed through self-assembling using the inorganic metals as nodes and organic ligands as linkers [28, 29]. They possess unique structure properties, such as ultrahigh specific surface area and high porosity, tunable pore structure, and easy functionalization. The specific surface area of MOFs are much higher than that of other porous materials such as activated carbon and zeolites. For example, the synthesized MOF-201 possesses a high BET specific surface area of ~6240 $m^2 g^{-1}$ [30], while zeolites possess specific surface area less than 600 $m^2 g^{-1}$. High porosity of MOFs also brings up a very low density (~0.13 g cm^{-3}) [23], which is important to the storage of fuels or the applications in energy conversion and storage. The pore structure of MOFs can be tuned by choosing different organic ligands or altering the length of organic ligands. It was reported that Deng et al. prepared a novel IRMOF (IRMOF-74 XI) with large apertures of ~9.8 nm, by expanding the length of its organic linker to ~5 nm [31]. Apart from the tunable pore structure, MOFs can be easily functionalized by decorating the pores, surfaces, or introducing guests into MOFs, thus resulting in a large amount of MOFs with various physicochemical properties [32]. Due to these unique properties, MOFs have been widely developed and applied in gas adsorption/separation [24], magnetism [25], optoelectronics [26], and catalysis [27] in recent years.

According to topological structure features, MOFs can be generally divided into four categories: isoreticular metal-organic frameworks (IRMOFs), zeoliticimidazolate frameworks (ZIFs), materials of institute Lavoisier frameworks (MILs) and pocket-channel frameworks (PCNs) [33, 34].

IRMOFs are a large family of MOFs, which are built up by $[Zn_4O]^{6+}$ and organic hydroxyl acid as metal nodes and ligands, respectively. In the IRMOFs family, MOF-5 is the typical one which was prepared by Li et al. as early as in 1999 [35]. MOF-5 is highly porous, and the specific surface area and the density are about 2900 $m^2 g^{-1}$ and 0.59 g cm^{-3}, respectively. Specially, the space access to guest substance reaches up to 55–61%.

The topological structures of pores of ZIFs are similar to aluminosilicate zeolite. Generally, imidazole or its derivatives and Zn or Co ions are used as ligands and metal nodes, respectively. The N atoms in imidazole and its derivatives can coordinate with Zn, Co, or other transitional metal ions. Compared with other kinds of MOFs, ZIFs show higher thermal and chemical stability. For example, as a typical ZIF material, ZIF-8 can sustain its structures in inorganic or organic solvents or even in boiling water for 1–7 days [36].

Generally, there are two categories of MILs. One is formed by using lanthanides or transition metals as metal nodes and dicarboxylic acids as organic ligands. The other is obtained using trivalent metals such as aluminum or vanadium as metal nodes, and terephthalic acids or trimesic acids as organic ligands. MILs are highly porous and possess ultrahigh specific surface area. MIL-100 and MIL-101 are typical MILs. In MIL-100, Cr^{3+} ions are metal nodes and BTC (1,3,5-benzenetricarboxylate) is used as organic ligands. It possesses a high specific surface area of ~3100 m^2/g and mesopores with the pore size of ~2.9 nm [37]. In addition, MIL-100 exhibits excellent thermal stability below 275°C [37].

During the synthesis of PCNs, Cu ions or oxo-clusters are generally used as metal nodes, and tricarboxylic acids, 4,4′,4″-s-triazine-2,4,6-triyltribenzoate (H_3TATB) or s-heptazine tribenzoate (HTB) is usually used as an organic ligands. PCNs have pocket and three-dimensional orthogonal channels which are connected through small sized windows. As a typical PCN, Cu-BTC is formed by using $Cu_2(COO)_4$ as metal nodes and BTC as organic ligands. Two typical channel structures can be observed in Cu-BTC. One is a small octahedron pocket, while the other is the three-dimensional orthogonal channels (~1 nm) [38].

To prepare MOFs, various synthetic methods have been proposed, such as solvothermal (hydrothermal) method, diffusion method, microwave-assisted method and ionothermal method. During the solvothermal (hydrothermal) process, water or organic solvents are usually used as reaction medium in an airtight reactor. High temperature and pressure condition can be achieved through heating the airtight reactor. Thus, some compounds with poor solubility at room temperature and atmospheric pressure can be dissolved and recrystallized to obtain the desirable MOFs. In addition, high crystallinity and controllable particle size for the resulting MOFs can be obtained through the solvothermal (hydrothermal) process. Therefore, the solvothermal (hydrothermal) method is effective to produce MOFs with good orientation and perfect crystals [19, 39].

The diffusion methods include vapor diffusion, liquid diffusion, and gel diffusion methods. The products are obtained in the two-phase interface through slow crystallization [20]. The diffusion methods have two advantages, including mild synthesis conditions and high quality crystal MOFs. However, the efficiency of this method is usually low, which requires a long synthesis time, up to 1 week. Furthermore, this method also requires precursors with good solubility.

