

Review



# Metal–Organic Frameworks Toward Electrocatalytic Applications

# Jun-Hong Li, Yi-Sen Wang, Yu-Chuan Chen and Chung-Wei Kung \*

Department of Chemical Engineering, National Cheng Kung University, 1 University Road, Tainan City 70101, Taiwan; willan9802@gmail.com (J.-H.L.); aa86424576@yahoo.com.tw (Y.-S.W.); rudychen21@gmail.com (Y.-C.C.) \* Correspondence: cwkung@mail.ncku.edu.tw; Tel.: +886-6-275-7575 (ext. 62629)

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**Abstract:** Metal–organic frameworks (MOFs) are a class of porous materials constructed from metal-rich inorganic nodes and organic linkers. Because of their regular porosity in microporous or mesoporous scale and periodic intra-framework functionality, three-dimensional array of high-density and well-separated active sites can be built in various MOFs; such characteristics render MOFs attractive porous supports for a range of catalytic applications. Furthermore, the electrochemically addressable thin films of such MOF materials are reasonably considered as attractive candidates for electrocatalysis and relevant applications. Although it still constitutes an emerging subfield, the use of MOFs and relevant materials for electrocatalytic applications has attracted much attention in recent years. In this review, we aim to focus on the limitations and commonly seen issues for utilizing MOFs in electrocatalysis and the strategies to overcome these challenges. The research efforts on utilizing MOFs in a range of electrocatalytic applications are also highlighted.

**Keywords:** carbon dioxide reduction; conductive MOF; electrocatalysis; electrochemical sensor; oxygen reduction; porous material; redox hopping; water splitting

## 1. Introduction

Electrochemical reactions are the redox reactions which take place solely at the interface of an electrode and the electrolyte. Due to their attractive advantages, such as the simple control of reaction rate via changing the applied bias and the easy separation of reaction products from both half reactions, electrochemical systems have been utilized in various practical applications, including electrochemical sensors [1], supercapacitors [2], electrolysis [3–5], fuel cells [6,7], batteries [8], and electrochromic devices [9]. Frequently, a layer of electrochemically active materials is coated on the surface of the electrode as a thin film; the thin film deposited on the electrode can be served as either the active material for the corresponding application or the material that can further enhance the performance of the corresponding application (e.g., electrocatalysts for electrolysis, fuel cells, and some electrochemical sensors, capacitive materials for supercapacitors, materials enabling ion intercalation for batteries, and electrochromic materials for electrochromic devices). For electrocatalytic applications, the design of thin-film electrocatalysts thus becomes crucial to achieve a faster reaction rate at a relatively lower overpotential. The reaction rate of the thin-film electrochemical process can be affected by the following factors [10–12]: (1) the total number of electrochemically active sites presented in the entire thin film, (2) the charge-transport rate between those active sites and from the active sites to the underlying electrode, (3) the rate of physical diffusion of the active sites within the film (if there is any), and (4) the diffusivity of counter ions within the thin film for maintaining electroneutrality. The total number of electrochemically active sites is directly related to the accessible surface area of the thin film deposited on the electrode. Therefore, to achieve a high reaction rate for the electrochemical reaction occurring at the active thin film, which is beneficial for electrocatalytic applications, electrocatalytically active

thin films composed of nanoporous materials with high surface area, facile charge-transport rate, and rational porosity for ion diffusion are highly desirable.

