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Analysis of Electrocatalytic Metal-Organic Frameworks

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Abstract

The electrochemical analysis of molecular catalysts for the conversion of bulk feedstocks into energy-rich clean fuels has seen dramatic advances in the last decade. More recently, increased attention has focused on the characterization of metal-organic frameworks (MOFs) containing well-defined redox and catalytically active sites, with the overall goal to develop structurally stable materials that are industrially relevant for large-scale solar fuel syntheses. Successful electrochemical analysis of such materials draws heavily on well-established homogeneous techniques, yet the nature of solid materials presents additional challenges. In this tutorial-style review, we cover the basics of electrochemical analysis of electroactive MOFs, including considerations of bulk stability, methods of attaching MOFs to electrodes, interpreting fundamental electrochemical data, and finally electrocatalytic kinetic characterization. We conclude with a perspective of some of the prospects and challenges in the field of electrocatalytic MOFs.

Keywords

metal-organic frameworks; electrochemistry; electrocatalysis; electroactive thin films

1 Introduction

Humanity is moving rapidly towards increasingly dire consequences of climate change and environmental destruction [1,2] and there has been a clear need for many decades to address the root causes of these negative outcomes. Consequently, we and many others have been working to develop the necessary knowledge to create devices which synthesize clean fuels (e.g., hydrogen from water or alcohols from carbon dioxide and water). Significant work towards this goal has been carried out [3–6], and the resulting research has been diverse. Within the chemistry community, two general conclusions to date stand out to us. **First**, *molecular* catalysis driving fuel synthesis offers enormous potential for fine tuning product selectivity and rate [7–10]. **Second**, such molecular catalysts when in homogeneous phase usually do not survive long enough to be practical, even if they are made from relatively inexpensive earth-abundant elements [11]. In other words, fantastic molecular catalysts have been developed which nonetheless are generally not relevant to industrial applications.

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Great strides towards addressing this problem have been made through incorporation of promising molecular catalysts into materials [12–14]. This approach provides several benefits: unwanted bimolecular decomposition pathways between catalysts can be avoided, the matrix can be used to tune the selectivity and activity of the molecular catalyst, and, in the case of incorporation of molecular catalysts into electrolytic devices, the catalytic sites can theoretically be kept constantly supplied with electrons via contact with the electrode.

Next-generation site-isolated electrocatalysts have leveraged the established knowledge in materials chemistry (e.g., metal oxide electrodes [15,16] and polymer scaffolds [17,18]). Metal organic frameworks (MOFs) have proven to be one such versatile platform for the embedding of molecular catalyst units. MOFs themselves take advantage of molecular chemistry via use of well-defined multidentate molecular linkers and metal clusters (referred to as secondary building units, or SBUs) as the components for the bulk framework [19,20], a method which can result in porous materials with exceptionally high internal surface area. As the components themselves are molecular, both molecular organic and inorganic chemistry techniques can be used to modify MOFs, such as through the incorporation of molecular catalyst units [19,20] and via advanced bimetallic electrocatalyst MOF systems [21,22].

Despite the potential of MOFs as components in fuel-forming electrocatalytic devices, the vast majority of MOFs are insulating materials. Designing MOFs which permit electron flow has seen sustained attention over the last decade, with two general strategies pursued (Figure 1): 1) building intrinsically conductive or semi-conductive MOFs by carefully overlapping the molecular orbitals of the molecular components [23,24] and 2) building a MOF of redox-active components which allow electron/hole charge hopping [25–27]. These efforts are maturing, and consequently building MOFs which incorporate molecular electrocatalysts has become feasible.

While we will not focus on the factors for designing next generation MOF electrocatalysts, it is worth noting the clear trend towards MOFs which leverage outer coordination sphere effects such as proton transfer relays and hydrogen bonding, leading to the suggestion that catalytic sites in MOFs could approach the tunability and complexity of enzyme active sites [28]. Additionally, it is also clear that engineering of MOF pores to facilitate rapid electrolyte and substrate access to catalyst active sites will be crucial for achieving high current densities [29].

Excellent recent reviews on the field of MOF electrocatalysis exist [30–33], with an increasing emphasis on questioning long-term stability [34] and contextualizing the underlying fundamental electrochemical and diffusional processes at play [35]. However, to date the key concepts required to build and analyze MOF electrocatalyst materials have not been summarized. While these concepts are known to various degrees throughout the MOF electrocatalysis field, *here we seek to collect the latest methods into one resource.*

To do so, we draw on resources and lessons learned by our counterparts in the molecular electrochemistry community as well as the rich redox polymer literature. Our hope is that this review will provide a springboard for new researchers to jump into this rapidly

expanding field, as well as provoke conversation regarding cutting-edge topics in MOF electrocatalysis.

We begin this tutorial-style review by discussing bulk MOF stability in **Part 2**, a crucial starting point when exploring the electrochemistry of a new MOF. Such knowledge can help the MOF electrochemist understand if the observed electrochemical results are due, in fact, to the actual electrochemistry experiment or an unanticipated instability issue. In **Part 3** the common methods for preparing MOFs for electrochemical analysis are presented. Specifically, we seek to answer the question “how are MOFs attached to electrodes for subsequent analysis?” Over the course of **Part 4** we explore common methods for investigating basic electrochemical properties of a MOF material (drawing significant parallels with the homogeneous electrochemistry community), and in **Part 5** we discuss methods for probing the electrocatalytic properties of MOFs.

2 Bulk MOF Stability

Stability is a fundamental parameter of any prospective functional material. However, in MOF-related research, including articles on electrochemical properties, rigorous characterization of stability is yet to become a standard entry. In this section, we review (i) different aspects of MOF stability, (ii) methods of stability assessment, and (iii) design factors affecting MOF stability.

2.1 Features of stability

2.1.1 Definition of stability—Stability of a given MOF is not an absolute and universal feature as it depends on the intended application. MOF stability has been defined as “the resistance of MOF structure to degradation upon exposure to the operating conditions” [36], stressing the importance of considering the purpose of the MOF in the definition of its stability. The authors identify (i) chemical stability and (ii) mechanical stability as factors relevant to MOFs. We would also name (iii) *stability under electrochemical conditions* as a key factor for electrocatalysis. It is clear that these categories can be related to each other, e.g., elevated temperatures may speed up existing chemical degradation processes, yet they provide a convenient guideline for consideration of destabilizing factors. Some authors also distinguish between thermodynamic and kinetic stability [37], the latter referring to stabilization by a high activation barrier of decomposition – a dichotomy useful in designing stable materials.

MOF degradation conventionally refers to drastic changes in MOF structure, such as full or partial pore collapse, and is most often detected as stark changes in diffraction pattern, high-magnification images, and/or internal surface area. Meanwhile, milder processes, such as formation of defects and partial framework dissolution, are not always considered, although these latter processes can change the properties of a MOF dramatically [38–40], and leached-out components can affect the surrounding media and impair electrochemical studies. While a particular set of conditions might not be harsh enough to lead to structural collapse, it can still induce defect formation. With this in mind, we propose a modified definition of MOF stability: “the resilience of MOF structure *and composition*, including defect formation, upon exposure to given operating conditions.”

2.1.2 Aspects of stability—In this section we review aspects of MOF stability as outlined above.

Chemical stability

1. Solvent and coordinating substances

In general, the weakest part of the MOF structure tends to be the linker-SBU bond [41]. In the presence of coordinating molecules (e.g., water, alcohols, carboxylates, phosphates), the bond may become labile and enter an equilibrium where the linker and the guest molecule compete for the electrophilic SBU, leading to partial linker detachment. In fact, this phenomenon can be exploited to introduce electrocatalysts in solvent-assisted linker exchange (SALE) and post-synthetic exchange (PSE) [42–45].

If a MOF is to be used in conjunction with liquids, a critical destabilizing factor to consider is the solvent, for it is present both inside and outside of the MOF. Thus, it is important to choose experimental conditions that avoid introducing undesirable coordinating ligands. For instance, phosphate or acetate buffers that are frequently used electrolytes have been known to cause framework collapse in multiple carboxylate-based frameworks [46]. In an illuminating study, Marreiros et al. found that prolonged exposure of UiO-66 to methanol generates missing-linker defects, equilibrating at approximately one missing linker per unit cell [47]. While this does not necessarily lead to framework collapse, the defect makeup and porosity may be altered in an unpredictable way. If a MOF is not kept in anaerobic conditions, its stability in water needs to be considered even if it is not purposely exposed to aqueous solutions, as even atmospheric humidity can promote linker detachment [48,49]. Regarding water stability in particular, Burtch et al. provide a comprehensive review and guidelines for application-related tests [37].

2. Acid/base

Aqueous media at extreme pH levels present an additional stress for the MOF structure. In acidic or basic conditions that are often used for electrocatalytic fuel production or water oxidation, protons and hydroxides can compete with SBUs and linkers, respectively, leading to an equilibrium-controlled ligand dissociation. In acidic solutions, the SBU-linker bonds can be broken by protonation at the linker binding group (e.g., carboxylate, phosphonate, azolate), while in basic solutions, hydroxide ions may coordinate to the SBU. In a recent review by Yuan et al. [50], the authors pointed out that, although there are exceptions, MOFs constructed using low-valent metals and azolate linkers tend to be stable under alkaline conditions while being readily hydrolysed by acids. On the other hand, MOFs built from high-valent metal ions and carboxylate ligands tend to be stable in acids and decompose in basic solutions. This phenomenon is explained through the differing affinities of SBUs and linkers toward hydroxides or protons, respectively, depending on valence state of the metal and the pK_a of the ligand. These general rules of SBU/ligand affinity are demonstrated by experimental investigations of MOF stability as summarized by Howarth *et al.* [51] in their pH stability chart of common MOFs (Figure 2).

