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Recent progress of 2D metal-organic frameworks and their derivatives for oxygen evolution electrocatalysis

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Abstract: The development of high-performance transition metal-based electrocatalysts for the oxygen evolution reaction (OER) is paramount for electrochemical secondary metal-air batteries and water splitting. Two-dimensional (2D) metal-organic framework (MOF) nanosheets have recently emerged as a novel class of efficient electrocatalysts for the OER due to a high specific surface area, ultrasmall thickness and abundance of active sites. Here, we summarize recent progress in the preparation and characterization of 2D transition metal-based MOFs (e.g. Ni, Co and Cu), as well as their composites and derivatives, including metals/alloys, metal oxides/chalcogenides and metal phosphides/hydroxides, as OER electrocatalysts reported over the past several years. Design principles and preparation routes are presented. The performance of the electrocatalysts is directly compared in terms of η (thermodynamics) and electrocatalytic current density (kinetics), as well as operational stability (economics). Many of these materials exhibit superior catalytic activity compared to the noble-metal based catalysts such as RuO₂ ($\eta < 300$ mV at 10 mA cm⁻²), and considerable stability with negligible decay with operation over several hours to days. Challenges and perspectives of applying 2D MOFs and their derivatives for OER electrocatalysis are also discussed.

Keywords: 2D MOF; MOF derivatives; oxygen evolution reaction; electrocatalysis.

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1. Introduction

Green energy technologies are urgently needed due to forthcoming insecurity of fossil fuel supply, increasing global energy demand and critical environmental concerns.^[1-8] Rechargeable metal-air batteries and electrochemical water splitting (Figure 1a)^[9] are promising systems for the storage and conversion of renewable electricity, for example, from solar and wind energy. They have attracted considerable attention due to their environmental friendliness, high efficiency, and high safety.^[10-13] The electrochemical oxygen evolution reaction (OER) is a core process in such devices, highlighting the importance of high-performance OER electrocatalysts.

The OER is the process in which H₂O or OH⁻ is oxidized to dioxygen gas at the anode of an electrolyzer cell. Ideally, the process proceeds around the thermodynamic limit of 1.23 V versus the reversible hydrogen electrode (RHE), but typically requires overpotentials of several hundreds of millivolts. The OER mechanisms vary depending on pH of the electrolyte and catalyst surface.^[14, 15] The well-accepted OER model process includes four separate steps with overall four-electron transfer in acidic (eq. 1) or alkaline (eq. 2) solution, respectively. X* indicates one active site on the electrocatalyst surface, while X*OH, X*O and X*OOH refer to different OER intermediates absorbed on active sites during the OER (Figure 1b).^[14, 16]

The benchmark OER electrocatalysts are noble metal-based catalysts e.g. of ruthenium (Ru) or iridium (Ir).^[17, 18] Nevertheless, the low crustal reserve, high cost and poor stability of these metals are obstacles for large-scale implementation of the noble-metal based electrocatalysts. As an alternative, earth-abundant and cost-effective transition metal-based electrocatalysts are promising candidates for OER.^[19-22] Rossmeisl and associates.^[16] constructed a volcano-type plot showing the relationship between adsorption free energy descriptors (ΔG_{O^*} and ΔG_{HO^*}) and OER overpotential (η), which can be used as a guide in searching for good OER catalysts. According to their description, η is determined by the critical step forming the *O (eq. 1.2) or *OOH (eq. 1.3) adduct. The difference in adsorption free energy for *OH and *OOH (Figure 1c) is a constant (about 3.2 eV).^[16, 23] Disregarding solvent dynamic effects (reorganization free energies)^[24], the theoretical η at standard conditions can be obtained by^[16]

$$\eta = \{\max [(\Delta G_{O^*} - \Delta G_{HO^*}), 3.2 \text{ eV} - (\Delta G_{O^*} - \Delta G_{HO^*})]/e\} - 1.23 \text{ V} \quad (3).$$

RuO_2 is located close to the top of the volcano (Figure 1d), but some non-noble transition metal oxides, e. g. NiO and Co_3O_4 , are found very close to RuO_2 . Transition metal-based catalysts could be optimized by adjusting $(\Delta G_{O^*} - \Delta G_{HO^*})$.^[25, 26] For example, Ho and co-workers have reported that the (012) facet of $\alpha\text{-Fe}_2O_3$ (Figure 1e) has an optimal adsorption/desorption position for favorable OER.^[25]

Figure 1. a) Schematic illustration of rechargeable metal-air batteries and electrochemical water splitting. The magenta dashed box highlights the key process, *i.e.* OER in both devices. b) The OER mechanism under acidic (blue round) and alkaline (orange round) conditions. Not drawn to real scale. c) The universal scaling relation plot between adsorption energies of HOO^* and HO^* on perovskites, rutiles, anatase, Mn_xO_y , Co_3O_4 , and NiO oxides. The red star indicates the ideal electrocatalyst. Reprinted with permission from Ref.^[16]. Copyright (2011) WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. d) Volcano plot of the computed OER overpotential against the descriptor value of $\Delta G_{O^*} - \Delta G_{HO^*}$ for selected transition-metal oxides. Reprinted with permission

from Ref.^[16]. Copyright (2011) WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. e) Impact of facets on the OER activity descriptor. Inset, e_g occupancy of six- and seven- coordinated configurations. Reprinted with permission from Ref.^[25] Copyright (2018) WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

As an emerging group of transition metal-based materials, metal-organic frameworks (MOFs) are a class of highly porous crystalline materials composed of transition metal units and strongly coordinating organic ligands.^[27] MOFs are being studied extensively with wide-ranging application prospects, *e.g.* in gas storage and separation, batteries, catalysts *etc.*, benefiting from their high specific surface area, tunable porosity and abundance of active metal sites.^[28, 29] To date, a large library of MOFs has been fabricated with a wide spectrum of metal units or clusters (“nodes”) and organic linkers.^[9, 30] Besides the variety of components and structures, different morphologies of MOFs have been designed and prepared, including zero-dimensional (0D, *e.g.* nanoparticles or quantum dots), one-dimensional (1D, *e.g.* nanowires or nanorods), two-dimensional (2D, *e.g.* nanosheets or plates) and three-dimensional (3D, *e.g.* networks) structures.^[31-35] These different morphologies and microstructures open new research opportunities for OER if using them as precursors or templates for good OER catalytic performance.

Since the discovery of graphene,^[36] 2D materials (*e.g.* MoS₂, MXenes and black phosphorus) have been widely studied in the past decades due to their unique physicochemical features.^[37-42] OER is an interfacial reaction that is strongly dependent on the surface physicochemical features of the catalysts. Graphene is composed of a single atomic layer of sp²-hybridized carbon atoms. MXenes are transition metal carbides with hydrophilic nature due to their hydroxyl- or oxygen-terminated surfaces.^[43] Different from graphene and MXenes, 2D MOFs are made by linking metal nodes and organic linkers with coordination bonds. 2D MOFs themselves show OER catalytic activity, offering additional advantages, *i.e.* easily tailored surface atom and bonding organization for superior OER electrocatalysis. However, so far MOFs have been considered to have low electrical conductivity and often poor OER performance. Recently, π -conjugated 2D MOFs with benzene- or phthalocyanine-based organic groups have been synthesized, and directly used for OER with high intrinsic electrical conductivity.^[44, 45] 2D MOFs further combined

with conductive agents (carbon components or conductive substrates), or pyrolysis of 2D MOFs have been adopted to improve the conductivity and enhance OER catalytic activity. It is therefore not surprising that 2D MOF-based materials are emerging as novel type efficient OER electrocatalysts, but there are so far only few reviews focusing on the advances in 2D MOF-based OER electrocatalysts.

