METAL-ORGANIC FRAMEWORKS AND DERIVED MATERIALS FOR FUTURISTIC ENERGY APPLICATION: OXYGEN EVOLUTION REACTIONS

Abstract

Metal-organic frameworks (MOFs) are an emerging class of porous crystalline materials, synthesized by combining organic linkers and secondary building blocks. Their remarkable designs and flexibility facilitate functional linkers and engineering synergies between the metal nodes, making them appropriate platforms for an extensive variety of applications. The high surface area, controllable porosity, and good stability make them promising materials. The oxygen evolution reaction is the important half-cell reaction that plays a key role in energy conversion and storage devices such as water electrolyzers, regenerative fuel cells, and rechargeable metal-air batteries. The main obstacle in the OER is the sluggish kinetics, the four-electron transfer process requires high overpotential for OER. The development of sophisticated electrocatalysts with high activity and stability based on non-noble metal elements remains a great challenge.

Keywords: Metal-organic frameworks, Industrial applications, electrocatalysts, Metals, Water splitting

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I. INTRODUCTION

Metal-organic frameworks are newly discovered crystalline and highly porous solid materials having various chemical and physical properties[1], many research communities have grabbed immense attention due to achieving a great variety of aesthetically fascinating structures that could be more interesting for extensive applications in many areas related to high porous materials, including separation, catalysis, storage, drug delivery, electrocatalysts, which completely rely on the pore size, shape or morphology as well as the host-guest interplays between them[2]. MOFs are highly porous and crystalline materials, the inorganic secondary building units (SBU), metal ions, and organic ligands or polydentate organic ligands could be utilized to construct excellent network structures, much abundant diversity and flexibility in the structure and composition of MOFs and, can be transmuted from angstroms to nanometers by controlling the length of bi and multi-pedal rigid ligands and different metal ions, made up valuable and remarkable material for various applications[3,4]. MOFs exhibited a huge variety of uniformly distributed metal sites or complexes in a highly porous structure of organic ligands, due to their higher porosity (up to 90% free volume), superior internal pores, or ultra-high surface areas. MOFs possess micro and mesoporous materials and ultrahigh surface areas of 10,000 m^2/g, which is more of zeolites and activated carbons, measured by Brunauer−Emmett−Teller (BET)[5]. To study on the synthetic design or construction of MOFs and their various applications have been pioneered by groups including, Yaghi[6], Moore[7], Robson[8], Kitagawa[9], and Fé rey[10], in 1990, near about more than 20,000 MOFs have been reported and some MOFs are commercially producing in tons' scale by BASF, available at Sigma-Aldrich, MOF technologies and strem Chemicals. The MOFs HKUST – 1, Fe-BTC, MIL-53, and ZIF-8 are most extensively used which plays a vital role in gas storage[11], chemical sensing[12], drug delivery, proton conductivity, catalysis[13] chiller[14], and energy conversion. With MOF-74, the mixed-metal approach was used to create a MOF with two distinct metal nodes for future adsorption chiller applications. During synthesis, the reasonably priced Zn salt was used to partially replace the Ni salt precursor. By using the less expensive Zn salt instead of the more expensive Ni salt, the bimetallic MOF-74 was demonstrated to have effective H2O adsorption capability, greatly reducing the material costs of industrial scale synthesis/applications, and in industrial applications[15] such as textile industries, oleo-chemicals, transportation, food packaging, all electric automobile prototypes and respiratory systems.

