Showcasing research from Prof. Nikolay Kornienko at the University of Montreal, Department of Chemistry, Montreal, Canada.

*Operando* spectroscopy of nanoscopic metal/covalent organic framework electrocatalysts

Metal and covalent organic frameworks (MOFs and COFs) are increasingly finding exceptional utility in electrocatalytic systems. In order to obtain insights into their function, mechanism and dynamics under electrocatalytic conditions, *operando* spectroscopy, which is performed as the catalyst is functioning, has been increasingly applied. This review highlighted emerging research in recent years that have used *operando* spectroscopic techniques to investigate electrocatalytic MOFs and COFs.

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Nikolay Kornienko

Metal and covalent organic frameworks (MOFs and COFs) are increasingly finding exceptional utility in electrocatalytic systems. Their chemically defined porous nature grants them key functions that may enhance their electrocatalytic performance relative to conventional molecular or heterogeneous materials. In order to obtain insights into their function, mechanism, and dynamics under electrocatalytic conditions, operando spectroscopy, that which is performed as the catalyst is functioning, has been increasingly applied. This mini review highlights several key works emerging in recent years that have used various operando spectroscopic techniques, namely UV-vis absorption, Raman, Infrared, and X-ray absorption spectroscopy, to investigate electrocatalytic MOFs and COFs. A brief introduction to each technique and how it was applied to investigate MOF/COF-based electrolytic systems is detailed. The unique set of data obtained, interpretations made, and progress attained all point to the power of operando spectroscopy in truly opening the functionality of MOFs and COFs across many aspects of catalysis.

Introduction

As research into renewable energy becomes increasingly urgent, more emphasis is placed on the development of electrochemical technologies and the electrocatalysts that drive them.1,2 Such systems carry the potential to be completely powered by renewable-derived electricity and simultaneously be economically competitive with established routes to meet many of society’s energy, fuel, and material demands.3 In fact, the scope of electrosynthetic systems is also being significantly expanded, ranging from water electrolysis and CO2 reduction,4,5 to biomass valorization,6 peroxide electrolysis,11 methane oxidation12 and eventually to a whole host of reactions that may electrify the chemical industry.13,14

Within the context of electrocatalyst research, traditionally catalysts have been divided between molecular and heterogeneous, with each featuring a unique set of strengths and limitations. In contrast to these defined boundaries, many works are beginning to emerge using hybrid systems that in various capacities blend aspects of molecular and heterogeneous catalysts to generate functional systems that combine their advantages and minimize drawbacks.15 Notable examples of these systems include nanoparticles exhibiting functional molecular entities grafted onto their surfaces (ex. Cu/arylpyridinium interfaces16), polymeric catalysts (ex. Co-terpyridine grafted polymers17), and heterogenized homogeneous catalysts (ex. graphite conjugated porphyrins18).

Within this framework, one group of hybrid systems that particularly stands out is metal and covalent organic frameworks (MOFs and COFs). MOFs and COFs are crystalline, permanently porous systems featuring metal nodes (in the case of MOFs) linked together by organic species.19 Their appeal in terms of electrocatalyst design lies in their exceptional tuneability, in which the nodes and organic likers can be tuned, and therefore the porosity and hydrophilicity can be rationally designed a priori.20,21 Further, catalytically active sites, whether they are situated on the organic linker or on coordinatively-unsaturated sites on the inorganic node, can be designed with atomic precision. Finally, the pockets within the MOF/COF framework can be functionalized to act in an enzyme-mimetic manner through secondary coordination sphere effects.22,23 Here, the catalytic pockets stabilize intermediates, minimize reorganization energies and thermodynamically and/or kinetically direct the reaction to efficiently proceed solely through the desired pathway.