Herein, we critically summarize recent progress in the preparation and characterization of 2D transition metal-based MOFs (*e.g.* of Ni, Co and Cu), as well as their derivatives including the corresponding metals/alloys, metal oxides/chalcogenides and metal phosphides/hydroxides for OER electrocatalysis. Design principles and preparation routes are presented. The performance of the electrocatalysts is directly compared in terms of η (thermodynamics) and electrocatalytic current density (kinetics), as well as operational stability (economics). Challenges and perspectives are also discussed. Tables 1-3 provide numerical overview of reported materials based on Ni, Co, Cu and derivatives, and performance metrics, while Figure 9 gives a graphical summary of the evolution of publications, overpotential and achieved stabilities.

2. Preparation and characterization of 2D MOFs

2D MOFs can be synthesized *via* either top-down or bottom-up approaches.^[9, 30, 46, 47] More detailed review focusing on synthesis methods of 2D MOF materials are available in literature^[47, 48]. The top-down methods include physical^[49, 50] and chemical exfoliation^[51, 52], which rests on breaking the weak van der Waals interactions between layers in bulk layered materials. For example, Moorthy and co-workers^[49] synthesized 2D Cd-DP MOF nanosheets by ultrasonically layered Cd-DP MOFs in ethanol. Scanning electron microscopy (SEM) (Figure 2a) showed the presence of stacked 2D sheets from the solvothermal formation of the bulk MOF. Transmission electron microscopy (TEM) of the 2D Cd-DP MOF obtained after ultrasonication displayed a sheet-like morphology with wrinkles (Figure 2b). The thickness of 2D Cd-DP nanosheet, determined by atomic force microscopy (AFM, Figure 2c and d) was about 3 nm. Zhang and associates^[52] fabricated 2 nm 2D Co₆-O(dhbdc)₂(OH)₂(H₂O)₁₀ (dhbdc: 2,3-dihydroxy-1,4-benzenedicarboxylic) nanosheets (2D-Co-NS) through electrochemical exfoliation by removing the pillar ligands (H₄dhbdc) in the 3D MOF. The prepared 2D-Co-NS showed a catalytic OER

performance on nickel foams (NFs) with a low overpotential of 0.2 V. 2D MOFs synthesized by top-down methods often exhibit inhomogeneous morphologies and thicknesses, attributed to numerous surface defects originating from the breakup of interlayer interactions in the 3D MOF precursors. Moreover, the abundant surface defects on the 2D MOFs are helpful for catalytic applications.^[48, 52]

Figure 2. Examples of top-down (left) and bottom-up (right) approaches to 2D MOF synthesis. a) SEM image of pristine Cd-DP crystals show the presence of stacked 2D sheets. b) TEM and c) AFM images and d) height profile of 2D Cd-DP nanosheets. Reprinted with permission from Ref.^[49]. Copyright (2018) Elsevier. e) Digital photograph, and f) Scheme that shows the spatial arrangement of different liquid regions during the synthesis of CuBDC MOF nanosheets. Regions labelled i, ii and iii correspond to benzene 1, 4-dicarboxylic acid (BDCA) solution, intermediate solution region containing the generated CuBDC MOF, and the aqueous solution of Cu^{2+} ions, respectively. g) AFM image of CuBDC MOF nanosheets. h) Height profiles measured along the blue and red lines in (g). Reprinted with permission from Ref.^[53]. Copyright (2014) Nature Publishing Group.

In contrast to the top-down method, the morphology and thickness of synthetic 2D MOFs by bottom-up approaches can be well controlled, leading to high-quality and high-yield production. Common bottom-up strategies include two-phase interfacial/intermediate layer growth^[53, 54] or

surfactant/template-assisted approach^[55, 56]. For example, Gascon and co-workers^[53] prepared dispersible 2D copper 1,4-benzenedicarboxylate MOF (CuBDC) nanosheets through the two-phase method (Figure 2e). Cu²⁺ ions and BDC linkers slowly diffuse to the interface of two solutions, generating highly diluted 2D CuBDC nanosheets. AFM images (Figure 2f-h) demonstrate lateral dimensions above one micrometer and thicknesses in the range 5–25 nm. Zhang *et al.*^[56] synthesized 2D zeolitic imidazolate framework-L (ZIF-L) nanosheets by template-assisted deposition. Horizontally aligned 1D halloysite nanotubes were used as templates, acting as nucleation sites and guiding the vertical growth of the 2D MOF. Although the weak structural stability and surface additives of 2D MOFs fabricated by bottom-up approaches are obstructive for the application in surface-related applications, it is easy to control the formation of various metal-doped 2D MOFs.^[48, 57]

Hybrid 2D MOFs resulting from the introduction of hetero-components (atoms, molecules *etc.*) into the 2D MOF structure could efficiently inherit the controllable morphology but modify the electronic structure to facilitate the catalytic activity for the OER. The most universal and facile approach to synthesizing hybrid 2D MOFs is adding extra metal ions or metal-organic compounds during the formation of 2D MOFs, the metal nodes of which are thus partially replaced or modified by the foreign metal ions or metal-organic compounds. In addition, the template-assisted approach is another emerging method to fabricate hybrid 2D MOFs featuring superior interfacial connection for good electrical conductivity, robust structural stability and thus good catalytic performance. For example, Dong and associates^[58] used the template-assisted approach to prepare ultrathin Co₉Ni₁-MOF nanosheet arrays on Co₉Ni₁ foam substrates. The surface layer of the metallic Co₉Ni₁ self-dissociated in the presence of benzenedicarboxylic acid (BDC) solution during a hydrothermal process, forming 2D Co₉Ni₁-MOF nanosheet arrays on the substrate. This 2D MOF exhibited good OER catalytic activity with an overpotential η of 215 mV at 10 mA cm⁻².

The morphology and structure of 2D MOFs can be characterized by a variety of techniques. SEM and TEM can be used for the observation of the spontaneous curling at 2D MOF edges after drying, while the thickness can be precisely measured by AFM. Further, the atomic arrangement in 2D MOFs can be identified *via* scanning TEM (STEM) with near-atomic resolution and high Z-contrast.^[59] The crystallinity of 2D MOFs can be examined by bulk powder X-ray diffraction (PXRD)

or selected-area electron diffraction (SAED) of individual nanosheet. The elemental composition can be obtained by energy dispersive spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS), which also allows for chemical analysis of the elemental components in the 2D MOF. In addition, EDS mapping using STEM can image the distribution of metal nodes in bimetallic or trimetallic 2D MOFs with high resolution. X-ray absorption spectroscopy (XAS) with synchrotron radiation can help to analyze oxidation states, local atomic structure and unoccupied metal electronic states in 2D MOFs associating with intrinsic OER catalytic activity.^[60]

Different electrode substrates and electrode preparation routes are employed when 2D MOF-based materials are used for OER electrocatalysis. Drop-casting of the as-fabricated 2D MOF inks onto a glassy carbon electrode (GCE), fluorine-doped tin oxide (FTO) on glass, or carbon cloth (CC) is a widely used approach.^[8, 45, 61, 62] It allows efficient control of the mass loading of the catalyst on the substrate for quantitative investigation of the intrinsic catalytic OER activity. However, the interface between the substrate and the catalysts may suffer considerable impedance as insulating binders are typically used in the ink, leading to reduced OER performance. *In-situ* strategies to grow 2D MOFs directly on conductive substrates, such as NFs, is an alternative, more promising approach.^[63, 64] The resulting 2D MOF electrodes not only maintained good electronic connection between substrate and catalyst improving the electrical conductivity, but also inherit the hierarchical frameworks of the substrates for improved O₂ mass transport away from the catalyst surface and good OER performance. However, determination of the precise mass loading of catalysts in these systems is difficult. Furthermore, it is recommended to report the catalyst loading and effective surface area so that appropriate comparison of OER performance across studies can be made.

3. 2D MOFs for the OER

2D transition metal-based MOFs (*e.g.* of Ni, Co and Cu) have attracted extensive attention. Among these, 2D Ni-based and Co-based MOFs have demonstrated excellent catalytic performance for OER.