In the microwave-assisted process, the charging particles are placed in electromagnetic fields. These charging particles collide with high speed, forming the final products. Due to the high frequency of microwave, the microwave-assisted method is considered as a high energy efficiency method [21]. It has many advantages, such as uniform heating, high reaction rate, selective heating, and no hysteresis effects.

For the ionothermal synthesis, ionic liquids and eutectic mixture are usually used as solvents [22]. Ionothermal synthesis can avoid the high-pressure reaction condition, and produce final MOFs in an open condition, because ionic liquids have almost no vapor pressure.

In MOFs, the organic ligands cannot only be used as linkers, but also adsorb gas molecules through Van der Waals force. This is the reason that MOFs materials can be used for gas

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adsorption/separation [24]. Till date, most of the studies on MOFs still focus on gas adsorption/separation. Because some metals such as group VIII metals possess excellent magnetic properties, MOFs are also popular in magnetism field by using magnetic metal ions as nodes, and they possess paramagnetic or antiferromagnetic properties [25]. Similar regularity was observed of MOFs in the optoelectronics area. Luminescent lanthanide(III) ions which are utilized as nodes for MOFs are always designed as luminescent centers [26]. Due to the high specific surface area and tunable pore structure, MOFs have also been applied in electrocatalysis involving energy conversion and storage in recent years [32]. For instance, MOFs can be directly used as electrocatalysts in the applications for HER and/or OER. However, the electric conductivity of most MOFs is poor. The combination of MOFs and highly conductive substrates (such as graphene, carbon nanotubes, Ni foams and conductive glasses) is an efficient protocol to enhance the electrocatalytic performance of MOFs [27]. In addition, MOFs also can serve as precursors to form derived catalysts such as metal oxides, metal (oxides or carbides or sulfides or phosphides)/nanocarbon hybrids or porous nanocarbons, which is another effective way to take advantage of MOFs for HER and/or OER [40].

3. HER/OER

The growing concern of energy crisis and environment pollution promotes the development of highly effective clean energy storage and conversion systems, such as water splitting [1], metal-air batteries [2], and fuel cells [3]. In such systems, oxygen- and hydrogen-involving electrocatalytic processes, including oxygen reduction reaction (ORR), hydrogen oxidization reaction (HOR), hydrogen evolution reaction (HER), and oxygen evolution reaction (OER) are the most mentioned key components in determining the practical performance of these energy storage and conversion systems. The former two reactions consume oxygen and hydrogen to provide power, but the premise is that the available oxygen and hydrogen are generated from water splitting through OER and HER, respectively. The OER/HER involved in water splitting can be given in the following equations [9, 41]:

Hydrogen evolution reaction:

$2H^+ + 2e \rightarrow H_2$ in acid solution

$2H_2O + 2e \rightarrow H_2 + 2OH^-$ in alkaline solution

Oxygen evolution reaction:

$2H_2O - 4e \rightarrow O_2 + 4H^+$ in acid solution

$4OH^- - 4e \rightarrow O_2 + 2H_2O$ in alkaline solution

Water splitting can produce pure hydrogen and oxygen which can be directly utilized as raw materials for fuel cells or for other industrial processes individually. Apart from water splitting, HER or OER can be associated with other electrochemical processes. For instance, OER is also a key reaction for rechargeable metal-air batteries [2] and regenerative fuel cells [3] when being charged. Rechargeable metal-air batteries and regenerative fuel cells

are seen as promising ways to produce electricity in the future and may effectively reduce our dependence on traditional fossil fuels and relieve environmental pollution.

Unlike HOR/ORR, HER/OER don't maintain a constant value at high overpotential. In other words, HER/OER are not limited by the mass transfer rate and they obey Butler-Volmer model even in high overpotential. Generally, the HER/OER catalytic mechanisms differ from each other. Even so, the descriptor (ΔG_{H^*}, hydrogen binding energy/adsorption free energy) is widely used to reflect HER activity for catalysts, while the descriptor (ΔG_{O^*}-ΔG_{OH^*}) is used to evaluate the OER activities [5]. HER involves the two-electron transfer processes, while OER includes more complex processes with the multistep charge-/proton-transfer. These complex processes result in the low efficiencies of HER/ORR and make it difficult for them to satisfy practical applications. Therefore, the development of efficient electrocatalysts for HER/OER to accelerate the kinetics and reduce the overpotentials is of great significance for the commercialization of HER/OER-related devices.

Currently, the HER/OER electrocatalysts mainly include precious metal catalysts and non-precious metal catalysts [5, 42].The precious metal catalysts have been widely developed due to their extremely excellent catalytic performance. For instance, precious metal catalysts for HER are mainly dependent on Pt-based catalysts since they exhibit the best HER electrocatalytic performance in basic solution with a low onset overpotential. IrO_2 and RuO_2 have been demonstrated as the benchmark OER electrocatalysts (Pt-based catalysts barely show any OER catalytic activity), and even show remarkable stability in acid solution. However, although the precious metal catalysts possess excellent catalytic performance, their scarcity and high price hamper their large-scale applications. Thus, non-precious metal catalysts with low-cost and earth-abundance for HER/OER are urgently needed.

