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***In situ/Operando* studies of electrocatalysts using hard X-ray spectroscopy**

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Abstract

This review focuses on the use of X-ray absorption and emission spectroscopy techniques using hard X-rays to study electrocatalysts under *in situ/operando* conditions. We describe the importance and the versatility of methods in the study of electrodes in contact with the electrolytes, when being cycled through the catalytic potentials during the progress of the oxygen-evolution, oxygen reduction and hydrogen evolution reactions. The catalytic oxygen evolution reaction is illustrated with examples using Co, Ni and Mn oxides, and Mo and Co sulfides are used as an example for the hydrogen evolution reaction. A bimetallic, bifunctional oxygen evolving and oxygen reducing Ni/Mn oxide is also presented. The various advantages and constraints in the use of these techniques and the future outlook are discussed.

Keywords

X-ray spectroscopy; Electrocatalysis; Electronic structure

1. Introduction

The environmental threat posed by climate change, largely caused by the increase in the use of fossil fuels worldwide over the last century, has provided a powerful and sufficient enough incentive to convert from an economy based on fossil fuels to one based on carbon-neutral renewable fuels.

Renewable energy sources such as solar, wind, tidal or hydro power all have in common a problem of intermittent production and hence availability, some functioning over a day/night cycle and others on a seasonal, yearly cycle. It follows that the energy produced by the conversion of renewable energy sources has to be stored, in order to be re-used at other times and locations than where it is produced, to match the needs of society that do not adapt to intermittent utilization of energy. Batteries are one important and viable energy storage

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option, but another one is the conversion of energy into chemical bonds [1,2]. One system that has drawn much attention as early as the 70's is the electrolysis of water, also known as water-splitting (eq. 3). This reaction combines two half-reactions occurring in a single electrochemical cell: water oxidation (the oxygen evolving reaction, OER) at the anode (eq. 1) and proton reduction (the hydrogen evolving reaction, HER) at the cathode (eq. 2).

The dioxygen and hydrogen produced during the reaction are stored separately and can be recombined in a fuel cell to regenerate water and recover, with some losses, the energy that was originally used to 'split water'. These reactions require, however, catalysts based on noble metals such as iridium (for OER) or platinum (for HER) to minimize the overpotential required and also kinetic barriers. The cost of these catalysts based on expensive metals not available abundantly is one important reason that prevents these reactions and the associated hydrogen-based technologies from being used more widely.

For the last decade, much effort has been directed towards the replacement of these expensive catalysts with cheaper ones, using earth-abundant elements. In the case of noble metal catalysis, improvements have consisted in decreasing the amount of expensive elements used by decreasing the size of the particles, alloying them or developing high surface area materials, such as core-shells or hollow spheres. The case of earth-abundant materials is different, since the challenge is not to decrease their amount for cost reasons, but increase the efficiency, both thermodynamically and kinetically. Rather than a purely empirical approach, such improvements require a detailed understanding of the fundamental processes that govern these reactions, through a structure-activity relationship. Several aspects of electrocatalytic phenomena need to be understood in order to describe a fuel-producing electrochemical device with a comprehensive view.

The local geometry, *e.g.* the phase and the level of order, as well as the electronic structure of a catalytic material are at the heart of its activity. These aspects govern properties such as conductivity, stability over time and interactions at the interface with the substrate-containing media, where bond-forming or breaking reactions occur. Several spectroscopic techniques can probe structural or electronic structures, but only a few of them can be applied to *in situ/operando* catalytic experiments. Vibrational (IR [3] and Raman [4]) spectroscopies have been used to study materials under catalytic conditions. These techniques provide very important information on specific bond formation or breaking, but they cannot access the electronic structure with much detail. Electronic paramagnetic

resonance (EPR) is a powerful tool to probe paramagnetic samples, but the instrumental setup requiring a large magnet with a specific configuration is a severe constraint for *in situ* catalytic reactors. X-ray absorption (both X-ray absorption near edge spectroscopy (XANES) and extended X-ray absorption fine structure (EXAFS) and emission spectroscopy are well suited to study the electronic and geometric structure of the catalysts, and because of the ability of X-ray photons to penetrate matter at the micrometer or even millimeter scale (depending on the photon energy), X-ray spectroscopies hold a place of choice in catalytic *in situ/operando* studies. X-ray methods allow studying materials behind a solid support, which can act as a liquid-vacuum separating membrane, a solid-liquid interface, an electrode, or these three components at the same time.

