

Metal–Organic Frameworks for Electrocatalysis: Catalyst or Precatalyst?

Metal–organic frameworks (MOFs) have popularly been engaged directly in electrochemical applications, particularly as electrocatalysts in energy-related reactions.¹⁻⁴ The well-demonstrated efficiency and selectivity of MOFs are commonly attributed to their structures: their high specific surface area can expose abundant catalytic active sites to the surface; their pores of predetermined size/geometry allow rapid mass transport of selected substrates to the active sites; and the isolated metal nodes (typically, ions and clusters) of MOFs can serve as the active sites, providing great mono-dispersibility and atomic efficiency close to 100 %. Meanwhile, the functionalization of organic ligands enables extra chemical and structural selectivity over both reactants and products.

However, the coordinate bonding between metal nodes and organic linkers, by nature, is generally weaker than the ionic bonding in inorganic solids. Therefore, the structural robustness of MOFs under electrochemical environments is questionable. A typical electrocatalysis involves chemical species in the electrolyte, dynamic electrochemical double layer interface, inner sphere electron transfer, and surface redox reactions that break and form bond(s). These can be classified as chemical and electrochemical environments (**Figure 1**). The possible reconstruction of MOFs under these environments brings a question to their role during electrocatalysis: *are they the real catalysts or merely the precatalysts that produce active phases during the electrochemical treatment?* Furthermore, depending on the reaction conditions (potential, electrolyte, pH, *etc.*), a robust electrocatalyst for one reaction may be a vulnerable precatalyst for another. The blurred line between catalyst and precatalyst has previously raised concerns in transition metal carbides-, pnictides-, and chalcogenides-based catalysts.⁵⁻⁷ To initiate a deeper discussion on MOFs, in this

Viewpoint, we provide an analysis of their roles during electrocatalysis and our suggestions on reporting MOFs as catalysts.

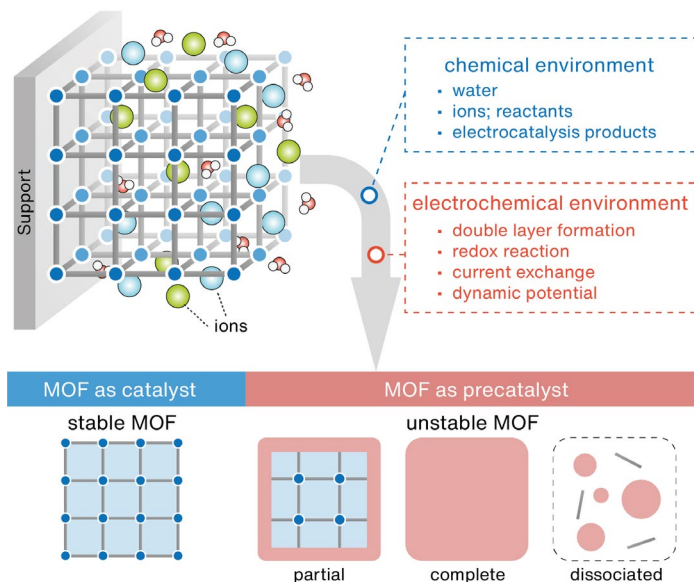


Figure 1. Chemical and electrochemical environments of MOFs during electrocatalysis and possible scenarios: stable and unstable (partial and complete conversion; dissociation).

CHEMICAL ENVIRONMENTS

The chemical environment includes water, reactants, ions, and products from electrocatalysis. Water promotes the hydrolysis of the metal–linker coordination sites, which irreversibly destroys the framework and produces hydroxide/hydrated metal species (in basic electrolytes) and/or protonated linkers (in acidic electrolytes) that further diffuse to the electrolyte.⁸ Generally, the hard and soft acid–base (HSAB) theory (**Figure 2A**) applies: the pairs of (hard Lewis acids)–(hard Lewis bases) and (soft Lewis acids)–(soft Lewis bases) have much stronger interactions than other combinations.^{9–10} Depending on the desired reaction, the chemical environments of electrocatalysts vary. **Figure 2B** lists the typical species for different reactions. For example, industrial alkaline water electrolysis is conducted in 20 ~ 30 wt.% KOH aqueous solution at 50 ~ 80 °C under high