3.1 2D Ni-based MOF hybrids

2D Ni-based MOFs consisting of single-metal Ni units with different organic linkers have been investigated in the past few years, as summarized in Table 1.^[45, 62, 65] Du *et al.*^[45] utilized a phthalocyanine (Pc) unit as a key organic fragment to construct a π -conjugated 2D NiPc-MOF *via* a bottom-up method, exhibiting a layered morphology (thickness: 100–200 nm) as confirmed by AFM. The NiPc-MOF registered an OER η of 350 mV at 10 mA cm⁻² on a fluorine-doped tin oxide (FTO) substrate. It could be concluded that lack of heteroatom doping in the 2D NiPc-MOF and low loading may limit the OER performance (Table 1). Similarly, a 2D pure Ni-based MOF, which was prepared by physical exfoliation by ultra-sonicating 3D pillared-layer MOFs ([M₂(BDC)(dabco)]-guest (M = Ni, BDC = 1,4-benzenedicarboxylate, dabco = 1,4-diazabicyclo[2.2.2]octane)) in water, showed an OER η of 581 mV at 10 mA cm⁻² on CC.^[62] However, there is still ample room for improvement in OER performance (Table 1). Recently, some researchers have introduced metal heteroatoms to 2D Ni MOFs as hybrid electrocatalysts, enabling improved OER performance.^[44, 66, 67] Tang and co-workers^[44] fabricated NiCo-based ultrathin 2D MOF (NiCo-UMOFNs) consisting of Ni²⁺/Co²⁺ and organic linkers of BDC nanosheets with a uniform thickness of 3.1 nm *via* sonication, exhibiting superior OER catalytic activity with a lower η (250 mV at 10 mA cm⁻²) than that of the single-metal 2D Ni-UMOFN (321 mV). *In-situ* X-ray absorption spectroscopy (XAS) indicated that the Ni K-edge peaks of NiCo-UMOFNs shifted to higher binding energy after applying a potential in the range of 1.43 to 1.53 V vs. RHE, confirming that the Ni sites in NiCo-UMOFNs were more easily oxidized to high valence for enhanced catalytic sites than in bulk NiCo-MOFs.^[44, 68] Density functional theory (DFT) calculation results further revealed that coordinatively unsaturated metal atoms were the main active sites and the coupling effect between Ni and Co metals was crucial for the enhancement of electrocatalytic activity. In addition, the nanometer-thick 2D structure increases the amount of exposed surface and thus of unsaturated active metal sites.^[44] Following this report, a number of bimetallic 2D Ni-based MOFs hybrids (NiFe-UMNs^[66] and Ni_{0.75}Fe_{0.25} BDC^[67]) have been explored by a similar bottom-up synthetic method with high quality and yield. For instance, Wang and associates^[66] synthesized NiFe 2D ultrathin MOF nanosheets with a thickness of ~10 nm, showing a η of 260 mV at 10 mA cm⁻². Meanwhile, Li *et al.*^[67] tuned the Fe doping in a 2D Ni MOF, with the optimized Ni_{0.75}Fe_{0.25}

BDC registering a η of 310 mV at 10 mA cm⁻². These reports indicate that the heteroatom (Co, Fe) doping in the 2D Ni MOFs could efficiently maintain 2D morphology and modulate the electronic structure for excellent OER performance. Introduction of metal heteroatoms in the 2D MOFs is facile. Unsaturated metal atoms exposed at the surface of 2D MOFs can be easily replaced by metal heteroatoms.

Table 1. OER activity of reported 2D Ni-based MOFs electrocatalysts in 1 M KOH. The widely different Tafel slopes are notable and indicative of quite different rate determining OER steps on the different MOF surfaces.

Catalyst	Overpotential @ 10 mA cm ⁻² (mV)	Tafel slope (mV dec ⁻¹)	Catalytic stability (h)	Loading (mg cm ⁻²)	Substrate	Ref.
NiPc-MOF	350	N/A	50	0.076	FTO	[45]
2D-Ni-single-layer	581	182	N/A	0.2	CC	[62]
NH ₂ TA-MOF	356	105	3.3	N/A	GCE	[65]
Ni-UMOFNs	321	65	N/A	0.2	GCE	[44]
Ni BDC	420	92.5	N/A	0.2	GCE	[67]
Ni-MNS/NF	425@ 50 mA cm ⁻²	100	N/A	N/A	NF	[63]
Ni-MOF	370	139	N/A	0.2	GCE	[69]
NiCo-UMOFNs	250	42	120	0.2	GCE	[44]
NiFe-UMNs	260	30	2.8	0.4	GCE	[66]
Ni _{0.75} Fe _{0.25} BDC	310	43.7	11.1	0.2	GCE	[67]
Ni-MOF@Fe-MOF	265	82	N/A	0.2	GCE	[69]
Ni-BDC/Ni(OH) ₂	320	41	20	0.19	GCE	[70]
NiFe MOF/OM-NFH	270	123	11.1	0.4	GCE	[71]
NiFeZn-MNS/NF	350@ 50 mA cm ⁻²	49	120	N/A	NF	[63]
Ni-ZIF/Ni-B@NF-4	234	57	36	N/A	NF	[72]

N/A: not available.

In addition, incorporating heterogeneous components into 2D Ni-based MOFs can also enhance the catalytic ability for water oxidation.^[69-72] Rational design of the composition and structure could efficiently mitigate the aggregation of 2D Ni MOF. For example, Sun *et al.*^[69] synthesized hybrid 2D dual MOFs (Ni-MOF@Fe-MOF) by *in-situ* generation of Fe-MOFs nanocrystals on the surface of 2D Ni MOFs, resulting in a 100 mV lower overpotential (to 265 mV at 10 mA cm⁻²). Qiao and coworkers^[70] developed a 2D Ni-BDC/Ni(OH)₂ heterostructure for OER electrocatalysis, exhibiting a η of 320 mV at 10 mA cm⁻² and a good catalytic durability of 20 h. Besides, Zhu *et al.*^[71] designed a unique 2D NiFe MOF nanosheets inlaid on a 3D ordered macroporous NiFe

hydroxide template (NiFe MOF/OM-NFH), with partial NiFe hydroxide of the template *in-situ* transformed into 2D NiFe MOF nanosheets. The combination of the highly exposed active centers in the ultrathin NiFe MOF nanosheet inlay and efficient electron/mass transfer in the 3D hierarchical structure ensured excellent OER catalytic activity, with a η of 270 mV at 10 mA cm⁻². In addition, generating hybrid 2D Ni MOFs on porous NF skeletons could accelerate mass/charge transfer. Wei and co-workers^[63] grew NiFeZn-based MOF nanosheets containing Fe₂O₃ nanoparticles (size < 5 nm) on NF substrates (NiFeZn-MNS/NF), registering better OER performance (350 mV@ 50 mA cm⁻²) than the pure Ni-MNS/NF (425 mV@ 50 mA cm⁻²). It is notable that crystalline-amorphous interfaces on the crystalline surface of Ni-based MOFs could optimize the adsorption energy of OER intermediates for enhanced OER performance. Wu and associates^[72] synthesized ultrathin Ni-ZIF/Ni-B nanosheets with abundant crystalline-amorphous phase boundaries *via* room temperature boronization of as-prepared Ni-ZIF nanorods on NF (Figure 3a). High-resolution TEM (HRTEM) (Figure 3b-d) clearly showed the crystalline-to-amorphous transformation process from Ni-ZIF to Ni-B with boronization time. The optimal samples (Figure 3c) with 4 h boronization (Ni-ZIF/Ni-B@NF-4) contained a large number of crystalline-amorphous phase boundaries. The corresponding STEM and EDS mapping (Figure 3e) revealed the co-existence and uniform dispersion of C, N, Ni and B. Among various controls, Ni-ZIF/Ni-B@NF-4 exhibited the best catalytic activity for OER (Figure 3f and g) with the lowest η of 234 mV at 10 mA cm⁻² and highest catalytic stability, with negligible decay after 36 h at 10 mA cm⁻² by maintaining the initial 2D nanosheet morphology (inset of Figure 3g). DFT calculations indicated that the potential-determining step (PDS) of Ni-ZIF was the adsorption of *OH (2.36 eV at U =1.23), while the PDS was the formation of *OOH (1.23 eV at U =1.23) for amorphous Ni-B. The combination of 2D Ni-ZIF and amorphous Ni-B reduced the energy barrier of adsorption of *OH and formation of *OOH, leading to enhanced intrinsically OER catalytic activity.