As a first approximation, the following guidelines are proposed to engineer acid/base-stable MOFs [50] (Scheme 1):

- 1) **Stability in acid** is promoted by using ligands with low pK_a s which, in turn, should be combined with high-valence metals.
- 2) **Stability in base** is promoted by using low-valent metal ions which should be combined with high- pK_a ligands.

Mechanical stability

Mechanical stability is a major point of concern when performing MOF activation (evacuation of the pores), as some MOFs can undergo irreversible pore collapse upon removal of guest molecules [52,53]. Caused by the capillary forces, this effect is more pronounced when removing solvent with higher surface tension, like water, and can be mitigated by preliminary exchange for a solvent with lower surface tension [52], or activation using supercritical CO_2 [54]. Frameworks with large pores and long, flexible linkers are more susceptible to collapse upon activation than MOFs with short, rigid linkers and dense structure [36].

Stability under electrochemical conditions

Similarly to the fact that some molecules cannot be reversibly reduced or oxidized in homogenous electrochemical experiments, it should be considered whether the individual building MOF blocks, i.e. the SBUs or organic linkers, may also be susceptible to irreversible changes upon reduction or oxidation. Fortunately, many common linkers and SBUs used for MOF construction are electrochemically inert over standard potential ranges. Indeed, this is often a major obstacle to the building of electrochemically addressable MOFs! On the other hand, electrochemical stability is of crucial importance for MOFs that are envisaged for electrocatalysis applications.

The origins of MOF instability under electrochemical/electrocatalytic (both without and with substrate present) conditions are varied, and can include: 1) delamination of the whole MOF from the electrode, perhaps due to charging of the MOF, 2) degradation of a specific component (e.g., linker, SBU, catalyst) after addition or removal of electrons, or 3) bulk collapse of the MOF framework which may inhibit substrate or counterion access. Techniques for assessing whether a MOF is stable under electrocatalytic conditions will be discussed in detail in section 4.

2.2 Methods for evaluating MOF stability

As noted previously, no standard procedure or standard testing protocols has yet been established for assessing MOF stability [36,51]. Most MOF-related articles report either powder X-ray diffraction (PXRD) only or PXRD + Brunauer–Emmett–Teller (BET) stability tests, as these are the most accessible tools. However, exposure of a MOF to liquids can introduce defects without disrupting the overall structure, making them undetectable by PXRD alone, and, if the detached linkers stay trapped in the pores, possibly invisible by the BET method [36,47]. Therefore, the integrity of a MOF may not be completely assured, at least in liquid or in the presence of solvent vapours, based only on these two characterization

methods. Burtch et al. [37] proposed the measurement of solid phase mass loss after exposure to liquid as a test for solvent stability, a valid method as long as one ensures complete evacuation of non-coordinated guest species (e.g., detached linkers) from the pores. To test stability in a given solvent, we propose the existing common techniques be complemented by incubation in the solvent for at least the duration of the relevant electrochemical experiments followed by characterization not only of the MOF, but also the supernatant, to probe for possible leached-out MOF components. If a leached-out MOF component is detected in the supernatant, it is reasonable to repeat the incubation-measurement cycle several times to test whether the component keeps leaching out, which would indicate an equilibrium, or the leaching stops after several cycles. It is possible that only weakly bound linkers, such as those in defect sites, decoordinate and diffuse out, in which case the initial leaching will subside after multiple soaking cycles. The presence of MOF components in the supernatant can be assessed by the appropriate method such as spectroscopic techniques (e.g., NMR and UV-vis) or ICP (inductively-coupled plasma). This complementary approach increases the likelihood of uncovering partial decomposition which is otherwise difficult to detect.

2.2.1 X-ray diffraction methods—PXRD is the most basic method for characterizing structural quality of MOF materials. It allows assessment of overall crystallinity and, given a high-resolution pattern, estimation of basic cell parameters of the material. Although its capacity to provide *ab initio* structural data is rather limited (the Rietveld analysis, where a predicted pattern is refined to match the experimental one, relies on a rational initial structure estimate), the method allows for the qualitative detection of changes in the structure through comparison to reference patterns or by watching the pattern of the same material evolve following exposure to the given experimental conditions. Variations of this technique exist, including PXRD performed in solvent [55]. The variable temperature XRD (VT-XRD) method is especially useful to assess thermal stability [56]. For thin MOF layers or highly dispersed materials such as many individual surface-mounted MOF (SURMOF) crystals, when the sensitivity of classical PXRD is too low, the grazing incidence X-ray diffraction (GIXRD) method is used [57,58]. For materials with mesoscopic structural features, the wide-angle PXRD (WA-XRD) can be used to probe the stability of those features [59]. Evidence for partial loss of crystallinity in PXRD patterns can be seen in the broadening of reflections and/or appearance of the halo indicative of an amorphous material, while irreversible pore collapse leads to a new set of reflections accompanied by appearance of a broad halo [53] (see Figure 3).

2.2.2 Brunauer–Emmett–Teller (BET)—PXRD methods alone cannot identify randomly distributed defects: their nature, abundance or localization, nor can they detect randomly oriented guest molecules in the pores. Thus, BET surface area measurements are often used to supplement stability characterization. Based on adsorption and desorption of an inert gas, this method helps to determine the total internal surface area [48] and allows the calculation of pore dimensions distribution using a modification of the Barrett-Joyner-Halenda (BJH) method [59,60]. From the point of view of MOF stability, this family of methods can assess the integrity of the crystalline structure by comparing internal surface area and pore size distribution before and after the sample is subjected to stress conditions,

and detect changes in defect concentration [61]. Collapsed MOF structures tend to have dramatically decreased internal surface area compared to uncompromised lattices, while introduction of defects tends to lead to a slight increase of the internal surface area (per gram), provided the overall framework structure is intact [40,61]. It should be noted that while BET is a powerful method for assessing *bulk* MOF stability, it is much more difficult to apply BET to MOF thin films such as those used in electrocatalytic application. Precedent does exist using krypton as the analyte gas for MOF thin film BET measurements [62], though the method may be challenging to broadly apply to MOF thin films.

2.2.3 Thermogravimetric analysis (TGA)—In thermogravimetric analysis (TGA), the weight change of a solid sample is monitored as a function of temperature (usually during heating) under varying ambient conditions (normally air, inert gas, or oxygen). As such, the method is primarily used to study thermal or temperature-induced oxidation stability of MOFs [63], but can sometimes be used for other purposes. For example, it was possible to quantify missing-linker defects in UiO-66 by comparing experimental weight loss of the linker to the expected one [64]. The method can also be used to provide information about absorbed/guest species [64–66], especially if coupled with a mass spectrometer [64]. TGA is a useful supplement to other methods, though again is much more applicable to bulk MOF materials than MOF thin films on electrodes.

2.2.4 Spectroscopic methods—While X-ray diffraction, BET, and TGA are useful methods for assessing *bulk* MOF stability/crystallinity, more direct evidence of the (in)stability of a MOF's *molecular* components can be obtained using spectroscopy. For example, infrared spectroscopy has been one of the leading techniques used to identify and characterize the chemical nature of MOF defect sites [67]. With an appropriate instrumental setup, infrared spectroscopy can be routinely performed on thin films – such as a thin MOF film on an electrode. Alternatively, X-ray photoelectron spectroscopy (XPS) can quantify relative atomic ratios and answer questions such as ‘Has the number of ligands relative to metal clusters changed?’, in addition to directly probing changes in metal oxidation state. In general, XPS, infrared spectroscopy, and a wealth of other available spectroscopic methods in principle allow assessment of if the molecular components of a MOF remain intact after exposure to the conditions of interest. We elaborate on the use of spectroscopic methods to probe MOF stability after electrochemical analysis below (Part 4.1.4, Electrochemical stability).

2.3 Improving MOF stability at the design level

The bond between the linker and the SBU is perhaps the most crucial factor providing stability to a MOF [41], especially when considering applications in polar liquid media or in contact with water. Thus, the most intuitive approach to improving the stability is by strengthening the ligand-SBU bond.

2.3.1 SBU type—The strongest ligand-SBU bond often forms by using Lewis acidic metal cations of higher oxidation states and high charge density [36], such as Zr^{4+} , Cr^{3+} , Ti^{4+} . Multiple authors have also recommended consideration of Pearson's hard/soft acid/base principle (HSAB) when choosing MOF building blocks [37,50,68], matching high-

charge metal ions with low- pK_a ligands, and less charged metal cations with “soft” linker types, such as azolates (Scheme 1). As pointed out above in the acid/base stability section, for some applications (e.g., in basic aqueous media) the latter combination is actually preferable.