To this end, operando spectroscopy,24–29 that which is performed as the catalyst is functioning, is playing a substantial role in aiding researchers in their efforts to fully understand the function of electrocatalytic MOFs and COFs, and from this understanding, develop design rules towards the construction of next-generation systems. The primary spectroscopic techniques include, but are not limited to, UV-Vis absorption, Raman, infrared, and X-ray absorption spectroscopy (Fig. 1). Key insights obtained include the determination of the catalyst redox state, detection of reaction intermediates, and the...
unveiling of charge transfer pathways. Often, such information is not obtainable through the standard array of electroanalytic techniques or through *ex situ* measurements performed before or after catalysis.

In general, UV-Vis absorption spectroscopy is the easiest to use amongst the techniques listed. Its main use is to probe the catalyst electronic structure through measuring electronic transitions of molecular species within MOFs induced by the absorption of UV or visible light. Generally, it is highly sensitive and its main limitation is that it cannot measure reaction intermediates or provide direct structural information about MOFs. Raman spectroscopy measures inelastically scattered light that has lost energy to excite molecular vibrations that feature changes in molecular polarizability. The resultant information can inform on catalyst redox state, catalyst structure, and reaction intermediates. Its low sensitivity often makes the use of resonance Raman or surface-enhanced Raman necessary. This can also be used advantageously as the former can selectively probe a chromophore (e.g. porphyrin) and the latter is exceptionally surface sensitive (nm level) that is sensitive enough to detect sub-monolayer concentrations of molecular species. Infrared spectroscopy also measures molecular vibrations that exhibit changes in the molecular dipole moment. This can also inform of MOF structural dynamics and reaction intermediates. In the most commonly used configuration (attenuated total reflection mode), the infrared source penetrates approx. 1 µm deep into the electrolyte. IR spectroscopy does not require any resonance or surface enhancement to obtain high-quality spectra. Finally, XAS is an element specific spectroscopy that can inform researchers on both the elemental electronic state, through analysis of the shape/position of absorption peaks, and on the element’s local chemical environment, through investigation of the extended fine structure of the absorption. Through this combination, the depth of information on catalyst behavior is exceptionally high. The limitations of XAS is that this technique usually cannot probe reaction intermediates and that specialized facilities that supply high-intensity X-ray light are necessary.

This mini review aims to highlight several key works in recent years that have utilized various *operando* spectroscopic techniques to shed light on nanoscale electrocatalytic MOFs/COFs and to lay out promising avenues to pursue in order to fully take advantage of this exciting array of materials.

**UV-Vis absorption spectroscopy**

UV-Vis absorption spectroscopy is arguably the most accessible technique mentioned in this text as most laboratories are equipped with a suitable spectrometer capable of carrying out these measurements. Often, this is performed in transmission mode with the catalyst grown on a transparent conductive substrate. By monitoring characteristic features in the absorption spectrum, both the MOF/COF redox state in steady state conditions as well as the rate of which charge moves through the framework can be recorded.

A Co-porphyrin based MOF (CoPIZA) was first evaluated with UV-Vis to understand the nature of its redox processes.

![Operando spectroscopy techniques and illustrations of typical spectroelectrochemical cells utilized to probe the function of electrocatalytic frameworks.](image-url)
The steady-state absorption spectra and in particular, the spectral changes corresponding to the porphyrin redox states, were used to extract the redox potential of the Co units in this MOF. Beyond recording the redox potentials corresponding to the Co(II/III) couple, the authors also recorded the apparent diffusion coefficient of charge passing through their MOF by fitting their time-dependent Co(II/III) redox change to a modified Cottrell equation. The derived value of $7.55 \pm 0.05 \times 10^{-14}$ cm$^2$ s$^{-1}$ corresponded to electrons hopping between redox-active porphyrin sites. This seminal work laid out a foundation for spectroelectrochemically evaluating electrochromic MOF films. A similar measurement was subsequently performed on Co-porphyrin bearing conductive COFs to demonstrate that electrons transport through at approximately 1–2 orders of magnitude faster in this case.37

