Modulating metal–organic frameworks for catalyzing acidic oxygen evolution for proton exchange membrane water electrolysis

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Abstract

Proton exchange membrane (PEM) water electrolysis represents one of the most promising technologies to achieve green hydrogen production, but currently its practical viability is largely affected by the slow reaction kinetics of the anodic oxygen evolution reaction (OER) in an acidic environment. While noble metal-based catalysts containing iridium or ruthenium are excellent catalysts for the acidic OER, their practical use in PEM electrolyzers is hindered due to their low abundance and high cost. Most recently, metal–organic frameworks (MOFs) have been demonstrated as a perfect platform to facilitate the design of acidic OER catalysts with both high efficiency and cost-effectiveness. Here, we provide a timely and comprehensive overview of the recent progress on MOF-based acidic OER catalysts. The fundamental mechanisms of the acidic OER are first introduced, followed by a summary of the development of pristine MOFs and MOF derivatives as acidic OER catalysts. Importantly, a number of catalyst design strategies are discussed aiming at improving the acidic OER catalytic performance of MOF-based candidates. The integration of MOF-based catalysts into real PEM water electrolyzers is also included. Finally, future research directions are provided to achieve better MOF-based catalysts operational in acidic environments and PEM devices.

KEYWORDS

acidic water oxidation, electrocatalysis, hydrogen production, metal–organic frameworks, oxygen evolution reaction, proton exchange membrane water electrolysis

1 | INTRODUCTION

Over the past century, fossil fuels (oil, coal, and natural gas) have supplied humanity with sufficient energy to achieve social and economic development, but their continued use has also raised growing concerns over global warming and climate change associated with the carbon dioxide emission.¹–³ Hydrogen (H₂) has long been considered as a cleaner alternative because its generation, consumption, and regeneration involve only water as a product and thus can significantly reduce carbon emissions.⁴ More importantly, hydrogen possesses a
mass-based energy content higher than any other fuels, that is, nearly thrice that of gasoline (120 vs. 44 MJ kg\(^{-1}\)).\(^5\) In addition, hydrogen is storable and can be easily used and distributed in transport and industry sectors, as well as households, adding to its suitability as a replacement for fossil fuels to achieve carbon neutrality. Currently, nearly 90% of H\(_2\) is produced by steam reforming, a process that consumes fossil fuels as energy sources and is, therefore, not sustainable.\(^6\) Alternatively, water electrolysis, a simple means to split water molecules (H\(_2\)O) into oxygen (O\(_2\)) and H\(_2\), can produce high-quality hydrogen, and if facilitated by electricity generated from renewable energy (e.g., solar and wind), can further reduce the carbon footprint.\(^7\) Depending on the operating conditions, there are mainly three types of water electrolysis technologies available, namely, solid oxide electrolysis,\(^8\) anion exchange membrane water electrolysis,\(^9\) and proton exchange membrane (PEM) water electrolysis.\(^10\) Of note, PEM water electrolysis has received soaring interests by virtue of its many advantages, including higher energy efficiency, lower gas crossover, more compact cell design, and exceptionally longer life.\(^10–13\) Therefore, it is of great importance to develop high-performance PEM water electrolyzers to achieve green hydrogen production in an efficient way.

Water splitting involves two half-reactions, namely, the hydrogen evolution reaction (HER) at cathode and the oxygen evolution reaction (OER) at anode.\(^9,14\) Because of the inherent energy barrier, a practical water electrolyzer often operates at a cell voltage higher than the theoretical value (i.e., 1.23 V under standard conditions 298 K and 1 atm).\(^15\) In particular, a majority of the extra energy input is associated with the energy losses at the anodic OER, which is kinetically more sluggish than the HER due to a complex four-electron process.\(^16,17\) Therefore, developing efficient electrocatalysts holds the key to accelerate the water-splitting kinetics. However, in PEM water electrolyzers, there exist more stringent requirements on the OER catalysts because they must be able to withstand the harsh acidic environments. This results in a limited number of catalytic candidates in acidic OER, in stark contrast to the case of OER in alkaline solutions. To date, noble metal iridium (Ir), ruthenium (Ru), and their derivatives are still the best candidates for acidic OER because of their suitable electronic structures and high resistance against the corrosive and oxidative conditions.\(^18,19\) Nonetheless, the low abundance and high cost greatly hinder the deployment of these noble metal-based catalysts on a larger scale. One general strategy to develop low-cost, active, and stable alternatives is to dilute noble metals in a framework made up of non-noble elements, which reduces the usage of noble metals while offering comparable or even better catalytic performance due to a well-tailored electronic effect. Successful examples include single-atom catalysts,\(^20,21\) perovskites,\(^22–25\) pyrochlores,\(^26\) and other metal oxides.\(^27–29\)

Metal–organic frameworks (MOFs), a class of porous materials that are periodically assembled by metal ions/clusters and organic linkers via coordination bonding,\(^30\) offer a perfect platform to meet the above requirement for the design of acidic OER catalysts. In fact, MOFs and their derivatives have attracted considerable research attention for versatile applications owing to their ultrahigh porosity, large surface area, tunable morphology, flexible structure, and synergy between metal centers and organic ligands.\(^31–40\) More recently, MOF-based materials have received burgeoning interest as candidates for catalyzing the acidic OER.\(^41–69\) Here, we provide a timely and comprehensive review summarizing these most recent achievements (Figure 1). It is noted that Prussian blue analogues (PBAs), which are cyanide-bridged coordination polymers produced by the reaction between metal ions and transition-metal cyanometalates,\(^70\) are considered one category of MOFs and thus are also included for discussion. We first introduce the fundamental mechanisms of the OER under acidic conditions, followed by an overview of the recent development of pristine MOFs and MOF derivatives as acidic OER catalysts. We then present a range of catalyst design strategies that aim to improve the acidic OER catalytic performance of MOF-based candidates. We also briefly discuss their integration into real PEM water electrolyzers. Finally, we provide future research directions to achieve better MOF-based catalysts operational in acidic environments and PEM devices. We hope this review could help promote the development of MOF-based catalysts for acidic OER catalysis to eventually realize efficient hydrogen production in a cost-effective manner.

## 2 | FUNDAMENTALS OF ACIDIC OER

Generally, based on the contribution of oxygen in the dioxygen production, the OER in acidic solutions can proceed through two types of reaction mechanisms, including the adsorbate evolution mechanism (AEM) and the lattice-oxygen participated mechanism (LOM).\(^71,72\) Presented in Figure 2 are two proposed pathways for the AEM and LOM, respectively.\(^71\) Note that among many other possibilities, these proposed mechanisms are recognized to be the most accepted ones to date, and that there is ongoing debate over the exact reaction pathways, in particular, for the LOM mechanism.\(^71–73\) Interested readers are directed to some excellent review articles for a detailed understanding of the OER mechanisms.\(^72,73\)

In the AEM process, the oxygen production is originated from the absorbed water molecules, which involves
a four proton–electron transfer process taking place on the metal active sites (M) on the catalyst surface. In detail, as described in Figure 2A, water molecules are first adsorbed onto the surface of active site, generating the hydroxyl intermediate species (M-OH$_{ads}$) via a one-electron process. The M-OH$_{ads}$ intermediate species is then oxidized to form the M-O$_{ads}$. Afterward, the intermediate M-OOH$_{ads}$ is formed via adsorbing another water molecule, followed by releasing an oxygen molecule and recovering to the initial state (M). 74 As for the LOM pathway, the first two steps are the same as the AEM process with the formation of M-OH$_{ads}$ and M-O$_{ads}$ intermediate species. Differently, in the following steps, the oxygen from the lattice of the catalyst can directly participate in the oxidation process and the formation of O$_2$ molecules. 75,76 As shown in Figure 2B, the lattice oxygen is coupled with the adsorbed M-O$_{ads}$ species to release one O$_2$ molecule. This step leaves behind an oxygen vacancy, which is subsequently replenished by water dissociation and further recleneed to recover to the initial M site.