In this article, we will review our own efforts, as well as those of others, in studying various aspects of electrocatalytic, energy-related reactions using X-ray spectroscopies. We will cover some methodological aspects and describe the progress made in understanding the OER or HER reactions using *in situ/operando* X-ray absorption spectroscopy, but also more advanced techniques such as X-ray emission spectroscopy.

2. *In situ/Operando* hard X-ray spectroscopy methods

As a preamble, we are giving here a definition of *in situ* and *operando* experiments. An *in situ* experiment probes the subject of a study such as a material, a molecule or an enzyme under conditions that are relevant to its native or applied use. Probing a proton-conductive membrane set in a fuel cell stack, a molecular catalyst dissolved in the solvent that will be used for catalysis or an enzyme under physiological conditions are *in situ* experiments. These conditions will show the interactions between the studied object and its neighboring components: i.e. the diffusion of nearby elements in its structure, the coordination of solvent to a metallic center or a conformational effect induced by external ions or solvent molecules. If the subject of the study is probed while performing the function it is intended to, then it is an *operando* experiment. As for the examples mentioned above, the proton-exchange membrane might change its organization and internal hydrogen-bond network, the catalyst might be converted into another intermediate and an enzyme might completely rearrange its active site under functioning conditions. Very often, *operando* experiments are evolutions of *in situ* experiments, which are augmented by the addition of an external stimulus and with a time-resolution component.

In situ or *operando* X-ray experiments have been performed for several decades, with the intent of studying interface phenomena such as those found in heterogeneous catalysis [5], fuel cells [6], or batteries [7]. Up to now, the main challenge of *in situ* or *operando* X-ray experiments was in the design of the cell and its components. Transmission or back-reflection setups have been described for absorption and fluorescence experiments, respectively. Total electron yield (TEY) experiments have also been described recently, which require a specific procedure if electrochemical data are to be recorded from the same electrode as that of the TEY signal [8]. The more recent experiments have taken advantage of the widespread use of thin film deposition. It is possible, nowadays, to deposit virtually any conductive material as a thin layer (from a few to hundreds of nm) onto another material that will have the mechanical properties suited to separate a liquid-containing vessel from

the outer environment (which can be under vacuum). The commercial availability of very thin (tens of nanometer) silicon nitride membranes that are almost transparent to X-rays with a very good mechanical and chemical resistance have also played a crucial role in these technological advances. Certain materials can even play both the role of a separating membrane and of an electrode, such as glassy carbon films, boron-doped diamond or thin metallic foils. The balance between conductivity, mechanical and chemical resistance and thickness is not always easy to match, and it gets more difficult as the energy of the photons used decreases. From the data collection point of view, most experiments consist in applying a constant potential between the reference and working electrodes for a time long enough to record XAS spectra with a sufficient signal to noise (S/N) ratio.

Fig. 1 shows a typical example of an electrochemical cell that has been used by our group and others for *in situ/operando* characterization of electrochemical materials with hard X-ray techniques. To avoid the effects of bubbles that form during the OER and HER reactions as well as to avoid interference of X-rays with electrolyte layers, we used a setup in which the back side of the X-ray transparent window faces the incident X-rays and the front side of the window with the catalyst on a conductive layer faces the electrolyte. The window consists of Si_3N_4 or amorphous carbon, with conductive layers, such as ITO (Indium-doped Tin Oxide), FTO (Fluorine-doped Tin Oxide), or Au being used as the working electrode (WE). The counter electrode (CE) is isolated from the main compartment and the reference electrode (RE) is placed close to the WE. X-ray absorption was measured as a fluorescence excitation spectrum using a multi-element, energy discriminating solid-state Ge detector.