Metal-organic frameworks (MOFs) consist of a class of porous materials constructed from metal-rich nodes and organic linkers [13,14]. Compared to other categories of nanoporous materials such as zeolites, nanoporous carbons, and inorganic oxides, MOFs exhibit several attractive characteristics, including regular, interconnected and permanent porosity, high structure tunability, and ultrahigh specific surface area. The experimental Brunauer-Emmett-Teller (BET) specific surface area of MOFs has achieved more than 7000 m<sup>2</sup>/g [15,16], which is much higher than those of conventional nanoporous materials. Besides, due to their crystallinity, MOF-based materials are more structurally characterizable compared to amorphous materials. Owing to these unique features, MOFs have attracted great attention in several applications such as gas storage [17], separation [18,19], and chemical sensors [20] over the past two decades. Moreover, the periodic intra-framework functionality of MOFs, either provided by the metal-based nodes or organic linkers, may be further utilized to install well-separated and accessible active sites within the entire framework with a high active-site density [21,22], which renders MOFs attractive porous supports for a range of catalytic applications [23–25]. Although the majority of MOFs still show poorer chemical and thermal stability compared to other nanoporous materials, several MOFs possessing water stability and moderately thermal stability have been designed during the past decade [26–28], which further extends the feasibility of utilizing MOFs in aqueous systems and high-temperature catalysis. One can thus expect that the MOF-based materials installed with three-dimensional (3D) arrays of well-separated active sites should be excellent candidates as the thin-film catalysts for electrocatalysis due to their high "accessible" active-site density and regular porosity for ion diffusion; the choice of water-stable MOFs can further extend the use of these materials in the electrocatalytic applications that need to be operated in aqueous solutions, such as water splitting and electrochemical sensors. However, most MOFs are electrically insulating at low bias [29,30], which hinders the charge transport between the active sites in MOFs and strongly limits the practical use of MOFs in electrochemical applications. Thus, rendering efficient charge transport within the catalytic MOF thin film and maintaining the framework stability in the electrolyte solution become the main challenges for utilizing MOFs in electrocatalytic applications. Although it still constitutes an emerging subfield, the use of MOFs and relevant materials for electrocatalytic applications has attracted much attention in recent years, as revealed in Figure 1. In this review, we aim to focus on the strategies to overcome the aforementioned challenges for utilizing MOFs in electrocatalytic applications, and some examples are highlighted to show the recent progress in utilizing MOFs for electrocatalysis and relevant applications.



**Figure 1.** The number of papers with the topics of metal–organic frameworks (MOFs) and electrocatalysis, electrocatalytic, or electrochemical senor, published in each year, obtained from Web of Science database. It should be noted that all publications using MOF-derived and MOF-templated materials are counted.

## 2. Charge Transport in Metal–Organic Frameworks (MOFs)

Due to the electrically insulating or low conducting feature of most MOFs, rendering a facile charge–transport rate within the framework becomes one of the main challenges for achieving promising performance with MOF-based electrocatalysts. Based on the charge-transport mechanism, approaches to rendering charge transport in MOFs can be briefly classified into two categories: redox hopping and band transport [31].

## 2.1. Redox Hopping

Redox-hopping mechanism occurring in polymeric thin films has been known for more than two decades [32,33]. At an appropriate applied potential, redox hopping can happen in the polymer with anchored redox-active sites that are spatially close to each other and possess a similar redox potential; the transport of electrons can oxidize or reduce all the redox-active sites and render the entire polymeric thin film electrochemically addressable. The diffusion of counter ions from the bulk electrolyte also plays an important role in the redox-hopping process. Counter ions need to diffuse through the polymeric thin film and adsorb on or desorb from the redox-active sites in order to maintain the local electroneutrality and enable the redox hopping to take place smoothly. Similarly, the redox-hopping mechanism applies to MOFs. When redox-active linkers or metal-base clusters are presented as repeating units within the framework, the transport of electrons via redox hopping may take place to render the MOF thin film electrochemically addressable at a reasonable applied potential. As the physical movement of the redox-active sites within most rigid MOFs is theoretically impossible, the overall rate of the electrochemical process presented in such redox-active MOF thin films is controlled by either the rate of charge hopping rate, the rate of diffusion for counter ions, or the total amount of redox-active sites presented within the MOF thin film. The redox-hopping behavior in MOF thin films was first observed by D. M. D'Alessandro et al. in 2012 [34]; the redox-active linkers presented in a zinc-based MOF can enable charge transport and render the MOF thin film electrochemically active. Similar behaviors were also observed by M. Dincă et al. [35]. In the study, the redox-active naphthalene diimide (NDI)-based linkers were utilized to electrochemically address most linkers presented in the zinc-based MOF thin film, and such MOF thin films were found to exhibit electrochromic behavior. In 2013, A. J. Morris et al. reported the similar findings in the thin film of a cobalt-based MOF constructed from redox-active porphyrinic linkers, and investigated the charge hopping mechanism in the MOF thin film via electrochemical and spectroelectrochemical approaches [36]. By utilizing the redox-hopping mechanism, even though the framework is not electrically conductive, the MOF thin film may still show a remarkable electrochemical performance in the presence of counter ions and an applied potential. For example, in 2013, J. T. Hupp et al. observed the redox-hopping behavior in the thin films of a zirconium-based MOF (Zr-MOF), NU-901 (Figure 2) [37]. Although NU-901 is electrically insulating [38], by electrochemically oxidizing the pyrene-based linkers in the presence of counter ions in the electrolyte, more than 90% of the pyrene units within the micrometer-thick MOF thin film can be electrochemically addressable; the resulting MOF thin film exhibits remarkable electrochromism with reversibility. Such redox-hopping strategies have been widely utilized in a range of MOF thin films for electrochemical purposes and their mechanistic insights have been investigated during recent years [31,39–41]. Very recently, S. Ott et al. found that the thin films of a Zr-MOF constructed from NDI-based linkers can perform stable redox-hopping behavior in aqueous electrolytes [42]. It should be noted that since the charge transport in these MOFs relies on the redox reaction of the repeating units within the framework, the redox hopping may not be stable during electrochemical operations if the redox reaction is not reversible in certain electrolytes; the charge transport may be ceased to work at this situation even though the framework is still structurally intact. In some examples, the redox hopping in MOF thin films is not efficient enough, which strongly limits the overall reaction rate of the electrocatalytic process and hinders the corresponding electrochemical performance [43,44].