The non-precious metal catalysts for HER mainly include transition-metal sulfides, phosphides, alloys, etc. Through element selection, Co sulfides or phosphides are seen as the most promising HER catalysts, but they suffer from low stability. The alloys have been developed by integrating Ni with Mo or Cu [12, 13]. Diverse structures and composition are the advantages to those alloyed catalysts, but their restriction of activity limits their applications. The non-precious metal catalysts for the OER mainly contain transition metal oxides [14–16], sulfides [17, 18], hydroxides [43], and carbons [44], etc. Among them, metal oxides in single phase or in mixed phases are the most developed ones as efficient OER electrocatalysts due to their diverse compositions, superior stability, and remarkable OER performance. Thus, metal oxides are widely explored as promising OER catalysts, but the mechanism of OER is very sensitive to the compositions and structures of the catalysts, which requires further design, preparation, and optimization of OER catalysts. In spite of rapid development of the HER/OER electrocatalysts with relatively good performance, to date, no one catalyst can satisfy the practical demands. More researches for highly efficient HER and OER electrocatalysts are needed.

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4. MOFs-based catalysts for HER

In recent years, MOFs have been widely explored to store hydrogen fuels due to high specific surface area, tunable pore structures, and various functions [45]. Meanwhile, they also have been developed as electrocatalysts for the HER through electrochemical splitting of water. Generally, MOFs can be directly used as catalysts or served as precursors for the derived catalysts for HER. Recently, Gong et al. synthesized $Cu_3(Mo_8O_{26})(H_2O)_2(OH)_2(L1)_4$ (L1 = 4H-4-amino-1,2,4-triazole) and $Ag_4(Mo_8O_{26})$-$(L2)_{2.5}(H_2O)$ (L2 = 3,5-dimethyl-4-amino-4H-1,2,4-triazole) MOFs via a hydrothermal process [46]. The former had a chain-like structure, while the latter possessed a 3D structure. Both of them showed electrocatalytic activity for HER in 0.5 M H_2SO_4 with low overpotentials. $Cu_3(Mo_8O_{26})(H_2O)_2(OH)_2(L1)_4$ had better HER activity than $Ag_4(Mo_8O_{26})$-$(L2)_{2.5}(H_2O)$. Their HER activities were related to the redox of $[Mo_8O_{26}]^{4-}$ polymolybdate anions. Qin et al. developed another polymolybdate (POM)-based MOF for HER [47]. This novel 3D open structure was formed by connecting POM fragments as nodes and H_3BTB (H_3BTB = benzene tribenzoate) or H_3BPT (H_3BPT = [1,1′-biphenyl]-3,4′,5-tricarboxylic acid) as ligands. POM-based MOFs had excellent HER activity likely due to the combination of the redox of POM and the porosity of MOFs. Noticeably, the POM-based MOFs were stable not only in air but also in acid or basic solutions. Among these catalysts, NENU-500 ($[TBA]_3[\varepsilon$-$PMo^{V}_8Mo^{VI}_4O_{36}(OH)_4Zn_4]$ $[BTB]_{4/3}\cdot 18H_2O$, TBA^+= tetrabutylammonium ion) exhibited excellent HER activity with an onset overpotential of about 180 mV and Tafel slope of 96 mV dec^{-1} in 0.5 M H_2SO_4. What's more, this catalyst could maintain its catalytic activity after 2000^{th} cycles in 0.5 M H_2SO_4 solution.

Cobalt dithiolene species are highly efficient molecular catalysts for HER. Cloigh et al. integrated cobalt dithiolene into metal-organic surface (MOS, $[Co_3(BHT)_2]^{3+}$and $[Co_3(THT)_2]^{3+}$ (BHT= benzenehexathiol, THT=triphenylene-2,3,6,7,10,11-hexathiol) materials to obtain effective catalysts for HER [48]. The prepared catalysts Co/MOS possessed a two-dimensional layer structure with high surface/volume ratio, resulting in high charge transfer efficiency and high surface active site concentration. The catalysts, especially $[Co_3(BHT)_2]^{3+}$, showed not only remarkable stability in acidic solutions, but also excellent HER catalytic activity under wide pH conditions, and the current densities at 0.5 V (vs. Standard Hydrogen Electrode, RHE) increased with decreasing electrolyte pH. The mechanism of HER of the MOS involved Co^{3+}/Co^{2+} redox reactions, following protonation of the S sites on the ligands.

Recently, MOFs also have been combined with 2D materials, such as graphene and metal dichalcogenide nanosheets, to form nanocomposites with unique properties and wide applications [49]. A Cu-MOF/graphene oxide (GO) nanocomposite catalyst for HER was successfully synthesized via a solvothermal process [27]. The Cu-MOF was prepared using $Cu(NO_3)_2$, 1,4-benzenedicarboxylic acid and triethylene-diamine as precursors. The integration of Cu-MOF with graphene oxide (GO) can effectively enhance the electron transfer, which further significantly improve HER activity. It was also found that the GO content affected the HER activity of the nanocomposite catalysts. The optimized GO content was about 8%. The HER current density of the (GO 8 wt%) Cu-MOF was high up to -30 mA cm^{-2} at an overpo-

tential of -0.2 V in N_2-saturated 0.5 M H_2SO_4, whereas the overpotential of 20 wt% Pt was -0.06 V at the current density of -30 mA cm^{-2}.