In the experimental configuration shown in Fig. 1, X-rays can penetrate into both the catalysts and the electrolyte. Considering an experiment at the Mn K-edge XAS, for example, the transmission of 6.6 keV X-rays through a 100 nm Si_3N_4 membrane with 100 nm thick gold layer is more than 90%. The out-going Mn $\text{K}\alpha$ fluorescence signal (5.9 KeV) will be further attenuated by a similar path, and as a consequence, we expect 80% of the incident photons to be used to probe the catalytic material of interest. For Mo $\text{L}_{2,3}$ -edges at ~ 2500 eV, much higher attenuation occurs and therefore the window thickness and the conductive layer materials/thickness become more critical. The spectroscopic data obtained by this approach is dominated by the bulk character of the catalysts, unless the electrocatalyst itself is a monolayer or thin layers. As described in the next section, however, almost all of the electro-deposited OER and HER catalysts, *i.e.* Mn, Co and Ni oxides for OER and MoS_x for HER, are porous and consist of electrolyte-permeable structures. Therefore, spectroscopic changes under applied potentials are noticeable, without requiring more surface-sensitive methods. This was demonstrated, for example, by the study of a manganese oxide catalyst with two different thicknesses (100 and 200 nm). While the electrocatalytic current scaled linearly with the thickness of the material, the spectroscopic signature remained identical. This indicated that the entire thickness of the material was active, and not only the topmost layer [9]. Similarly, Klingan et al. showed that the bulk region of CoO_x -based catalysts is active for oxygen evolution owing to the formation of a highly accessible $\text{Co}^{\text{III}}\text{O}(\text{OH})$ layered structure, in which water and electrolyte can efficiently diffuse and intercalate between the different layers [10].

XAS techniques include XANES and EXAFS, the latter requiring a significant data treatment and simulation effort as compared to the former. XANES allows determining the average oxidation state of a material by comparing its rising edge energy (which can be determined by the position of the maximum value in the first derivative spectrum or by the position of the half edge-jump, *i.e.* the position where the normalized intensity is equal to 0.5) with that of reference model compounds. Although the edge position is not an absolute marker of oxidation state, comparisons between similar compounds or between different states of a material give indications on oxidation state changes which are essential to propose mechanistic pathways. XANES, and particularly the so-called pre-edge region, can also give information on the nature of neighboring atoms, the symmetry or the spin-state of the excited central atom.

Fourier transform EXAFS allows, using mathematical simulations, determining the number and the distances of the neighbors around the central atom to a distance of about 5.0 Å, depending on the system. It also allows estimating the degree of order of a material and the size of the largest domains. For example, an infinite lattice will give a number of first neighbors for the excited atom. When crystallites are very small (below 2 nm), the average number of neighbors is decreased, since the atoms at the edge of a domain will have fewer neighbors than those in the center. The relationship between the number of neighboring atoms and the cluster size can also be reflected in the longer-range M–M–M interactions (where M is the central metallic atom). It is thus possible to roughly estimate the average size of the smallest ordered domain in a material that does not yield any diffraction pattern.

3p to 1s XES ($K\beta$ emission), is mostly sensitive to the oxidation state of a molecule or material, and is much less influenced by the neighboring atoms. Although energy shifts are smaller for a given change in oxidation state, it reflects better the oxidation state of the central atom, without charge delocalization considerations. The so-called ‘satellite’ $K\beta'$ peak corresponds to the degeneracy of the 3p to 1s transition and reflects the amount of unoccupied valence shell orbitals, thus probing the oxidation and spin state of the excited atom.

3. Operando studies of OER-active amorphous metal oxide catalysts using hard X-rays

First row transition metal oxides, such as MnO_x [11,12], CoO_x [13,14], NiO_x [15] and $FeNiO_x$ [16] have been shown to function as catalysts for the oxygen evolution reaction (OER). There have been intensive studies to identify the chemically active forms of the catalysts and their catalytic mechanism using X-ray spectroscopic methods [9,17–20]. A series of studies, including earlier work by our group [17,18], have shown that these electro-deposited oxide catalysts are ‘amorphous’, and that they do not possess any crystalline nature within the resolution of the powder X-ray diffraction method. For such materials, X-ray absorption spectroscopy becomes a unique tool for determining the local structure around the metals of interest.