**Figure 2.** Charge transport via redox hopping between the pyrene units presented in one-dimensional channels of the NU-901 thin film [37].

## 2.2. Band Transport

In addition to redox hopping, another approach to facilitate the charge transport in MOFs is building up the electrical conductivity. Although most MOFs are electrically insulating, MOFs with semiconducting or conducting characteristic may be synthesized via rational structural design [29,30]. It should be noted that for most MOFs, their highest occupied molecular orbitals (HOMO), lowest unoccupied molecular orbitals (LUMO) and therefore band gaps can be experimentally measured. However, such observations do not suggest that the frameworks are semiconducting and behave like conventional inorganic semiconductors since the electrons are highly localized in most MOFs; charge carriers can not travel among unit cells through the entire MOF crystal. It is thus more reasonable to consider MOF as a periodic array of self-assembled molecular units with discrete absorption modes instead of classic semiconductors [45,46]. Therefore, to design a "real" semiconducting or conductive MOF that can facilitate the long-range movement of charge carriers in the domain of the bulk crystal, the conducting pathways for electrons must be constructed periodically within the entire MOF structure. A number of strategies have been proposed to design the electrically semiconducting or conductive MOFs. For example, O. M. Yaghi et al. synthesized the two-dimensional (2D) MOFs constructed from copper nodes and 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP) linkers, which can render the charge transport between the 2D layers and achieve an electrical conductivity of about  $2 \times 10^{-1}$  S/cm [47]; recently this MOF was also found to exhibit superior supercapacitive performance [48]. Similar design of 2D MOFs with  $\pi$ -conjugation to rendering the framework conductive was also demonstrated by M. Dincă et al. [49]. The resulting 2D MOF (Ni<sub>3</sub>(HITP)<sub>2</sub>, HITP = 2,3,6,7,10,11-hexaiminotriphenylene, see Figure 3a) achieved an even higher electrical conductivity (40 S/cm) and can be utilized as the active material for electrochemical charge storage [50]. A few examples of other 2D MOFs which exhibit electrical conductivity also got reported recently [51–54]. The formation of such  $\pi$ -stacked pathways can also be constructed in 3D MOFs. For example, the selection of zinc-based nodes and tetrathiafulvalene(TTF)-tetrabenzoate linkers results in the 3D MOF that contains columnar stacks of TTF to facilitate charge movement [55]. In addition to the formation of  $\pi$ -stacked pathways, the electrical conductivity of MOFs can also be acquired by using sulfur-containing ligands to facilitate charge delocalization within the framework [56,57]. Introducing both the electron-donating and electron-accepting units within the framework structure is another strategy to design the conductive MOFs [58]. For example, S. Takaishi et al. synthesized the MOF constructed with the electron-donating Cu(I) ions and electron-accepting Cu(III)(2,3-pyrazinedithiolate)<sub>2</sub> linkers, and the charge transfer by virtue of donor-acceptor interactions within the obtained MOF results in an electrical conductivity of  $6 \times 10^{-4}$  S/cm [59]. Similar donor-acceptor charge transfer can also be designed by incorporating either the electron donor or electron acceptor as guest molecules into the MOF consisting electron-accepting or electron-donating building blocks. In 2014, M. D. Allendorf et al. incorporated 7,7,8,8-tetracyanoquinododimethane (TCNQ) as the electron acceptor into an electron-donating copper-based MOF ( $Cu_3(BTC)_2$ , BTC =