Under steady state conditions, a Co-porphyrin containing MOF, active towards CO$_2$ reduction to CO, was investigated with UV-Vis absorption spectroscopy.38 By recording the characteristic absorption of the Co-porphyrin, the authors determined that a Co(i) species was built up under catalytic conditions and that this was the species responsible for initially reacting with CO$_2$. Recently, a MOF featuring catalytic cobaloxime linkers was synthesized and found to be active towards the hydrogen evolution reaction (HER).39 The authors used UV-Vis absorption spectroscopy to demonstrate the reversibility of the Co species between the Co(i) and Co(II) redox states, and a lack of reversibility between the Co(i) and Co(III) states (Fig. 2b–d). These measurements are particularly important as redox transitions and the evaluation of reversibility are not always evident through conventional cyclic voltammetry (CV) measurements due to large capacitive currents and sluggish charge transport through MOF/COF films.

### Raman spectroscopy

Raman spectroscopy measures inelastically scattered light upon irradiating a sample with a visible or ultraviolet laser. Raman active vibrations are those that feature a change in the polarizability in the material/molecule. A limitation to this technique is the small fraction of photons that are inelastically scattered (1 out of every $10^6$) and thus, techniques to enhance this such as resonance Raman (RR)40 or surface-enhanced Raman spectroscopy (SERS)41 are often employed. The advantage of Raman spectroscopy, especially in the context of operando experiments, is that the simple setup (Fig. 3b), often operated in reflection mode, is highly amenable to a host of reactor designs. Often either a long working distance objective or a water immersion objective is utilized, situated just above the catalyst-containing working electrode. Depending on the exact system, both catalyst structure, redox state, and reaction intermediates can be deciphered as a function of time, voltage, or other relevant parameters.

Recently RR was utilized to identify active sites within a phthalocyanine-based Co–Cu bimetallic MOF active towards the oxygen reduction reaction (ORR), a key component in various types of fuel cells.42 The spectra, acquired under simulated reaction conditions in an alkaline electrolyte, revealed O and OH adsorbed onto the Co species of the Co–O$_4$ sites in conjunction with the redox changes of the Co between the Co(III) and Co(II) states. The Cu–N$_4$ sites within the phthalo-
cyanine units were deemed instead to be catalytically inert in this case. A combination of UV-Vis absorption and Raman spectroscopies unveiled structural dynamics within ZIF-67 water oxidation catalysts (Fig. 3a and b). The starting material, ZIF-67, featured Co atoms coordinated to the four nitrogens of the 2-methylimidazole linkers in a tetrahedral geometry. As the potential was poised in the positive direction in which water oxidation begins to occur, features in both, the UV-Vis absorption and Raman spectra attributed to the ZIF-67 began to disappear (Fig. 3c and d). In turn, Co-(OH)$_2$, and finally CoOOH signatures emerged in the spectra. This data, in conjunction with ex situ X-ray diffraction and X-ray photoelectron measurements, lead the authors to conclude that the ZIF-67 first undergoes a series of ligand substitutions, replacing imidazole to OH$^-$, then finally goes through a phase transition to yield the CoOOH catalyst (Fig. 3e). The exact nature of these steps was deemed important as the two types of CoOOH formed exhibited significantly different water oxidation activities.

Infrared spectroscopy

Infrared spectroscopy, highly complementary to Raman spectroscopy, records light absorbed in the infrared region whose energy is used to excite vibrational modes featuring a change in the molecule's dipole moment. In the context of operando electrochemical experiments, IR spectra are usually acquired in an attenuated total reflection (ATR) setup in which a catalyst film is deposited onto an ATR waveguide and the IR light comes from below and reflects back to the detector (Fig. 4a). This configuration enables researchers to selectively measure within 1 µm of the waveguide/catalyst-electrolyte interface and avoids having the solvent signal completely overwhelm the spectra. For higher surface-sensitivity, surface-enhanced IR absorption spectroscopy (SEIRAS) can be performed with the use of nanostructured metal films.