pressure.¹¹ The hydrolysis is expected to proceed much faster than in pure water. Other ions beyond H^+ and OH^- are also destructive. The PO_4^{3-} anion in phosphate buffered (PB) solution is a hard Lewis base that strongly interacts with high-valency metal ions. UiO-66, an acid-stable MOF, is a good example: UiO-66 completely disassembles within a few minutes in PB solution.¹² Recently, Mirsaidov's group visualized the conversion of ZIF-8 (**Figure 2C**) to a layered double hydroxide using liquid-phase transmission electron microscopy (TEM), showing that the Zn^{2+} -2-methylimidazole connection was broken within minutes in Co^{2+} -containing solution, and the Zn^{2+} ions were released into the surroundings to form $ZnCo(OH)_x$.¹³ Product(s) from electrocatalysis are currently overlooked but can also cause instability of MOFs. For gas evolution reactions, nanobubbles are generated at the active sites, posing both mechanical and chemical challenges to structural integrity.¹⁴⁻¹⁵ Other products, such as formate/ CH_3OH from CO_2 reduction reaction (CO_2RR) and NH_4^+ from nitrogen reduction reaction (NRR), may pose a similar doubt.

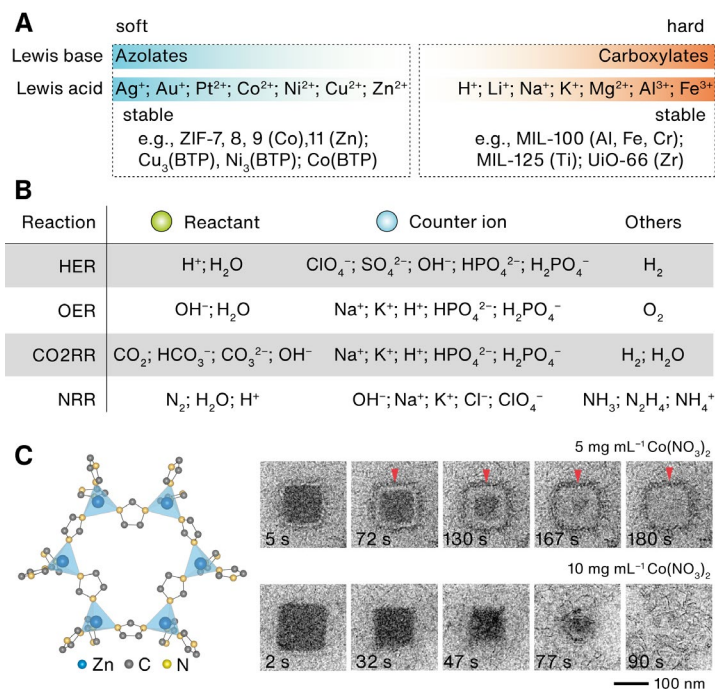


Figure 2. (A) Hard and soft acid–base theory for stable MOF design. (B) Chemical environments in aqueous electrolytes of some common electrocatalytic reactions (HER: hydrogen evolution

reaction; OER: oxygen evolution reaction; CO₂RR: CO₂ reduction reaction; NRR: nitrogen reduction reaction). (C) Left: structure of ZIF-8; Right: time series of images showing the structural evolution of a ZIF-8 nanocube in 5 (top) and 10 mg mL⁻¹ (bottom) Co(NO₃)₂ solution. Reprinted from Wang *et al.*¹³