benzene-1,3,5-tricarboxylic acid; also known as HKUST-1) [60]. The resulting thin films of TCNQ@ HKUST-1 become electrically conductive by means of the donor-acceptor charge transfer between the copper clusters in the framework and TCNQ guests (Figure 3b). Recently, the incorporation of guest molecules to engender the intra-framework donor-acceptor charge transfer has been demonstrated in cooper-based, cobalt-based, and manganese-based MOFs to facilitate the electron conduction within those frameworks [61–63]. The donor-acceptor strategy was also utilized to render the water-stable Zr-MOFs electrically conductive very recently. O. K. Farha et al. demonstrated the incorporation of nickel(IV) bis(dicarbollide) as the electron acceptor into NU-1000, a mesoporous Zr-MOF containing electron-donating pyrene-based linkers (Figure 3c); much improved electrical conductivity and electrochemical performance were achieved with the help of the electron-accepting guest molecules [64]. J. T. Hupp et al. also utilized a similar strategy to render another Zr-MOF (NU-901) electrically conductive by incorporating fullerene as the electron-accepting guest [38]. Besides the aforementioned approaches, other strategies may be used to design the electrically conductive MOF materials. For example, T. Uemura et al. demonstrated the polymerization of conducting polymer within the channels of the MOF to prepare the electrically conductive MOF-polymer composite materials (Figure 3d) [65], and J. T. Hupp et al. utilized self-limiting techniques to construct conducting and continuous molecular bridges within the MOF channels to rendering the framework electrically conductive [66,67]. The design of electrically conductive MOFs is not only beneficial for the use in electrocatalysis and relevant applications, but also helpful for developing MOF-based resistive gas sensors [68].



**Figure 3.** Examples of electrically conductive metal–organic frameworks (MOFs) designed by utilizing (a) 2D  $\pi$ -conjugation [49]. Reproduced with permission from [49], Copyright American Chemical Society, 2014. (**b**,**c**) incorporation of guest molecules [60,64]. Reproduced with permission from [60,64], Copyright The American Association for the Advancement of Science, 2014 and Copyright American Chemical Society, 2018. And (**d**) MOF-polymer composite [65]. Reproduced with permission from [65], Copyright American Chemical Society, 2016.

In addition to the strategies that render charge transport in MOFs mentioned above, another common approach to prepare electrically conductive MOF-based materials is transforming MOFs into MOF-derived porous carbons and metal oxides at high temperature [69]. Due to the remarkable electrical conductivity of carbon materials, these MOF-derived materials usually perform well in electrochemical applications. However, such MOF-derived materials lose the regular pore structures and chemical functionality of the parent MOFs. Since MOF-derived materials are no longer crystalline

MOFs, the use of MOF-derived materials for electrocatalytic applications is beyond the scope of this review.

### 3. The Stability of Metal–Organic Frameworks (MOFs) under Electrochemical Environments

Besides the efficient charge transport and facile diffusion of counter ions within the framework, the stability of MOFs during electrochemical operations is another crucial factor for utilizing MOFs in electrocatalytic applications. If the MOF is not chemically stable in the electrolyte, the framework may collapse during or before the electrochemical operation; dissolution of the MOF or formation of the MOF-derived metal oxides tethered with organic ligands may occur [70]. The resulting modified electrode may exhibit a stable electrochemical performance with long-term stability, but in fact the active electrode material that shows the electrochemical activity is no longer the crystalline MOF with regular porosity. For example, the early findings suggest that a cobalt-based MOF constructed from 1,4-benzenedicarboxylic acid linkers shows exceptional pseudocapacitive performance in alkaline electrolytes [71,72], but the active material achieving the observed capacitive behavior is indeed cobalt hydroxide derived from the MOF in the electrolyte [73]. Another example is Cu-BTC, i.e., HKUST-1, a common copper-based MOF that has been found to be unstable in water [26], but got reported sometime for the electrocatalytic applications in aqueous electrolytes. In some circumstances, the collapse of MOF may solely occur on the surface of MOF crystals, which generates a layer of electrochemically active MOF-derived metal hydroxide covering the inactive MOF [74]. Thus, to avoid recognizing the electrocatalytic activity originated from MOF-derived materials as the property of the crystalline MOFs, it is crucial to examine the chemical stability of the targeted MOF in the electrolyte before utilizing the MOF for corresponding electrocatalytic applications. As mentioned previously that more than 90% of existed MOFs are not stable in water, for the electrocatalytic applications that need to be operated in aqueous electrolytes such as water splitting, oxygen reduction, and most of the electrochemical sensing systems, the use of water-stable MOFs is necessary.