In terms of the AEM process, the relative adsorption energies of the oxygen intermediates are generally linearly correlated with each other (ΔG$_{M-OOH_{ads}}$ − ΔG$_{M-OH_{ads}}$ = 3.20 eV), obeying a so-called “scaling relationship.” 77 On the one hand, the scaling relationship enables the rapid screening of electrocatalysts from a trial-and-error approach toward a theory-guided approach. Additionally, the adsorption energy calculated by density functional theory (DFT) computations allows to establish a catalytic activity trend of a series of electrocatalysts in the form of a “volcano plot,” which brings about considerable activity descriptors, such as ΔG$_{M-O_{ads}}$ − ΔG$_{M-OH_{ads}}$. 16,78 The well-established relations are regarded as a low-cost and powerful method to predict the OER activity of the theory-guided materials. On the other hand, the best activity for the series of catalysts, which is often located on the
top of the volcano plot, also sets a limitation for further catalyst design. To realize the ultimate goal of decreasing the overpotential, more effective design strategies are desired to break the unfavorable scaling relationship. Of note, LOM is capable of breaking the scaling relationship due to the generation of the M-OOH ads intermediate being circumvented. Thus, LOM is regarded as a promising scheme to design high-performance OER catalysts.

3 | MOFS AND THEIR DERIVATIVES AS ACIDIC OER CATALYSTS

3.1 | Pristine MOFs

For pristine MOFs to directly catalyze the acidic OER, they need to be stable both in acidic water and under oxidative bias, a stringent prerequisite that few MOFs can satisfy. Despite increasing reports on using pristine MOFs for the alkaline OER,79,80 those for the acidic OER are rarely seen. This is mainly because most of the pristine MOFs are prone to decompose due to the ligands being easily protonated in acidic electrolytes.81 In addition, low electrical conductivity could be another roadblock to the use of pristine MOFs as acidic OER electrocatalysts.82,83

Recently, Voznyy et al. for the first time demonstrated the acidic OER catalysis of a pristine, Mn MOF prepared by coordinating Mn to the terephthalic acid (TPA) (MnTPA) (Figure 3A).41 MnTPA alone, however, was found with poor OER activity, due to the poor electrical conductivity of Mn and the electrically insulating TPA ligands. To address this issue, carbon black (CB) as an electrical conductor was introduced to composite with MnTPA (Figure 3A). The optimized composite with a MnTPA-to-CB mass ratio of 1:2 (MnTPA/CB) achieved current densities of 10 and 50 mA cm$^{-2}$ at overpotentials of 539 and 765 mV, respectively, in a 0.05 M H$_2$SO$_4$ electrolyte with 0.5 M K$_2$SO$_4$ (pH 1.3), much better than a similarly prepared MnO$_2$/CB composite catalyst (715 and 898 mV) (Figure 3B). This gain in activity relative to the transition metal oxide counterpart highlights the promise of developing pristine MOFs based on non-noble metals for catalyzing the acidic OER. When held chronoamperometrically at an initial current density as high as 10 mA cm$^{-2}$, MnTPA/CB showed an exponential decrease in current density, indicating poor catalytic stability, although still better compared to MnO$_2$/CB. Future efforts are required to improve the stability of pristine MOF catalysts in acidic OER, for example, by means of exchanging the chelating ligands to those with different donor groups.

By comparison, PBAs generally show greater structural stability than conventional MOFs and have recently been designed for OER catalysis under mildly acidic pH conditions.42–45 For instance, the Galán-Mascarós group directly grew cobalt hexacyanoferrate (CoFe PBA) on a conductive fluorine-doped tin oxide (FTO) substrate through a facile chemical etching approach, which remained stable, both chemically and electrochemically, during bulk water electrolysis in the pH range 2–13.42 In a pH 2 electrolyte (0.1 M KPi + 1 M KNO$_3$ + H$_3$PO$_4$), Tafel analysis of the polarization data gave an overpotential of ∼520 mV at 1 mA cm$^{-2}$, while chronopotentiometric stability measurements revealed an overpotential of ∼820 mV at 10 mA cm$^{-2}$. The same group also evaluated the acidic OER activity of a physical mixture of CoFe PBA nanoparticles and antimony-doped tin oxide (ATO) nanotubes using the rotating disk electrode methodology.43 The composite with 17% in weight of CoFe PBA, which was optimized taking into consideration the conductivity, delivered a current density of 0.2 mA cm$^{-2}$ at a ∼640 mV overpotential in 0.1 M H$_2$SO$_4$. Despite the impressive durability in acidic electrolytes, these CoFe PBA candidates are still far from being competitive in terms of catalytic activity. More recent investigations demonstrated that the acidic OER activity can be enhanced by doping foreign elements44 or forming core@shell hybrids.45 However, the electrochemical analysis of these materials was not performed in a thorough manner, hindering an in-depth understanding of the
structure–activity relationships. This again invites future research inputs into exploring pristine PBAs for acidic OER, in particular, under more strongly acidic conditions.

### 3.2 MOF derivatives

Compared to pristine MOFs, their derivatives are generally more stable in acids. Therefore, more research is focused on using MOFs as precursors for preparing a variety of acidic OER catalysts, including metals, metal oxides, carbons, and their composites.\(^{46–69}\) Till date, the most used method to synthesize MOF-derived materials is pyrolysis, during which parameters, such as temperature, atmosphere, and duration, can be facilely tuned to regulate the products’ properties. Because metal nodes are evenly distributed at the atomic level in the MOF matrix, the derived materials usually favor a homogenous distribution of the metal elements, in the form of metals supported on carbon or metal components within an oxide lattice. The diversity of metal nodes in MOFs also means that MOF derivatives can be tailor-made by appropriate selection of the pristine MOFs.

Another major advantage of MOF derivatives is that they often inherit the morphological features of their respective starting MOFs. For example, the octahedral shape of the Ru-incorporated Cu-BTC was maintained after forming Cu-doped RuO\(_2\),\(^{55}\) and the nanorod structure of the Ru-exchanged Zn-BTC was preserved after converted to Zn-doped RuO\(_2\).\(^{57}\) Also inherited are the high surface area and rich porosity of the MOF precursors. In addition, the removal or evaporation of certain metal species during pyrolysis (e.g., Zn) can generate a large amount of meso/macropores, contributing further to enhanced surface area and porosity. For instance, Zn evaporation during the heating treatment of a bimetallic Zn-Ir-MOF resulted in the formation of an Ir/C catalyst with surface areas of up to \(\sim 1000\ \text{m}^2\ \text{g}^{-1}\).\(^{50}\)

Furthermore, the pyrolyzed MOFs, often in the form of carbons or doped carbons, can be exploited as precursors or substrates to prepare more complicated multimetallic structures.\(^{62–69}\) In these catalysts, MOF derivatives mainly serve as a conductive support to allow for good dispersion of the catalytically active materials while offering high conductivity and porosity necessary for charge transfer and mass transport. It should be noted that the stability of these carbon-based catalysts may pose a challenge for use in acidic environments, especially under high oxidative bias and high-temperature testing conditions for real PEM water electrolysis devices, although electrochemical measurements in room-temperature, half-cell conditions suggest otherwise.