Figure 3. a) Schematic illustration of the synthesis process of Ni-ZIF/Ni-B@NF. HRTEM images of b) Ni-ZIF, c) Ni-ZIF/Ni-B-4, and d) Ni-B@NF-24. e) STEM and the corresponding EDS elemental mapping of Ni-ZIF/Ni-B-4. f) OER performance of Ni-ZIF@NF, Ni-ZIF/Ni-B@NF-2, Ni-ZIF/Ni-B@NF-4, Ni-ZIF/Ni-B@NF-9, and Ni-B@NF-24 characterized by LSV with a scan rate of 1 mV s^{-1} in 1.0 M KOH . g) The operational stability of Ni-ZIF/Ni-B@NF-4 at 1.464 V vs. RHE . Inset in (g) is an SEM image of the cycled Ni-ZIF/Ni-B@NF-4 catalyst after long-term test. Reprinted with permission from Ref.^[72]. Copyright (2019) WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

In summary, 2D Ni-based MOFs hybrids used for OER have been studied over several years recently. Most pristine 2D Ni MOFs demonstrate relatively weak OER catalytic capacity due to the poor catalytic activity of active sites and strong tendency to agglomerate during OER, in turn leading to limited catalytic stability. Heterogeneous metal atoms or compounds are therefore introduced in the 2D Ni MOFs to modulate the electronic structure for enhanced intrinsic catalytic activity and in the agglomeration for improved catalytic stability. Some improvement has been achieved (Table 1), while the detailed understanding of OER catalytic mechanism is still ahead of us.

3.2 2D Co-based MOF hybrids

2D Co-based MOFs also exhibit high catalytic OER performance, as summarized in Table 2. 2D single-metal Co-based MOFs with a range of organic linkers have been studied recently.^[52, 64, 73-75] For example, Fischer and associates^[73] utilized 2D cobalt ion (Co^{2+}) and benzimidazole (blm) to prepare zeolite-imidazole framework (Co-ZIF-9(III)) nanosheets (thickness: 2–4 nm), *via* mechanochemical grinding and subsequent ultrasonication assisted liquid-phase exfoliation. The 2D Co-ZIF-9(III) nanosheets exhibited a η of 380 mV at 10 mA cm^{-2} , better than that of bulk Co-ZIF-9 counterparts (η : 420 mV), which can be explained by more accessible active sites and faster mass diffusion than bulk MOF crystals. Similarly, the introduction of a second organic linker to 2D Co-based MOFs^[74, 75] by top-down approaches can also enhance OER catalysis outperforming bulk Co MOFs. Bu and co-workers^[64] provided a bottom-up method for *in-situ* growth of quasi-2D Co MOF nanoarrays consisting of Co^{2+} and organic linkers of thiophenedicarboxylic acid (H_2TDC) on NF substrates (Co MOF/NF), with a slight reduction in η relative to drop-casting the same MOF powders on NF (270 vs 297 mV at 10 mA cm^{-2}). The enhanced catalytic performance was mainly attributed to the well-connected attachment of the catalyst on the hierarchical, porous NF skeleton for fast electron/ion transfer.

Table 2. OER activity of reported 2D Co-based MOFs electrocatalysts in 1 M KOH.

Catalyst	Overpotential @ 10 mA cm^{-2} (mV)	Tafel slope (mV dec^{-1})	Catalytic stability (h)	Loading (mg cm^{-2})	Substrate	Ref.
Exfoliated Co-ZIF-9(III)	380	55	10	0.21	GCE	[73]
2D-Co- NS@Ni	211	46	96	N/A	NF	[52]
Ultrathin Co- MOF	263	74	3.3	0.25	GCE	[74]
Co-MONs	309	75.7	30	N/A	Cp ^a	[75]
Co MOF/NF	270	75	30	N/A	NF	[64]
Co-UMOFNs	371	103	N/A	0.2	GCE	[44]
Co-MOF	341	111	N/A	N/A	GCE	[76]
Co@HPA- MOF	386	61	N/A	0.21	GCE	[77]
CoNi(1:1)- MOF	265	56	20	N/A	Cu foil	[76]

Co-Ni@HPA-MOF	320	58	N/A	0.21	GCE	[77]
Co ₃ Fe-MOF	280	38	10	0.42	GCE	[78]
FeCo-MNS-1.0	298	21.6	13.9	0.36	GCE	[79]
CoNi-MOFNA	215	51.6	300	2.0	Co ₉ Ni ₁ foam	[58]
CoFe-MOF	277	31	N/A	0.34	GCE	[80]
Ti ₃ C ₂ T _x -CoBDC	410	65	N/A	0.21	GCE	[81]
Co-BPDC/Co-BDC-3	335	72.1	80	0.28	GCE	[82]
CoBDC-Fc-NF	178	51	80	1.80	NF	[83]

^a CP: carbon paper.

In contrast to pure 2D Co MOFs, 2D hybrid Co-based MOFs with metal heteroatoms (e.g. Fe, Ni), inheriting the controllable morphology and allowing for tailoring of the electronic structure, have demonstrated improved OER catalytic activity.^[58, 76-80] For example, Lee *et al.*^[76] grew 2D CoNi-MOFs with different atom ratios of Co and Ni on Cu foil substrates using a hydrothermal procedure. The optimal material, CoNi(1:1)-MOF (thickness: 5.3 nm), showed a η of 265 mV at 10 mA cm⁻², which was lower than that of pure Co MOF (341 mV). *In-situ* conducting AFM and two-point conductivity measurements indicated that the good catalytic activity was related to the dominant (2 $\bar{2}$ 0) facets with enhanced conductivity along the Z-axis, facilitating electron transfer from the substrate to active centers. Similarly prepared 2D bimetallic Co-based MOFs including Co-Ni@HPA-MOF (HPA: hypoxanthine)^[77] and Co₃Fe-MOF^[78] also showed enhanced OER performance compared to the corresponding single-metal Co MOFs.

In addition, Zhu and co-workers^[79] designed a unique template-assisted approach to the synthesis of iron-cobalt MOF-74 nanosheets (FeCo-MNS) by solvothermal reactions (Figure 4a). As-prepared iron-cobalt oxide nanosheets (FeCo-ONS) were used as sacrificial templates for the reaction with different amounts of 2,5-dihydroxyterephthalic acid (H₄dobdc). TEM and AFM images (Figure 4b-c) indicated that FeCo-ONS transformed to the optimal FeCo-MNS-1.0 nanosheets (thickness: 2.6 nm). FeCo-MNS-1.0 (Figure 4d) showed superior OER performance with a lower η (298 mV at 10 mA cm⁻²) and an unusually low Tafel slope (21.6 mV dec⁻¹) compared with those of FeCo-ONS, cobalt MOF-74 nanosheets (Co-MNS) and iron-cobalt bulk MOF-74

(FeCo-MB). X-ray absorption fine structure (XAFS) characterization demonstrated an increased amount of coordinatively unsaturated metal sites (CUMSs) on FeCo-MNS-1.0, which contributed to the superior OER activity. Construction of 2D FeCo-MNS nanosheets with 2.6 nm thickness enriches the CUMSs that act as active centres for enhanced OER performance. Besides, Jia and associates^[80] prepared hierarchically structured 2D CoFe-MOFs using ultrasound-assisted synthesis and subsequent solvothermal treatment. This route could remove unstable domains and generate continuous mesopores on the 2D MOFs *in-situ*, resulting in 2D CoFe-MOFs with hierarchical porosity using holey ultrathin crystalline nanosheets (thickness: 1.3 nm). The designed 2D porous structure significantly improved the OER catalytic performance with a η of 277 mV at 10 mA cm⁻².