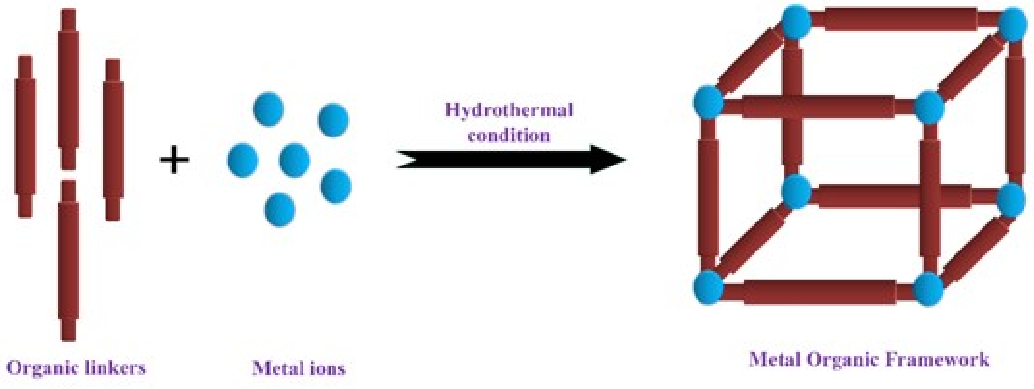

Figure 1: Metal Organic Framework

In the past decades, enormous efforts have been made to synthesis new MOF structures and explore their variety of applications in sustainable energy[14]. Nevertheless, MOFs show drawbacks like low conductivity and chemical stability that obstruct their use in large-scale applications with full potential. In order to achieve appropriate and accurate applications of MOFs, it is desirable to introduce new functionality to increase further the properties such as conductivity, chemical stability, and so on. The MOFs combine with various functional materials which mitigate the deficiency of both the components and fortunately enhance the active performance. The investigation of MOF composites furnishes new synthesis protocols for highly active performance with well-sophisticated architecture composite materials[16]. One MOF is combined with one or more functional materials to form the MOF composites materials, including, graphene, carbon nanotubes (CNTs), metal nanoparticles (NPs), polyoxometalates (POMs), quantum dots (QDs), polymers, and biomolecules, can be effectively combined and therefore, to improve the active performance of composite materials, new physical and chemical qualities should be developed[17]. The synergistic coupling of MOF with other functional materials improves the performance of MOF composite materials, making them ideal for a variety of applications. To achieve appropriate MOF composite materials by utilizing existing literature on porous crystals. MOFs have good flexibility, high porosity with uniform crystallinity, and functional materials having various kinds of unique properties like catalytic, magnetic, optical, and electrical conductivity, after combining make them superior active composite materials for various applications

II. SYNTHESIS

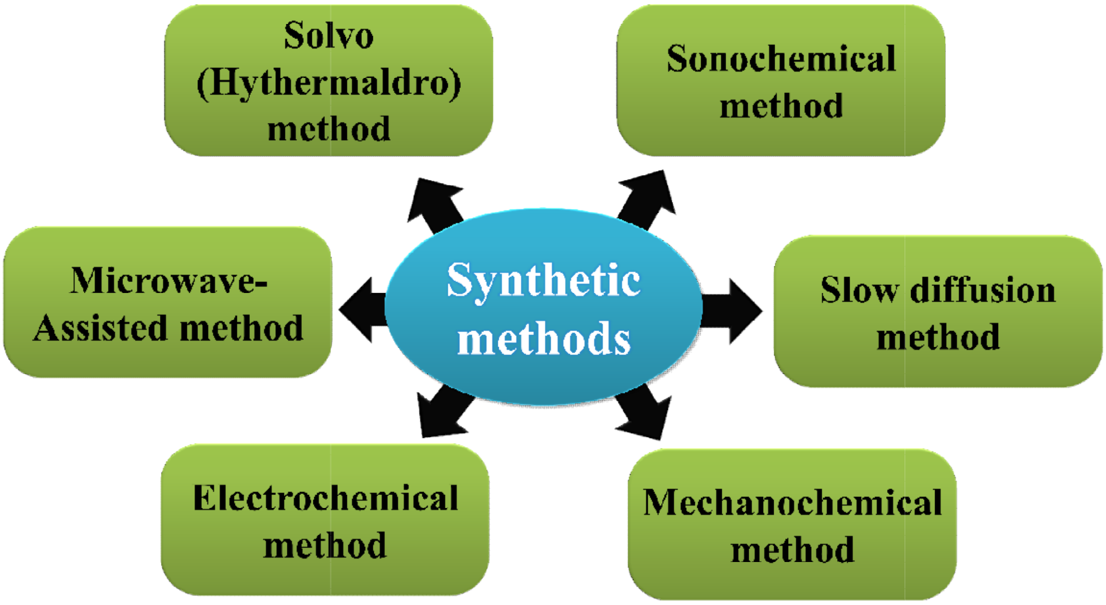

Figure 2: Synthetic methods used to obtain MOFs.