2.3.2 Linker type—The key stability factor in linker topology is the connectivity number [50]. From an entropic standpoint, in an equilibrium of dissociation and reassociation with the SBU, a linker with 3-4 coordinating groups is less likely to detach from the framework completely than the corresponding bidentate linker. Sometimes, as in the case of PCN-601, the number of SBU connections per individual linker is named as the crucial stability factor over individual bond strength [69]. Related to this factor, linker rigidity also plays an important role in kinetic framework stabilization. Similar to the connectivity number, a rigid linker restricts its detachment from the SBU upon partial substitution by solvent molecules [70].

The internal pore lining of the MOF is eventually determined by the body of the linker, so introducing functional groups into it is a classical approach to tuning framework stability [71]. For example, decoration of the MOF pores with hydrophobic groups or using highly hydrophobic linkers improves stability in aqueous media [72], and sterically shielding an SBU with linker-borne bulky groups can protect it against coordinating agents [73] – an example of kinetic stabilization.

The most prominent stable MOF linker type in the literature is carboxylate-based. Using carboxylate linkers, some of the most stable MOFs have been introduced, such as UiO-66 [74] and MIL-100 [75]. More recently, BUT-8(Cr) MOFs have been introduced, demonstrating high stability in concentrated hydrochloric and sulphuric acids [76]. When designing a carboxylate framework, it is reasonable to keep in mind that, although there are exceptions [71], most carboxylate-based MOFs tend to decompose in aqueous base while having higher stability in neutral to acidic conditions than other linker types [50].

While the MOF field is dominated by carboxylate-based frameworks, other linkers may be interesting to consider for specific applications. One such unconventional linker type is phosphonate-based, which may be of interest for electrocatalysis-related applications considering, for example, the emerging field of highly proton-conductive phosphonate MOFs [77]. In 2012, Taylor and coworkers reported a highly water-stable MOF (CALF-25) by using phosphonate monoester linkers [73], where the stability was attributed to shielding of the Ba^{2+} SBU by the phosphonate-borne ethyl esters. Two years later, Taddei *et al.* synthesized a zirconium phosphonate MOF (UPG-1) which was more stable towards hydrolysis than UiO-66 [78]. This year, Zorlu and coworkers presented a cobalt arylphosphonate MOF with high thermal stability (up to 500 °C) [79]. These benefits are normally attributed to the metal-phosphonate link being stronger than the corresponding metal-carboxylate link [79,80], possibly due to higher bond multiplicity between an individual SBU and the ligand (see above). On the other hand, the high affinity of phosphonates to metal ions complicates the formation of porous, high-quality crystalline materials, and amorphous or layered structures are often formed instead [80,81]. For more

information on phosphonate-based MOFs, we direct the reader to reviews by Gagnon *et al.* [80], Taddei *et al.* [82] and Yücesan *et al.* [83].

Another unconventional linker type is sulfonate-based, which was early on hypothesized as a promising linker for engendering high proton conductivity in MOFs [81]. In general, the sulfonate-metal bond is rather weak, making purely sulfonate-based frameworks the least stable in the family [81]. However, there are reports of water-stable sulfonate MOFs, such as copper- or terbium-based frameworks built with combined carboxylate/sulfonate linkers introduced by Dong *et al.* [84,85] which exhibit high proton conductivities. More recently, a water-stable NDI-sulfonate (NDI = naphthalene diimide) MOF was reported possessing high Li^+ conductivity [86].

Azolate-based MOFs are a large group of frameworks boasting some very stable members such as ZIF-8 [87] and PCN-601 [69]. A common feature of azolate-based MOFs is good stability under basic conditions (sometimes as harsh as boiling in concentrated NaOH [69]) due to the relatively high $\text{p}K_{\text{a}}$ of the linker. Utilizing this feature, a MOF-based glucose sensor, where basic medium is a requirement for the electrochemical detection, has been reported this year [88], showing both environmental and electrochemical stability of the imidazolate-based MOF (MAF-4- Co^{II}). The group of Long has synthesized a MOF with universal stability in both acidic and alkaline conditions created using the tritopic pyrazolate linker 1,3,5-tris(1*H*-pyrazol-4-yl)benzene. This material remains stable in boiling aqueous media at pHs ranging from 2 to 14 for two weeks [89]. Following the previously mentioned HSAB analysis, it is recommended to combine azolate-based linkers with soft, low-valence metals to achieve the highest stability.

2.3.3 Preparation considerations—Preparation procedures play an important role in structural quality and stability of the resulting MOF and knowledge from these studies can be translated to the direct solvothermal synthesis of thin films described in section 3. For example, defects and associated thermal stability of UiO-66 as a function of synthesis temperature has been investigated with the temperature ranging from 100°C to 220°C [90]. The experiment showed that higher temperatures during synthesis led to fewer defects, with the best material quality achieved at the highest temperature probed, 220°C.

If the SBU is not a single metal ion but rather a cluster or polyoxometalate, the conventional preparation method is via forming the SBU particles *in situ* during synthesis. This approach can lead to some of the SBUs being defective – such as being partially formed or irregularly capped – when they are incorporated into the framework (for example, an illuminating discussion of this topic for a specific MOF, UiO-66, is available [91]) This issue can be avoided by using *pre-formed* SBUs, improving crystal quality and associated stability of the corresponding MOF. Using this method, Zhou *et al.* created a series of PCN frameworks using pre-formed $[\text{Fe}_2\text{M}(\mu_3\text{-O})]$ SBU clusters, reporting greatly improved crystal quality and stability in the resultant MOFs [92]. In a similar approach, DeStefano *et al.* used pre-formed $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{OAc})_{12}$ acetate-capped SBUs, enabling room-temperature synthesis of nearly defect-free UiO-66 [93].

It is well known that isorecticular expansion of a framework by using longer linkers produces less stable MOFs, eventually leading to frameworks amenable to collapse or intergrowth. Cai et al. [94] presented a way to combine both high porosity and high stability in a single MOF by engineering defects into hierarchical pores. For example, the hierarchically porous UiO-66 analogue HP-UiO-66 exhibits mesoporosity while retaining the same stability as the parent UiO-66 structure.

Another crucial aspect of MOF synthesis is the use of modulators [95,96]. A modulator is normally a small molecule possessing the same nucleophilic group as the linker. For example, typical modulators for carboxylate-based MOFs are acetic, benzoic and formic acids. The mechanistic purpose of a modulator is to compete with linkers for SBU coordination, introducing an alternative equilibrium. This slows down crystal nucleation and allows *in situ* correction of lattice errors, improving overall crystal quality. However, these benefits come at a price of introduction of modulator-occupied (missing linker) defects.

3 Preparing MOF-modified electrodes

Electrochemical analysis of MOFs requires interfacing of the MOF with an electrode. While the methods of attaching MOFs to conductive substrates suitable for use as electrodes has rarely merited standalone investigations, the means of preparation has important implications. At one extreme, electroactive MOFs are synthesized directly on electrodes, and at the other extreme, MOFs are first grown and then attached. Each method has different considerations including mechanical stability (will the MOF easily detach?), preparation time, and ease of electron transfer between the conductive electrode substrate and the MOF.

MOFs are generally prepared for electrochemical studies by four methods: dropcasting, electrophoretic deposition, direct solvothermal growth on a bare or SAM-modified electrode surface, and layer-by-layer epitaxial methods (Figure 4). A fifth method which uses a metal oxide film deposited on an appropriate substrate by atomic layer deposition (ALD) will also be discussed. Other methods for attaching MOFs to electrodes which are outside of the scope of this review include electrochemical syntheses [97–104] and spin or dip coating [105,106]. Additionally, a plethora of methods exist for building well-ordered MOF films on non-conductive substrates, and we expect that these methods can be applied for the specific case of attaching MOFs to conductive substrates for electrochemical analysis. For readers interested in a more comprehensive review, please see the excellent contributions by Genesio *et al.* (which focuses on transparent conductive oxide substrates) [105], that of Liu and Wöll (on general methods for growing thin MOF films on substrates) [107], and an electrochemical-focused review by Li *et al.* [101].

In general, we note that considerable variation exists in the electrochemical MOF community for preparing MOFs on electrodes. The connection between electrode and MOF is a crucial factor in the resulting electrochemical response – specifically regarding the rate of electron transfer between the electrode and the first MOF layer as well as how much of the bulk MOF is electrochemically accessible. Both points will be discussed in more detail in Part 4. The type of MOF/electrode attachment can also have a large impact on the strength of mechanical adhesion, with poor adhesion resulting in delamination [34,108]. To date we

are unaware of broad systematic efforts comparing electron transfer kinetics and MOF adhesion based on the electrode preparation method – though such studies would be quite valuable. The limited examples available indicate that clear differences should exist [34].

3.1 Dropcasting

The simplest method to attach MOFs to electrode surfaces is by dropcasting. This technique consists of suspending a pre-prepared bulk MOF in a volatile solvent (typically by sonication) and subsequently ‘dropping’ a small volume of this suspension onto an electrode surface. The electrode is then left to dry with the solvent evaporating to leave a thin film of the MOF dispersed on the electrode for electrochemical analysis. This procedure has seen wide use [31,109–111].