Figure 4. a) Schematic illustration of the sacrificial 2D metal oxide approach to achieving the conversion of M-ONS to M-MNS in the presence of H₄dobdc ligand. b) TEM image of FeCo-ONS. c) TEM image of FeCo-MNS-1.0. d) OER polarization curves of FeCo-ONS, FeCo-MNS-1.0, iron-cobalt bulk MOF-74 (FeCoMB) and Co-MNS in 0.1 M KOH. Reprinted with permission from Ref.^[79]. Copyright (2019) WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

There are also reports focusing on the combination of heterogeneous components and 2D Co-based MOFs to optimize the electronic structure.^[81-83] Such hybridization can also assist in preventing MOF nanosheet agglomeration. For instance, Huang's group^[81] incorporated 2D cobalt 1,4-benzenedicarboxylate (CoBDC) with Ti₃C₂T_x nanosheets *via* an inter-diffusion reaction-

assisted process. An OER η of 410 mV at 10 mA cm⁻² was obtained with the hybrid Ti₃C₂T_x-CoBDC, which was an improvement over the pure CoBDC. Metal-like Ti₃C₂T_x nanosheets promoted the charge transfer kinetics of the hybrid material and prevented the porous CoBDC MOF layers from aggregating. Besides, Ni and associates^[80] reported a 2D Co-BPDC (BPDC: 4,4'-biphenyldicarboxylate)/Co-BDC heterojunction nanostructure for OER electrocatalysis. Co-BPDC was grown on pre-synthesized Co-BDC nanosheets under stirring at 80 °C for different periods of time. The optimal electrocatalyst, Co-BPDC/Co-BDC-3, showed better OER performance (η of 335 mV at 10 mA cm⁻²) than that of Co-based MOFs. Li and co-workers^[83] incorporated non-bridging linkers such as carboxyferrocene (Fc) into Co₂(OH)₂(C₈H₄O₄) MOF nanosheets (CoBDC-Fc). DFT simulation suggested that the modification of the electronic structure for CoBDC-Fc could change the band gap and charge distribution, thus optimizing adsorption strengths of OER intermediates (Figure 5a). SEM and TEM images (Figure 5b-d) of CoBDC-Fc showed nanosheet-like morphologies and EDS mappings (Figure 5e) clearly indicated that Fc was homogeneously incorporated. CoBDC-Fc (Figure 5f-i) gave a low η of 178 mV at 10 mA cm⁻², a Tafel slope of 51 mV dec⁻¹ and long-term stability (80 h) at a high current density of 100 mA cm⁻². The improved OER performance of CoBDC-Fc indicates that OER activity of MOFs can be indeed facilitated by tuning electronic structure via introducing Fc. DFT calculations showed that the PDS for CoBDC was the formation of *OH with a large energy barrier (3.74 eV). This was reduced significantly on Fc incorporation, which shifted the PDS to the generation of *O with a much lower energy barrier (1.85 eV).

Overall, 2D Co-based MOFs hybrids have been widely investigated for OER. Heterogeneous metal atoms or compounds are introduced in the 2D Co-based MOFs to tune the electronic structure and surface physicochemical features for enhanced OER catalytic activity. Compared with 2D Ni-based MOFs hybrid, a wider range of 2D Co-based MOFs hybrids are obtained (Table 2), demonstrating better OER catalytic performance and deeper understanding of the catalytic mechanisms.

Figure 5. a) Modulating the electronic structure of CoBDC MOF *via* introduction of Fc for improved OER. b-c) SEM and d) TEM images of CoBDC-Fc-NF. e) STEM image and STEM-EDS mappings of CoBDC-Fc-NF. f) LSV curves, g) overpotentials at different current densities and h) Tafel plots of different catalysts toward OER in 1 M KOH. i) Operational stability of CoBDC-Fc-NF for 80 h at 100 mA cm⁻² in 1 M KOH. Reprinted with permission from Ref.^[83]. Copyright (2019) Nature Publishing Group.

3.3 2D Cu-based MOF hybrids

In addition to the widely investigated 2D Ni- or Co-based MOF hybrids for OER electrocatalysis, the potentials of other 2D MOFs, especially Cu-based MOFs have been explored.^[84-86] For example, Fu and associates^[84] prepared CoNi-Cu(BDC) electrocatalysts by utilizing Cu(BDC) as a template with a facile one-step impregnation approach, delivering a lower η of 327 mV at 10 mA cm⁻² than the pure Cu(BDC). The enhanced OER activity may be attributed to the transformed 2D lamellar morphology and synergistic effects of the metal species. Thus, doping transition metal heteroatoms (Ni, Co) into the 2D Cu-based MOFs to modify the electronic structure could be a promising route. Further, combining the hybrid 2D Cu-based MOFs with conductive materials (say, graphene) can improve the electrical conductivity for fast electron transfer, leading to enhanced OER catalytic activity. As an example, a 2D bimetallic porphyrinic MOF (Co-CuTCPP) combined with reduced graphene oxide (Co-CuTCPP/rGO) exhibited a OER catalytic performance,

with a η of 396 mV at 10 mA cm⁻² and a Tafel slope of 58 mV dec⁻¹.^[85] In addition, Fang's group^[86] combined CoCu-based zeolitic imidazolate framework nanosheets (CoCu-ZIF NSs) and graphdiyne (GDY), to obtain good OER catalytic activity with a low η of 250 mV at 10 mA cm⁻² and Tafel slope of 57 mV dec⁻¹. This material is believed to benefit from the fast electron transport ability and large number of exposed active sites. Considering that the price of Cu is lower than the price of Ni and Co, approaches to preparing 2D Cu-based MOFs as efficient OER electrocatalysts are very appealing.

4. 2D MOF derivatives for the OER

Although 2D MOF electrocatalysts are intensively studied in the past few years, the unsatisfactory stability and conductivity of 2D MOFs limit their further OER application. For example, Biradha and associates^[65] synthesized a Ni MOF (NH₂TA-MOF) composed of a flexible tripodal tris-pyridyl ligand and 2-aminoterphthalate (H₂NTA), displaying a η of 356 mV at 10 mA cm⁻² and a poor stability of 3.3 h. Alternatively, 2D MOF derivatives, either with or without metal component, obtained *via* pyrolysis in certain atmosphere and other post-treatment routes can potentially overcome these challenges.^[48, 87] Among these, MOF-derived metal-free carbon materials exhibit relatively poor OER catalytic performance,^[88, 89] which is likely due to water oxidation occurring at overpotentials, where oxidation of the carbon components can occur, compromising the structure. This highlights the importance of metal components, which can be oxidized to high-valence states and recycled between valences during OER catalysis, as the OER active site. 2D MOF-derived metal-based components (e. g. metals/alloys, metal oxides/chalcogenides or metal phosphides/hydroxides etc.) containing carbon materials demonstrate enhanced OER activity and stability.^[48, 90] 2D MOF derivatives can not only efficiently inherit the morphology and structure of the 2D MOF precursors, but display porous or hierarchical nanostructures of carbon with exposed metal sites on the surface for improved mass transfer. Moreover, the carbonaceous components formed originating from the organic linkers can improve the electrical conductivity for fast electron transfer and impart structural stability during OER. In this section, we summarize recent advances (Table 3) in 2D transition metal-based MOF derivatives for OER electrocatalysis.

Table 3. OER activity of reported 2D MOF-derived electrocatalysts in 1 M KOH.