ELECTROCHEMICAL ENVIRONMENTS

A MOF's *chemical stability* (or electrolyte stability) does not guarantee its *electrochemical stability*, let alone *electrocatalytic stability*. With a voltage bias applied, the surface of MOF is either negatively (for cathodic catalysis) or positively (for anodic catalysis) charged, attracting ions of the opposite charges to establish an electrical double layer (EDL), including a closely fixed layer of adsorbed ions (inner Helmholtz plane, IHP), a loosely attracted layer of ions (outer Helmholtz plane, OHP), and a diffuse layer (**Figure 3A**). The concentration of species within the EDL region is significantly different from bulk solution, depending on both applied potential and exchange current.¹⁶ For example, the local pH in EDL is contributed by the electrically adsorbed H⁺/OH⁻ and electrolysis that generates/consumes H⁺/OH⁻ species. In neutral PB buffer solution, Yang *et al.* demonstrated that the local pH in EDL could drift by 5 units to strongly basic during CO₂RR to produce hydrocarbons (-1 V vs. RHE).¹⁷ The EDL expands to the nanopores due to the diffusion of water molecules and ions (**Figure 3B**).¹⁸ The previous conclusion of chemical stability in the bulk electrolyte may not apply anymore since the newly established EDL region has different chemical environments. An example is given in **Figure 3C**: a MOF that is stable in a neutral solution but unstable in alkaline electrolytes cannot be claimed as a stable electrocatalyst for CO₂RR in neutral media because the real chemical environment of the MOF is strongly basic. Also, cyclic voltammetry (CV) applies an increasing/decreasing potential (**Figure 3D**) to form a dynamic EDL, and the MOFs are repeatedly exposed to cation/anion-concentrated chemical environments. Even a MOF that can resist cation-condensed EDL during cathodic electrocatalysis

may not show good stability during cyclic voltammetry studies. For example, we showed that ZIF-67 (**Figure 4A**), when subjected to non-Faradaic CV analysis, would experience morphologic and structural changes to Co(OH)_2 nanosheets (**Figure 4C**).¹⁹ In another report, Tian *et al.* demonstrated that a 3 nm-thick oxyhydroxide layer was instantly formed on the surface of MOFs upon the application of potential, and MOFs could be wholly converted to metal oxyhydroxide nanosheets in 20 s by CV potential sequence.²⁰

The redox reactions at metal nodes and organic linkers (**Figure 3E**) also can be destructive. If a specific potential is reached, metal species can be reduced or oxidized. Such metal valence changes can affect the hardness and coordination environments of the metal nodes. Heidary *et al.* recently reported that the electrochemical reduction of Mn^{3+} to Mn^{2+} resulted in the restructuring of Mn-MOF, releasing porphyrin carboxylate ligands.²¹ Also, electrocatalysis requires extensive chemical bond breaking and/or formation on the metal sites, which implies that some coordination sites need to lose linkers to accommodate reactants.²² Meanwhile, some reactions produce radical intermediates (*i.e.*, $\cdot\text{OH}$ and $\cdot\text{O}$) that may react with organic linkers. Therefore, it is vital to pre-determine the linkers' electrochemical stability window to avoid any undesired oxidation/reduction of linkers at operating potentials.

A real-world electrocatalyst requires low resistance and small overpotential for high energy efficiency. Currently, MOFs' conductivities are not comparable to the conventional electrocatalysts.²³ Therefore, at a high reaction rate, a considerable portion of electric energy is converted to thermal energy due to Joule heating,²⁴ posing thermal stability issues to MOFs.