Dropcasting of MOFs has been performed from suspensions consisting solely of MOF particles [111] as well as mixtures of MOF particles with additives to improve conductivity such as carbon black [112–114] and graphite [33,115,116], as well as binders like Nafion to improve electrode immobilization [111,116]. Additionally, electrode preparations have been reported by the application of a single drop of these suspensions or by the repeated dropcasting onto the same electrode until the desired surface coverage was achieved. Dropcasting has been applied to a variety of electrode surfaces, including glassy carbon [43,115] and conductive metal oxides [117].

Despite the widespread use of dropcasting, our survey of the field revealed that there is a clear lack of consistency in how dropcasting is performed. Consequently, direct comparison between different studies using dropcasting – especially those reporting catalytic turnover frequencies (TOFs) – is not straightforward. Furthermore, the inclusion of additives and binders while dropcasting – such as Nafion and carbon black [43,113] – may introduce non-innocent components to the electrochemical system. Even within the same lab, including our own, electrodes prepared by dropcasting may result in films that vary from sample to sample in terms of surface coverage, thickness, orientation, and overall adhesion. In one example of the effects that may arise from differences in films dropcast onto electrodes, it was reported that varying film thicknesses may affect charge transport from the electrode surface throughout the MOF film, impacting the calculation of kinetic parameters such as TOF and turnover number (TON) for electrocatalytic MOFs (see Part 4 for more detail).

3.2 Direct solvothermal synthesis

Apart from dropcasting, perhaps the most utilized method for attaching MOFs to electrodes is direct growth of MOFs on conductive substrates. This approach is attractive because if a successful solvothermal synthesis has been identified for a new redox-active MOF the synthesis can often be readily adapted for direct growth onto an electrode. Usually, adapting the procedure is as straightforward as placing the electrode in the solvothermal vessel with the standard MOF precursors and heating as normal [105]. The electrode surface can provide nucleation sites for MOF crystallization. In some cases, pre-soaking the electrode in a dilute linker-only solution is required; this ideally results in an adsorbed monolayer of linkers which then serve as binding sites for the first SBU layer and thus initiating further growth [43].

An advantage of the direct solvothermal synthesis approach compared to dropcasting is that direct attachment of the MOF to the electrode surface avoids the need for any additional additives which would have to be considered in all subsequent electrochemical analysis and would make mechanistic studies quite challenging. In one example, Miner *et al.* first reported the direct growth of the Ni-based MOF $\text{Ni}_3(\text{HITP})_2$ (HITP = 2,3,6,7,10,11-hexaiminotriphenylene) onto glassy carbon electrodes for electrocatalytic O_2 reduction [118]. Further experimental and computational studies revealed that ORR is centered at the HITP ligand and that the Ni center does not participate in the catalytic cycle but does affect the electronic nature of the ligand [119]. Such clear mechanistic determination for ORR may have proven extremely difficult in the presence of additional additives.

In at least one case, direct solvothermal synthesis was found to be superior to dropcasting for growing electrocatalytic MOFs. In work using the Co-azolate framework $[\text{Co}_2(\mu\text{-OH})_2(\text{bbta})]$ (H_2bbta = 1*H*,5*H*-benzo(1,2-*d*:4,5-*d'*)bistriazole) as a catalyst for the oxygen evolution reaction, the MOF was initially deposited onto glassy carbon electrodes using Nafion as a binder, and subsequently grown directly on Cu foil by solvothermal synthesis of the MOF in the presence of the Cu surface [120]. The direct growth method produced electrodes with improved catalytic performance as compared to the dropcasting method, reaching current densities of 10 mA cm^{-2} at a minimum overpotential of 292 mV. In contrast, 489 mV of overpotential was required to reach 2 mA cm^{-2} at the glassy carbon/MOF/Nafion electrodes.

3.3 Electrophoretic deposition

An additional method for immobilizing MOF crystallites that were prepared *ex situ* at an electrode surface is by electrophoretic deposition (EPD). Here, pre-synthesized MOF crystals are suspended in a non-polar solvent and the mixture placed into a two-electrode cell setup. Application of an electric field between the electrodes can then result in attraction of MOF particles to one of the two electrodes and formation of an adhered film. MOFs are hypothesized to have surface defects which give rise to partial charges [121]; it is these partial charges that result in attraction to the appropriately oppositely biased electrode surface (Figure 5).

EPD provides certain advantages over other immobilization techniques. Similar to the dropcasting method, no new procedures need to be developed if a redox-active MOF synthesis is already known for the bulk material. Additionally, the length of time over which EPD is performed can result in thicker, more densely packed MOF films [121]. Interestingly, it was reported that by increasing the deposition time, a higher percentage of the electroactive NU-1000 could be addressed electrochemically (Figure 6). It was first demonstrated that longer deposition times of NU-1000 resulted in higher surface immobilization of the MOF at the FTO electrode until full surface coverage was achieved at a deposition time of 180 minutes. It was then hypothesized that the longer deposition times resulted in better physical particle-particle connectivity at the FTO surface, and that this physical connectivity results in better electrochemical contact between the individual MOF particles in the resulting films. Therefore, only a small percentage of the MOF particles must have electrochemical contact at the electrode-film interface to allow for electrochemical

addressability of a vast majority (reported greater than 95%) of the MOF particles in the deposited films [121].

EPD has been used to prepare a wide variety of both redox-active and electrocatalytic MOF-modified electrodes, and at least a dozen different MOFs have been electrophoretically deposited directly on a variety of conducting substrates [101,122,123].

3.4 Liquid phase epitaxy (LPE)

Growing MOFs directly on substrates using the related techniques of layer-by-layer (LbL) and liquid phase epitaxy (LPE) was kickstarted in the late 2000's with the first reports of SURMOFs by Wöll and coworkers [124]. In the seminal example, a gold substrate pre-coated with thiol self-assembled monolayers (SAMs) presenting carboxylic acid moieties were soaked first in a metal salt solution, rinsed, and then soaked in a ligand solution, and rinsed again before the cycle was repeated. In this fashion, essentially layer-by-layer growth of a MOF was achieved with a very high degree of orientation with respect to the surface. Significant subsequent work demonstrated that the final orientation can be controlled by SAMs presenting different functional groups to the bulk solution [62,108,125–127].

In the decade-plus since the original SURMOF work, SURMOFs and related epitaxial growth methods have been heavily researched [106,128]. Some of these reports have dealt specifically with introducing electroactive – and electrocatalytic – moieties directly onto conducting substrates. For example, the epitaxial growth method was used to grow a Re-containing MOF on FTO which was capable of reducing CO₂ to CO [129]. However, to date, few reports have leveraged epitaxial growth to generate redox-active MOFs. As discussed below, the *thickness* of an electroactive MOF can dramatically influence the electrochemical response. We see a clear potential for the LPE method to systematically grow electroactive MOF films of varying thickness.

3.5 Atomic layer deposition (ALD)-based methods

Atomic layer deposition (ALD) of metal oxides provides an intriguing option for controlling MOF film thickness. In this method (based on the principle of pseudomorphic replacement) metal oxide layers provide a template for MOF growth [130]. Specifically, the SBUs of the MOF are constructed from the pre-positioned metal atoms in the oxide phase which react with organic linkers in solution to form MOF layers.

For example, electrocatalytic MOF films of well-defined thickness for CO₂ reduction were prepared by combining a Co tetrabenzoate porphyrin linker with ALD-deposited alumina films on glassy carbon disks [131]. In this case, the final thickness of the MOF film could be controlled by the number of ALD cycles utilized. Given the potential of this dissolution-recrystallization technique to build well-ordered MOF thin films with controlled crystallization sites and thickness, it may be a critical tool in the electrocatalytic MOF community, especially for establishing parameters related to optimal surface coverage or kinetic limitations.

4 Electrochemical analysis of MOFs

Electrochemical data provides information on both the thermodynamics and kinetics of a reaction. It is assumed that the reader is familiar with the basics of electrochemical analysis and the kinetics of homogeneous molecular catalysis of electrochemical reactions [132–134]. Briefly, when probing the reaction $P + e^- \rightleftharpoons Q$ by cyclic voltammetry (CV), the midpoint potential of the redox couple gives the energetic positioning of the species being analyzed – that is, how much electrochemical potential is required to reduce or oxidize the redox-active center. A redox couple can be chemically and/or electrochemically reversible.

For an electrode-immobilized molecule, chemical reversibility (Q is chemically stable on the time scale of the CV measurement) is indicated by equivalent areas under the anodic and cathodic peaks, evidence that the same concentration of molecules is participating in electron transfer in the absence of side phenomena (e.g., irreversible chemical reactions or catalysis), which would decrease the current on the return scan. Conversely, for a freely diffusing molecule in solution, the charge passed during the forward and reverse sweep are now asymmetric (the concentration profiles of P and Q are not completely restored when returning the potential to its initial value). Consequently, the ratio of the forward and reverse peak currents is used as a diagnostic for reversibility. If $i_{pa}/i_{pc} = 1$ (i_{pa} is the anodic peak current and i_{pc} is the cathodic peak current), then the redox couple is chemically reversible [135], provided, for example for a reductive process, that the scan is reversed sufficiently more negative than the cathodic peak potential and if baseline corrections to the anodic peak current on the return scan can be made.