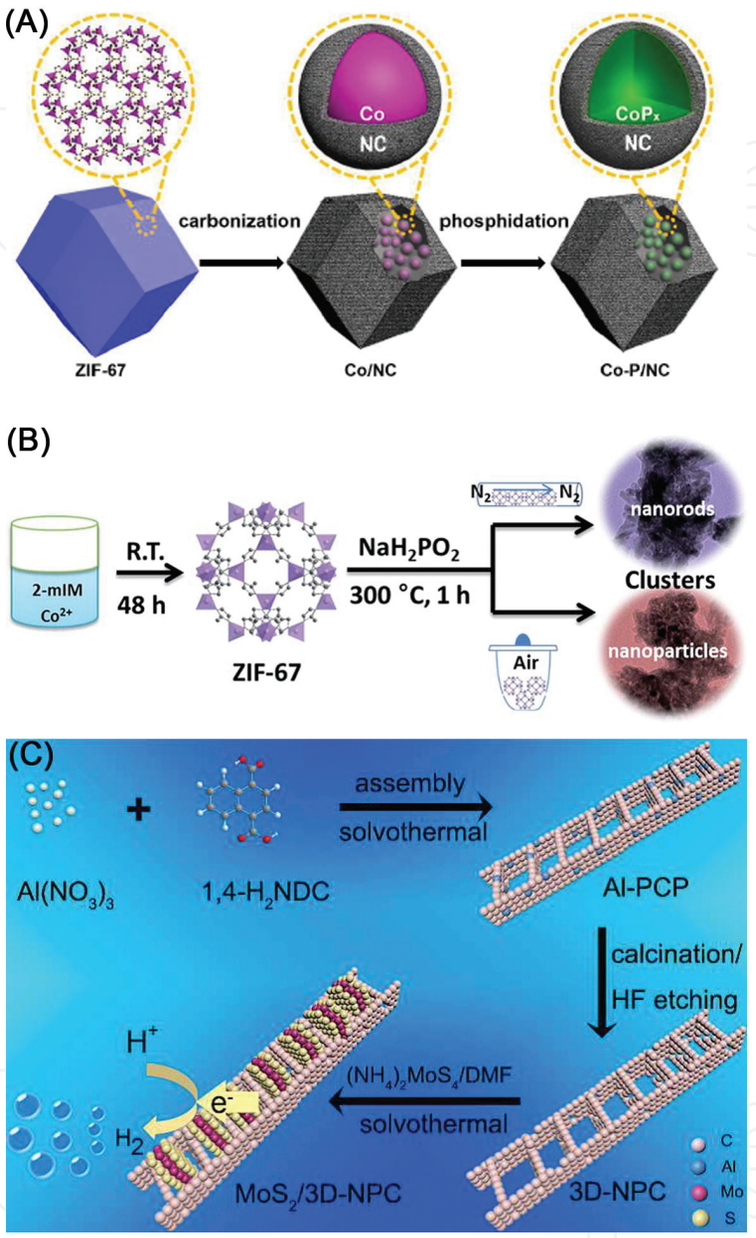


Figure 1. Schematic illustration of (A) synthesis of Co-P/NC [50]; (B) formation of CoP NPCs and CoP NRCs derived from ZIF-67-Co [51]; (C) the space-confined synthesis of MoS_2/3D-NPC composites and its application in HER [53].

Because MOFs possess structural diversity, high specific surface area, and large pore volume, MOFs are regarded as ideal precursors to prepare various inorganic nanomaterials as electrocatalysts, such as porous carbon, metal-oxide nanoparticles/porous carbon or metallic nanoparticles/carbon. It has been reported that cobalt species are active for HER. Among them, cobalt phosphides as HER electrocatalysts have been widely investigated in recent years. You et al. prepared a Co-P/NC catalyst by embedding CoP_x nanoparticles into N-doped carbon

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through carbonizing Co-ZIF-67 and a subsequent phosphidation (**Figure 1A**) [50]. After carbonization, the obtained Co-ZIF-67 inherited the morphology of polyhedron-like ZIF-67, in which the metallic Co nanoparticles were wrapped by the porous N-doped carbon shells. Through the following phosphidation, the products also preserved the polyhedron-like morphology of ZIF-67, while the metallic Co nanoparticles were transformed into CoP_x nanoparticles. The optimal Co-P/NC catalyst afforded a high specific surface area of 183 m^2 $g^{-1}$and a high pore volume of 0.276 cm^3 g^{-1}. The overpotentials of the catalyst at 10, 20, and 100 mA cm^{-2} were ~154, 173, and 234 mV respectively in 1 M KOH solution, indicating an outstanding HER activity. Such high HER activity can be attributed to its unique structures, such as abundant HER active species (CoP_x and N-doped carbon), 3D interconnected mesopores, and the porous N-doped carbon shells. Jiang et al. synthesized several cobalt phosphides by directly phosphating Co-ZIF-67 under mild conditions [51]. The CoP nanorod assemblies (NRAs) were obtained by calcined precursor in N_2 atmosphere, while the CoP nanoparticle assemblies (NPAs) were obtained by thermally treated precursor air atmosphere (**Figure 1B**). The CoP NRAs showed better HER electrocatalytic performance than CoP NPAs. The CoP NRAs only needed overpotential of about 181 mV at 10 mA cm^{-2} in 0.5 M H_2SO_4, whereas the overpotential for CoP NPAs was 393 mV at 10 mA cm^{-2}. After 1000th CV cycles, CoP NRAs and CoP NPAs both have slight loss of initial current density. The high efficiency of HER for CoP might be related to the charge transfer from Co to P, similar to the charge transfer process between hydride-acceptor and proton-acceptor of hydrogenase.