IR spectroscopy was used to probe the accessibility of molecular H$_2$ evolving catalysts grafted into amino functionalized MIL-101(Cr) MOFs. The reduction of the catalyst, [Fe$_2$(cbdt)(CO)$_6$] (FeFe, cbdt = 3-carboxybenzene-1,2-dithiolate) with chemical reductants was monitored over time to probe the functional accessibility of these species deep within the MOF structure. Complete reduction, signified by several key marker bands in the IR spectrum, took place within the hours and at short time scales was found to be hindered by the ions of the reduced catalyst and oxidized reductant formed within the pores. This work pressed for careful consideration of mass transport in the design of catalytic MOFs.

Fig. 3 Spectroelectrochemical setup used for operando UV-Vis absorption (a) and Raman (b) spectroscopies. UV-vis absorption (c) and Raman (d) spectra point to the structural evolution of the ZIF-67 structure into CoOOH as the true water oxidation catalyst (e) under applied oxidizing voltages. Reprinted with permission from ref. 43: W. Zheng, M. Liu and L. Y. S. Lee, ACS Catal., 2020, 10, 81–92. Copyright 2020 American Chemical Society.
A series of bimetallic MOFs, comprised of Cu/Zn phthalo-cyanine units with Cu/Zn –N4 coordination linked via Zn/Cu-O4 clusters, was found to be exceptionally active towards electrochemical CO2 conversion to CO. The MOF was deposited onto a roughened gold surface and SEIRAS was subsequently used to probe the mechanism of this system. A CuO4-H intermediate was detected at 1850 cm–1, as were CuN4-CO and CuO4-CO species at 1933 and 2071 cm–1, respectively. However, no intermediates were detected on the CuN4 sites, nor any on either of the Zn sites, possibly due to their transient nature. This led to the interpretation the Cu is active for proton adsorption, which either facilitates hydrogen evolution or protonation of the CO2 intermediates situated on the Zn sites in a synergistic manner.

A combined UV-Vis, Raman and IR study was used to unveil the structural reorganization of a Mn-porphyrin containing MOF thin film under electrochemical bias. First, UV-Vis absorbance measurements, following the spectroscopic signatures of the Mn(II/III) redox couple, showed that the complete reduction of the system occurred within several seconds but the re-oxidation, while being fully reversible, took tens of minutes. Raman and IR measurements (Fig. 4a–d) revealed that the redox process was coupled with a ligation change and unveiled the partial detachment of the porphyrin carboxylate units to the Zn centers, the latter of which matched the timescales of the rapid reduction/slow oxidation. This allowed the researchers to put forth a model of how this system restructured under applied bias (e). IR was further extended to probe the CO2– and CO intermediates of this system en route to CO2 to CO conversion, enabling the construction of a catalytic reaction mechanisms.

As mentioned in the introduction, a key strength of electrocatalytic MOF systems is that functional units may be grafted in to promote catalysis via secondary coordination sphere effects. To this end, pyridine units were grafted into a metal-organic layer containing Co-porphyrins as the catalytic site. The protonation of the pyridine to pyridinium under catalytic conditions was captured with operando IR spectroscopy and it was this species that was thought to stabilize the intermediates of the CO2 as it was reduced to CO, thereby enhancing the rate of this process.

Finally, the mechanism of bifunctional MOFs, catalytic towards oxygen reduction and water oxidation, was deciphered with operando IR spectroscopy. The series of ultrathin (20 nm) MOFs, featuring octahedral Ni- and Fe-oxo nodes and 2,6-naphthalenedicarboxylate linkers, were solvothermally synthesized and subsequently irradiated with UV light to induce lattice strain within their structure. This modulated their electronic structure and consequently their catalytic activity. Under both oxygen reduction and water oxidation conditions, a band at 1048 cm–1 was evident which corresponded to the superoxide *OOH species built up under steady state conditions. This observation, coupled to isotope-labeled experiments and operando XAS measurements, was key to elucidate the complete catalytic cycle of this system for both reactions.