Among MOFs constructed from carboxylate-based linkers, zirconium-based MOFs and their hafnium-based analogs have been reported to exhibit exceptional stability in water due to the stronger bonds incorporated in these frameworks [27]. The most common example of zirconium-based MOFs is UiO-66 developed by K. P. Lillerud and coworkers in 2008 (Figure 4a), which possesses a thermal stability up to 500 °C and a superior chemical stability in acidic and neutral aqueous solutions [28]. Due to the remarkable stability and high structural tunability, numerous zirconium-based MOFs have been designed for a range of applications [75]. However, it is still quite challenging to find zirconium-based MOFs that can show chemical stability in strong alkaline solutions or concentrated solutions containing strongly coordinating ions such as phosphate [27]; such characteristics limit the use of zirconium-based MOFs in the electrocatalytic systems operated in phosphate buffer solutions or strong base. Except zirconium-based MOFs and their hafnium-based analogs, MOFs constructed from anionic and nitrogen-containing linkers usually exhibit stability in water. The most common example is ZIF-8, one of the zeolitic imidazolate frameworks (ZIFs), which can preserve its crystallinity in strong alkaline solutions. Such a remarkable stability is in part attributed to the small and hydrophobic pore opening of ZIF-8 that excludes the penetration of liquid water [27,76]. Another example of MOFs constructed from nitrogen-containing linkers is pyrazolate-based MOFs. MOF constructed from nickel-based nodes and pyrazolate-based linkers has been reported to show a chemical stability in aqueous solutions ranging from pH 2 to pH 14 [77]. Series of nickel-based MOFs constructed from pyrazolate-based redox-active linkers, i.e., PCN-601 and PCN-602 (Figure 4b), were also reported recently to show high chemical stability in strong alkaline solutions and concentrated phosphate solutions [78,79]. Such MOFs with exceptional chemical stability should be served as potential candidates for the electrochemical systems in alkaline electrolytes.



**Figure 4.** Crystal structures of (**a**) UiO-66 [28] and (**b**) PCN-601 and PCN-602 [78,79]. Lime green: Zr; red: O; grey: C; malachite: Ni; light slate blue: N. Hydrogen atoms are not shown for clarity.

### 4. Recent Progress in Utilizing MOFs for Electrocatalysis and Relevant Applications

## 4.1. Hydrogen Evolution

Photoelectrochemical water splitting has attracted great attention and been considered as a potential route to generate renewable energy [3]. Except the photosensitizers that can render charge separation, electrocatalysts are also required for both the anode and cathode to accelerate the rates and reduce the overpotentials for both half reactions [4]. Platinum is the typical electrocatalyst on the cathode side to catalyze the half reaction that converts water into hydrogen gas. Besides, metal sulfides, metal selenides, and metal phosphides have been proposed as the highly active electrocatalysts for hydrogen evolution to replace platinum [80]. In 2011, A. Dolbecq and coworkers reported the use of polyoxometalate-based MOFs for electrocatalytic hydrogen evolution [81]. By utilizing the redox hopping between those polyoxometalate-based units presented within the framework, the MOF thin film was found to exhibit significant electrocatalytic activity for hydrogen evolution. H. C. Zhou et al. further designed another polyoxometalate-based MOF (NENU-500) that possesses a much higher porosity and larger pore size compared to the previous one [82]. With the help of a better porosity, the resulting NENU-500 thin film achieved a current density of 10 mA/cm<sup>2</sup> for hydrogen evolution at a relatively low overpotential of 237 mV. On the other hand, the use of a zirconium-based MOF (NU-1000) thin film electrodeposited with a layer of nickel sulfide for electrocatalytic hydrogen evolution was demonstrated by J. T. Hupp and coworkers (see Figure 5) [83]. The presence of highly robust NU-1000 framework along with nickel sulfide was found to facilitate proton transport during the electrocatalysis process in acidic electrolytes, which resulted in a much better electrocatalytic activity compared to that of the pristine electrodeposited nickel sulfide. To further increase the density of active sites within the MOF thin films, J. T. Hupp et al. also utilized NU-1000 as a porous support to deposit the spatially well-separated molybdenum sulfide nanoclusters for hydrogen evolution [84]. With the help of redox mediators to facilitate charge transport between those catalytically active sites decorated in the framework, the resulting electrocatalytic activity for hydrogen evolution can be significantly improved. Recently, W. B. Lin and coworkers demonstrated the use of carbon nanotube-supported hafnium-based MOF constructed from cobalt (III) porphyrinic linkers for electrocatalytic hydrogen evolution [85]. With the help of carbon nanotubes as the conductive support to facilitate charge transport between MOF crystals, the electrocatalytic activity of the composite material was found to be significantly enhanced compared to that of the pristine MOF. A recent finding also shows that an iron-based MOF, MIL-53(Fe), can exhibit electrocatalytic activity for hydrogen evolution [86].