### 3.3 Benchmarking with state-of-the-art catalysts

It is meaningful to present performance benchmarking with state-of-the-art catalysts to identify any research gaps and stimulate further research endeavors. Table 1 provides an exhaustive comparison of the MOF-based acidic OER catalysts reported to date, with some of the excellent candidates also included. All electrochemical data were obtained in a three-electrode, half-cell mode at ambient temperature. The activity is assessed by several parameters. One that is most reported is the overpotential needed to reach a geometric current density of 10 mA cm\(^{-2}\) (\(\eta_{10}\)), a parameter widely adopted for benchmarking purposes due to its close relation to solar fuels production.\(^{84}\) Here, the overpotential is defined as the difference between the applied potential and the equilibrium potential for water oxidation, which is 1.23 V versus the reversible hydrogen electrode. Tafel slope (in mV dec\(^{-1}\)), a parameter independent of catalyst surface area or mass loading,\(^{85}\) is also included to compare the catalyst kinetics; the smaller the Tafel slope, the faster the kinetics. Turnover frequency (TOF), defined as the number of O\(_2\) gas evolved per active site per unit time at a given potential (in s\(^{-1}\)), is also compared, but its accurate estimation remains a challenge due to the difficulty in unambiguously measuring the number of active sites,\(^{86}\) thus only a limited number of publications reported this parameter. Considering the need to reduce noble metal usage in acidic OER, mass activity based on the content of noble metals in the catalysts is also compared to evaluate the cost effectiveness. In the meantime, stability is evaluated, most often by means of chronopotentiometry with the catalyst held at a constant current density of 10 mA cm\(^{-2}\) to continuously catalyze the acidic water oxidation, under which a catalyst that can sustain longer operation is considered more stable. Other approaches, such as the accelerated degradation test by running hundreds of thousands of cyclic voltammetry (CV) scans, may also be employed. Note that it is also important to assess the catalyst degradation by measuring cation dissolution in electrolytes (however, is not included in Table 1 due to the current lack of such practice).

Despite the scattered electrochemical testing conditions across the research community (e.g., differences in electrolyte, substrate, and catalyst loading), a rough comparison can still be made. Remarkably, noble metal-based MOF derivatives demonstrate excellent performance, with some candidates comparing favorably to the state-of-the-art, Ir/Ru-based catalysts in terms of both catalytic activity and stability. On the contrary, pristine MOFs and MOFs made of non-noble metals exhibited much poorer catalytic performance in acids, leaving plenty of room for improve-
| Catalyst                      | MOF involved | Electrolyte          | Loading (mg cm⁻²) | η₁₀ (mV) | Tafel slope (mV dec⁻¹) | TOF (s⁻¹) | MA (A g⁻¹)² | Stability         | Ref. |
|------------------------------|--------------|----------------------|-------------------|----------|------------------------|-----------|-------------|------------------|------|
| **Pristine MOFs**            |              |                      |                   |          |                        |           |             |                  |      |
| MnTPA/CB                     | MnTPA        | 0.05 M H₂SO₄ with 0.5 M K₂SO₄ | CP /              | 539      | /                      | /         | N.A.        | Decay half life of 1121 s @ 10 mA cm⁻² | 41   |
| **Non-noble metal-based MOF derivatives** |              |                      |                   |          |                        |           |             |                  |      |
| NC-CNT/CoP                   | Co-MOF       | 0.5 M H₂SO₄         | CC 1.5            | 350      | /                      | /         | N.A.        |                  | 46   |
| P-NSC/Ni₄Fe₅S₈               | NiFe-PBA     | 0.5 M H₂SO₄         | GCE 0.4           | ~500     | 72.1                   | 0.013     | /           | 10 000 CV cycles | 47   |
| **Noble metal-based MOF derivatives** |              |                      |                   |          |                        |           |             |                  |      |
| RuIrOₓ                      | ZIF-8        | 0.5 M H₂SO₄         | RDE 0.01          | 233      | 42                     | /         | /           | 3000 CV cycles  | 48   |
| Ir nanosheet                 | MIL-88A      | 0.5 M H₂SO₄         | GCE 0.285         | 254      | 72.5                   | 0.25 @ 330 mV | 1200 @ 320 mV | 50 h @ 100, 20, 10 mA cm⁻² | 49   |
| Ir/C                        | Ir@MOF-5     | 0.5 M H₂SO₄         | GCE 0.197         | 359      | 229                    | /         | 416 @ 300 mV | 5.6 h @ 10 mA cm⁻² | 50   |
| Mg-RuO₂                      | Mg-MOF-74    | 0.5 M H₂SO₄         | GCE /             | 228      | 48.66                  | /         | /           | 30 h @ 10 mA cm⁻² | 51   |
| Cu₀.₆Ru₀.₄O₂                 | MIL-101 (Cr) | 0.5 M H₂SO₄         | GCE 0.283         | 178      | 58                     | 0.15 @ 260 mV | /           | 10 h @ 10 mA cm⁻² | 52   |
| Mn-RuO₂                      | Mn-BTC       | 0.5 M H₂SO₄         | GCE 0.275         | 158      | 42.94                  | 0.391 @ 250 mV | 596.38 @ 270 mV | 10 h @ 10 mA cm⁻² | 53   |
| Cu₀.₈Ru₀.₂O₂                 | ZIF-67       | 0.5 M H₂SO₄         | GCE 0.283         | 169      | 49                     | /         | /           | 50 h @ 10 mA cm⁻² | 54   |
| Cu-RuO₂                      | Cu-BTC       | 0.5 M H₂SO₄         | GCE 0.275         | 188      | 43.96                  | 0.0528 @ 250 mV | /           | 8 h @ 10 mA cm⁻² | 55   |