Metal ions or clusters are combined with organic ligands during the creation of metal-organic frameworks (MOFs), which result in highly organized, porous, and crystalline structures. (Figure 1). MOFs have received a lot of attention in a number of disciplines because of their flexible characteristics and diverse application possibilities. Selecting suitable metal ions or clusters, as well as organic ligands, to create the required MOF structure with the desired attributes[18,19]. The final structure and properties of the MOF will depend on the metal ion and ligand that are selected. There are various known methods[20] to synthesizing MOFs such as solvothermal or hydrothermal synthesis, slow diffusion synthesis, Microwave-Assisted synthesis, Electrochemical synthesis, Mechanochemical synthesis, Sonochemical synthesis etc. (Figure 2). These methods are less expensive, rapid, high yield and good yield cleaner products[21,22].

The general steps for synthesizing MOFs are as follows:

1. **Solvo(Hydro)thermal Method:** The most common approach to MOF synthesis is the solvothermal method. In this method, the metal ions and organic ligands are mixed together in a solvent at an elevated temperature in a sealed container (autoclave) to promote the formation of the MOF crystals. The choice of solvent is crucial as it affects the formation and growth of MOF crystals. The reactions are conducted in Teflon-lined autoclaves utilizing polar solvents at temperatures ranging from 100 to 400 ^{0}C, with lengthy reaction durations of hours to occasionally days. The temperature of the reaction can be raised to promote simple bond formation, suitable crystallization, and the use of kinetically inert metal ions. The shape of the crystal structure may also benefit from the higher temperature, and a longer reaction time may result in a better end product composition. The cooling rate of reaction must be very slow; which notable affect the crystal growing process. Most frequently solvents are used such as ethanol, methanol, water, acetone, dimethylformamide (DMF), diethylformamide (DEF), acetonitrile, and their mixtures. In the solvo(hydro)thermal reaction conditions, the starting reagent goes through surprising chemical transformations that are not conceivable under straightforward, milder synthetic pathways, which results in the in-situ creation of novel ligands.

2. **Slow Diffusion Method:** Another method involves slow diffusion, where a metal salt solution is layered on top of a solution containing the organic ligand. Slow mixing allows for controlled nucleation and crystal growth, resulting in well-defined MOF structures. This technique works at room temperature without the usage of an energy source, using low boiling point liquids to speed up the process. At the point of interface layer's crystals are formed, the precipitate solution separated into layers during slow diffusion. The slow diffusion method is typically employed with partially soluble materials. The advantage of this method is that low cost and without heat energy crystals are formed.

3. **Microwave-Assisted Synthesis:** Microwave-Assisted Synthesis have been depending on the reaction between electromagnetic waves with a movable electric charge. In an electromagnetic and oscillating field, the polar portion of the solution attempts to self-orient, which causes the molecules to permanently change their alignment. The collision between the molecules will take place by using the appropriate frequency, leading to an enhancement in the kinetic energy of the system. Thus, homogeneous and high heating rate is possible during the reaction. Microwave irradiation can accelerate the MOF synthesis process, reducing reaction times and improving the purity and crystallinity of the resulting MOF.

4. **Sonochemical Method:** Sonochemistry branch of research deals with ultrasonic waves and the chemical transformation of molecules via high ultrasonic radiations. When the reaction solution is exposed to ultrasonic radiation, bubbles form and hot spots with high pressure and temperatures are produced, which promote chemical reactions and the quick production of crystals[23]. Ultrasonic waves can assist in the formation of MOFs by promoting mixing and enhancing mass transfer, leading to faster and more efficient synthesis.

5. **Mechanochemical Synthesis:** In mechanochemical synthesis, MOFs can be formed by grinding the metal salts and organic ligands together in the absence of solvent. This technique is gaining popularity as it is environmentally friendly and can lead to the formation of new MOF structures. In 2006 first MOF was reported using this method. There are multiple reasons to synthesize MOF in this way as environmental issues. Reactions are carried out in the absence of organic solvent at room temperature within the short time range of 10 to 60 minutes, and giving a large yield of product is very advantageous. At some times metal oxides are used as a starting material except metal salts, resulting in the formation of water as by product.