Catalyst	Overpotential @ 10 mA cm ⁻² (mV)	Tafel slope (mV dec ⁻¹)	Catalytic stability (h)	Loading (mg cm ⁻²)	Substrate	Ref.
Ni@NC	280	45	10	0.31	GCE	[91]
HXP@NC800	307	48	8	0.4	GCE	[92]
Co-NCS@CNT	360	92.9	N/A	0.17	GCE	[93]
Co@N-carbon	400	61	N/A	0.21	GCE	[94]
FeNi@CNF	356	62.6	24	0.34	GCE	[95]
Ni-MOF-250	250@50 mA cm ⁻²	88.6	20	N/A	NF	[96]
Co ₃ O ₄ /C _{BDC}		50.1	36	N/A	Ni foil	[97]
nanosheet arrays						
CoTFBDC/EG_250	365	39.8	10	0.25	GCE	[98]
Co ₃ O ₄ flakes array	205	65.3	24	N/A	NF	[99]
M-Co ₃ O ₄	370	74.0	25	N/A	NF	[100]
Co-MOF/H ₂	312	89.7	40	N/A	NF	[101]
CC@NiCo ₂ O ₄	340	72	20	0.60	CC	[102]
Fe ₁ Co ₃ /V ₀ -800	260	53	15	N/A	CC	[103]
NiCo/Fe ₃ O ₄ /MOF-74	238	29	36	0.76	GCE	[104]
FeNi ₃ -Fe ₃ O ₄	234	37	20	0.28	GCE	[105]
NPs/MOF-CNT						
Ni-BDC@NiS (12h)	330@20 mA cm ⁻²	62	12	0.20	Ni foil	[106]
Ni-Ni ₃ S ₂ @Carbon		56	8	0.20	GCE	[107]
Nanoplates						
Co ₉ S ₈ @TDC-900	330	86	7	N/A	GCE	[108]
Ni-Co-S HPNA	270	74	24	N/A	CC	[109]
Co-P@/NC-800	370	79	12	0.28	GCE	[110]
CoP-NS/C	292	64	24	0.14	GCE	[111]
HP-CoP NA/NF	258	91.7	12	N/A	NF	[112]
Co _{0.7} Fe _{0.3} P/C	270	27	N/A	0.40	GCE	[113]
CoNi	324	33	2.8	0.20	GCE	[114]
hydroxide UNSs						
FeCo _{0.5} Ni _{0.5} -LDH	248	38	50	N/A	Cu foil	[115]

4.1 Metals/alloys

Metal/alloy nanostructures can be synthesized from 2D MOF precursors at high temperature (> 600 °C) and inert atmosphere. The metal/alloy nanostructure and carbonaceous components generated, originating from the metal units and organic ligands in the 2D MOFs, respectively, ensure high conductivity and active site concentration for OER.^[91-95] Metal nanoparticles (e. g Ni or Co) embedded in carbon components with different compositions and morphologies derived from 2D MOFs are of special interest. Xu and associates^[91] synthesized Ni nanoparticles (Ni NPs) locked in few-layered nitrogen-doped graphene (Ni@NC) obtained by high-temperature

annealing of Ni MOFs in nitrogen atmosphere (Figure 6a). SEM and TEM demonstrated a hierarchical structure of the Ni MOFs comprising aggregated 2D nanosheets with a lateral size of 500–800 nm (Figure 6b and c). The carbonized product (Ni@NC) displayed a spheroidal nanostructure (diameters: 20–30 nm, Figure 6d and e). TEM and HRTEM further revealed that the spheres were composed of Ni nanoparticle cores and 3–5 layers graphene shells (Figure 6f and g). Ni@NC exhibited a low η of 280 mV at 10 mA cm⁻² and excellent catalytic stability (duration of 10 h at 1.52 V vs. RHE) for OER (Figure 6h and i). Liu and associates^[92] designed a novel approach to prepare distorted hexagonal (3,4)-connected Ni₂(BDC)₂(DABCO) (BDC = 1,4-benzenedicarboxylic acid, DABCO = 1,4-diazabicyclo[2.2.2]octane) framework nanoplates, which were transformed to Ni@N-doped carbon nanoplates by pyrolysis, exhibiting a η of 307 mV at 10 mA cm⁻². Meanwhile, Dong and associates^[93] reported 2D carbon framework-encapsulated highly dispersed Co nanoparticles from which N-doped carbon nanotubes grew (Co-NCS@CNTs) by carbonizing 2D ZIF (ZIF-L) nanosheets in an atmosphere of H₂ and Ar. The prepared Co-NCS@CNTs exhibited OER catalytic activity with a η of 360 mV at 10 mA cm⁻². Similar Co@N-carbon nanosheets^[94] were also synthesized, showing a η of 400 mV at 10 mA cm⁻². 2D MOF-derived alloy nanoparticles including carbon components have been also explored for OER electrocatalysis. Alloys can provide additional synergetic effects between the metal components and tenability of the electronic structure for enhanced OER performance.^[116, 117] Gao and associates^[95] prepared FeNi alloy nanoparticles incorporated in carbon nanoflowers (FeNi@CNFs) using 2D bimetallic nanosheet-assembled nanoflower-like MOFs as precursors. The optimized FeNi@CNFs showed a η of 356 mV at 10 mA cm⁻², benefiting from the aligned nanosheets and complex nanoflower morphology for rich active sites and fast electron transfer. Synthetic 2D MOFs derived metal/alloy nanostructures can thus be formed by reduction of the metal units of the 2D MOFs with the organic linker as the reducing agents at high temperature. Most current related catalysts exhibit relatively weak catalytic stability (Table 3). New strategies are needed to explore for robust OER electrocatalysts.

Figure 6. a) Schematic illustration of the preparation of Ni@NC materials from Ni-based MOF precursors. b) SEM and c) TEM images of the Ni-based MOFs. d and e) SEM, f) TEM, and g) HRTEM images of Ni@NC-800. The inset of (g) is a schematic illustration of the Ni@NC structure. h) The OER polarization curves of various Ni@NC samples and commercial IrO₂ catalyst in 1.0 M KOH solution. i) Polarization curves before and after 1000 potential cycles of Ni@NC-800. The inset of (i) is the chronoamperometric curve at 1.52 V vs. RHE for 10 h. Reprinted with permission from Ref.^[91]. Copyright (2017) WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

4.2 Metal oxides/chalcogenides

2D MOF-derived metal oxides can be prepared with morphologies and structures from the 2D MOF precursors maintained, because only relatively low annealing temperatures (200–600 °C)

are needed. The derived carbon components can serve as conductive and protective frameworks by enclosing the metal oxides formed from the metal sites of the 2D MOFs.^[48, 90] 2D MOF-derived metal oxides, such as NiO^[96, 97], Co₃O₄^[97-100] and hybrid metal oxides encapsulated in carbon nanostructures^[101-105], are attracting growing attention. For instance, He and associates^[96] fabricated ultrafine NiO nanoparticles (NPs) within ultrathin 2D Ni MOFs by partial heating decomposition. Benefiting from the ultrathin 2D nanosheet-like structure and highly active sites from the defect-rich NiO NPs, the optimized Ni-MOF-250 demonstrated excellent OER catalytic performance with a η of 250 mV at 50 mA cm⁻², achieving an industrially relevant current density of 1000 mA cm⁻² at a small η of 410 mV. Besides, Li and co-workers^[97] prepared 2D Co₃O₄/C_{BDC} composites on Ni foil by annealing, exhibiting a η of 208 mV at 10 mA cm⁻². This was attributed to the improved conductivity and more exposed active sites offered by the 2D structure with rich hierarchical pores of the derived carbon.