Fig. 2 shows the XANES of Co and Ni electrodeposited catalysts, together with a typical cyclic voltammogram and the proposed structures based on EXAFS studies for these

materials. In Fig. 2A, we show the spectra of Co-Pi (where Pi stands for inorganic phosphate, PO_4^{3-} , as described by Kanan and Nocera [13]) under resting and catalytic conditions. For the Co catalyst films with about 40–50 nmol Co ions/cm² deposited at 1.25 V vs. NHE (Normal Hydrogen Electrode), the XANES spectrum under catalytic conditions is shifted to higher energy (7722.1 eV) by 0.3 eV relative to the spectrum under resting conditions (7721.8). A comparison of the edge position under catalytic conditions with model compounds indicated an average Co valency of ~3 for the Co-Pi samples under OER conditions, although it is difficult to determine metal valency based only on XANES spectra due to their sensitivity to the geometry and ligand environment. Thinner films (~monolayer thickness) were also studied (data not shown) and we observed that the degree of XANES shift is larger in the thin Co-Pi film as compared to the thicker ones. We also determined from EXAFS data that the average cluster size is in the order of ~2 nm, and is larger in a relatively thick film than in an extremely thin one. These observations correspond to a high surface/bulk ratio in the thinner films and therefore indicate a higher porosity for these films [17].

In addition to the information about Co valency, our studies led us to a model of Co-Pi based on structural parameters extracted from fits to the EXAFS data measured under OER conditions. The Co-O and Co-Co distances of 1.89 and 2.82 Å, respectively, indicate that this catalyst consists of Co oxo/hydroxo clusters. Given the number of Co-O and Co-Co interactions (6.0 and 4.5, respectively), the clusters can be described as edge-sharing CoO_6 octahedra, with a maximum size of *ca.* 2 nm. This structural motif is the same as the one found in the extended planes of cobaltates [21]. However, cobaltates themselves are stable in water, and cannot be OER catalysts. Therefore, the OER activity of Co-Pi likely arises from the small size of the Co-oxo/hydroxo clusters, in which the reaction occurs at the edges. This structural model has also been supported by other groups using a similar approach [22] or other *in situ* techniques [23,24]. In particular, pair distribution function (PDF) studies, that use high-energy X-rays, are beneficial for capturing long range order of the clusters beyond the short-range interactions ($< \sim 5$ Å) that EXAFS can provide. Using this technique, Tiede et al. showed the effect of the buffer on the cluster size distribution and the stack domain size [24]. In the presence of phosphate buffer, the CoO_x catalyst likely consists of monolayer domains, but when borate buffer is used, it organizes as stacks, and its lattice structure can be best described as that of anionic cobaltates, like LiCoO_2 . This result points out the influence of chemical nature of the buffer and of pH on the nanoscale organization of CoOOH domains.

Regarding mechanistic implications for amorphous Co oxides, the membrane-inlet mass spectroscopy (MIMS) experiments by Messinger's group provided interesting insights of where the O—O bond formation occurs [25]. By following the time-resolved ^{18}O -labelling isotope-ratio with MIMS, they concluded that the O—O bond formation of the amorphous Co-oxide nanoparticles (Co/methylenediphosphonate (Co/M2P)-oxide) occurs via intermolecular oxygen-coupling between two terminal Co- OH_x ligands, without the involvement of bridging oxygens. Unlike bridging oxygens, these terminal oxygens are proposed to be exchangeable with bulk water. Using the same method, they determined the number of Co per catalytic site to be $\sim 2.1 \pm 0.5$. This rather small number of Co centers

involved in the catalytic reaction implies that a small, amorphous-like cluster is important for the OER reaction.

The above mechanism of the OER by amorphous Co-oxide based on conclusions from the water exchange results differs from what was concluded from light induced time-resolved FT-IR studies [26] and theoretical calculations [27] performed on crystalline Co_3O_4 -based OER catalysts, in which the nucleophilic addition of water to a $\text{Co}^{\text{IV}} = \text{O}$ site is proposed as the O—O bond formation step. It should be noted that such photocatalytic pump-probe experiments and *operando* spectroelectrochemical measurements may not probe exactly the same situation, since in the former case charges arrive sequentially, while in the latter they are constantly supplied to the catalytic material.

More recently, Bergmann et al. showed the reverse-amorphization of a spin-coated Co_3O_4 film surface (a sub-nm thick near-surface region), using *in situ* GI-XRD and *quasi-in situ* XAS (freeze-quenched) methods. This surface species was identified as $\text{CoO}_x(\text{OH})_y$ with $\text{Co}^{3+}/\text{Co}^{4+}$ mixture [28], and demonstrated that transformation to the active (catalytic) phase is accompanied by reversible amorphization of $\text{Co}^{(\text{II,III})}_3\text{O}_4$ to $\text{Co}^{(\text{II,III})}\text{O}_x(\text{OH})_y$. If this is the case, a similar mechanism to what is observed in amorphous Co oxides could be plausible for the OER activity present in Co_3O_4 crystalline materials. This may corroborate the mechanistic aspects of electrocatalysis proposed by Görlin et al., which consists in a dynamic system from a structural point of view [29]. Along this idea of multiple phase material, Yang et al. have demonstrated that it is possible to tailor an efficient CoO_x catalyst layer by creating a two-phase assembly, where a $\text{Co}^{(\text{II})}(\text{OH})_2$ phase is present atop of a mixed $\text{Co}^{(\text{II,III})}_3\text{O}_4$ oxide [30].