6. **Electrochemical Synthesis:** Electrochemical synthesis of Metal-Organic Frameworks (MOFs) is an innovative approach to fabricating these porous materials, which are composed of metal ions or clusters linked by organic ligands. Electrochemical synthesis, offers several unique advantages such as fine-tuned control over reaction parameters such as current density, potential, and electrode composition, which can influence the size, shape, and crystallinity of MOFs, and the direct deposition of MOFs onto conductive substrates. This can be advantageous for applications such as catalysis, sensing, and energy storage, require less solvent compared to traditional methods, making them more environmentally friendly and efficient. The electrochemical synthesis of MOFs generally involves the use of a conductive electrode, often made of materials like metal or conductive polymers, immersed in a solution containing metal ions and organic ligands. Applying a potential or current to the electrode initiates the formation of MOFs through reduction or coordination reactions between the metal ions and ligands. The growth of the MOF crystals on the electrode surface can be controlled by adjusting the electrochemical parameters. Researchers continue to explore and develop new electrochemical methods to create MOFs with enhanced properties and functionality for various technological applications.

It's important to note that the specific synthesis method and conditions can vary depending on the chosen metal ion, organic ligand, and intended application of the MOF.

III. ELECTROCATALYTIC APPLICATION: OXYGEN EVOLUTION REACTIONS (OER)

Develop sustainable energy storage and conversion techniques for the generation of renewable energy to reduce environmental pollution and the potential for a shortage of energy. The electrochemical water splitting is an efficient method, that offers a renewable, clean, less expensive process, in which water is splitting into oxygen and hydrogen ($H_2O \rightarrow H_2 + \frac{1}{2}O_2$) has an important and promising strategy to convert renewable light and electrical energy into chemical fuel as a renewable energy[24]. The fuel of the future, hydrogen gas has the highest mass-energy density and burns cleanly in the air. The anodic oxygen evolution reaction (OER), an obstacle one-half reaction involving the sluggish kinetics of the four-electron transfer, significantly impairs efficient water splitting. Therefore, it is important to explore a highly efficient and cost effective OER electrocatalyst is a critical requirement to diminish the activation barriers, and accelerate the reaction, Consequently, enhances the efficiency of energy conversion. This chapter focus particular attention is dedicated to oxygen evolution reaction, which occurs at anode, and requires a more potential above the minimum set of thermodynamics.

1. **Thermodynamics of Water Splitting:** The thermodynamic potential for the electrochemically water splitting, $2H_2O(l)$ - $2H_2(g) + O_2(g)$, is $E_o = -1.23$ V. This overall reaction involves two half reactions, relying on the pH of electrolyte the reaction is carried out. Scheme 1 shows the two half reactions and the related thermodynamic potentials for the exceedingly pH = 0 as acidic and pH = 14 as basic. The reaction carried out in acidic conditions, water is oxidized to produce gaseous oxygen, protons and electrons at the anode and the recombination of protons and electrons to produce gaseous H_2 at the cathode[25]. The reaction carried out in basic conditions, the oxidation of hydroxyl anions to produce oxygen, water and electrons at the anode and the reaction of water and electrons to produce gaseous H_2 a hydroxyl anion at the cathode[26]. The two half reactions are associated to as the oxygen evolution reaction (OER) and the hydrogen evolution reaction (HER).

In Aqueous acid (pH = 0)

$$2H_2O\,(l) \longrightarrow O_2\,(g) + 4H^+ + 4e^- \qquad E = E^0 = 1.23\text{ V}$$

$$4H^+ + 4e^- \longrightarrow 2H_2\,(g) \qquad E = E^0 = 1.23\text{ V}$$

$$2H_2O\,(l) \longrightarrow O_2\,(g) + 2H_2\,(g) \qquad E = E^0 = 1.23\text{ V}$$

In aqueous base (pH = 14)

$$4OH^- \longrightarrow O_2\,(g) + 2H_2O\,(l) + 4e\text{-}\ E = 0.40\text{ V}$$

$$4H_2O\,(l) + 4e^- \longrightarrow 2H_2\,(g) + 4OH^- \qquad E = -0.83\text{ V}$$

$$2H_2O\,(l) \longrightarrow O_2\,(g) + 2H_2\,(g) \qquad E = E^0 = 1.23\text{ V}$$

Scheme 1: Half reactions of water-splitting in aqueous acid and base.