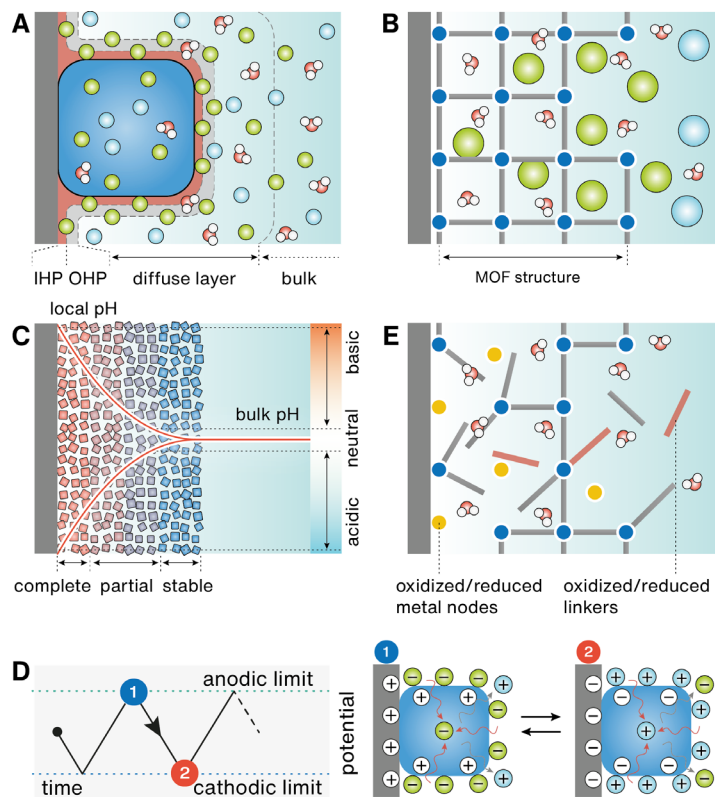


Figure 3. (A) Established EDL structure on the surface of a MOF particle; (B) Diffusion of ions/molecules into the framework of MOF in the established EDL; (C) Cross-sectional illustration of MOF-coated electrode in neutral electrolyte. The charged surface creates a concentration gradient of ions (H^+ in this case), causing the local pH in EDL to drift to acidic/basic ends and result in complete/partial destruction of the neutrally stable MOFs; (D) EDL formation and ion diffusion on the surface/inside the pores of MOFs (right) due to the dynamic potential sweeping (left); (E) Structural destruction of MOFs due to the redox reaction of metal nodes and/or organic linkers.

PITFALLS IN CLAIMING MOFs AS ELECTROCATALYSTS: CASE ANALYSES

As the MOF family grows, papers directly using MOFs in electrocatalysis appear daily. Many share a similar structure: material characterization of MOFs in pristine form; electrochemical analysis of MOFs; electrocatalytic performance evaluation; and/or post-analysis of MOFs. Despite the increasing number of reports showing the stability issues of MOFs, numerous reports assigned

the active sites to the metal nodes of MOFs regardlessly. Here, we revisit some representative examples demonstrating 'stable' MOF electrocatalysts to understand whether the evidence can support their claim, as well as the common pitfalls.

One typical way of claiming the 'stability' of MOFs is, as in many early reports, to compare the electrochemical performance during long-term electrocatalysis or before/after catalytic reactions. If no or minor differences were observed, the authors often declared the MOF a 'stable electrocatalyst' and assigned the active sites to the metal nodes.²⁵⁻²⁷ However, the current–potential profile cannot reveal the structural information, and such an interpretation is a result of mistaking *electrochemical 'performance' stability* as *electrochemical stability*. Stable performance does not mean the stability of structure. For example, if the destruction of MOFs occurs rapidly, the associated current drop/increase will be hidden inside the initial charging current spike, and the following long-term electrocatalytic activity should be attributed to the new phase derived from the MOFs. Alternatively, if the destruction is slow, the newly generated species on MOFs' surface may act as the active sites to show stable electrochemical performance even when the MOFs are not electrocatalytic active. The misuse of electrochemical performance stability to claim electrocatalytic stability of MOFs often leads to contradictory results. One archetypal example is HKUST-1, a hydrophilic MOF with Cu nodes linked by benzene-1,3,5-tricarboxylate molecules. Although the HKUST-1 is known by the MOFs community to be unstable even in moisturized conditions (water binds strongly to unsaturated Cu sites),²⁸⁻²⁹ a few reports claimed it as the 'stable' electrocatalyst for NRR,²⁶ CO₂RR,³⁰ and oxygen reduction reaction³¹ in an aqueous electrolyte based on the electrochemical data.

As the post-electrocatalysis analysis tools, electron microscopy (EM: TEM and scanning electron microscopy, SEM) and X-ray diffraction (XRD) are frequently engaged to reveal the

morphologic and structural changes of MOFs.³² With no significant changes of EM and the diffraction patterns before and after long-term electrocatalysis, the conclusion of a stable MOF electrocatalyst was often drawn.³³⁻³⁴ Still, these validation methods are flawed due to the limitation of the techniques. On the one hand, the ability to retain its shape/size after electrocatalysis does not necessarily mean that the chemical structure of MOF is stable. A MOF precatalyst of which surface is slowly converted to a new phase during electrocatalysis would not display significant changes in its overall shape. Some MOFs, even after being carbonized, still exhibit the same polyhedral shape.³⁵ On the other hand, XRD patterns only reveal the diffraction signals from highly ordered structures with large crystalline sizes. Amorphous structures and particles with crystalline size below 2 nm do not produce discernible diffraction patterns in conventional XRD,³⁶ especially when the signals from the MOF are overwhelmingly intense. Thus, if only the surface region of a MOF is transformed into amorphous phases with the thickness of a few nanometers while the bulk MOF structure remains (partially degraded MOFs), the XRD results before and after electrocatalysis would not show distinguishable differences, as many has pointed out.^{2, 37} Besides the technical limitation, the X-ray radiation can induce the amorphization of some MOFs,³⁸ creating a 'Schrodinger's cat' situation: once examined with XRD, one may not know if the new phase is created by electrocatalysis or X-ray radiation. Similar electron beam damage of MOFs' structure during EM observation (especially, high-resolution ones) is also known.³⁹⁻⁴⁰