**Figure 5.** The NU-1000 thin film electrodeposited with a layer of nickel sulfide for electrocatalytic hydrogen evolution [83]. Lime green: Zr; red: O; grey: C. Hydrogen atoms are not shown for clarity.

## 4.2. Oxyben Evolution

Although the main purpose of water splitting is to produce hydrogen fuel instead of the oxygen gas, the design of better electrocatalysts for oxygen evolution is still crucial due to the higher kinetic barrier and thus higher overpotential in general for oxygen evolution compared to those for hydrogen evolution [87]. The typical heterogeneous electrocatalysts for oxygen evolution are  $IrO_2$  and  $RuO_2$ , which can reveal remarkable electrocatalytic activity at relatively low overpotentials in both acidic and alkaline electrolytes [87]. Cobalt phosphate-based electrocatalyst, usually termed "Co-Pi", is another common candidate that can generate oxygen from water in neutral solutions [88]. Besides these options, most electrocatalysts for oxygen evolution such as nickel hydroxide, cobalt oxide, and nickel-iron oxide require alkaline electrolytes [87,89]. As the number of MOFs that are stable in strong alkaline solutions is quite limited, examples of stable MOFs providing electrocatalytic activity for oxygen evolution are relatively rare. A variety of nickel-based, cobalt-based, nickel-iron-based, and cobalt-iron-based MOFs have been applied for electrocatalytic oxygen evolution in strong alkaline media previously [90–96]. The transformation of MOFs into metal oxides and/or (oxy)hydroxides that truly provide electrocatalytic activity during electrocatalysis in alkaline solutions has been also reported [94]. In 2016, A. J. Morris et al. reported the use of a Zr-MOF constructed from nickel (II) porphyrinic linkers for electrocatalytic oxygen evolution in the electrolytes with neutral pH [97]. In addition, the same group also demonstrated the incorporation of electrocatalytically active ruthenium-based complex into a Zr-MOF; the obtained MOF thin films exhibit activity for oxygen evolution in neutral electrolytes (see Figure 6) [41]. Similar concepts also got reported by S. Ott and coworkers at the same time [98]. On the other hand, J. T. Hupp et al. reported the spatially well-separated cobalt oxide nanoclusters decorated in a Zr-MOF, NU-1000, which can be used for electrochemical oxygen evolution in weakly alkaline solutions [99]. A recent finding reported by X. Liu and coworkers shows that the Zr-MOF incorporated with electrocatalytically active iridium-based complex can catalyze oxygen evolution at neutral pH [100]. Very recently, S. Y. Lu et al. designed the highly active electrocatalyst for oxygen evolution based on a nickel-iron-based MOF, NH<sub>2</sub>-MIL-88B, which was found to exhibit superior electrocatalytic activity in strong alkaline electrolytes and maintain its crystallinity after long-term electrolysis [101].



**Figure 6.** The use of a Zr-MOF (metal–organic framework) incorporated with ruthenium-based complex for electrocatalytic oxygen evolution [41]. Reproduced with permission from [41], Copyright John Wiley and Sons, 2017.

## 4.3. Oxyben Reduction

Electrochemical oxygen reduction plays an important role in electrochemical energy conversion in fuel cells. The kinetics of oxygen reduction that involves four-electron transfer is usually very slow, therefore, efficient electrocatalysts are required on the cathodes of fuel cells [6]. Platinum is the most common electrocatalyst for oxygen reduction; other less pricey alternatives include metal oxides, metal sulfides, metal nitrides, and nitrogen-doped carbons [7,102]. As the oxygen can also get reduced through the two-electron pathway to produce the undesired hydrogen peroxide, in addition to achieving the low overpotential and high catalytic current density, the number of electrons transferred is also crucial for these electrocatalysts. In 2012, K. P. Loh et al. demonstrated the use of a composite material composed of an iron-based MOF and graphene for electrochemical oxygen reduction, and a number of electrons transferred of 3.82 was achieved in alkaline electrolytes [103]. A range of copper-based, cobalt-based, iron-based, and manganese-based MOFs have been directly applied for electrochemical oxygen reduction in alkaline electrolytes and found to show remarkable activity [104–108]. In 2017, A. Fateeva et al. showed that an aluminum-based MOF constructed from cobalt (III) porphyrinic linkers exhibits significant activity for electrochemical oxygen reduction in acidic solutions, and the observed activity is originated from the cobalt (III) porphyrinic centers [109]. A. J. Morris and coworkers also demonstrated the use of porphyrinic MOFs for electrochemical oxygen reduction (see Figure 7) [110]. With the Zr-MOF constructed from electrocatalytically active iron (III) porphyrinic linkers, a number of electrons transferred of 3.8 can be achieved in the acetic acid-based electrolyte. On the other hand, M. Dincă et al. utilized the 2D electrically conductive MOF, Ni<sub>3</sub>(HITP)<sub>2</sub> (see Figure 3a for the structure), as the electrocatalyst for oxygen reduction [111,112]. The conductive MOF was found to reveal chemical stability in alkaline electrolytes and show remarkable electrocatalytic activity for oxygen reduction, with an onset potential of +0.82 V vs. reversible hydrogen electrode (RHE) and a number of electrons transferred of 2.25.