(Continues)
| Catalyst                  | MOF involved       | Electrolyte  | Substrate | Loading (mg cm\(^{-2}\)) | \(\eta_10\) (mV) | Tafel slope (mV dec\(^{-1}\)) | TOF (s\(^{-1}\)) | MA (A g\(^{-1}\)) | Stability                      | Ref. |
|---------------------------|--------------------|--------------|-----------|---------------------------|-----------------|--------------------------------|-----------------|----------------|-------------------------------|------|
| Cu-RuO\(_2\)             | Cu-BTC (Cu-MOF)    | 0.5 M H\(_2\)SO\(_4\) | GCE       | 0.704                      | 201             | 55                             | /               | /              | 24 h @ 10 mA cm\(^{-2}\)     | 56   |
| Zn-RuO\(_2\)             | Zn-BTC             | 0.5 M H\(_2\)SO\(_4\) | GCE       | 0.275                      | 206             | 45.65                          | /               | /              | 30 h @ 10 mA cm\(^{-2}\)     | 57   |
| Ir\(_{0.06}\)Co\(_{2.94}\)O\(_4\) | ZIF-67             | 0.1 M HClO\(_4\) | Au electrode | 0.102                      | 292             | 45                             | 1.25 @ 300 mV | 251 @ 300 mV | 200 h @ 10 mA cm\(^{-2}\)     | 58   |
| Fe\(_3\)O\(_4\)/RuO\(_2\)/NEU-7 |                  | 0.5 M H\(_2\)SO\(_4\) | GCE       | 0.255                      | 450             | 305                            | /               | /              | 4 CV cycles (not stable)     | 59   |
| RuO\(_2\)/(Co,Mn)\(_3\)O\(_4\) | CoMn–PBA           | 0.5 M H\(_2\)SO\(_4\) | CC        | /                          | 270             | 77                             | /               | 366.5 @ 300 mV | 24 h @ 10 mA cm\(^{-2}\)     | 60   |
| Fe-IrO\(_2\)/\(\alpha\)-Fe\(_2\)O\(_3\) | Fe-MIL-101         | 0.1 M HClO\(_4\) | Ti plate | 0.2                        | 260             | 54                             | /               | ~680 @ 420 mV | 11.1 h @ 10 mA cm\(^{-2}\)    | 61   |
| RuO\(_2\)/Co\(_3\)O\(_4\)–RuCo@NC | ZIF-67             | 0.5 M H\(_2\)SO\(_4\) | GCE       | 0.35                       | 247             | 89                             | /               | /              | 8 h @ 10 mA cm\(^{-2}\)      | 62   |
| RuCo-RuCoO\(_2\)@NC      | ZIF-L-Co           | 0.5 M H\(_2\)SO\(_4\) | GCE       | 0.35                       | 228             | 76                             | 0.244 @ 300 mV | 933 @ 300 mV | 12 h @ 10 mA cm\(^{-2}\)     | 63   |
| Ni/RuO\(_2\)/C          | NiRu-MOF           | 0.5 M H\(_2\)SO\(_4\) | RDE       | 0.35                       | 211             | 46                             | 0.121 @ 250 mV | /              | 12 h @ 10 mA cm\(^{-2}\)     | 64   |
| RuIr@CoNC                | ZIF-67             | 0.5 M H\(_2\)SO\(_4\) | GCE       | 0.05\(^{b}\)              | 223             | 45                             | /               | 2041 @ 300 mV | 40 h @ 10 mA cm\(^{-2}\)     | 65   |
| Ir\(_3\)Ni\(_2\)/BMNC   | Zn-Co-ZIF          | 0.1 M HClO\(_4\) | GCE       | 0.424                      | 321             | 108.7                          | /               | 303 @ 350 mV | 11.1 h                    | 66   |
| Pt\(_{0.1}\)La\(_{0.1}\)-IrO\(_2\)@NC | ZIF-8              | 0.5 M H\(_2\)SO\(_4\) | CP        | 0.55                       | 205             | 50.9                           | 5.71 @ 280 mV | /              | 135 h @ 10 mA cm\(^{-2}\)    | 67   |
| Ce\(_{0.2}\)-IrO\(_2\)@NPC | ZIF-8              | 0.5 M H\(_2\)SO\(_4\) | CP        | 0.4                        | 224             | 55.9                           | 3.48 @ 300 mV | 6990 @ 300 mV | 100 h @ 10 mA cm\(^{-2}\)    | 68   |

(Continues)
| Catalyst                  | MOF involved | Electrolyte | Substrate | Loading (mg cm\(^{-2}\)) | \(\eta\) (mV) | Tafel slope (mV dec\(^{-1}\)) | TOF (s\(^{-1}\)) | MA (A g\(^{-1}\)) | Stability | Ref.  |
|--------------------------|--------------|-------------|-----------|--------------------------|--------------|-------------------------------|-----------------|-----------------|-----------|------|
| Sn-RuO\(_2@NPC\)        | ZIF-8        | 0.5 M H\(_2\)SO\(_4\) | CP        | 0.5                       | 178          | 60.6                          | /               | /               | 150 h @ 10 mA cm\(^{-2}\) | 69   |

State-of-the-art catalysts

| Catalyst                  | MOF involved | Electrolyte | Substrate | Loading (mg cm\(^{-2}\)) | \(\eta\) (mV) | Tafel slope (mV dec\(^{-1}\)) | TOF (s\(^{-1}\)) | MA (A g\(^{-1}\)) | Stability | Ref.  |
|--------------------------|--------------|-------------|-----------|--------------------------|--------------|-------------------------------|-----------------|-----------------|-----------|------|
| Ru\(_1–Pt\(_2Cu\)       | /            | 0.1 M HClO\(_4\) | GCE       | 0.00192\(^{\text{b}}\)   | 220          | /                             | /               | 6615 @ 280 mA cm\(^{-2}\) | 28 h @ 10 mA cm\(^{-2}\) | 20   |
| Ir–MnO\(_2\)             | /            | 0.5 M H\(_2\)SO\(_4\) | CP        | 4                        | 218          | 59.61                         | 7.7 @ 300 mV    | 786 @ 300 mV   | 650 h @ 10 mA cm\(^{-2}\) | 21   |
| IrO\(_x/SrIrO\(_3\)     | /            | 0.5 M H\(_2\)SO\(_4\) | SrTiO\(_3\) subtracts | /            | 270–290                  | ~40             | /               | /               | 30 h @ 10 mA cm\(^{-2}\) | 22   |
| SrCo\(_0.9Ir\(_0.1O\(_3–\delta\) | /            | 0.1 M HClO\(_4\) | GCE       | 0.255                     | ~295         | /                             | 2.56 ± 0.15 @ 270 mV | /               | 3 h @ 10 mA cm\(^{-2}\) | 23   |
| Ba\(_2PrIrO\(_6\)       | /            | 0.1 M HClO\(_4\) | Au electrode | 0.015                     | ~330         | 54±3                          | /               | /               | 1 h @ 10 mA cm\(^{-2}\) | 24   |
| CaCu\(_3Ru\(_2O\(_12\)  | /            | 0.5 M H\(_2\)SO\(_4\) | GCE       | 0.25                      | 171          | 40                            | 1942 @ 270 mV   | /               | 24 h @ 10 mA cm\(^{-2}\) | 25   |
| Y\(_2Ru\(_2O\(_7–\delta\) | /            | 0.1 M HClO\(_4\) | GCE       | 0.0255                    | 270 @ 1 mA cm\(^{-2}\) & oxide | 55                  | 0.13 @ 300 mV   | /               | 8 h @ 1 mA cm\(^{-2}\) & oxide | 26   |
| 3R-IrO\(_2\)            | /            | 0.1 M HClO\(_4\) | GCE/C     | 0.255                     | 188          | 52                            | 5.7 @ 270 mV    | 690.4 @ 270 mV | 511 h @ 10 mA cm\(^{-2}\) | 27   |
| GB-Ta\(_0.1Tm\(_0.1Ir\(_0.8O\(_2–\delta\) | /            | 0.5 M H\(_2\)SO\(_4\) | Au electrode | 0.041                     | 198          | 64                            | 3126 @ 266 mV   | 500 h @ 10 mA cm\(^{-2}\) | 28   |
| Co\(_3O\(_4/\text{CeO}_2\) | /            | 0.5 M H\(_2\)SO\(_4\) | CP        | /                        | 347          | /                             | /               | /               | 50 h @ 10 mA cm\(^{-2}\) | 29   |

Abbreviations: CC, carbon cloth; CP, carbon paper; GCE, glassy carbon electrode; RDE, rotating disk electrode.

\(^{a}\)Current density normalized by the mass of noble metals in the catalysts.

\(^{b}\)Loading based on the amount of Ru/Ir noble metals.

\(^{c}\)Assuming that all the Ni/Ru atoms are active sites.
ments. These observations again highlight the formidable challenge as well as the urgent need to develop MOF-based acidic OER catalysts with reduced use of noble metals.