In addition to Co species, Ni species are also considered to be active for HER. Nickel phosphides (Ni_2P and $Ni_{12}P_5$) were prepared by phosphatizing Ni-MOF (Ni-BTC) in mild conditions [52]. During the preparation of Ni-BTC, nickel nitrates and BTC (benzene-1,3,5-tricarboxylic acid) were used as Ni sources and organic ligands, respectively. Then Ni_2P and $Ni_{12}P_5$ were obtained by phosphating from sodium hypophosphite at 275 and 325°C, respectively. The prepared $Ni_{12}P_5$ nanoparticles show similar morphology to the Ni_2P nanoparticles. However, the average diameter of the Ni_2P (25 nm) was smaller than that of the $Ni_{12}P_5$ (80 nm). The HER activity of the Ni_2P was better than that of the $Ni_{12}P_5$ nanoparticles in 0.5 M H_2SO_4, due to the similar effects of CoP on the HER activity [51]. The durability of the Ni_2P nanoparticles was further evaluated by chronoamperometric durability test, and current density was reduced to 75% of the original value after 6 h test.

The two-step synthesis method was also utilized by Liu et al. to prepare MoS_2-based HER catalyst with 3D hierarchical structure, in which MoS_2 nanosheets grew in the nanopores of MOFs-derived 3D carbons (MoS_2/3D-NPC) (**Figure 1C**) [53]. An Al-PCP was formed first by a solvothermal process, and a 3D-NPC was obtained through calcination. The 3D-NPC possessed randomly assembling nanopores, benefiting the intercalating of Mo precursors. After a solvothermal process, The MoS_2/3D-NPC catalyst was finally obtained, where MoS_2 nanosheets were dispersed well in nanoporous 3D-NPC. This unique 3D hierarchical structure can provide exposed active site and enhanced conductivity, thus resulting in the high performance for HER. The MoS_2/3D-NPC catalyst requires overpotentials of 180 and 210 mV to achieve current densities of 1 and 10 mA cm^{-2} in 0.5 M H_2SO_4 solution, respectively.

In addition to MoS_2, MoC_x has also been widely studied for HER. The porous MoC_x nano-octahedrons were prepared through an MOFs-derived strategy [54]. Cu-based MOF [HKUST-1; Cu_3 $(BTC)_2(H_2O)_3$] was first used to hold the Mo-based Keggin-type POMs ($H_3PMo_{12}O_{40}$), forming an MOF, i.e., NENU-5 nano-octahedrons. The MoC_x-Cu intermediate was prepared by carbonizing NENU-5 in inert atmosphere, and the final MoC_x porous nanoparticles were obtained by removing Cu by Fe^{3+} etching. The obtained porous MoC_x catalysts were evaluated for HER in both acidic and basic aqueous solutions. The polarization curves showed that the overpotentials of this catalyst were only 142 and 151 mV to deliver a current density of 10 mA cm^{-2} in acidic and alkaline solutions, respectively.

In summary, the highly porous MOFs containing redox sites have been developed as HER catalysts. However, their low conductivity limits their electrocatalytic performance for HER. Their combination with highly conductive substrates is an efficient way to enhance their HER activities. Furthermore, many researches have demonstrated that the MOFs-derived catalysts may exhibit greatly improved performance in HER. These MOFs-derived catalysts were obtained mainly through carbonization and a following phosphidation or sulfuration of MOFs containing active metal species (usually Co, Ni and Mo) at appropriate temperatures in inert or air atmosphere. Due to the active species, the novel porous structures, the enhanced conductivity and the protection from the heteroatom doped carbons, these MOF-derived catalysts usually exhibit higher activity and stability as compared to the pristine MOFs catalysts. Hence, because of these unique structures and properties, the MOF-derived materials benefit the development of HER catalysts with low costs and high performance.