Like cobalt, nickel can be electro-deposited as thin film from solutions of $\text{Ni}(\text{aq})^{2+}$ in a proton-accepting electrolyte. The NiO_x electrocatalyst thus formed in borate electrolyte (denoted as Ni-Bi, Bi standing for inorganic borate) shows high oxygen evolution activity under alkaline conditions ($\sim \text{pH } 9.2$) [15]. Fig. 2B shows the typical cyclic voltammograms recorded during the electrode-position process. The current intensity increases as the amount of material deposited increases. Unlike the analogous Co system, however, the Ni electrocatalyst requires an oxidative pre-treatment (anodization) to maximize OER activity. We therefore performed *in situ/operando* experiments when poisoning the electrode at the resting, pre-catalytic (before anodization) and catalytic potentials (after anodization, poised at 1.1 V for 2.5 h), as described in Fig. 2B. The XANES spectra displayed in Fig. 2C show that the Ni-Bi sample under resting conditions is $\text{Ni}(\text{OH})_2$, while under pre-catalytic and catalytic conditions, it is very similar to NiOOH . It can also be clearly seen that the anodized Ni-Bi has a higher edge energy (by 1.3 eV) than that of the non-anodized one, thus showing an increased fraction of oxidized Ni centers in the Ni-Bi catalyst. The estimated valency from the edge position as well as from coulometric measurements is ~ 3.0 in the non-anodized (pre-catalytic) sample and > 3.6 in the anodized (catalytic) one. This overall trend led us to conclude that the presence of $\text{Ni}(\text{IV})$ is important for the OER. The analysis of the EXAFS data shows that the Ni-O and Ni-Ni distances found in the pre-catalytic and catalytic Ni-Bi samples correspond precisely to those found in β - NiOOH and γ - NiOOH , respectively. The β and γ phases of NiOOH are allotropes that only differ by the insertion of cations, potassium in the present case, between the oxide sheets. Since these two phases are

very similar, it is worth mentioning that they were differentiated by the presence of two Ni-O distances (1.90 and 2.10 Å) with a ratio of 4:2 in the pre-catalytic sample, which were identical to the bond lengths and ratio observed in the β -NiOOH phase. This bond length anisotropy arises from the Jahn-Teller distortion observed for Ni(III) ions, the oxidation state under which nickel is found in the β -NiOOH phase. The accuracy of this EXAFS analysis further confirms the +3.0 oxidation state observed in the non-anodized, pre-catalytic Ni-Bi sample and its attribution to the β -NiOOH phase. Similarly to the Co-Pi sample, the minimal cluster size in Ni-Bi was obtained from the number of neighbors to the central atom in the EXAFS fits and was determined to be *ca.* 2 nm. The fact that the conversion from the β to the γ phase of NiOOH leads to an improved catalytic activity suggests that both a high valence of nickel and the presence of alkali ions in the vicinity of the active layers have a beneficial effect [18].

In a later study on this system, Trotochaud et al. showed the incidental presence of Fe in the Ni-oxide electrocatalysts because of leaching from glass [16]. Their work emphasized the importance of impurities in heterogeneous electrocatalysts; the presence of trace Fe contaminant even increases the OER activity, while a purified NiO_x without Fe is a poor electrocatalyst. They suggested that the role of Fe may be to increase a partial-charge transfer activation effect. Their observation of higher OER activities of γ -NiOOH with respect to β -NiOOH matched well with our own study of this system [18]. Thus, the earlier observation of the increased activity of NiO_x after the anodization process described above is likely due to the incorporation of Fe ions in the oxide sheets themselves.