2D MOF-derived bimetallic or trimetallic oxides are believed to have unique hetero-structures and modulated electronic structure, thus leading to better OER catalytic performance than single metal oxide-based electrocatalysts. Zhou and associates^[103] performed plasma-enabled Fe doping in 2D Co MOF nanosheets with considerable oxygen vacancies (V_O), which were carbonized into triangular-shaped “cheese-like” Fe/Co-carbon nanosheets. The optimized Fe₁Co₃/V_O-800 exhibited a good OER performance with a η of 260 mV at 10 mA cm⁻². The authors claimed that filling the oxygen vacancies with Fe heteroatoms helped to achieve the unique heterostructure for fast electron transfer. Li and associates^[104] reported a controlled partial pyrolysis of trimetallic NiCoFe-MOF-74 in nitrogen atmosphere at 400 °C for 60 min to prepare robust NiCo/Fe₃O₄ heteroparticles within 2D MOF-74 (Figure 7a). STEM imaging of NiCoFe-MOF-74 (Figure 7b) showed a nanosheet-like structure. Numerous uniform nanoparticles were formed in the 2D MOFs structure after carbonization (Figure 7c). High-resolution STEM images and corresponding STEM-EELS elemental mapping of NiCo/Fe₃O₄ nanoparticles (Figure 7d-h) indicated the presence of metallic NiCo alloy cores with thin Fe₃O₄ shells. The as-prepared NiCo/Fe₃O₄/MOF-74 delivered remarkable OER performance (Figure 7i-j) with a η as low as 238 mV at 10 mA cm⁻² and catalytic stability of 36 h. DFT calculations revealed the PDS of pure Fe₃O₄ was the escape of the O₂ product with an energy barrier of 1.56 eV, while the PDS was the

formation of $\cdot\text{O}$ on the NiCo/Fe₃O₄ surface representing a slightly smaller energy barrier (1.48 eV). These results confirm that the underlying NiCo alloy promoted the OER activity of Fe₃O₄ through exchanging stabilized active oxygen species. Compared with other 2D MOFs derivatives, 2D MOFs derived metal oxides could maintain stable crystalline structure easily in ambient conditions with high catalytic activity. Meanwhile, the facile synthetic process can promote the scalable production with low cost.

Figure 7. a) Scheme of the fabrication of trimetallic NiCoFe-MOF-74 and the partial pyrolysis of NiCoFe-MOF-74 to NiCo/Fe₃O₄/MOF-74. STEM images of b) NiCoFe-MOF-74 and c) the derived NiCo/Fe₃O₄/MOF-74 after controlled partial pyrolysis at 400 °C for 1 h. d) High-resolution STEM

image of NiCo/Fe₃O₄ nanoparticle and (e) corresponding STEM-EELS elemental mappings of NiCo/Fe₃O₄ showing the hierarchical elemental distributions of Ni, Co, and Fe. f–h) Enlarged high-resolution STEM images taken from the areas highlighted in d), with simulated atomic models overlapped on the images. i) OER polarization curves of NiCoFe-MOF-74 and the derived partial and completely pyrolyzed samples at 1600 rpm in O₂ saturated 1.0 M KOH. j) Relative chronoamperometric test under a constant potential of 1.47 V. Reprinted with permission from Ref.^[104]. Copyright (2018) American Chemical Society.

Similar to the features of 2D MOF-derived metal oxides for OER electrocatalysis, 2D MOF-derived metal chalcogenides (Ni-, Co- or NiCo-based) are also explored as oxygen evolution electrocatalysts.^[106–109] The MOF-derived transition metal chalcogenides have a tunable metal-sulfur coordination environment and good electrical conductivity for OER.^[118] For example, Li *et al.*^[106] developed a liquid-state partial sulfurization procedure to prepare Ni-BDC@NiS catalysts. The 2D [Ni₃(OH)₂(1,4-BDC)₂·(H₂O)₄].2H₂O (Ni-BDC; 1,4-BDC = 1,4-benzenedicarboxylate) MOF was *in-situ* grown on the surface of Ni foil, which was then immersed in a thioacetamide (TAA) solution for sulfurization at different durations. The optimal Ni-BDC@NiS (12 h sulfurization treatment), with ordered Ni-BDC nanosheets for more accessible active sites and efficient mass transfer, demonstrated a η of 330 mV at 10 mA cm⁻². In comparison to liquid-state partial sulfurization, solid-state sulfurization is better controllable and the generated carbon species could further enhance the electrical conductivity and improve the structural stability during the OER process. Liu and co-workers^[107] reported 2D free-standing nitrogen-doped Ni-Ni₃S₂@carbon nanoplates by annealing NiSO₄ based MOF nanoplates as the precursor through a “self-sulfidation” procedure in an inert atmosphere. The resulting nanoplates were constructed by Ni-Ni₃S₂ nanoparticles homogeneously embedded in a carbon matrix, exhibiting a η of 284.7 mV at 10 mA cm⁻² for OER. Similar self-sulfidation methods have been adopted to synthesize N, O and S-tridoped carbon matrix encapsulated with Co₉S₈ nanocomposites (Co₉S₈@TDC) *via* direct carbonization of a 2D Co MOF [Co(BDC)₂(SPDP)₂(DMF)(H₂O)] (H₂BDC: 1,4-benzenedicarboxylic acid, SPDP: 4,40-(sulfonylbis(4,1-phenylene))dipyridine, DMF: N,N-dimethylformamide). The Co₉S₈@TDC obtained showed reasonable OER performance with a η of 330 mV at 10 mA cm⁻². Zhou and associates^[109] synthesized hierarchical porous metal sulfide (Ni-Co-S) nanosheets

arrays (HPNA) directly on conductive carbon cloth (CC) substrates using 2D CoNi MOF nanosheet arrays as precursors, which underwent initial annealing and subsequent sulfurization. The hierarchical porous nanostructures, affording high specific surface area, abundant active sites and short diffusion paths, ensured a better OER performance of the Ni-Co-S HPNA with a η of 270 mV at 10 mA cm⁻² than that of Co-S HPNA. Compared with 2D MOF-derived metal oxides (Table 3), most 2D MOF-derived metal chalcogenides electrocatalysts suffer from insufficient stability, most likely due to the fact that metal chalcogenides are transformed to metal oxides to be active for OER,^[118, 119] thus suffering irreversible component and structure change in long-term operation. Exploring novel hybrids to find more robust 2D MOF-derived metal chalcogenides could be a possible solution. In summary, 2D MOFs derived metal oxides/chalcogenides have been widely investigated as OER electrocatalysts, and much progress on the OER catalytic capability and understanding of the catalytic mechanisms have been obtained over the past several years.

4.3 Metal phosphides/hydroxides

Metal phosphides are emerging as a class of OER catalysts that display good electrical conductivity and metalloid characteristics.^[120, 121] The organic ligands of the 2D MOF-derived carbon layers are expected to enhance the electron transfer and limit the agglomeration of metal phosphide nanoparticles. Thus, 2D MOF-derived metal phosphide-carbon composites show appealing OER electrocatalytic properties.^[110-113] For example, Du and associates^[110] reported the synthesis of cobalt phosphide nanoparticles embedded in N-doped carbon materials (Co-P@NC) using 2D Co-based porphyrin paddlewheel framework-3 (PPF-3) nanosheets as the sacrificial template. The template was initially carbonized followed by low temperature phosphorization using NaH₂PO₂ as the phosphor source. The Co-P@NC demonstrated a η of 370 mV at 10 mA cm⁻² for OER. Using a similar phosphorization approach, Zhu and co-workers^[111] prepared a cobalt phosphide nanosheet and amorphous carbon composite (CoP-NS/C) using as-prepared 2D Co-ZIF nanosheets as the template. The MOF-derived porous crystalline CoP nanosheets provided highly-exposed active sites. The existence of carbon afforded fast electron transfer, ensuring the good OER performance with a η of 292 mV at 10 mA cm⁻². Further, constructing metal phosphide based composites on the NF substrate structure shows enhanced OER performance, due to highly

exposed active sites, shortened ion diffusion path and promoted gas release during OER. Gong and co-workers^[112] designed hierarchical porous CoP nanoarrays on NF (HP-CoP NA/NF) that exhibited good OER electrocatalytic activity with a low η of 258 mV at 10 mA cm⁻². A three-step procedure was followed: i) Interconnected 2D cobalt-based MOFs were grown on NF *via* an aqueous solution reaction at room temperature; ii) The MOFs were uniformly converted into porous CoP arrays through a Co²⁺-etching process and iii) subsequent phosphorization. Additional metal doping to the 2D MOF-derived metal phosphides is believed to modulate electronic structures to lower energy barriers, resulting in bimetallic phosphides typically outperforming monometallic counterparts for OER. Wang and associates^[113] fabricated Co_{1-x}Fe_xP/C nanosheets using 2D CoFe MOFs as precursors, retaining the well-defined 2D morphology of the MOFs. The optimized Co_{0.7}Fe_{0.3}P/C showed good OER catalytic performance with η as low as 270 mV at 10 mA cm⁻². The enhanced OER performance was attributed to the 2D morphology of the carbon matrix and the ultrafine character of Co_{1-x}Fe_xP nanoparticles. Moreover, moderate iron doping preserved the catalytically active sites and improved the oxidation ability of the surfaces of the Co_{1-x}Fe_xP nanoparticles. Overall, 2D MOF-derived metal phosphides demonstrate relatively good OER catalytic performance, but in-depth understanding of OER catalytic mechanism is still lacking. More *in-situ* technologies and DFT simulations to study the OER active sites of 2D MOF-derived metal phosphides are critically required.