**Figure 7.** The use of a porphyrinic Zr-MOF (metal–organic framework) PCN-223(Fe), for electrocatalytic oxygen reduction [110]. Lime green: Zr; red: O; grey: C; light slate blue: N; orange: Fe. Hydrogen atoms are not shown for clarity.

## 4.4. CO<sub>2</sub> Reduction

Via electrochemical processes, carbon dioxide can be transformed into useful fuels such as carbon monoxide, formic acid, methanol, methane, ethanol, ethylene, and ethane [5,113]. With the help of protons to render proton-coupled multi-electron steps, the electrochemical reduction of CO<sub>2</sub> is not thermodynamically unfavorable at all, but its high kinetic barrier strongly hinders such electrochemical reactions to occur. Moreover, proton reduction that generates hydrogen gas may take place simultaneously as a side reaction. Therefore, the design of efficient electrocatalysts that can reduce the overpotential for CO<sub>2</sub> reduction as well as facilitate the selectivity against hydrogen evolution becomes crucial. Metal complexes consisting of macrocyclic or bipyridine ligands are common homogeneous electrocatalysts for the reduction of CO<sub>2</sub> [5], while metallic copper, gold, and silver are common heterogeneous electrocatalysts [114]. Among these catalysts, copper is the unique candidate that shows a proclivity to produce  $C_2$  or even  $C_3$  hydrocarbons from  $CO_2$  electrochemically [115]. MOFs constructed from copper-based nodes have been widely applied for electrocatalytic  $CO_2$ reduction [116–120]. In 2015, P. Yang et al. demonstrated the use of an aluminum-based porphyrinic MOF for electrocatalytic CO<sub>2</sub> reduction [121]. With the cobalt (II) porphyrinic linkers as the catalytically active units, the MOF thin film can catalyze the reduction of proton and  $CO_2$  to produce hydrogen and carbon monoxide. At the same time, J. T. Hupp and coworkers also reported that a Zr-MOF constructed from iron (III) porphyrinic linkers, MOF-525(Fe), can be utilized as an active electrocatalyst to produce hydrogen and carbon monoxide from CO<sub>2</sub> and a proton source [44]. As reported by B. X. Dong et al., another porphyrinic Zr-MOF, PCN-222(Fe), was also found to show electrocatalytic activity to convert CO<sub>2</sub> to CO [122]. Beside porphyrinic MOFs, J. T. Hupp et al. also utilized thin films of a Zr-MOF (NU-1000) as the support to install metallic copper nanoparticles [123]; the resulting MOF thin films incorporated with copper nanoparticles were found to exhibit electrocatalytic activity to convert CO2 to carbon monoxide and formic acid. Recently, X. Wang and coworkers reported the ZIF-8 doped with electrocatalytically active 1,10-phenanthroline, which can show significant electrocatalytic activity to convert  $CO_2$  to CO [124].

## 4.5. Electroanalysis

If the electrode surface can selectively react to a certain species electrochemically, the electrochemical system can be utilized to determine the concentration of the targeted species with current response as the output signal. Most of such amperometric sensors rely on the two-step  $EC_{cat}$  mechanism [125], which implies that these electrochemical sensing systems in fact belong to electrocatalytic applications.