5. MOFs-based catalysts for OER

MOFs possess high specific surface area and tunable pore structures, and they are easily functionalized by different metal centers and organic linkers, highlighting their great potentials in electrocatalysis. Similar to those utilized for HER, MOFs have already been developed for OER catalysis basically in two ways: direct and indirect ones. In the first case, MOFs will be received directly as electrocatalysts, and therefore element selection plays a key role to construct coordination modes which should facilitate oxygen-species adsorption/desorption and water dissociation. While in the second case, MOFs will be transformed into other composite materials in which metal, in the form of metallic–, oxide– or nitrite–phase, is associated with carbon. Despite having potential, MOFs-derived materials are at the expense of MOFs. For instance, the specific surface area decreased and the ordered porosities were destroyed. Therefore, structure modification is crucial to make the materials maintain higher specific surface area and hieratical pore structures through pyrolysis in order to maximize the catalytic site density and provide accessible channels for mass transfer.

Regarding element selection, metal-O, metal-N, or mixed N-metal-O coordination modes have already been developed to construct OER catalysts. In MOFs, the metal ion redox typically involves in the electrochemical process, and the electron-accepting ability of the nitrogen and oxygen atoms in organic linkers may polarize the adjacent metal atoms to afford better catalytic performance.

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Babu et al. [55] investigated the electrocatalytic activity of commercially available Fe(BTC) MOF (Basolite™ F300), with BTC=bezene-1,3,5-tricarboxylate. When studying the hydroxide on the voltammetric responses for Fe(BTC), a well-defined hydroxide oxidation response was clearly observed if NaOH was added to a 0.1 M KCl background electrolyte. Such an oxidation current was ascribed to OER current. However, such a current could be seen only by prescanning the Fe(BTC)-modified electrode lower than 0.5 V vs. saturated calomel electrode (SCE), a reduction potential zone where the hydrous iron oxide intermediates could be formed. Fe(III/II) played a key role in determining the electrochemical behavior of Fe(BTC).

Gong et al. [56] prepared two Co^{II} metal-organic frameworks, complex **1** (using 4,5-di(4′-carboxylphenyl) phthalic acid and 4,4′-bipyridine as co-ligands) and complex **2** (using 4,5-di(4′-carboxylphenyl)phthalic acid and azene as co-ligands) as electrocatalysts. The OER catalytic activity of these two complexes in an aqueous buffer solution (pH = 6.8) was investigated. The results showed that complex **1** possessed an oxidation peak of water at a more negative potential of 1.02 V vs. SCE accompanied by a much higher OER current than bare glassy-carbon (GC) electrode and ligand-modified glassy-carbon electrode. As confirmed by electrochemical impedance spectra, complex **1**-modified GC showed lower charge-transfer resistance than the bare GC, indicating that the framework promoted the charge-transfer, thus the OER catalytic activity. When applied complex **2**, the **2**-modified GC showed lower OER overpotential and higher OER current than complex **1**-modified GC. Such an enhancement could be ascribed to the better charge build-up of complex **2** than that of complex **1**, further due to the different co-linkers and frameworks in the two MOFs.

To verify the Co contributions for OER in MOFs, Yin's group [57] first synthesized an MOF(Fe) catalyst by hydrothermal process using Fe^{III} as metal precursor and 1,3,5-BTC as organic ligand. The synthesized MOF(Fe) afforded a specific surface area up to 1600 $m^2\ g^{-1}$. MOF(Fe) afforded excellent OER activity with a delivered current density of 2.30 $mA{\cdot}cm^{-2}$ at 0.90 V vs. Ag/AgCl in 0.1 M KOH, higher than the activated carbon (Super P). Further, they prepared an MOF(Fe/Co) as ORR/OER catalyst by a hydrothermal process using Fe and Co as mixed metal precursors, and the same organic ligand [58]. Surprisingly, MOF(Fe/Co) exhibited an improved OER activity with a delivered current density of 2.97 $mA{\cdot}cm^{-2}$ at 0.90 V vs. Ag/AgCl than the aforementioned MOF(Fe). Although MOF(Fe/Co) possessed lower specific surface area (~1070.1 $m^2{\cdot}g^{-1}$) than MOF(Fe), MOF(Fe/Co) exhibited better OER activity than MOF(Fe) in 0.1 M KOH electrolyte, primarily due to the aid of Co species.

Wang et al. [59] synthesized a cobalt-based ZIF (Co-ZIF-9) by assembling Co ions with benzimidazolate ligands for water oxidation. Co-ZIF-9 had open-framework structure, in which Co ions were coordinated by N atoms in benzimidazolate linkers. It had been found that this catalyst was thermodynamically feasible for catalytically oxidizing water molecule by density functional theory (DFT) calculation because Co ions had redox function and could bond -OH resulting in low activation barriers. In addition, the nearby benzimidazolate also promoted the OER reaction by accepting the eliminated -H atoms. Thus, Co-ZIF-9 showed obvious OER activity in wide pH basic solutions. Besides, the activity stability of Co-ZIF-9 was also investigated and there was no obvious deactivation in current density after 25 h test in potassium phosphate buffer.

Tan et al. [60] synthesized an MOF-74 to study the water dissociation mechanism on open metal sites in MOFs through *in situ* IR spectroscopy and first-principles calculations (**Figure 2**). The *in situ* IR spectroscopy provided a direct evidence of water reaction occurred on the metal centers. The water dissociation mechanism in MOF-74 primarily depended on two aspects: (1) the covalent bond between water and metal center and (2) the hydrogen bonding between the O atoms of the linker and the H atoms of the water molecule. This work was of significance to demonstrate the coordinatively unsaturated metal centers as active sites for water dissociation.