Figure 8. a) Schematic illustration of *in-situ* synthesis of layered double hydroxides (LDHs) from oxalate MOFs. SEM images of (b) FeCo_{0.5}Ni_{0.5}-MOF and (c) FeCo_{0.5}Ni_{0.5}-LDH. d) HRTEM images of FeCo_{0.5}Ni_{0.5}-LDH. e) STEM images of FeCo_{0.5}Ni_{0.5}-LDH and corresponding EDS mapping of C, O and Fe, Co and Ni. f) iR-corrected LSV curves and g) Tafel plots of various catalysts in 1 M KOH. h) Operational stability of FeCo_{0.5}Ni_{0.5}-LDH. Reprinted with permission from Ref.^[115]. Copyright (2019) Elsevier.

2D MOF-derived metal hydroxides, especially layered double hydroxides (LDHs) with better ionic conductivity than the conventional bulk LDHs, are attracting intensive attention for the OER.^[114, 115] For instance, Ding and associates^[114] prepared 2D CoNi hydroxide ultrathin nanosheets (UNSS) *via* liquid exfoliation of a CoNi MOF precursor in 0.1 M KOH. The CoNi hydroxide UNSS obtained

demonstrated a η of 324 mV at 10 mA cm⁻² for OER. In addition, Gu and co-workers^[115] have initially prepared a series of oxalate MOFs (Fe_xNi_{1-x}-MOF) grown on Cu foils, which were *in-situ* transformed into LDHs in 1 M KOH for 30 min (Figure 8a). FeCo_{0.5}Ni_{0.5}-MOF (Figure 8b) showed an octahedral morphology with a clearly layered structure. The derived FeCo_{0.5}Ni_{0.5}-LDH showed a rougher structure (Figure 8c and d) composed of ultrathin hierarchical nanosheets (thickness: 1 nm). The STEM images of FeCo_{0.5}Ni_{0.5}-LDH and the corresponding EDS mapping images (Figure 8e) showed a uniform distribution of elemental C, O and Fe, Co and Ni. The optimized FeCo_{0.5}Ni_{0.5}-LDH gave superior OER catalytic activity (Figure 8f-g) with a low η of 248 mV at 10 mA cm⁻², a Tafel slope of 38 mV dec⁻¹ and long-term catalytic stability over 50 h. The dynamic OER process at the electrocatalyst surface was characterized by *in-situ* Raman spectroscopy. The Raman spectra of FeCo_{0.5}Ni_{0.5}-LDH exhibited a signal at $\sim$ 530 cm⁻¹ at 1.1 V vs. RHE (no OER), ascribed to the Ni-O stretching mode.^[122] When the potential was raised to 1.6 V vs. RHE (OER on-going), the Raman spectra showed new peaks at $\sim$ 470 and 550 cm⁻¹, which were identified as arising from the NiOOH,^[123] indicating that the OER active sites were Ni atoms. Besides, electron paramagnetic resonance (EPR) spectroscopy of FeCo_{0.5}Ni_{0.5}-LDH indicated a modulating effect of Co cation on the electronic structure of FeNi-LDH. In contrast to other MOFs derivatives, 2D MOF-derived metal hydroxides have recently attracted increasing interest for OER electrocatalysis due to high electrocatalytic activity and easy preparation. Hetero-components (atoms, molecules *etc.*) can straightforwardly be incorporated in the layered host matrix for tunable electronic structure and enhanced OER catalytic activity, but further comprehensive studies of the OER focused on the metal hydroxides are needed as noted.

Figure 9. a) The number of related publications during the past years (2016-2019). Data also presented in Table 1, 2 and 3. b) Chronological trend in overpotential of OER catalysts including 2D Ni-based MOFs, 2D Co-based MOFs and 2D MOFs derivatives in alkaline electrolytes. The grey dashed line shows the overpotential of RuO₂ in alkaline electrolytes. Red line shows the corresponding trend of overpotential. c) The experimental data summary between overpotential and catalytic stability of 2D Ni-based MOFs, 2D Co-based MOFs and 2D MOFs derivatives in alkaline electrolytes during the recent five years.

5. Summarizing conclusion and perspectives

We have summarized the progress in the areas of preparation, characterization, and use of 2D transition metal MOFs and their derivatives as OER electrocatalysts. The number of related publications keeps increasing over the past five years (Figure 9a), with the performance summarized in Figure 9b-c. As shown in Figure 9b, many of these materials exhibit superior catalytic activity compared to the noble-metal based catalysts such as RuO₂ ($\eta < 300$ mV at 10 mA cm⁻²), and considerable stability with only negligible decay after tens of operating hours as shown in Figure 9c and Table 1-3. Comparing to the evolution of other OER catalysts^[124] where the overpotential dropped from around 400 mV to 200 mV over 7 years, the evolution of performance has been similar for 2D MOFs, with no clear trend of any specific type seeming likely as best leading to future improvements. Although exciting scientific achievements have been reported, challenges to be overcome and new perspectives to be explored still remain in this field: First, the limited stability and strong tendency of pristine 2D MOFs to agglomerate during OER are limitations to their long-term applications. Despite approaches such as introduction of metal ion/metal-organic components into the 2D MOFs and *in-situ* 2D MOF generation on NF have been adopted to improve the structural stability of 2D MOFs and prevent agglomeration, more efficient and facile strategies should be developed. Damage to surface morphology and pore structure of 2D MOF derivatives during operation is also a critical issue, which could be addressed, for example by a partial annealing method such as reported by Li et al.^[104] Second, the presently reported 2D MOFs rely on expensive organic ligands and their derivatives, obtained by highly energy-consuming processes, and the OER electrocatalysts obtained are mostly evaluated under

alkaline solution conditions. Exploring cheap raw materials and scale-up strategies for reproducible 2D MOF-based electrocatalysts with superior OER catalytic activity and high stability over a wide range of pH values are urgently needed, especially those that can operate in neutral electrolytes. Third, there are only few reports on the structural and morphological evolution of 2D MOFs and their derivatives during the OER process followed by *in-situ* techniques (e.g. *in-situ* XAS, Raman, TEM etc.). In comparison to *ex situ* characterization, *in-situ* techniques combined with computational simulation is a powerful route to localizing the intrinsic active sites and understanding the reaction mechanisms. Fourth, bifunctional electrocatalysts that are capable of simultaneously catalyzing hydrogen evolution reaction and OER, or dioxygen reduction reaction and OER, will hold great prospects for simplifying setups for water splitting and secondary metal air batteries.

Notes

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915 Two-dimensional (2D) metal-organic frameworks (MOFs) with transition metal based nodes
916 (e.g. Ni, Co and Cu) are emerging as oxygen evolution reaction (OER) electrocatalysts. The
917 preparation, characterization and performance of 2D MOFs and the derivatives for OER are
918 summarized and analysed, providing guidelines for further electrocatalyst development.

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920 Mr. Wei Huang, Dr. Jing Tang, Ms. Fangyuan Diao, Dr. Christian Engelbrekt, Prof. Jens Ulstrup,
921 Dr. Xinxin Xiao and Dr. Kristian Mølhave

922 **Recent progress of 2D metal-organic frameworks and their derivatives for oxygen evolution**
923 **electrocatalysis**

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