4 RATIONAL DESIGN OF MOF-BASED ACIDIC OER CATALYSTS

In theory, the activity of an electrocatalyst can be improved by two ways. One is to increase the intrinsic activity of each catalytically active site by leveraging the electronic effect, and the other is to increase the number of the overall active sites (i.e., extrinsic activity) by utilizing the geometric effect. In this section, material design strategies that aim to develop improved MOF-based acidic OER catalysts are overviewed, spanning efforts from morphology tuning, compositional regulation, defect engineering, surface structure control, composite formation, to catalyst-support interaction. To bring about the best catalytic activity, a combination of multiple strategies may be adopted. Where applicable, efforts that address the catalyst stability are also included.

4.1 Tuning morphologies

One major advantage of MOF derivatives lies in their morphological characteristics inherited from or facilitated by the pristine MOFs, which often feature high surface area and porosity that could afford a large number of accessible active sites and thus lead to superior catalytic activity. Recently, Zhuang et al. developed a dispersing–etching–holing strategy to fabricate a three-dimensional (3D) open nano-netcage RuIrO$_x$ nanometric catalyst using ZIF-8 as the precursor (Figure 4A). In this approach, Ru$^{3+}$/Ir$^{4+}$ sources were first dispersed in ZIF-8 to allow for exchange with Zn$^{2+}$, which all underwent hydrolysis during solvothermal reaction leading to an etched internal ZIF-8 core. Subsequent annealing resulted in the formation of RuIrZnO$_x$ hollow nanoboxes, and an additional in-situ electrochemical etching removed the amphoteric ZnO from and hole the walls of the RuIrZnO$_x$ hollow nanobox, eventually yielding RuIrO$_x$ with a 3D open nano-netcage morphology. Based on theoretical calculation from surface area data, such nano-netcage morphology can afford an effective-surface-area ratio much higher than the nanoparticle structure (∼70% vs. 3–24%) (Figure 4B), thereby contributing to a significantly improved atomic utilization of Ru/Ir noble metals. As a result, the RuIrO$_x$ nano-netcage catalyst delivered exceptional OER activity in 0.5 M H$_2$SO$_4$, significantly higher than commercial RuO$_2$ and IrO$_2$ catalysts (with a reduction of $\eta_{10}$ by 159 and 200 mV, respectively) (Figure 4C). This work highlights the importance of developing MOF derivatives with unique morphologies for highly efficient acidic OER catalysis.

Over the years, loads of acidic OER catalysts with diverse morphologies, including hollow porous polyhedron, nanosheet, nanorod, and nano-netcages, have been obtained using MOFs either as a template or as a precursor. For example, an iron-based MOF, MIL-88A, was employed as a hard template to synthesize an Ir nanosheet catalyst, which exhibited higher acidic OER activity compared to an Ir nanoparticle catalyst prepared in the absence of the MIL-88A template. In general, the morphology of MOF-derived materials can be tuned through tailoring the synthesis method, for example, by altering the nature of MOF or modifying the pyrolysis conditions (e.g., temperature and atmosphere). However, research efforts that address the precise morphology tuning of MOF-based materials and its effect on acidic water oxidation are still lacking.

4.2 Regulating compositions

The acidic OER catalysis is directly related to the constituent elements of a catalyst. To regulate the chemical compositions, incorporating foreign elements into a parent lattice structure through elemental doping is one of the most used strategies. As proposed by Nocera et al., introducing a structural element into a catalytic element-containing parent oxide to form mixed oxides is a viable approach to decouple activity from stability in the acidic OER catalysis and to eventually obtain both active and stable catalysts. In the past years, there have been growing interest in developing non-noble metal (structural element)-doped Ru/Ir (catalytic element) oxides for acidic OER using MOFs as an excellent material synthesis platform. Various MOFs, including Mg-MOF-74, MIL-101 (Cr), Mn-BTC, ZIF-67 (Co), Cu-BTC, and Zn-BTC, have been applied as precursors to prepare RuO$_2$ oxides doped by the metals present in these MOFs (i.e., Mg, Cr, Mn, Co, Cu, and Zn, respectively). In a typical synthesis, Ru source is loaded into the pores of the target MOF, followed by annealing under air atmosphere to form an oxide solid solution, as exemplified by the Cr-doped Cr$_{0.3}$Ru$_{0.7}$O$_2$ (Figure 5A,B). The as-derived oxides can have large surface area and pore structures, depending on the annealing conditions, which also influence the crystallinity of the oxides. The doping amount can be controlled by varying the Ru loading to obtain optimum catalytic activity (Figure 5C), although there can be a doping limit due to the saturation adsorption limit of the MOF. The incorporation of alien elements can result in a profound change in the electronic structure of Ru and consequently boost the catalytic activity and stability (Figure 5D). As revealed by DFT calculations based on the
AEM mechanism on a Ru site, Cr-doping could lead to a reduction in the free energy change of the $^{\bullet}\text{O} \rightarrow ^{\bullet}\text{OOH}$ (i.e., M-O$_\text{ads}$ $\rightarrow$ M-OOH$_\text{ads}$) rate determining step (RDS) by 0.15 eV (Figure 5E,F). For other doped RuO$_2$ oxides, similar catalytic enhancements have been observed, although the fundamental origin as to how each dopant affects the Ru electronic structure may differ. 51,53–57 These studies suggest that by selecting the proper type of MOF precursors and by varying the noble metal loading amount, active and stable Ru-based acidic OER catalysts can be rationally designed.

By applying a similar synthesis approach but significantly reducing the noble metal loading, Shan et al. obtained an Ir-doped Co$_3$O$_4$ spinel oxide (Ir$_{0.06}$Co$_{2.94}$O$_4$) from ZIF-67 (Figure 6A).58 Unlike other doping cases, here Ir is preferentially accommodated into the octahedral site of the spinel framework in the form of single atoms, featuring a short-range order and a spatial correlation identical to the host lattice (Figure 6B,C). Such a strong interaction between Ir and Co$_3$O$_4$ enables excellent OER activity in 0.1 M HClO$_4$, much higher than the conventionally prepared single-atom Ir catalyst supported on Co$_3$O$_4$ (Ir SA@Co$_3$O$_4$), which suffers from a weak Ir–Co$_3$O$_4$ interaction (Figure 6D). Remarkably, Ir$_{0.06}$Co$_{2.94}$O$_4$ demonstrated significantly enhanced corrosion resistance in the long-term OER testing showing minimal metal dissolution over 200 h (Figure 6E,F), which is further evidenced by the absence of surface phase evolution or electronic structure change during in situ Raman and X-ray absorption near-edge structure (XANES) measurements. More importantly, HAADF high-resolution scanning transmission electron microscopy (HAADF-HRSTEM) images taken before and after OER suggest that the short-range correlation of Ir sites was well preserved (Figure 6G,H). These results highlight the great potential of utilizing MOFs to integrate correlated noble-metal sites into non-noble metal oxide frameworks for efficient and robust OER catalysis in acids.