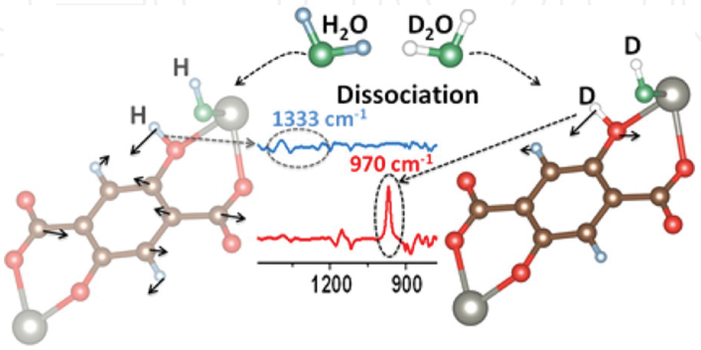


Figure 2. Schematic illustration of the OER catalytic mechanism on MOF-74 [60].

Based on the above results, it has been theoretically or experimentally demonstrated that bare MOFs can be designed by element selection to show excellent OER catalytic activity. However, compared with the noble metal-based and transition metal oxide-based electrocatalysts, MOFs are still insufficient to catalyze OER with higher current probably due to their intrinsic poor electronic conductivity. Therefore, Loh et al. [27] prepared a Cu-centered MOF from copper nitrate trihydrate, 1,4-benzenedicarboxylic acid and triethylene-diamine in the presence of GO. An optimal composition (GO 8 wt%) Cu-MOF afforded an OER onset potential of 1.19 V vs. RHE in acid electrolytes, a ~200 mV positive shift than that of pure Cu-MOF. The 8 wt% GO-incorporated Cu-MOF also showed fast OER kinetics with a smaller Tafel slope of 65 mV·dec $^{-1}$ than pure Cu-MOF (89 mV·dec^{-1}). The results demonstrated that the enhanced electrocatalytic properties and stability in acid of the GO-MOF composite was due to the unique porous scaffold structure, improved charge transport, and synergistic interactions between the GO and MOF.

Because of the high specific surface area and the well-defined porosities, MOFs are excellent catalyst support materials. Therefore, doping MOFs with other active species in the forms of oxides, ions, and complexes can open up a new route for MOFs in OER electrocatalysis.

Yin et al. [61] prepared α-MnO_2/MIL-101(Cr) catalyst through a hydrothermal process. In this catalyst, α-MnO_2 particles were embedded in MIL-101(Cr) matrix, resulting in strong interactions between α-MnO_2 and MIL-101(Cr). The OER catalytic activity of the composite was tested using a carbon paper containing this catalyst as working electrode. The results revealed that α-MnO_2/MIL-101(Cr) composite afforded an excellent OER catalytic activity with a delivered current density of 23.67 mA cm^{-2} at 0.9 V in 0.1 M KOH solution which was about two times higher than that of pure α-MnO_2 under the same conditions. The high specific surface

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area of MIL-101(Cr) and abundant micropores of MIL-101(Cr) were advantageous for the diffusion of electrolyte and the high dispersion of α-MnO_2 particles made it easy to contact the electrolyte, resulting in enhanced OER catalytic activity.

Subsequently, Yin's group [62] decorated MIL-101(Cr) with Co ions with various oxidization states through impregnation followed by post-treatment under oxidant or reducing reagents. The Co species were highly dispersed on the MOF surface and showed various Co^{III}/Co^{II} ratios. Primary results demonstrated that the OER activity is related to the Co^{III} contents since the catalyst showed better OER catalytic activity as the surface Co^{III} content increased. The reason might be the Co^{III} species could promote the OH^- adsorbed onto the electrocatalyst surface. In addition, the porous and open structures of MIL-101(Cr) support were in favor of the contact between oxygen species and the active Co sites.

Wang et al. [19] decorated a Zr-MOF, namely UiO-67, with **1-3** Ir-containing complexes to form MOF **1-3**, respectively. Many MOFs lack stability in water, but UiO-67 is one of the exceptions. The OER performance of the samples was investigated in a pH = 1 solution with Ce^{4+} as an oxidant. The Ce^{4+} was reduced to Ce^{3+}, while water was oxidized to form oxygen. The results showed that after the incorporation of Ir-containing complexes in UiO-67, MOF **1-3** were the effective water oxidation catalysts with turnover frequencies of up to 4.8 h^{-1}. The parent UiO-67 showed negligible OER catalytic activity, demonstrating the significance of the Ir-containing dopants as active centers.

The OER current density at 10 $mA \cdot cm^{-2}$ is a criterion used to judge an OER catalyst since such a current density is an important metric for practical solar fuel production. Unfortunately, most of the aforementioned MOF-based OER catalysts fail to reach such a current density even at high overpotentials. Apart from directly being the OER catalysts, MOFs can be converted into other forms of materials through pyrolysis. Through pyrolysis, the organic linkers can be transformed into carbon materials, and the well-dispersed metal centers in the MOFs' frameworks can be transformed into phosphate- or oxide-phase but still maintain excellent dispersion in carbons. Such a strategy is helpful to obtain materials with excellent charge-transfer properties.