These limitations of EM and XRD can invalidate the claim of electrochemically stable MOFs and lead to controversial conclusions. In 2016, Tang and co-workers reported an ultrathin NiCo-MOF that showed an excellent electrocatalytic OER performance under alkaline conditions, which is one of the first 'stable' MOF electrocatalysts for OER and has quickly gained broad interest (>1k citations so far). They claimed excellent stability of the MOF based on stable current, unchanged

morphology, and XRD pattern and proposed that the surface atoms of the MOF (Ni and Co) were the active centers for OER.³³ Such justification was later challenged by Najafpour *et al.* in 2020, who showed that the pristine NiCo-MOF was not the true catalyst but merely a precatalyst.⁴¹ Combing the pieces of evidences from X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, Fourier-transform infrared spectroscopy (FTIR), UV–vis spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, EMs, and X-ray absorption spectroscopy (XAS), they convincingly proved that, during OER, the as-mentioned MOF was decomposed to Co/Ni oxides that have been well known to be OER active. In a recent report, Tang's group acknowledged the structural transformation of their MOFs to $\text{Ni}_x\text{Co}_y\text{OH}$ during OER using *in situ* XAS, to which the high activity attributed.⁴²

Another example is a recent study by us regarding the electrochemical instability of ZIF-67 (**Figure 4A**),¹⁹ a commonly used MOF' electrocatalyst' claimed to be stable and OER active.⁴³ Comprehensive analysis revealed that the ZIF-67 could not retain its structure even in mild electrochemical tests (**Figures 4B-C**). Using *in situ* Raman and UV–vis spectroscopies, the ZIF-67 was shown to irreversibly transform into OER-active alpha- $\text{Co}(\text{OH})_2$ and beta- $\text{Co}(\text{OH})_2$, and longer reaction time or higher overpotential led to a quicker collapse of the structure (**Figure 4D**). Therefore, by no means can ZIF-67 be claimed as the electrocatalyst. Similar structural transformation of MOFs to their metal hydroxide intermediates, as the OER active sites, were recently reported by a number of researchers.⁴⁴⁻⁴⁶ In these cases, the MOFs were utilized as precatalysts to generate active sites by electrochemical environment.