Electrochemical reversibility is indicative of the degree to which the redox couple adheres to Nernstian behavior ($E = E^\circ + RT/F \ln ([P]/[Q])$ for the reaction at equilibrium $P + e^- \rightleftharpoons Q$ with the formal potential E°) and is characterized by the peak separation of the redox peaks. An ideal reversible one-electron couple in solution should have a peak separation of 57 mV at 25 °C [132,135], and in theory, an immobilized species has no peak separation since diffusion of the analyte to the electrode is no longer a factor [136]. Furthermore, the peak width at half maximum current is predicted to be 90 mV for an ideal redox couple not limited by charge transfer [137].

4.1 Key factors in electrochemical analysis of MOFs

4.1.1 Midpoint potentials—Perhaps the most straightforward measurements to take when analyzing a new electroactive MOF are cyclic voltammograms (CVs) of the MOF and the redox-active molecular linker separately (using the same solvent and electrolyte). A standard 3-electrode cell can be used for many cyclic voltammetry experiments [135,138]. If large surface area MOF electrodes are to be used, or if bulk electrolysis is to be performed, a cell with separate compartments for the working and counter electrode should be used in order to keep separate the products generated at the working and counter electrodes [139]. A range of electrolyte and solvent combinations can be utilized (see reference [135] for some general selection considerations); for the experimental examples herein we have explicitly included these conditions. A MOF-electrochemistry specific factor to consider is possible size-exclusion of larger electrolyte ions by the MOF pores – if the counterions are too large

(or the MOF pores too small), no charge compensation can occur and so electrochemical responses may be artificially suppressed.

A MOF's observed redox features can often be quickly assigned by direct comparison with the homogeneous CVs taken of the molecular redox-active building block. For example, in a recent PIZOF-type MOF constructed from redox-active naphthalene diimide linkers, comparison of the homogeneous CV of the naphthalene diimide with that of the MOF clearly revealed that the observed redox features could be attributed to the naphthalene diimide components (Figure 7) [140]. Additionally, observation of a Faradaic current response much larger than that of a monolayer demonstrates that this particular MOF is capable of conducting charge via electron-hopping, which is equivalent to a diffusion process (see sections 4.2.3 and 5.1 for details).

The magnitude of the current response for a MOF containing redox-active components are not necessarily as high, nor the features as clear, as the data shown in Figure 7. For example, a UiO-66 thin film that was grown on FTO and post-synthetically modified with a FeFe hydrogenase active site mimic was found to have approximately 32-35% of the native redox-inert bdc linkers replaced with the redox-active FeFe moiety [141]. Analysis of this material by CV showed relatively weak redox features (Figure 8), which is likely attributed to the large percentage of redox inactive bdc units (66-68%), and the use of a bulkier counteranion in the electrolyte ([NBu₄][PF₆]) (as opposed to KPF₆ in Figure 7) which is expected to hinder counterion diffusion.

In 2016, Lytvynenko and Kolotilov reviewed the literature of coordination polymers studied by cyclic voltammetry and compared the observed redox values from the coordination polymers on electrodes to known values for the redox-active molecular fragment [142]. A clear linear relationship was observed (Figure 9), with the maximum difference approaching 350 mV (though the authors noted that the redox events observed for the coordination polymers were rarely reversible). These somewhat large deviations in formal potential between a linker in solution vs. within a MOF is perhaps expected, and mirrors to some extent the situation in enzymes where carefully-tuned protein environments can give for example iron sulfur clusters considerable variations in formal potential [143]. Indeed, the fact that the formal potential of the redox active unit can be so different once incorporated into a MOF strongly suggests that *rational* MOF pore modification could be performed. Extending the analogy to protein active sites further, perhaps even the transition state of a catalytic reaction within a MOF can be tuned.

Slight differences in the midpoint potential of redox centers in MOFs compared to their parent molecules have been attributed to electronic effects of the local MOF environment [26,144]. In comparing a thin film of UiO-67 with a Ru catalyst installed, the position of the [Ru^{IV}=O]²⁺/[Ru^{II}-OH₂]²⁺ was shifted $\approx$ 100 mV positive in the MOF when measured in aqueous conditions (0.1 M LiClO₄, H₂SO₄, pH 2.8) compared to that of the complex in homogeneous solution [145]. In thin films of pyrazolate MOFs comprising Zn nodes and NDI linkers, a shift to more negative potentials was observed for the NDI reductions measured in DMF containing 0.1 M *n*-Bu₄NPF₆ compared to that of the parent linker [26].

This additional potential required for the reductions was attributed to greater charge density in the MOF framework compared to the parent compound in solution.

4.1.2 Changes during repeated cycling—The comparison of subsequent scans of CVs can yield information on the stability and/or charge transfer within a film. At one extreme, redox features are observed only on the first scan, after which the film is irreversibly deactivated or delaminated, resulting in no further electrochemical signatures (see Figure 12 in the stability section below). For a stable film with no restructuring or changes in redox activity, consecutive scans will overlay each other. In reality, repeated cycles often are in an intermediate region to these extremes. In repeated scans of a thin film of a Ru-functionalized UiO-67 MOF at an FTO electrode in a 0.1 M KCl (pH 6.2) solution, the current attributed to the Ru^{III/II} couple initially decreases sharply and then stabilizes [43]. The authors postulate that this is likely due to initial loss of some loosely connected MOF particles of the film. Once the partial electrochemically induced delamination ceases, the film is stable and subsequent scans are reproducible. Examples of the opposite effect – that is, an *increase* in current upon scanning – has also been reported [26,140]. This phenomenon, referred to as “conditioning” or a “break-in phase” indicates slow counter-ion diffusion into the film. In cyclic voltammetry scans of an NDI-based MOF tested in DMF with 0.8 M KPF₆ as the supporting electrolyte, the current density increased over the first consecutive scans, reaching a maximum current density after 20 cycles (Figure 10). In this case, the percentage of the reduced (or oxidized) redox centers are limited by the concentration of ions within the film to balance the charge and allow for further charge transfer from the electrode to the film. One method to address this is by decreasing the size of the counterion to minimize the time needed for all electroactive centers to become electrochemically accessible or, with more difficulty, by decreasing the film thickness.

4.1.3 Electrolyte effects—The choice of counterion can significantly affect the electrochemical response of a MOF film, depending on the 1) size, 2) concentration, and 3) ion-pairing effects of the counterion. For example, a strong effect of electrolyte on MOF electroactivity was seen in a study using a Zr-based NU-1000 MOF composed of a pyrene-based linker [146]. The oxidation of pyrene could be seen in the parent MOF when tested at 0.05 M TBAPF₆ (tetrabutylammonium hexafluorophosphate) in acetonitrile, but upon incorporation of ferrocene at the Zr nodes, the pyrene was no longer electroactive (Figure 11). This was attributed to an exclusion effect in the MOF whereby the oxidized ferrocene blocked the entrance of cations, causing an unfavorable local environment for the further oxidation of the pyrene linker. Upon increase of electrolyte concentration to 0.5 M, the oxidation of pyrene was reinstituted.

4.1.4 Electrochemical Stability—Many molecular catalysts (including those incorporated as linkers into MOFs) undergo loss of ligands, dimerization, and/or decomposition to nanoparticles during redox cycling. The insights learned from the *molecular* electrocatalysis community can be applied to electrocatalytic MOFs where the linkers are built from molecular catalysts. For example, the well-studied cobaloxime catalyst for hydrogen evolution loses a chloride ligand upon the Co(III/II) reduction, and a second axial ligand also dissociates when further reduced to its catalytically relevant state, Co(I)

[134]. Surface immobilization can improve molecular stability during electrochemical cycling. Covalent attachment of Co-based hydrogen evolution catalysts to carbon nanotubes improved the turnover number (TON) of the catalysts compared to their non-immobilized counterparts, presumably by prohibiting deactivation pathways involving the interaction of two activated catalysts [147]. In addition, encapsulation of the cobaloxime $[\text{Co}^{\text{III}}(\text{dmgH})_2\text{pyCl}]$ (dmg = dimethylglyoxime) in a polymer network with excess pyridine ligands has been postulated to increase catalyst stability, likely by enhancing the effective ligand concentration which promotes re-formation of the catalyst [148,149]. In this context, a MOF framework may stabilize redox-active molecular species through confinement. For example, a cobalt porphyrin catalyst linked by imine bonds to form an extended covalent organic framework (COF) was studied for CO_2 to CO conversion in aqueous conditions. The turnover number (TON) for the COF-immobilized cobalt porphyrin was found to be 26 times higher compared to the TON of the parent catalyst in solution [29].

Electrochemical stability of a MOF takes a number of factors into consideration. In addition to bulk MOF stability (Part 2) and the stability of the molecular catalytic component, MOFs under electrochemical conditions must meet two additional stability requirements: 1) maintaining physical attachment to the electrode surface, and 2) remaining structurally intact under reducing and/or oxidizing conditions during electron flow through the framework. The likelihood of meeting the first stability challenge – the potential for delamination or generally loss of MOF from an electrode surface – depends to a large degree on how the electrode was prepared. The second stability issue of resisting degradation under electron flow while in the presence of substrate is a much more MOF-specific challenge. We are unaware of any comprehensive discussion of what chemical composition makes a MOF stable under reducing/oxidizing conditions, a distinct contrast to the rigorous studies available for bulk stability (see Part 1 above). However, the known examples to date show that a successful strategy for building MOFs which are stable under electrochemical conditions is by using molecules *known* to give reversible electrochemical responses as MOF ligands. For example, numerous electrochemically-stable MOFs have been successfully built from ligands based on a naphthalene diimide core [25,26,140], a moiety well-known to be stable when reduced. A more in-depth recent discussion is available in a recent review by Liu and Yin [33].