The potential (E) of any reaction at pH = 0 is identical to the slandered potential (E^0), which is defined for this pH, presuming that the assessment of E_0 for HER is 0.00V. The potential for every half reaction is completely rely on the Nernst equation, which at unit partial pressure of H_2 is given by $E_{HER} = -0.59$ x pH V for HER and O_2 is given by $E_{OER} = 1.23 - 0.59$ x pH V for OER. Since the experiments are carried out at different pH values, it is suitable to use potential to the reversible hydrogen electrode (RHE). Therefore, E_{OER} vs. the RHE is always 1.23 V.

Whatever the condition of pH, the exact potential necessary for the water splitting is higher cause of reaction barriers corresponds to the catalyst utilized at the anode and cathode. This additional potential, known as the overpotential, is a measure of the current density passed via the electrolyzer. Thus, increase in the overpotential with increasing the current density, and the performance of the several catalysts compared with the fix current density, which frequently taken to be 10 mA/cm^2, depending on the superficial area of the anode. The OER and HER overpotential is symbolized by η_{OER} and η_{HER}, respectively. The η_{OER} and η_{HER}, depends on the current density (j) is calculated by the Tafel equation, $\beta = d\eta_{OER}/ d\ln(j)$, where β is the Tafel slope. The equation elucidates the catalytic activity of OER catalyst.

In the process of HER at the cathode, overpotential required as low as 50 mV at 10 mA/cm^2 and for the OER at the anode, the overpotential required typically as low as 300 mV. Since ηOER is considerably larger than the ηHER, while maximum research in the field of the electrocatalyst water splitting has focused on the findings and the development of catalyst with low value of ηOER, and understanding the chemical compositions and structure affect the magnitude of parameters. It should be notice that, the various OER catalyst exhibited different value, which are compared on the basis of the value of ηOER at fixed anodic current density, the change in the value of ηOER due to the change in the preparation at different ways.

2. **Catalysts for the OER:** To encourage the OER catalyst under basic as well as acidic conditions, numerous reviews, book chapters, and articles have been published. In this chapter, we concentrate on the basic condition of OER catalysts. All studies showed that precious-metal electrocatalysts, such IrO_2 and RuO_2, are remarkable OER catalysts[27,28] in basic conditions but less stable in acidic conditions, which shows excellent OER catalytic activity in the basic conditions but some limitations and obstacles of the catalyst to the commercialization and large-scale production of catalyst, such as the scarcity and high cost.