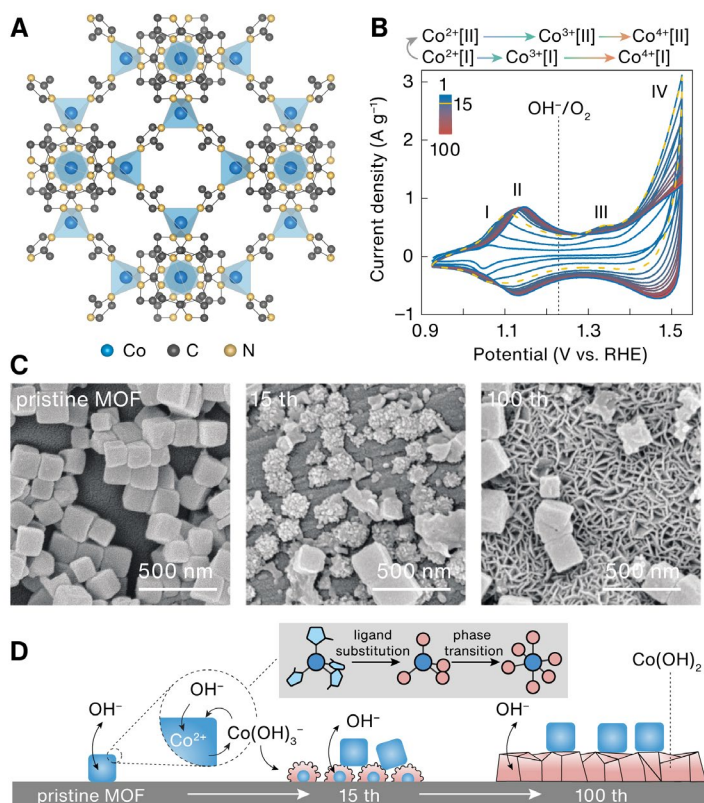


Figure 4. (A) Structure of ZIF-67. (B) CV profile of ZIF-67 from 1st to 100th cycle showing the gradual formation of active species. Oxidation of Co^{2+} and OER are involved within the CV range. (C) SEM images of ZIF-67 in its pristine form, after 15 CV cycles, and after 100 CV cycles. (D) Schematic mechanism of the morphological and structural evolution during CV study. Only capacitive charge/discharge is involved within the CV range. Inset shows the conversion of Co coordination sites to $\text{Co}(\text{OH})_2$. Panels B–D were reprinted from Zheng *et al.*¹⁹

HOW TO CLAIM A MOF AN ELECTROCATALYST

To prove that a MOF is an electrocatalyst is much more challenging than to disprove it due to the complexity of MOFs' structures and their possible conversion paths in electrocatalysis. It needs to be clarified that the instability of a MOF does not necessarily disqualify it for electrocatalyst. Even unstable MOFs can still be claimed as electrocatalysts if they show specific catalytic activities. The structural reconstruction of unstable MOFs, however, generates new phase(s) that may exhibit higher or lower catalytic activity, producing a better or worse electrocatalyst than the original

MOFs. Ideally, the MOF without catalytic activity, but can be transformed to an active catalyst, are precatalysts. However, the instant potential-driven structural reconstruction of MOFs during electrochemical analysis makes it extremely difficult to study the starting stage of electrocatalysis. Nevertheless, by gathering evidences from various techniques focusing on different aspects at different reaction stages (**Figure 5A**), we can get a glimpse of MOFs' role during electrocatalysis.

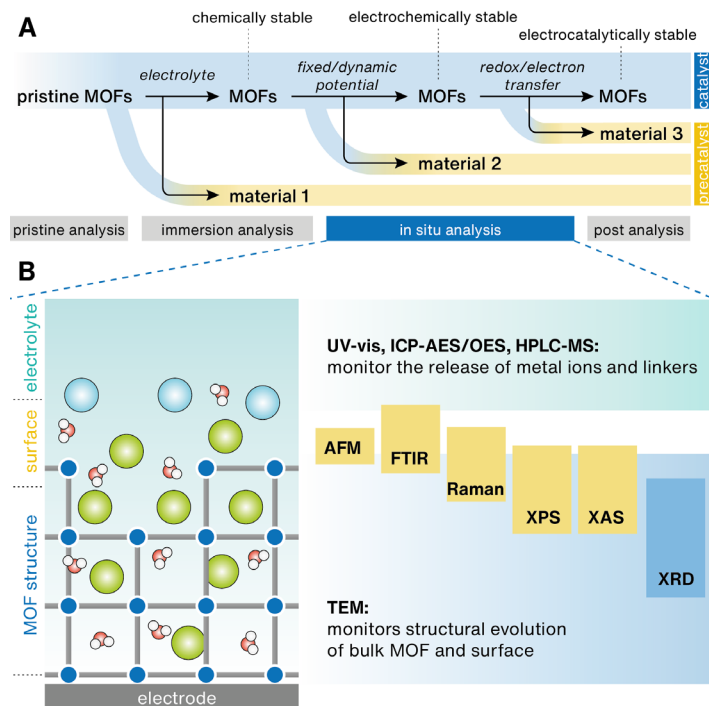


Figure 5. (A) Scenarios of MOFs' evolution at different steps of electrocatalytic study and the corresponding analysis stages, from immersion in the electrolyte to surface-charged with potential, and real operation conditions. (B) Map of detection regions for *in situ* techniques to study electrocatalysis using MOFs: from bulk to surface and electrolyte.