4.3 Engineering defects

Defect engineering is considered an effective way for tailoring electronic structure and optimizing intrinsic activity of electrocatalysts. 91 Importantly, oxygen defects in the form of oxygen vacancy in complex oxides (e.g., perovskites and pyrochlores) have been reported to promote the acidic OER catalysis. 92,93 In a broad sense, the presence of oxygen vacancy is deemed important in dictating the OER reaction pathways, in particular for the alkaline OER catalysis. 94,95 Recently, Tian et al. incorporated lower-
FIGURE 5 Cr-doped Cr$_{0.6}$Ru$_{0.4}$O$_2$ oxide solid solution for acidic OER catalysis. (A) Schematic depicting the preparation of Cr$_{0.6}$Ru$_{0.4}$O$_2$ through annealing of Ru-exchanged MIL-101 (Cr). (B) High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image and the corresponding energy-dispersive X-ray spectroscopy (EDS) elemental mapping showing the distribution of Cr, Ru, and O. (C) OER polarization curves for Cr-doped RuO$_2$ oxides with various Cr-doping amounts in 0.5 M H$_2$SO$_4$. (D) TOF values of Cr$_{0.6}$Ru$_{0.4}$O$_2$ and RuO$_2$ at the first and 10 000th cycle. (E) Schematic showing the four-step OER process on a five-coordinated surface Ru site. (F) Gibbs free-energy diagrams for RuO$_2$ and Cr$_{0.6}$Ru$_{0.4}$O$_2$ (based on a simulation model of Cr$_3$Ru$_3$O$_{16}$). Reproduced with permission. Copyright 2019, The Authors
**Figure 6** Ir$_{0.06}$Co$_{2.94}$O$_4$ with short-range ordered, spatially correlated Ir single-atom sites for acidic OER catalysis. (A) Schematic depicting the synthesis of Ir$_{0.06}$Co$_{2.94}$O$_4$. (B) Structural model of Ir-substituted Co$_3$O$_4$ in a polyhedral representation with Ir taking the octahedral site. (C) HAADF-HRSTEM image of Ir$_{0.06}$Co$_{2.94}$O$_4$. (D) OER polarization curves for Ir$_{0.06}$Co$_{2.94}$O$_4$, Ir SA@Co$_3$O$_4$ (single-atom Ir catalyst supported on Co$_3$O$_4$), Co$_3$O$_4$, and commercial IrO$_2$ in 0.1 M HClO$_4$. (E) Chronopotentiometric stability test of Ir$_{0.06}$Co$_{2.94}$O$_4$ at 10 mA cm$^{-2}$ for 200 h. Inset: CV data of Ir$_{0.06}$Co$_{2.94}$O$_4$ and Co$_3$O$_4$. (F) The dissolution of Co and Ir ions measured for Ir$_{0.06}$Co$_{2.94}$O$_4$ and Co$_3$O$_4$ in electrolyte by inductively coupled plasma mass spectrometry. (G, H) Mass fraction histograms of identified projected clusters with different numbers of correlated Ir dopant sites in the Ir$_{0.06}$Co$_{2.94}$O$_4$ catalyst (G) before and (H) after the acidic OER. Insets: distribution maps for correlated Ir sites on HRSTEM images taken in the $<233>$ direction. Reproduced with permission. Copyright 2021, American Chemical Society.

Valence Co dopants into the RuO$_2$ lattice by annealing a Ru-exchanged ZIF-67 precursor, which gave rise to the formation of abundant oxygen vacancies due to the need to maintain the overall charge balance (Figure 7A,B). Compared to the RuO$_2$ parent oxide, the optimized Co-doped sample, Co$_{0.11}$Ru$_{0.89}$O$_2$ (350) (here 350 denotes the annealing temperature of 350°C), demonstrated significant enhancements in both activity and stability for the acidic OER (Figure 7C). DFT calculations suggest that the OER proceeds preferentially via the LOM pathway on the vacant O site, showing a 0.24 eV lower energy barrier compared to the AEM pathway on the five-coordinated Ru site (Figure 7D,E). The authors also proposed that oxygen vacancy formation may effectively avoid the overoxidation of Ru to the soluble RuO$_4$, hence, rendering enhanced stability.
While oxygen vacancy formation may be beneficial to promoting acidic OER catalysis on MOF-based materials, a quantitative correlation between the vacancy content and activity increase remains to be explored. In addition, the catalytic stability for oxygen-deficient materials that utilize the LOM mechanism could present another challenge. In a recent report by Hao et al., both tungsten(VI) and erbium(III) dopants were introduced into the RuO$_2$ lattice (to form W$_{0.2}$Er$_{0.1}$Ru$_{0.7}$O$_{2-\delta}$) to inhibit the formation of oxygen vacancy and the participation of the LOM mechanism, thus suppressing the Ru dissolution rate and eventually achieving more acid-stable OER catalysts. Therefore, caution should be exercised when designing oxygen-deficient catalysts from MOF materials, and the effect of oxygen vacancy on the acidic OER catalysis should be assessed in a case-by-case manner.

### 4.4 Controlling surface structures

In principle, the electrocatalytic reactions take place in the near surface regions of a catalyst. Therefore, manipulating catalyst surface structures (e.g., surface atomic configuration and arrangement) holds key to the electrocatalytic performance. Su et al. reported that annealing Ru-exchanged Cu-BTC at a relatively low temperature of 300°C could yield Cu-doped RuO$_2$ nanocrystals with high surface exposure of high-index facets, which significantly boosted the acidic OER catalysis. The appearance of such high-index facets was found to be highly dependent on the annealing temperature. Elevating the annealing temperatures caused continued growth of nanocrystals and diminishing of high-index facets. Designing advanced synthetic approaches that can achieve controlled exposure of surface facets from MOF materials is highly desirable but remains quite challenging.

More recently, Xu and coworkers synthesized ZIF-67 derived cobalt–nitrogen–carbon (CoNC) supported RuIr nanocrystals with enriched surface atomic steps (RuIr@CoNC) (Figure 8A–D). The appearance of a large amount of surface atomic steps may be associated with the strong interaction between the Ru$^{3+}$/Ir$^{3+}$ species and the unsaturated pyrrolic-N groups present in the CoNC support. These surface atomic steps allow for greater exposure...
FIGURE 8 RuIr@CoNC with abundant surface atomic steps for acidic OER catalysis. (A, B) TEM images taken at different magnifications. Inset of (B): size distribution of RuIr nanocrystals. (C) HRTEM image. (D) HAADF-STEM image. Atomic steps are indicated by pink dotted lines. (E) OER polarization curves for RuIr@CoNC and other control catalysts in 0.5 M H₂SO₄. Mass activity is normalized by the loading of noble metal (all at 50 μg cm⁻²). (F) Electrochemically active surface area (ECSA) and the ECSA-normalized specific activity of RuIr@CoNC and other control catalysts in 0.5 M H₂SO₄. (G) Schematic illustrating the four-electron AEM reaction pathways for the acidic OER on the Ru₀.₅Ir₀.₅O₂ (120) step surface. Green, blue, red, and white spheres represent Ru, Ir, O, and H atoms, respectively. (H) Gibbs free-energy diagrams on the flat and step surfaces, calculated at 1.23 V. Reproduced with permission. Copyright 2021, American Chemical Society.

of catalytically active sites, which contributed to better utilization of noble metals and improved mass activity in acidic OER (Figure 8E). More importantly, the presence of abundant atomic steps optimizes the adsorption of reaction intermediates, leading to enhanced intrinsic OER activity (Figure 8F), as supported by comparison studies based on DFT calculations using flat and step surface models (Figure 8G,H). This work highlights how MOF-derived support materials can guide the synthesis of acidic OER-active components with high exposure of surface atomic surfaces.

4.5 Constructing composites

Constructing composite materials that contain MOFs or MOF derivatives can often lead to changes in the electrical or electronic properties, and is, therefore, considered an effective approach to promote the electrocatalytic OER performance in acidic electrolytes. For pristine MOFs, conductive agents (e.g., CB, FTO, and ATO) have been introduced, through either physical mixing or chemical blending, to compensate for any conductivity limitations and contribute to better acidic OER catalysis.⁴¹–⁴⁴ Beyond that, other types of MOF composites are largely underexplored. Given the diversity of MOF composites,⁹⁸ there remains much to be researched to testify their efficacy for catalyzing the acidic OER.