This activity increase upon Fe incorporation is in line with the fact that OER catalysts with both Ni and Fe have been shown to have the highest OER activity from large-scale combinatorial screening [31]. However, the mechanistic understanding of such a system is still debated. *Operando* XAS studies by Friebe et al. reported the structural and electronic role of Fe in the NiFeO_x OER electrocatalysts [32]. From the high energy resolution fluorescence detection (HERFD)-XAS, they showed that Fe³⁺ in Ni_{1-x}Fe_xOOH occupies octahedral sites with unusually short Fe-O distances, sharing edges with surrounding [NiO₆] octahedra. They concluded that Fe is the active site for the catalysis. In contrast, a more recent study by Gorlin et al. using *operando* differential electrochemical mass spectrometry (DEMS) and *quasi-in situ* XAS showed that Fe does not change its oxidation state, but Ni does, and that the more active one contains Ni²⁺ [33]. Unlike the former study, no phase separation of Fe and Ni at higher Fe stoichiometry, nor the formation of metallic Ni was observed under the conditions they used.

The *in situ* XAS method was also utilized by our group to study a OER/ORR (oxygen reduction reaction) bifunctional catalyst based on Mn oxides [9,12]. We found that the switch from ORR to OER potentials results in a structural change in the MnO_x catalyst on Au-Si₃N₄, and characterized the MnO_x phases present under both OER and ORR catalytic conditions. An ORR-relevant potential of 0.7 V *vs.* RHE (Reversible Hydrogen Electrode) produces a disordered Mn₃^{II,III,III}O₄ phase with negligible contributions from other phases. After the potential is increased to a highly anodic value of 1.8 V *vs.* RHE, that is relevant to the OER, we observe an oxidation of approximately 80% of the catalytic thin film to form a mixed Mn^{III,IV} oxide, while the remaining 20% of the film consists of a less oxidized phase,

likely corresponding to unchanged $\text{Mn}_3^{\text{II,III,III}}\text{O}_4$. The oxidized phase is a lamellar structure similar to that of birnessite. By studying catalyst films of different thicknesses, it was also shown that OER catalysis must occur throughout the whole catalyst structure and not just at the topmost geometric layer of the film, indicating porosity of the films. An evolution of this material into a NiMnO_x OER/ORR bifunctional mixed oxide was later studied by our group using XAS and XES, whose results are described in Section 5 of this manuscript.

4. Studies of transition metal sulfide HER catalysts using metal and ligand-centered X-ray spectroscopy

The search for hydrogen evolving catalysts based on earth abundant elements has been very active in the past decade. Inorganic materials based on transition metal sulfides [34], phosphides [35], carbides [36] or borides [37,38] have been shown to have electro-catalytic efficiencies that begin to be competitive with platinum. The family of materials that has been most widely studied is transition metal sulfides, possibly because of their long time use as catalysts in oil desulfurization processes [39]. This section describes our work and that of others on the use of X-ray spectroscopy to probe the structure of such HER-active catalysts.

Molybdenum sulfide (MoS_2), was shown about ten years ago to be an efficient HER catalyst. The seminal work of Jaramillo et al. in 2007 showed that nanocrystals of MoS_2 epitaxially grown on an Ag surface were most active when their size was the smallest [40]. This was explained by the large amount of edge site as compared to basal sites in small particles as compared to larger ones. This experiment demonstrated the implication of terminal disulfide ligands in the proton reduction reaction for well-ordered, crystalline MoS_2 materials. Several studies have followed inspired by this work, using MoS_x materials as HER catalysts. For example, Tang et al. described the preparation and activity towards HER of CdSe-seeded CdS nanorods coated with a MoS_x material [41]. In this study, we used X-ray spectroscopy at the molybdenum K-edge (particularly EXAFS) to show that the molybdenum sulfide catalyst was in a reduced form of MoS_3 , as shown by a shift to lower energies of the Mo K-edge and by a shortening of the Mo–Mo distance. In light of further studies performed since then, this material could probably be now described as amorphous MoS_2 (or MoS_{2+x}). Given the small amount of material deposited on the nanorods, it is clear that a crystalline form of MoS_2 could be ruled out (~ 3 Mo atoms per surface CdS unit).