Consequently, an extensive amount of research has been done on an alternative method for OER catalysts, the first raw transition metal oxides exhibit that excellent activity towards oxygen evolution, which attracts more attention for enhancing the intrinsic activity as well as the potential candidates for water splitting electrocatalysts. Accordingly, Chao Huang et al. successfully synthesized CoNPs@CNT composite material of Co and CNT through one step chemical vapour deposition method in alkaline condition, which exhibits a small overpotential of 380 mV at 10 mV/cm^2, with small Tafel slope of 82.2 mV/dec and shows excellent structural and electrochemical stability[29]. MOF derived composite material shows promising electrocatalytic activity for OER, the Jiahui Zhang et al. synthesized hallow Co_3O_4-C/rGO-W composites material through pyrolysis of ZIF-67/GO-W precursor. The as prepared nanocomposite electrode material shows appreciable activity towards OER, the overpotential is as 382 mV at current density 10 mV/cm^2 and low tafel slope at 62 mV/dec with optimistic stability[30]. Transition metal chalcogenides (TMCs), have great interest for oxygen evolution reaction, are promising candidate for this, Xiaobin Liu, et al. synthesized high performance electrocatalyst for OER made from MOF-derived $CoSe_2$ microspheres; in this case, Co-MOF is converting to CoSe2 microspheres at different temperatures. The $CoSe_2$-450 microspheres exhibits admirable activity in 1.0 M KOH electrolytic solution, shows overpotential of 330 mV at current density 10 mV/cm^2 and low Tafel slope of 82.2 mV/dec, with good electrochemical durability[31]. The high conductivity of boron plays a major role in the electrocatalysts, Yanqiang Li et al. successfully developed MOF derived Co-B/C catalyst based on the Co-MOF and boron as a precursor. The catalytic activity for OER is improved by the high conductivity of the carbon and Co-B. The derived material shows low overpotential of 320 mV at 10 mA/cm^2 with long term stability without loss of performance after 20 hrs[32]. The three-dimensional nanomaterials play an important role in the electrochemistry, the 3D hierarchical ZIF-67/CoNiAl-LDH/NF synthesized through hydrothermal method by Feng Li and group. The 3D hierarchical architecture of the material enhances catalytic activity for OER cause of the electrocatalytic active surface area and the synergistic effect between the LDH nanoplatelets building blocks and 2D ZIF-67 nano arrays. The overpotential for the prepared electrocatalyst is small as 330 mV the current density 10 mV /cm^2 and low Tafel slope near about 88 mv/dec[33]. Jahangeer Ahmed et al. recently developed a nanocomposite material $NiMoO_4$-NRs@RGO via simple hydrothermal route. The fabricated composite material shows superior electrocatalytic activity for oxygen evolution reaction in alkaline solution (0.5 M KOH), exhibits low overpotential of 185 mV for OER and very low Tafel slope 54 mV/dec with excellent stability[34]. Shaowei Chen and group developed promising electrocatalyst for OER, based on the Fe-Co synthesise $FeSe_2$@$CoSe_2$ nanoparticles which are supported on the rGO. In the catalyst $CoSe_2$ phase was situated on the surface of the $FeSe_2$ and formed a huge number of active sites for OER, which shows low overpotential as 260 mV at 10 mV/cm^2 in alkaline condition with strong stability[35].