Recently, more efforts have been devoted to acquiring MOF-derived composite materials as acidic OER catalysts. There are multiple ways to construct composite catalysts using MOFs as precursors. One most straightforward way is to directly pyrolyze MOFs that contain multiple metal elements (e.g., bimetallic MOFs). For example, the direct pyrolysis of [Fe₃Ru₂(terpy)₂(PF₆)₂]₉ (NEU-7), an MOF comprising an Fe metal node and a Ru metalloligand,⁵⁹ resulted in the formation of a composite consisting of the corresponding oxides of these two metals (Fe₃O₄/RuO₂@NEU-7). This composite, however, exhibited moderate activity and poor stability for the OER in 0.5 M H₂SO₄ due to the catalytic incapability of Fe₃O₄, suggesting the importance of selecting an active and stable component for achieving high-performance composite catalysts. In another work, the annealing of a Ru-exchanged CoMn–PBA led to the formation of a RuO₂/(Co,Mn)₂O₄ composite (Figure 9A).⁶⁰ It should be noted that in these two examples, the formation of composite phases instead of a single-phase solid solution is likely associated with the intrinsic lattice mismatch of the different oxide phases. It is further found that adjusting the component-phase composition could bring about enhanced acidic OER activity. As depicted in Figure 9B,C, Mn-doping in the
RuO$_2$/((Co,Mn)$_3$O$_4$) composite modified the d orbital of Ru, leading to weakened oxygen adsorption and facilitating the formation of *OOH (or M-OOH$_{ads}$) (i.e., the RDS).

Another way to obtain composite catalysts from MOFs is through more complex chemical syntheses that exploit the properties of MOFs. For instance, by taking advantage of the self-dissolving property of an iron-based MOF (Fe-MIL-101), Huang and coauthors reported the hydrothermal synthesis of a Fe-IrO$_x$@α-Fe$_2$O$_3$ composite. 61 In the hydrothermal process, Fe-MIL-101 underwent an inward collapse to release Fe$^{3+}$ species, which instantaneously formed the α-Fe$_2$O$_3$ substrate, with a small proportion coprecipitated with the Ir$^{4+}$ introduced to assemble into Fe-doped IrO$_2$ (Fe-IrO$_2$). Electrochemical measurements showed that Fe-IrO$_x$@α-Fe$_2$O$_3$ exhibited superior acidic OER activity compared to control samples synthesized in the absence of Fe-MIL-101, highlighting the important role played by MOF materials in achieving a fine assembly of
the composite phases with high catalytic performance. The Fe-IrO$_2$@α-Fe$_2$O$_3$ catalyst may suffer from cation leaching during prolonged OER testing in acids, due to the thermodynamically unstable nature of the α-Fe$_2$O$_3$ substrate, again signifying the importance of choosing MOFs containing acid-stable elements for designing composite catalysts.

Post-treating MOF derivatives represents another route to develop composite catalysts. For example, Fan et al. first pyrolyzed ZIF-67 to form a porous N-doped carbon matrix embedding uniformly distributed Co sites (Co@NC), and then combined a galvanic replacement reaction (with Ru$^{3+}$ to obtain RuCo alloys incorporated in the carbon framework [RuCo@NC]) with a subsequent oxidative annealing treatment to form a RuO$_2$/Co$_3$O$_4$–RuCo@NC composite (Figure 9D). The as-obtained composite feature a wealth of metal–metal oxide interfaces (Figure 9E–H), which created the Mott–Schottky effect favoring both electronic interaction and charge transfer (Figure 9I), leading to significantly improved OER activity and stability in acids. The OER activity could be further optimized by tuning the weight fractions of the component phases by adjusting the amount of Ru$^{3+}$ precursor.

Above works demonstrate that forming MOF-based composites could promote the acidic OER catalysis owing to the synergy between different phase components. However, a detailed understanding of this so-called synergistic effect is not known. One way to address this is through controllable interface engineering. Taking into consideration the unique properties of MOF materials, delicate material design should be developed to allow for precise control over the component phases and their interfaces in the composite catalysts.

4.6 Leveraging the catalyst–support interaction

In addition to abovementioned efforts in modifying the catalyst properties, leveraging the catalyst–support interaction represents another important means to improve the electrocatalytic OER under acidic conditions. An earlier research found that detaching CoFe PBA from the FTO substrate significantly compromised the acidic OER activity in a pH 2 solution, suggesting the critical role of the CoFe–FTO interface. On the other hand, conventional noble metal-based catalysts (e.g., Ir/C and Ru/C) have largely relied on conductive carbon (e.g., CB and carbon nanotube) as the support material, which may have an inhomogeneous dispersion of catalysts and a relatively weak catalyst–carbon interaction, giving rise to catalyst aggregation and/or migration under electro-oxidation conditions (especially in strongly acidic environments) that eventually result in losses of catalytic species and/or active surface area. In this regard, N-doped porous carbon derived from various MOF precursors has emerged as a distinguished support that can firmly immobilize catalysts on its surface in a homogeneous fashion. Notably, it was found that the presence and amount of the surface N functional groups in the CoNC support plays a key role in stably anchoring the RuIr nanocrystals. As shown in Figure 8E,F, the superior acidic OER activity of RuIr@CoNC clearly showcases the advantage of the CoNC support over the XC-72 support, one of the most commonly used carbon supports in commercial catalysts. In addition, mass production of the CoNC support has been demonstrated on a gram scale while not affecting the acidic OER performance. Despite these advances, more systematic investigations are still required to obtain an in-depth, atomic-level understanding of the catalyst–support interaction in order to develop better MOF-based acidic OER catalysts.

5 INTEGRATION OF MOF-BASED ACIDIC OER CATALYSTS IN PEM WATER ELECTROLYZERS

While quite a number of MOF-based candidates have demonstrated high efficiency in catalyzing the acidic OER, their integration into a PEM water electrolyzer at relevant testing conditions is rarely reported. Galán-Mascarós and colleagues investigated the cell performance of a CoFe PBA (CoHFe) in a PEM water electrolyzer using Nafion® 115 membrane at 80°C. CoHFe was interfaced with ATO to compensate for its low electronic conductivity, and the acidic OER activity was optimized at a CoHFe proportion of 17 wt% (denoted by ATO@17% CoHFe). Interestingly, ATO@17% CoHFe achieved current densities on the order of 0.05–0.10 A cm$^{-2}$ at a cell voltage of 2 V, which was well maintained over a continuous testing for 22 h (Figure 10). At cell voltages greater than 2 V, the leaching of antimony and tin became a major problem, causing a disruption of the conductive network and consequently the loss of catalytic efficiency.