The most commonly seen example is the amperometric glucose sensor [1], which has been widely available on the market. During the past five years, numerous zinc-based and copper-based MOFs have been utilized in electrochemical sensing systems operated in phosphate buffer solutions or alkaline electrolytes to detect a range of species including hydrogen peroxide [126–129], glucose [130], L-cysteine [131], L-tryptophan [132], ascorbic acid [132,133], dopamine [134], and nitrite [135,136]. In 2015, K. C. Ho et al. demonstrated the use of a Zr-MOF, MOF-525, to electrochemically detect nitrite in aqueous electrolytes with a natural pH (see Figure 8a) [43]. The free-base porphyrinic linkers can be served as the active sites to catalyze nitrite oxidation, and the framework was found to keep intact after the electrochemical operations. Since the sensing performance was strongly limited by the sluggish redox hopping in MOF-525, the authors also designed the nanocomposites composed of MOF-525 nanocrystals interconnected by graphene nanoribbons to improve the electrochemical sensing performance (see Figure 8b) [137]. A similar strategy was also utilized by K. C. W. Wu et al.; they synthesized the composite material consisting of MOF-525 nanocrystals and poly(3,4-ethylenedioxythiophene) (PEDOT) nanotubes, and the resulting material was found to outperform both the MOF-525 and PEDOT nanotubes for the electrochemical detection of dopamine [138]. Recently, L. Guo and coworkers also reported the use of MOF-525/marcoporous carbon composite for the electrochemical sensing application toward luteolin [139]. On the other hand, S. Ma et al. demonstrated the polymerization of aniline monomers in the presence of another Zr-MOF, UiO-66-NH<sub>2</sub>, to synthesize the composite material with Zr-MOF and polyaniline; the obtained material was utilized for the electrochemical detection of cadmium ions [140]. Besides, the same group also designed another porphyrinic Zr-MOF (MMPF-6(Fe)) incorporated with gold nanoparticles for the electrochemical detection of hydroxylamine [141]. Another similar example was demonstrated by B. Zeng and coworkers, who utilized UiO-66-NH<sub>2</sub> to immobilize gold-palladium nanoparticles and applied the resulting material for electrochemical nitrite sensing [142]. Beyond these Zr-MOFs, L. Wang et al. reported the encapsulation of microperoxidase-11 into an aluminum-based MOF, PCN-333 (Al), and utilized the material for electrochemical detection of hydrogen peroxide [143].



**Figure 8.** (a) The use of metal–organic framework (MOF)-525 thin film for electrochemical nitrite sensing [43]. Reproduced with permission from [43], Copyright Elsevier, 2015. (b) The design of nanocomposites composed of MOF-525 nanocrystals interconnected by graphene nanoribbons to improve the electrochemical sensing performance [137]. Reproduced with permission from [137], Copyright The Royal Society of Chemistry, 2016.

### 5. Conclusions and Outlook

In summary, utilizing MOFs and relevant materials for various electrocatalytic purposes has become an emerging subfield in the past five years. As a catalog of highly porous supports with interconnected pore structures and tunable intra-framework functionality, MOFs can provide an ultrahigh density of accessible active sites and thus are attractive for catalysis. The findings of redox hopping behavior in MOFs opened up the feasibility to utilize MOFs for electrochemical applications, and the rapid growth in the numbers of electrically conductive MOFs and water-stable MOFs provides more opportunity for MOFs to be served as novel electrocatalysts.

Although to date there are already several examples of electrochemically addressable MOFs that have been utilized in hydrogen evolution, oxygen evolution, oxygen reduction, CO<sub>2</sub> reduction, and amperometric sensing, the corresponding electrochemical performances are in general quite limited; the slow redox hopping or low electrical conductivity still makes MOFs quite far away from state-of-the-art electrocatalysts in most of the cases. MOF-derived materials, either obtained by pyrolysis or in-situ electrochemical transformation, usually perform better for electrocatalytic applications compared to the crystalline MOFs at the current stage. However, most of the MOF-derived materials lose the tunable chemical functionality and the regular and interconnected porosity given by the parent MOFs. To keep these benefits provided by MOFs and further improve the corresponding electrocatalytic performance, the charge-transport rate within the MOF-based thin films must be improved. One of the strategies is to design electrically conductive MOFs possessing high porosity and water stability. As the thickness of the electrocatalytic thin film deposited on the conducting substrate is usually in the range of a few hundred nanometers to a few micrometers, extremely high electrical conductivity may not be necessary to achieve a negligible overpotential originated from the resistance of the electrocatalyst. Another alternative approach is designing the nanocomposites to integrate the advantages from different materials. The advantages of MOFs are still preserved, but another conducting material, such as nanocarbons or conducting polymers, can be incorporated with MOF crystals to facilitate charge transport within the electrocatalytically active thin film. Further research efforts are still needed to design better MOF-based materials for achieving benchmarking electrocatalytic performance in practice.

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