Techniques for assessing if a MOF is stable under electrochemical conditions can be broadly grouped into two categories: *in situ* qualitative signs and *post mortem* methods. Both will be discussed here. A recent thorough discussion of reported (and under-reported) stability of specific MOFs during electrocatalytic conditions is available [34].

In situ methods: Cyclic voltammetry is a powerful method for diagnosing solution phase chemical mechanisms, and well-established methods exist for understanding the operating mechanisms for both discrete chemical reactions [132,135,138,139,150,151] and catalytic systems [132,152,153]. Literature also exists for recognizing the situation for when *degradation* is occurring, and when the starting material is actually a precatalyst for the active catalyst [154–158]. However, these key papers focus almost exclusively on cases when the starting analyte is homogeneous, rather than heterogeneous solid-state materials such as MOFs. Fortunately, the task of determining whether a MOF is electrochemically

stable is perhaps easier than that of a homogeneous molecular species as the material is at least initially attached to the electrode.

As pointed out above, repeated cyclic voltammetry scans can provide an idea of the redox stability. This also presents challenges. Unlike homogeneous solution cyclic voltammetry, fresh, unreacted analyte cannot be brought to the electrode surface by simply stirring the solution [132]. Specifically, if a scan potential window is selected in homogeneous cyclic voltammetry such that irreversible reduction or oxidation of the analyte occurs – thereby destroying the analyte – the solution can simply be stirred to bring new analyte to the electrode (Figure 12A). Conversely, for MOFs on electrodes, if a potential range is selected in which irreversible redox events occur, the MOF may be irreversibly damaged and subsequent scans will only probe degraded material (Figure 12B).

To avoid this scenario, the initial scan window should be based on the open circuit potential (where nominally no net charge is being passed and thus no net electrochemically driven changes to the MOF should be occurring) and any known details of the formal potentials of the building blocks (e.g., knowledge of the formal potential of the naphthalene diimide ligand used to construct the MOF) should be used to set the potential window. In a way, this is the same process to be followed when investigating homogeneous species with unknown electrochemical features [135].

Electrochemically irreversible redox events observed for MOFs do not necessarily mean that the MOF structure has irreversibly changed – the return redox event may be kinetically sluggish. If, however, repeated scans through the same scan window show a diminishing of the initially observed redox peak – be it irreversible or reversible – this is a strong indication that the MOF is not electrochemically stable at those applied potentials.

A number of electroactive films have been shown to be stable under cycling or sustained electrolysis. In work using porphyrin-based MOF-525 thin films on FTO, the MOF composed of the free-base porphyrin was stable for over 10 cycles of oxidative scanning in aqueous conditions (0.1 M KCl) [121]. A cobalt porphyrin-based MOF (CoPIZA) film was stable in 0.1 M LiClO₄/DMF after 24 hours of chronoamperometry at an applied potential equal to the potential of the Co cluster nodes [27]. However, when poisoning the electrode more negative, at the potential corresponding to the Co(II/I) reduction of the cobalt porphyrin linker, the film showed significant degradation after 24 hours. It was postulated that the main factor for film instability under these conditions was the reduction of the Co nodes.

Indications of irreversible degradation of MOFs on electrodes during electrocatalytic experiments – such as bulk electrolysis – is largely analogous to what is observed during degradation during homogeneous experiments. Loss of current over time indicates declining electrocatalytic ability (see Figure 13 and reference [159] for an example). Current loss can also result from simple bulk consumption of substrate; if this is the case, replacing the solution with fresh solution should regenerate the original current magnitude. Conversely, observation of an induction period where the catalytic current increases over time may indicate that the initial MOF material is a precatalyst for the true active catalyst.

Post-mortem methods: A diverse range of techniques is available to determine if a MOF remains unchanged during electrochemical experiments. These are largely classic surface techniques which have found great versatility in the homogeneous electrocatalysis community for verifying if heterogeneous catalytically active materials are formed during electrolysis [155,156,160–164]. In these studies, scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX, especially when coupled to SEM), X-ray photoelectron spectroscopy (XPS), X-ray absorption (XAS) and others can be used to directly investigate what material is present on the electrode surface.

For the case of MOF electrochemistry, comparison of a prepared electrode by one of these techniques *before* electrochemistry and *after* can answer the question: has the MOF changed? Reports of electroactive MOFs should include post-electrochemical studies of the molecular nature of the construct by examination of the chemical environment through techniques such as XPS, EXAFS and FTIR. PXRD and grazing incidence XRD (GIXRD) are powerful methods for assessing if the *bulk* MOF structure is maintained after electrochemical experiments. Ideally, PXRD patterns should be taken before and after electrochemical investigations, and especially after catalytic bulk electrolysis. Such data can provide a glimpse into the stability of an electrocatalytic MOF over time if PXRD after multiple electrolysis time points are taken, as were in the work by Chen and co-workers for an oxygen evolving MOF. PXRD showed that their MOF was stable after 24 hours of electrolysis, but ultimately degraded by 96 hours (Figure 14) [165].

4.2 Charge transport through MOF films

4.2.1 Electroactive coverage: An advantage of thin film electrochemistry is that, in contrast to homogeneous electrochemistry in which only a small fraction of the bulk species are activated in the diffusion layer, immobilization of redox-active species at an electrode provides a path for 100% of the analyte to be reduced or oxidized. In addition, immobilization allows compounds to be utilized in media in which they are insoluble, allowing the use of a broader range of catalysts, for example, for water splitting applications. However, surface attachment does not guarantee that all species at the electrode surface are electroactive, and in some cases, only a fraction of them can be reduced or oxidized. Here we review how to experimentally assess what that fraction is.

The *total surface coverage* Γ_P^{Tot} in mol cm^{-2} can be obtained from digestion of the MOF film and analysis of the resulting solution by ICP (inductively-coupled plasma) or UV-vis spectroscopy to obtain the total number of species present, n_P^{Tot} . The *total concentration* of immobilized species, C_P^{Tot} (mol cm^{-3}) is normally taken as the total moles divided by the geometric volume of the film ($C_P^{Tot} = n_P^{Tot}/S \times d_f$ and therefore, $\Gamma_P^{Tot} = C_P^{Tot} \times d_f$, with d_f being the film thickness as determined by ellipsometry or SEM cross section images, and S is the geometric surface area of the film). In contrast, the *electroactive surface coverage* Γ_P^0 , also in mol cm^{-2} , represents the portion of the immobilized redox centers that are able to be reduced or oxidized. Similarly, *electroactive concentration* C_P^0 (mol cm^{-3}) is given by $C_P^0 = n_P^0/S \times d_f$ and therefore $\Gamma_P^0 = C_P^0 \times d_f$, where n_P^0 is the moles of electroactive species.

The percent electroactive species is simply the ratio of these two concentrations ($[C_p^o/C_p^{Tot}] \times 100 = [\Gamma_p^o / \Gamma_p^{Tot}] \times 100$). Determining the number of electroactive species as well as the total number of immobilized molecules provides insight into how much of the film is electrochemically addressable.

A range of methods can be used to determine the electrochemically active portion of surface-immobilized molecules. The integration of the area under a redox wave reports on the amount of charge passed when utilizing slow scan rates where finite diffusion holds and a symmetrical redox wave is observed (current potential-response is equivalent to that of a surface immobilized redox-couple). In this limit, the peak current is expressed as [166,167]

$$i_p = FSC_p^o d f \frac{F \nu}{4RT}$$

where F is the Faraday constant, S is the geometric surface area, R is the ideal gas constant, T is temperature, C_p^o is defined as above, and ν is the scan rate. C_p^o can be found from the slope of a plot of i_p vs. ν , once the film thickness has been determined from an independent measurement. If electron-hopping diffusion is slow and this limit is never reached on the CV time scale, chronoamperometry may be used to allow access of electrons throughout the film on longer time scales, where the total charge passed is proportional to C_p^o after exhaustive reduction of the film. Spectroelectrochemistry is also a useful tool to analyze electrochemical species at transparent conductive electrodes. In this *in situ* approach, spectral changes associated with applied potentials report on the electroactive coverage.