Although these initial results may appear promising for the utilization of PBA anode catalyst in PEM water electrolyzers, the cell performance is too low to compare with the state-of-the-art catalysts based on Ir-Ru oxides (Table 2). This huge gap in cell performance necessitates the need to develop more active MOF-based catalysts in order to deliver a higher current density, in particular at moderate cell voltages of 1.6–1.9 V. Also importantly, the previously developed MOF-based catalysts with excellent half-cell OER performance should be employed for operation in full-cell PEM devices to examine their catalytic behavior under realistic conditions.
FIGURE 10  Integration of the ATO@17% CoHFe catalyst in a PEM water electrolyzer. (A) Polarization curves before and after a potentiostatic control at 2 V for 22 h. (B) Current versus time during the potentiostatic control at 2 V. Reproduced with permission.\(^{43}\) Copyright 2018, Royal Society of Chemistry

| Anode          | Cathode             | Membrane | Temperature (°C) | Current density (A cm\(^{-2}\)) | Ref.  |
|----------------|---------------------|----------|------------------|---------------------------------|-------|
| ATO@17% CoHFe (3 mg cm\(^{-2}\)) | Pt/C (0.5 mgPt cm\(^{-2}\)) | Nafion\(^{5}\) 115 | 80 | 0.05–0.10 @ 2 V | 43    |
| GB-Ta\(_0\)\(_2\)Tm\(_{0.1}\)Ir\(_{0.8}\)O\(_2\)–δ (0.2 mg cm\(^{-2}\)) | 20 wt% Pt/C (0.2 mg cm\(^{-2}\)) | Nafion\(^{5}\) 117 | 50 | 1.00 @ 1.766 V | 28    |
| Ir\(_{0.2}\)Ru\(_{0.8}\)O\(_{2}\) (1.5 mg cm\(^{-2}\)) | Pt/C (0.5 mgPt cm\(^{-2}\)) | Nafion\(^{5}\) 115 | 90 | 3.20 @ 1.85 V | 101   |
| Ir\(_{0.2}\)Ru\(_{0.8}\)O\(_{2}\) (1.5 mg cm\(^{-2}\)) | Pt/C (0.5 mgPt cm\(^{-2}\)) | Nafion\(^{5}\) 1035 | 80 | 1.00 @ 1.622 V | 102   |

### 6  | CONCLUSION AND PERSPECTIVES

PEM water electrolysis represents one of the most promising ways to produce green hydrogen, yet its efficiency is hampered by the slow OER kinetics under acidic environments. In this review, we have summarized the very recent achievements of MOF-based materials for catalyzing the acidic OER. A thorough overview of the use of pristine MOFs and their derivatives for the acidic OER is provided, and a comparison made with some of the state-of-the-art catalysts suggests the great potential of these MOF-based materials as low-cost, efficient alternatives. Of importance, diverse material design strategies centering on tuning the morphology, composition, defect, surface structure, and support of MOF-based materials and their composites are highlighted, which aims to serve as guidelines for the development of better acidic OER catalysts based on MOF materials. The applicability of MOF-based materials in PEM devices, although rare, is also discussed. Despite the progress made, there remains much to be done to realize green hydrogen production using PEM technologies and MOF-based catalysts. To pursue this goal, we present some of the most interesting research directions as follows.

#### 6.1 Standardizing performance reporting practices

Rigorous data reporting has long been a scientific pursuit. As mentioned earlier, the reporting of electrochemical data for the acidic OER can vary across different research groups (Table 1). Considering that MOF-based acidic OER catalysis is still at its infancy, it is important that standardized reporting practices be observed so as to enable better comparison and guide the development of this research field. For the assessment of catalytic activity, it is encouraging to see that in addition to simply reporting apparent activity numbers (e.g., \(\eta_{10}\)), more and more researchers begin to report specific activity measures (e.g., TOF) to reveal the catalysts’ true activity, as well as mass activity metrics (e.g., currents normalized to the noble metal mass) to evaluate the catalysts’ economic viability. Still, caution should be exercised in quantifying the number of true active sites or the amount of noble metals in the catalysts. As for analyzing catalyst stability, apart from comparing the duration for electrochemical measurements (e.g., chronopotentiometry), the adoption of other metrics, such as activity-stability factor\(^{103}\) and stability number...
(S-number), should be encouraged. In particular, S-number, defined as the ratio between the amount of oxygen evolved and the amount of noble metals dissolved, is independent of surface area, loading amount, or active sites, and has thus been recognized by the broader research community as a convenient, reasonable, and reliable factor for stability assessment. As for performance evaluation in PEM full cells, although testing and reporting of rigor is still lacking due to limited research activities in this area, practices that can allow fair comparison with publications are suggested to be employed.

6.2 Developing new catalyst materials

Given the currently limited number of MOFs studied, more research efforts should be devoted to exploring a wider range of MOF materials for the acidic OER. Some promising candidates include noble-metal containing MOFs, multimetallic MOFs (e.g., bimetallic, trimetallic, and tetrametallic MOFs), and MOF composites. Recently, there is increasing interest in developing multimetallic compound catalysts; the incorporation of other earth-abundant elements could shift the noble metal usage while modifying the noble metal electronic structure and hence catalytic performance. MOF candidates mentioned above are known to accommodate a range of metals in their matrix in a homogenous way, and are, therefore, highly suitable platforms for synthesizing multimetallic compound catalysts. To further increase the atomic utilization, single-atom catalysts based on MOFs should also be developed. In addition, noble metal-free catalysts derived from MOFs should be explored, although challenges in improving both activity and stability persist. To aid the development of these potential catalysts, recent insights from high-throughput theoretical calculations may be useful to the selection of catalytically active and acid-stable elements or structures. Of equal importance, novel synthesis methods other than pyrolysis should be developed and implemented to obtain MOF-based catalysts.

6.3 Elucidating reaction mechanisms

To improve the acidic OER catalysis also requires a better understanding of its reaction mechanisms. However, under the corrosive and oxidative conditions of the acidic OER, catalysts surfaces are prone to experience dynamic changes. The accurate detection of these structural evolutions is a prerequisite for identifying the active sites involved, but is largely limited by the temporal and spatial resolution of the current characterization techniques, causing difficulties in further exploring the reaction mechanisms. To address this, in situ/operando characterizations (e.g., XANES and Raman) are powerful tools, although currently they are relatively less explored in understanding the acidic OER process on MOF-based catalysts.

In addition, the structural information gained from these in situ/operando measurements can be integrated with theoretical calculations (e.g., DFT) to establish combined understanding from both experiments and theory. Another research direction of interest is to explore emerging reaction mechanisms, such as the LOM. Currently, a large majority of the research focuses solely on the AEM mechanism to design MOF-based catalysts, which could suffer from activity limitations due to the scaling relationship. Therefore, investigations into alternative reaction pathways that can bypass the limitations of the AEM mechanism should be encouraged. In this respect, electrochemical methodologies, such as online electrochemical mass spectrometry, could be another useful means to detect the OER intermediates/products and to gain insights into the reaction mechanism.

6.4 Evaluating practical use

Of all the MOF-based acidic OER catalysts reported to date, only one candidate was evaluated for use in practical PEM water electrolyzers, which exhibited performance much lower than the state-of-the-art Ir-Ru oxide catalysts (Table 2). Therefore, part of the future research efforts should be directed to the testing of some of the most promising candidates obtained in half-cell conditions. In this transition, essential engineering approaches need to be applied to bridge any potential gaps between these two testing scenarios (due to major differences in testing conditions and electrode design). The operational stability of MOF-based catalysts at elevated temperatures (e.g., 50–90°C) may present as a primary issue. Electrode design, in particular for the membrane electrode assembly, could be another challenge for PEM devices. Notably, MOF-based catalysts have the advantage in offering a porous electrode architecture, which could facilitate mass transport during the OER process in PEM devices. To conclude, there is a long way to go for realizing operational PEM water electrolyzers based on MOF-related acidic OER catalysts.

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CONFLICT OF INTEREST
The authors declare no conflict of interest.

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