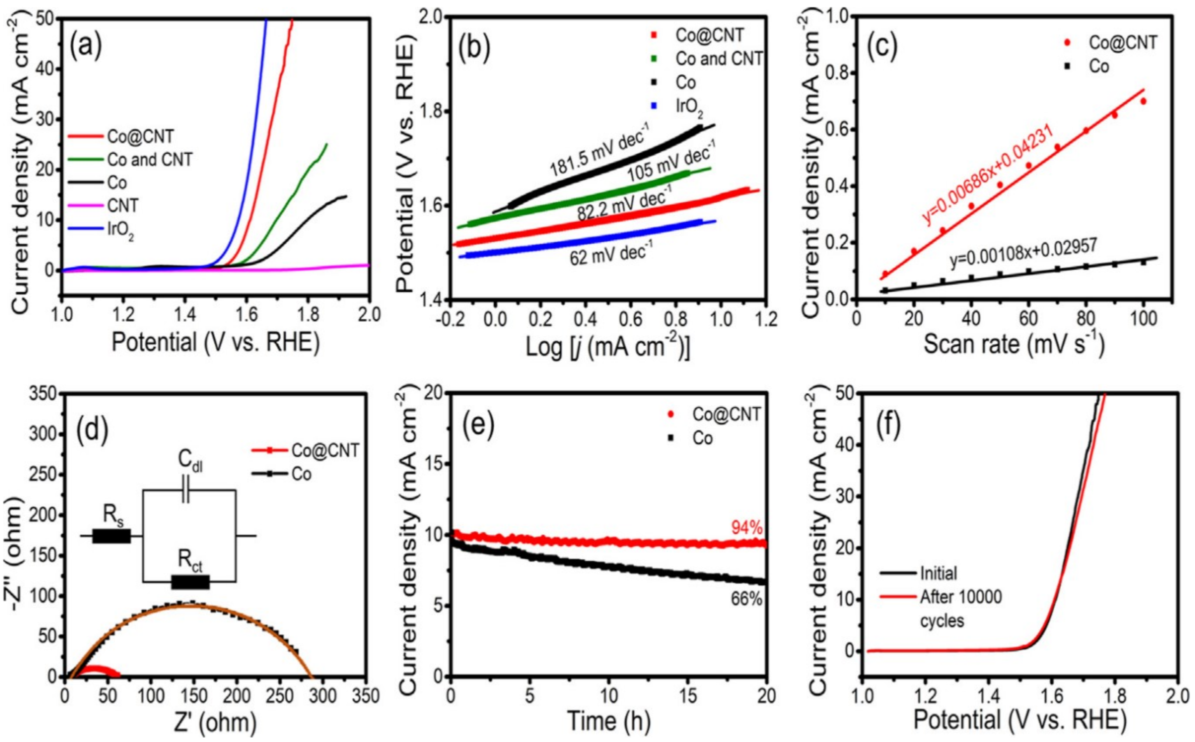

Figure 3: The Overall electrochemical study (a) OER polarization curves; (b) Linear Tafel slopes; (c) C_{dl} values; (d) EIS spectra with the inset displays the equivalent circuit model; (e) Investigation of the stability by chronoamperometry; (f) Stability of the LSV curves before and after 10,000 cycles. Reproduced from ref. [29]. Copyright Elsevier.

Yadong Li and group developed new strategy to partial pyrolysis of trimetallic NiCoFe-MOF-74 as precursor. In this strategy the MOF structure was preserved for substrate diffusion, which produce highly active nanoparticles. The constructed nanostructure shows amazing electrocatalytic activity, and stability with low overpotential as 238 mV at 10 mA/cm^2 and the small Tafel slop of 29 mV/dec[36]. Changsheng Cao et al. fabricated remarkable electrocatalyst based on the thin Ni(Fe)-MOF nanosheet as a precursor. The MOF nanocluster is perfectly binding with the surface of NF. The synthesised NiFe-NFF electrode material exhibits considerable OER activity in basic condition. The overpotential of 227 mV achieve at 10 mA/cm^2 with long term durability[37]. Yingwei Li and group successfully developed Co based MOF derived electrocatalyst through controlled two step pyrolysis process with nanoarchitectures embedded in hollow nitrogen-doped carbon polyhedral. The optimized Co_3O_4/HNCP-40 shows remarkable activity for OER. The Overpotential is low as 333 mV at 10 mA/cm^2 and a very small Tafel slope of 69 mV/dec with long term stability[38].

Table 2: Summary of Data on NPs in MOF Catalysts for OER

Sr. No.	Catalyst	Overpotential (mV)	Tafel slope (mV/dec)	Electrolyte	Stability tests	Ref.
1	CoNPs@CNT	380 mV	82.2	1 M KOH	20 h	29
2	Co_3O_4-C/rGO-W	382	62	0.1M KOH	500 cycles	30
3	$CoSe_2$	330	79	1 M KOH	5000 s	31
4	Co–B/C	320	75	1 M KOH	20 h	32
5	ZIF-67/CoNiAl-LDH/NF	303	88	1 M KOH	8 h	33
6	$NiMoO_4$-NRs@RGO	185	54	0.5 M KOH	1000 s	34
7	$FeSe_2$@$CoSe_2$/rGO-2	260	36.3	1 M KOH	1000 cycles	35
8	NiCo/Fe_3O_4/MOF-74	238	29	1 M KOH	36 h	36
9	NiFe-NFF	227	38.9	1 M KOH	1000 cycles	37
10	yolk@shell Co_3O_4/HNCP-40	333	69	1 M KOH	1000 cycles	38

IV. SCOPE

This chapter summarizes current advances in MOF, its derived nanomaterials, and its composites, which offer a promising substrate for superior oxygen evolution reactions. Due to its remarkable benefits, including its high specific surface area, porosity, ability to modify the composition or porosity, and ability to optimize the structure, much research is currently being conducted. By using different types of synthetic methods with a variety of ligands and metal clusters, achieve various morphologies such as nanocubes, nanorods, nanotubes, nanosheets, and nanowires and excellent catalytic properties. The highly porous structural combination, versatile nature of chemicals, and structural alteration of MOFs, with its low cost of production, has given many opportunities in the future to develop novel, multifunctional, large-scale, and commercialized MOF and its composites.

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