To illustrate how chronoamperometry and spectroelectrochemistry can be used to analyze the electroactive coverage, we will consider two case studies. In the first example, a MOF-525 composed of porphyrin struts was electrophoretically deposited onto FTO and post-metalated with iron centers [123]. When analyzed in acetonitrile (1 M TBAPF₆), three redox waves corresponding to three consecutive one-electron reductions of the Fe(III) centers were observed, showing that the porphyrin could be reduced within the MOF framework. In a chronoamperometry experiment, the electrode was poised at a potential negative of the Fe (III/II) couple, and an electroactive coverage of $6.2 \times 10^{-8} \text{ mol cm}^{-2}$ was calculated from the total charge passed, Q (in C), by employing Faraday's constant ($96485.33 \text{ C mol}^{-1}$), the geometric surface area, S (in cm²), and the number of electrons transferred ($n_e = 1$). Spectroelectrochemistry was performed to determine the percent electroactive Fe(III). By examining the decrease in oscillator strength at 419 nm during a potential step (corresponding to the reduction of the Fe(III) species), the percent electroactive coverage was found to be 77% (i.e.

percent electroactive = $[\Gamma_p^o / \Gamma_p^{Tot}] \times 100 = (1 - \{[Abs_{419}(t^{final})] / [Abs_{419}(t^{initial})]\}) \times 100$, where $t^{initial}$ is before any potential is applied, and t^{final} is after the potential step when the film is exhaustively reduced and the current drops to approximately zero).

In more recent work, redox-active naphthalene diimide-based linkers with hydroxyl moieties (dcphOH-NDI, 4,4'-(1,3,6,8-tetraoxo-1,3,6,8-tetrahydrobenzo[*lmn*][3,8]phenanthroline-2,7-diyl)bis(3-hydroxybenzoic acid)) were incorporated into a Zr-based UiO/PIZOF MOF [140].

When grown on SAM-modified FTO, this material forms films with a thickness of approximately one micron. The percent of electroactive NDI molecules was determined by calculating the concentrations of NDI and singly reduced $\text{NDI}^{\bullet-}$ from absorbance measurements taken in spectroelectrochemical experiments. The electrochemical potential was stepped from the open circuit potential to -1.26 V vs. Fc^+/Fc for the $\text{Zr}(\text{dcphOH-NDI})@\text{FTO}$ electrode in 0.8 M KPF_6 in DMF, and the absorbance of NDI at 385 nm and that of $\text{NDI}^{\bullet-}$ at 475 nm was monitored. The relative concentrations, $[\text{NDI}^{\bullet-}/\text{NDI}]$ was found to be 97%, illustrating that it is possible that almost all redox-active linkers in a MOF film can be electrochemically addressable.

4.2.2 Film thickness: Film thickness has important implications for electroactive MOFs. The interplay of the electroactive surface loading, Γ_p^o , (mol cm^{-2}), increased by thicker MOFs (larger d_f -values), with conductivity and substrate access has only begun to be investigated. The current lack of methods to control the film thickness of MOFs on conducting substrates severely limits the number of studies investigating this relationship, but examples of controlled growth can be found. Using metal oxide films as MOF templates (see Section 3.5) allowed the effect of film thickness on the CO_2 reduction activity of a catalytic cobalt porphyrin-based MOF to be monitored (Figure 15) [131]. The parent alumina film thickness was varied from 0.5 to 10 nm, and the catalytic activity (as measured by the current density) reached a maximum for electrodes prepared with 5 nm of alumina (MOF film thickness of 30 – 70 nm). The authors attributed the decrease in activity for thicker films to either charge transport limitations in thicker MOF films or impedance in unconverted portions of the alumina film.

4.2.3 Diffusion coefficients: The presence of multiple redox centers distributed throughout a thin film presents additional considerations in electrochemical analysis compared to discrete molecular species in a diffusion layer at the electrode. Guiding principles that can be extended to MOF films for kinetic analysis have already been described in the electrochemical analysis of polymer thin films [168,169]. Electron transport through the film (electron transfer steps between redox-active species), is driven by chemical potential gradients in the film, and is formally a diffusion process, despite the fact that the redox-active units are immobilized. There are several methods to determine equivalent diffusion coefficients (D_{app}) for MOF films with molecular redox-active linkers. Similar to the case of non-immobilized electroactive species at an electrode, semi-infinite diffusion occurs in the film under conditions where the diffusion layer thickness is significantly less than the film thickness (i.e. fast scan rates and/or thick films) and the peak current (i_p) assuming facile electrode kinetics is given by [166,167]

$$i_p = 0.4463 F S C_P^o \sqrt{\frac{F \nu D_{app}}{RT}}$$

The only difference between this expression and the classic Randles-Sevcik's equation is that now the diffusion coefficient is not that of the freely diffusing species in solution, but rather the apparent electron-hopping diffusion coefficient (D_{app}) which represents the charge transport process through the film. Plots of i_p vs. $\sqrt{\nu}$ will give a linear relationship, and the

slope can be used to extract D_{app} if C_P^0 can be accurately determined from the methods outlined in section 4.2.1. D_{app} also can be determined using potential step chronoamperometry and the Cottrell equation [139]:

$$i = \frac{FSC_P^0 D_{app}^{1/2}}{(\pi t)^{1/2}}$$

again using the data at short times (t in seconds) where the semi-infinite boundary condition is maintained. In other words, the validity of both equations above only holds when the diffusion layer thickness is significantly less than the film thickness i.e. $\sqrt{D_{app}t} \ll d_f$. While relatively few D_{app} values have been reported for MOFs, in general reported values range from 10^{-10} - 10^{-14} cm² s⁻¹, [27,29,43,123,131,145,170,171] though a very recent electrocatalytic MOF had an exceptionally high D_{app} of $3.6 (\pm 1.7) \times 10^{-8}$ cm² s⁻¹ [172].

The greatest source of error in these measurements is C_P^0 because d_f needs to be determined by an independent measurement. Errors in the measured film thickness can result in large variations in calculated D_{app} values, since d_f is always squared to find D_{app} . MOF films do not always display well-defined geometries and may have significant surface roughness, and in some cases the geometric volume ($S \times d_f$) might not be ideal for accurate determinations of the diffusion coefficient. More complex models can be built by taking into account roughness factors as well as, accessible thickness and accessible surface area [173] or even by taking into account the pore geometry [174].

5 Kinetic benchmarking of electrocatalytic MOFs

Molecular species incorporated into MOF assemblies forming microstructured films have demonstrated their viability for the catalysis of electrochemical reactions – primarily small molecule activation. A wide variety of MOF architectures (UiO, NU-1000, PCN, MOF-525) functionalized with molecular transition-metal catalysts, have been employed for CO₂ reduction [123,131], hydrogen evolution [111,175], oxygen reduction [27], and water oxidation [140,145]. A recent review highlights the scope of work in this field [34]. In the following sections, the focus is on briefly highlighting quantitative methods for the electrochemical analysis of MOF-based molecular catalysis, drawing from well-established theoretical and experimental studies.

5.1 Challenges in benchmarking—The foundation for rational benchmarking of homogeneous molecular catalysts by cyclic voltammetry has been well established in recent years by Savéant, Costentin and co-workers [176]. Meaningful kinetic parameters can be extracted when catalysis is fast and pure kinetic conditions are achieved [132], which holds when the catalytic reaction is fast relative to the CV timescale (RT/Fv). This ensures that the rates of diffusion and catalysis are matched so that a steady-state situation is reached, and the (time-independent) concentration profile of the active catalyst is confined to a small layer adjacent to the electrode. In this regime, the concentration of the active form of the catalyst can be determined from the size of the reaction-diffusion layer (ca. less than one micrometer) and used to extract a maximum TOF which is defined as the moles of product

generated per moles of active catalyst in a unit of time [153]. Efforts to obtain intrinsic rate constants, such as k_{cat} either from steady-state, S-shaped waves (by increasing the substrate concentration or raising the scan rate) or via tools such as FOWA (foot-of-the-wave analysis) [177–180] and catalytic Tafel plots [152,181], has allowed for quantitative characterization of the intrinsic activity of catalysts in the absence of side phenomena.

In comparison, benchmarking molecular catalysts incorporated in MOF thin film electrodes (either as linkers or nodes) in terms of intrinsic catalytic activity has yet to be experimentally demonstrated in a quantitative manner. Two main phenomena present complications when considering porous films: 1) the mode of electron conduction and 2) substrate diffusion inside and outside the film. In the vast majority of examples, MOF-imbedded catalysts display an electron hopping mechanism [27] that is equivalent to the formal diffusion of fixed redox-active centers [168], and as such, the balance between diffusion and any following chemical reactions must be considered when characterizing the kinetics of MOF-catalyzed reactions. When electron-hopping or substrate diffusion are significantly limiting compared to the rate of catalysis, the active catalyst may be confined to a small layer inside the film, leaving many catalytic sites dormant. Analogous to homogeneous catalysis outlined above, this situation requires a modification to the definition of TOF to include only the active catalyst concentration in the reaction-diffusion layer. An example is given below for a film operating where kinetic control is by electron-hopping diffusion as well as the catalytic reaction (see zone ER in reference [182]), substrate diffusion is considered to be fast compared to the other two processes, and the equilibrium partition coefficient of the substrate across the film-solution interface is unity (i.e. substrate concentration in the film is constant and equal to its bulk value in solution). When transport limitations are present, TOFs derived from total (or even total electroactive) catalyst concentrations (defined here as apparent turn-over frequencies, TOF^{app}) will greatly underestimate the true turn-over frequency (TOF^{true}), making a rational comparison between catalytic MOFs difficult [183].