First, the chemical stability of MOFs in electrolyte needs to be proved structurally and morphologically, which includes the analysis of surface species (XPS, FTIR), shape (EMs), chemical structure (Raman, XAS), crystalline structure (XRD, XAS), and porosity/surface area (BET: Brunauer–Emmett–Teller). Ideally, the post-analyses of MOFs after electrocatalysis need to show identical profiles. However, for most cases, hardly all results agree due to various issues.⁴⁷

In situ techniques coupled with electrochemistry are better choices than post-analyses.⁴⁸

Figure 5B summarizes *in situ* methods commonly engaged in electrocatalytic studies with their regions of interest. Researchers need to combine different techniques to acquire a complete understanding of the MOF's role in the targeted reactions. Considering that nearly all electrocatalytic reactions take place on the surface/interface region of the catalysts, methods that can monitor the surface structure of MOFs are indispensable, including Raman spectroscopy, XPS, XAS, and FTIR.^{46, 49} For any *in situ* techniques used to study MOFs, it should be noted that only the first profile can be used, *i.e.*, the first CV cycle or first anodic/cathodic sweeping. The sample should not be subjected to any electrochemical treatment before a baseline at OCP (open circuit potential) is collected.

It is also essential to monitor the changes in electrolytes, which can provide indirect evidences of MOF's instability. Methods such as UV-vis, ICP-AES/OES (inductively coupled plasma atomic emission spectroscopy/optical emission spectrometry), and HPLC-MS (high-performance liquid chromatography-mass spectrometry) are helpful to study the concentration of metal ions and linkers released to electrolyte. However, releasing metal ions/linkers during electrocatalysis does not necessarily disqualify MOFs as electrocatalysts but indicates their instability. Likewise, a minor release of metal ions or linkers does not prove stability. Direct structural evidence of the surface region is still required.

Once confirmed as the electrocatalyst, the assignment of active sites in MOFs is required to understand the reaction mechanism. The metal nodes, as previously mentioned, are widely proposed as the active sites for MOFs. However, other structural traits in MOFs that are currently overlooked may also contribute to electrocatalytic activity or even act as the active sites. Defects, for example, are often evident in MOFs in the form of unsaturated sites or missing linkers, and

such under-coordinated sites can interact with reactants.⁵⁰ It is likely that the local coordination environment of the defects can deliver higher efficiency and selectivity without involving structural reconstruction of MOFs. Still, these studies are lacking in the current literature since the electrocatalytic stability of MOFs remains unproven in many cases.

To summarize, we have discussed a currently blurred concept of catalyst and precatalyst in the content of MOFs for electrocatalytic applications. It is emphasized that, to gain an accurate understanding of the role of MOFs, the structural impact of chemical and electrochemical environments on MOFs needs to be considered for their electrochemical studies. Specifically, the concepts of *chemical stability*, *electrochemical stability*, *electrocatalytic stability*, and *electrocatalytic performance stability* need to be differentiated. Current pitfalls in claiming a stable MOF electrocatalyst are also pointed out, and *in situ* techniques are recommended to strengthen the claim.

Catalyst or precatalyst? This is a question to bear in mind when a MOF is engaged in electrochemical studies. As we are currently overwhelmed by numerous MOFs that show great potentials in electrocatalysis, we need to revisit the fundamental issues of electrocatalysts and try to provide a comprehensive story possible, especially regarding the structural evolution of MOFs at the operation conditions. Without a presumption that the metal nodes in MOFs are the electrocatalytically active sites, careful control experiments as well as *in situ* studies are advised to support the claim. Constantly, we find the 'minor/slight changes' is a description often encountered for 'so-claimed' stable MOF electrocatalysts. However, sometimes, it only takes small changes to significantly alter the electrocatalytic activity and even the reaction mechanism. We hope this Viewpoint can make researchers aware of current pitfalls and help them improve experimental design.

Weiran Zheng[†]

Lawrence Yoon Suk Lee^{*,†,‡}

[†]Department of Applied Biology and Chemical Technology, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong SAR, China.

[‡]Research Institute for Smart Energy, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong SAR, China.

AUTHOR INFORMATION

Corresponding Author

***Email:** lawrence.ys.lee@polyu.edu.hk

ORCID

Weiran Zheng: 0000-0002-9915-6982

Lawrence Yoon Suk Lee: 0000-0002-6119-4780

Notes

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