You et al. [50] prepared a CoP_x/NC catalyst derived from ZIF-67 and its polyhedron-like morphology survived from the pyrolysis. The specific surface area of CoP_x/NC was up to 183 $m^2 \cdot g^{-1}$, and the pore volume is 0.276 $m^3 \cdot g^{-1}$. In OER activity test, the overpotential of CoP_x/NC was about 354 mV at a current density of 10 mA cm^{-2}, while IrO_2 is about 368 mV at the same current density. Moreover, after 1000th continuous CV cycles, the overpotential of CoP_x/NC at 10 mA cm^{-2} showed only slight difference, demonstrating the excellent OER activity durability of the catalyst.

Apart from CoP_x, Co_3O_4 also has been reported to be active for OER, and can significantly improve the conductivity and stability properties of the catalysts when combined with carbon materials. The porous Co_3O_4-based hybrids were typically obtained through a one-step carbonization of Co-MOFs. Li et al. [63] introduced MWCNT to MOFs and obtained the Co_3O_4@MWCNTs by carbonization and subsequent oxidation process. The thermal oxidation led to Co_3O_4-N-C active sites uniformly dispersed on MWCNTs (20–50 nm). And the

introduction of MWCNT and the *in-situ* N-doped carbon carbonized from ligands could significantly improve the electronic conductivity of the catalysts. Thus, better OER activity was observed with an onset potential of only 1.5 V (vs. RHE). Ma et al. [64] synthesized MOF-derived Co_3O_4-carbon porous nanowire arrays. The Co_3O_4-carbon were directly prepared on Cu foil as a working electrode. Since this electrode is binder-free and carbon is formed *in situ*, the charge conductivity performance is greatly improved, resulting in excellent OER catalytic activity in 0.1 M KOH solution. It shows a sharp onset potential of 1.47 V (vs. RHE), very close to that of IrO_2/C (1.45 V vs. RHE). The durability is also an important criterion for OER catalysts. The chronopotentiometric response at a current density of 10 $mA{\cdot}cm^{-2}$ was also recorded, and only 6.5% attenuation was observed within 30 h on Co_3O_4-carbon, while that of IrO_2/C is 4.7 times lager under the same condition.

The above results demonstrate that MOFs-derived catalysts show much enhanced OER catalytic performance than pristine MOFs. There are likely several reasons for that. On one hand, carbon materials formed *in situ* or *ex situ* in catalysts can promote electronic conductivity and accelerate charge transfer. On the other hand, the OER active species can be well-dispersed on carbon materials, resulting in improved OER activity. In addition, the strong interactions between OER active species and carbon materials stabilize the OER active site structures, thus leading to enhanced OER activity durability.

6. Conclusions

MOFs-based electrocatalysts for HER and/or OER are rapidly developed in recent years due to unique structures of MOFs. These catalysts mainly include MOFs catalysts, MOFs supports for catalysts, and MOFs-derived catalysts. Due to the fact that the pore structures and functions are tunable and devisable, it is convenient to directly design and construct the active sites for HER and/or OER in MOFs during the synthesis process. However, the vast majority of the synthesized MOFs suffer from poor electronic conductivity, leading to low electron transfer efficiency, which restricts catalytic performance. MOFs are highly porous materials and have ultrahigh specific surface area, thus they are regarded as the most promising support materials for catalysts. The active species for HER or OER can be well dispersed at the surfaces of MOFs or embedded in MOFs matrix, resulting in improved catalytic performance for HER or OER. However, MOFs are microporous materials with small aperture size (<2 nm).On one hand, the active species are difficult to be introduced in their pore channels. Hence, one cannot obtain the catalysts with high activity and stability for HER or OER. On the other hand, the accommodation of electrolyte in the pore channels is very limited. Thus, the active centers in MOFs cannot access the electrolytes with high efficiency. In addition, the poor electronic conductivity of MOFs is another drawback of these catalysts. Some post-treatment methods can greatly improve the electrical conductivity of MOFs-derived catalysts. However, the collapse of the pore structures of MOFs usually occurs during the preparation of the MOFs-derived catalysts leading to a decreased specific surface area of the catalysts, which is adverse to the development of MOFs-derived catalysts with high catalytic performance for HER or OER.

Although many MOFs-based catalysts with high catalytic performance for HER and/or OER have been developed in recent years, there are still a lot of scientific and technical problems to solve before the developed MOFs-based electrocatalysts can meet the requirements for commercialization. The problems mainly involve how to improve the electronic conductivity of MOFs, enlarge pore channels of MOFs to accommodate more electrolytes, limit the collapse of pore structure of MOFs, and maintain high specific surface area during pyrolysis. In addition, the reaction mechanisms of HER and OER, the transfer and diffusion properties of reactants and products, and the effects of electrolyte on the catalytic performance of MOFs-based catalysts need to be clarified.

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