$$TOF_{max}^{app} = \left[\frac{\text{moles of product}}{(\text{total moles electroactive catalyst}) \cdot \text{time}} \right] = \frac{1}{d_f} \sqrt{D_e k_{cat}}$$

$$TOF_{max}^{true} = \left[\frac{\text{moles of product}}{(\text{moles electroactive catalyst in reaction-diffusion layer}) \cdot \text{time}} \right] = k_{cat}$$

given,

$$\left[\frac{\text{moles of product}}{\text{time}} \right] = \frac{i_{pl}}{F} = SC_p^o \sqrt{k_{cat} D_e}$$

$$[\text{reaction-diffusion layer thickness}] = \sqrt{\frac{D_e}{k_{cat}}}$$

$$[\text{total moles electroactive catalyst}] = SC_p^o d_f$$

$$[\text{moles of electroactive catalyst in reaction-diffusion layer}] = SC_p^o \sqrt{\frac{D_e}{k_{cat}}}$$

where i_{pl} is the plateau or limiting current (under steady-state and at a potential significantly more negative than the formal potential of the catalyst), C_p^o is the electroactive concentration of the catalyst (see section 4.2.1), S is the geometric surface area of the film, k_{cat} is the

intrinsic pseudo-first order rate constant for the catalytic reaction, D_e is the electron hopping diffusion coefficient, d_f is the film thickness, and t is time in seconds. As opposed to intrinsic catalytic rates, this TOF_{max}^{app} value will depend on the film thickness (very thick films with large transport limitations will display lower TOFs when derived from total catalyst concentration) [184]. Even though this is not reflective of the intrinsic activity of the MOF-imbedded molecular catalyst, TOF_{max}^{app} may give some indication of the efficiency of the catalytic film.

5.2 Kinetic analysis and rate-limiting phenomena—It is clear that a quantitative analysis of the different possible limiting processes (diffusion-like charge transport, substrate diffusion, or catalytic reaction) is required to accurately compare one MOF-based electrocatalyst to another. How the overall current-potential response depends on these three processes will result from the solution to a system of partial differential equations, each consisting of Fick's second law (to account for substrate diffusion or electron-hopping/diffusion) and a kinetic term resulting from the coupled catalytic reaction. Such kinetic models have been developed and well-studied for redox-polymer films [185–189] and bioelectrocatalytic films [190,191], but have yet to be applied to MOF-catalyzed electrochemical reactions. Costentin and Savéant have recently extended the analysis of the current-potential response of porous (multi-layer) electrocatalytic films from steady-state techniques (rotating-disk electrode voltammetry) to cyclic voltammetry [167,182,192]. Applied to molecular catalysts incorporated into MOF films, these methods would provide an easy and rapid determination of the relevant kinetic processes taking place within the film which may be rate-limiting, namely: the intrinsic catalytic reaction, permeation and diffusion of the substrate, and transport of electrons.

6 Conclusions

Development and analysis of electrochemically active MOFs benefits from knowledge in a variety of fields, including synthesis of coordination compounds, interface chemistry, and electrochemical studies. Considering the stability of the MOF in its bulk form can provide insights into possible degradation mechanisms of the MOF under electrochemical conditions and serve as an initial feasibility test for the electrochemical application of a MOF. An array of immobilization methods for MOFs at electrode surfaces is available, ranging in complexity from adding the pre-formed MOF directly to the electrode (e.g., dropcasting, EPD), to synthesizing the MOF at the electrode (e.g., direct solvothermal synthesis and LPE). The method of immobilization impacts interfacial charge transfer, with implications for the electrochemical activity of the MOF. Finally, MOFs at electrodes can be analyzed using classic electrochemical parameters, such as peak potential and peak separation. However, diffusion through the MOF film is an additional factor in MOF redox-active films compared to discrete redox-active components. Diffusion of charges through a film is non-trivial and, when it is the rate-limiting process, complicates analysis of catalytic parameters such as turnover rates. Thus, an important aspect in understanding fundamental processes in electrochemically active MOFs is being able to control film thickness and/or orientation to arrive at a better control of the interplay of interfacial electron transfer, charge transfer through the film, and maximum catalytic rates in electrocatalytic MOFs. These principles

should in turn inform the design of novel MOFs that capitalize on the strengths of MOFs to stabilize and tune electrocatalysts operating at high product production rates and selectivity.

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Figure 1.

Schematic representation of (A) through-bond and (B & C) through-space approaches to improving conductivity in MOFs. Panel (a) reprinted with permission from ref. [24].

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Figure 2.
pH stability ranges of representative common MOFs. Reprinted with permission from ref. [51] (Springer Nature, Copyright 2016).

Figure 3. PXRD patterns of the Zr-btba (btba = 4,4',4'',4'''-([1,1'-biphenyl]-3,3',5,5'-tetrayltetrakis(ethyne-2,1-diyl)) tetrabenzoate) MOF following activation under various conditions. The pattern (i), corresponding to thermal activation at 70 °C, contains the halo indicative of a new amorphous phase [53]. (Reprinted with permission from John Wiley and Sons, Inc.).

Figure 4.
Overview of methods for attaching MOFs to electrode surfaces.

(a) Anodic EPD

(b) Cathodic EPD

Figure 5.
Schematic of electrophoretic deposition in a) anodic and b) cathodic modes.

Figure 6.

Increasing the electrophoretic deposition time for the redox active NU-1000 MOF (A) resulted in a higher percentage of the total deposited MOF being electroactive (B). It was hypothesized that the films at higher deposition times had increased particle-particle contacts resulting in improved inter-particle redox connectivity. Adapted with permission from ref. [121]. Copyright (2014) Wiley.

Figure 7.

A) Structure of a MOF constructed using naphthalene diimide (NDI) redox-active linkers and B) cyclic voltammograms of the linker dissolved in solution with 0.1 M $n\text{-Bu}_4\text{NPF}_6$ in DMF (blue) and the corresponding MOF tested in 0.8 M KPF_6 in DMF (black). In this example, comparison of the CVs allowed quick assignment of the redox features seen in the MOF as arising from the NDI linker components. Panel A reprinted with permission from ref. [140]. Copyright (2018) American Chemical Society. Cyclic voltammetry data from ref. [140].

Figure 8.

Cyclic voltammograms in 0.1 M *n*-Bu₄NPF₆ in DMF of 1 mM Fe₂(dcbdt)(CO)₆ (blue) and a 2-5 μm UiO-66 film on FTO before (green) and after (red) post synthetic exchange of some of the linkers with Fe₂(dcbdt)(CO)₆ (dcbdt = 2,3-dithiolato-1,4-benzene dicarboxylate). Adapted with permission from Ref. [141]. Copyright (2015) The Royal Society of Chemistry.

Figure 9. Comparison of reported redox potentials for coordination polymer (CP, y-axis) modified electrodes with their respective redox-active *molecular* components (x-axis). Reprinted by permission from ref [142]. Copyright (2016) Springer.

Figure 10.

Illustration of increased current density of an NDI-based thin film MOF while cycling from the first (purple) to the last (dark red) scan. Reprinted by permission from ref [140].

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Figure 11.

(left) Comparison of films of the pyrene-based NU-1000 MOF with (red) and without (green) the solvent-assisted ligand incorporation (SALI) of ferrocene measured on FTO electrodes in a solution of 0.05 M TBAPF₆ in acetonitrile at a scan rate of 50 mV/s. (right) CVs of Fc-NU-1000 recorded in different concentrations of supporting electrolyte TBAPF₆. At concentrations of PF₆⁻ higher than that of the fixed Fc⁺ sites the oxidation of the pyrene linkers is restored. Reprinted with permission from ref [146]. Copyright (2015) American Chemical Society.

Figure 12.

Simulated electrochemically irreversible CVs of A) a homogeneous analyte and B) an electrode-attached electroactive MOF. In the case of the homogeneous analyte, stirring the solution between scans brings fresh analyte to the electrode surface and the same redox feature can be observed on the second scan. For the electrode-adsorbed MOF, however, the second scan reveals that the MOF was irreversibly changed on the first scan.

Figure 13.

Example of gradual current loss for a hydrogen-evolving 2D MOF during a bulk electrolysis. This represents an *in situ* electrochemical method for detecting irreversible degradation of an electroactive MOF. Reprinted with permission from ref [159]. Copyright (2015) American Chemical Society.

Figure 14.

PXRD patterns of an oxygen-evolving electrocatalytic MOF as-synthesized and after 24 and 96 hours of bulk electrolysis. Use of PXRD provided information on how long the bulk MOF structure was stable under electrocatalytic conditions. Reprinted with permission from ref [165]. Copyright (2017) American Chemical Society.

Figure 15.

Effect of MOF film thickness (as controlled by the number of ALD cycles) on catalytic current density for a $\text{Al}_2(\text{OH})_2\text{TCCP-Co}$ (TCCP = 4,4',4'',4'''-(porphyrin-5,10,15,20-tetrayl)tetrabenzoate) MOF capable of reducing CO_2 to CO. Reprinted with permission from ref. [131]. Copyright (2015) American Chemical Society.

Scheme 1. Strategies to construct stable MOFs as guided by HSAB theory.

Reprinted with permission from ref. [50]. BTP and BDP are 1,3,5-tris(1H-pyrazol-4-yl)benzene and 1,4-benzenedi(4'-pyrazolyl), respectively. Copyright (2016) Wiley.