**X-Ray absorption spectroscopy**

X-Ray absorption spectroscopy (XAS) uses high energy X-ray irradiation to probe electronic transitions between core and valence levels of the species of interest. This technique is
element specific and can be used to both, probe the electronic structure of the element of interest by examining the shape and energy position of the near-edge region (XANES) or to probe the element’s chemical environment by analyzing the extended fine structure region that extends several hundred eV past the edge (EXAFS). The depth of information provided is largely why these techniques are used across many areas of catalysis. However, the significant drawback to XAS is that high intensities of X-rays are required and only available in specialized facilities. In a typical XAS setup employing hard X-rays (above 5 keV), the catalyst/working electrode is placed in the path of the X-ray source in a thin electrochemical cell and either reflection or transmission mode may be used to collect signals. In the case of soft X-rays (below 5 keV), a high-vacuum environment is used with the catalyst deposited on one side of a conductive ultrathin window/electrode with electrolyte on one side and vacuum on the other.

XAS was recently used to highlight differences in electronic structure between a series of Co-Porphyrin containing COFs and the isolated porphyrin linkers active towards the reduction of CO2 to CO. An examination of the K-edge and L-edge spectra indicated that the COF structure imbibed an electron-withdrawing effect to the Co active site within the porphyrin units, in this case beneficial for catalysis. Furthermore, the reduction of Co(II) to Co(I) under CO2 reduction conditions was captured, successfully identifying the active species.

XAS was also crucial in the investigation of NiCo bimetallic ultrathin (3 nm) MOF water oxidation catalysts. The ultrathin MOFs were much more active than their bulk counterparts and this observation warranted a XAS study to explain. XANES at the Ni and Co K-edges, in conjunction with DFT simulations, was used to identify the undercoordinated sites involved in the catalysis. Operando XANES measurements revealed that a higher fraction of Ni and Co atoms were oxidized under positive water oxidation potentials in the ultrathin MOFs relative to the bulk analogues, highlighting the catalytic benefits of the ultrathin geometry. Recently, NiCo-MOF-74 and NiFe-MOF-74 MOFs were probed with XAS as they catalyze water oxidation. Through analysis of operando EXAFS spectra, the authors found a reversible oxhydroxide-hydroxide structural transformation between catalytic and pre-catalytic conditions. These materials behaved in contrast to what has been established for several porous catalysts, opening up pathways to further explore new modes of function with MOFs.

Concluding remarks

This mini review highlighted how operando spectroscopy can be leveraged to understand and fully harness the capacities of MOFs and COFs in the context of electrocatalysis. While detailing every study utilizing operando spectroscopy is out of the scope of this work, several key investigations in recent years were detailed. Each technique provides the researchers with a unique set of information and similarly has its own limitations. Therefore, many studies combine two or more operando experiments to arrive at a more conclusive data set and interpretation.

It must be mentioned that additional operando techniques not mentioned in this mini review have also been used to investigate electrocatalytic systems. These include X-ray photoelectron spectroscopy, X-ray diffraction, X-ray scattering, and quartz-crystal microbalance experiments, as well as spatially resolved techniques such as electrochemical microscopy and tip-enhanced Raman spectroscopy. Translating these to MOF and COF catalysts stands to further unveil the interesting complexity of their function. Finally, researchers should continually push to narrow the gap between the conditions used for spectroelectrochemical experiments and those in the actual catalytic experiments. A notable example lies within the field of CO2 reduction in which most spectroscopy is conducted within standard 3-electrode cells while catalytic experiments are increasingly being performed in gas-diffusion electrodes and flow cells. Beyond electrocatalysis, MOFs and COFs just been started to be applied in electrochemical contexts in the last handful of years, including the area of supercapacitors, batteries, and sensors and are already making sizeable impacts. Their versatility coupled to a greater understanding of how they function is envisioned to truly open up their use these fields.

Conflicts of interest

There are no conflicts to declare.

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References