The procedure introduced by Kanan and Nocera in 2008 for the electrodeposition of electrocatalytic materials [13] has been extended a few years later to transition metal sulfides for HER catalysis. An important example is the preparation of amorphous molybdenum sulfide films by electrodeposition processes that were described by the group of X. Hu [42,34,43]. While most research was focused on understanding the behavior of crystalline MoS_2 materials, which is convenient in terms of mechanistic hypotheses since its structure is known, a mechanism had to be found concerning the reactivity of this new class of amorphous materials. In a collaboration with this group, we used several X-ray spectroscopies to describe these materials' structure under dry, *in situ* and *operando* conditions, using Mo K-edge XANES and EXAFS, as well as sulfur K-edge and Mo L-edge spectroscopies [44]. Using these sets of data, we showed that the starting material is very

similar to MoS_3 and that it transforms, when placed in a $\text{pH} = 2$ aqueous buffer, into a sulfur-deficient form of MoS_3 , which can also be described as amorphous MoS_{2+x} [45]. When set under electro-catalytic conditions, three features stand out from our dataset (see Fig. 3A and 4B): a shift to higher energies of the S K-edge main peak, a shift to lower energies of the Mo $L_{2,3}$ -edge peaks and the disappearance of the Mo–Mo interaction in the Mo K-edge EXAFS signal. The energy shifts in the sulfur and molybdenum edge peaks can be explained by changes in their oxidation states, i.e. an oxidation for the sulfur and a reduction for the molybdenum. This information suggests the formation of disulfide units under hydrogen-evolving electrocatalytic conditions. In addition, the EXAFS data that indicate the breaking of the Mo–Mo interaction at $2.77 \text{ \AA}$ rule out the formation of bridging disulfide units, which are responsible for the aforementioned Mo–Mo interaction. It can therefore be concluded that, under electrocatalytic conditions, *terminal disulfide units* are formed in higher amount than in the resting state. It should be noted that *operando* spectroscopy on electrocatalytic systems is not time-resolved. It probes a mixture of states where the most abundant one is the longest-lived. On the basis of these considerations and of the collected data, we proposed a mechanism (see Fig. 3C) where terminal disulfide bridges are present in the most stable intermediate of the catalytic cycle and the rate-limiting step for the reaction is the protonation and reduction of these units. These results extend the findings of Jaramillo et al. on the implication of terminal disulfide units in crystalline MoS_2 [40] to amorphous molybdenum sulfide films.

In a similar line of research, Sun et al. published results on the electrodeposition of HER-active amorphous CoS_x films. We could show, using *ex situ* cobalt K-edge XANES and EXAFS that this material was indeed CoS , and remained as such even after a 3 h bulk electrolysis under catalytic conditions [46]. Later work by Kornienko et al. on this system using XAS at the cobalt K, L and M-edges showed that the as-synthesized material is partially oxidized CoS_2 , but ruled out an oxysulfide structure [47]. Further *operando* Raman and Co K-edge X-ray absorption spectroscopies performed in this study showed that, under operating conditions, the material is converted to CoS_2 -like molecular clusters. Although the amorphous and porous nature of the films suggest that activity is linked to the amount of available sulfur sites, the study did not conclude on the nature of the sulfur ligands involved in the catalysis. In this regard, the *ex situ* spectroscopic characterizations in our initial study of this system was not accurate enough to determine the precise stoichiometry of cobalt and sulfur. This points out to the fact that *operando* measurements are necessary to really assess a chemical structure, particularly for amorphous, low-order materials.

It appears from our studies and those of others that, for sulfide-based materials, sulfur ligands play an active role in the catalytic process. This concept has been confirmed by the efforts of other researchers to engineer materials where the amount of exposed sulfur ligands is particularly high [48,49]. Similar, phosphorus-based materials such as Ni_2P [35], CoP [50] or MoP [51,52] have also been shown to be HER-active. To which extent phosphide ligands are involved in the catalytic mechanism remains to be shown, and *operando* X-ray spectroscopy could certainly be helpful in this regard.

5. Multicolor XES to probe multi-element catalysts

Heterometallic catalysis based on the combined/concerted action of multiple metals has been explored extensively in the past few decades due to enhanced activity as compared to single metal-based systems [53,54]. Probing the changes in elements of interest separately under catalytic conditions can make the comparisons very tricky due to the systematic errors originating from concentration and volume distribution of the sample, data normalization and temporal errors. Based on X-ray emission spectroscopy (XES), we have developed an experimental method to detect changes in the electronic structure of multiple elements simultaneously under experimental conditions [55]. Unlike other X-ray spectroscopies, XES can simultaneously probe multiple metal sites since a single incident X-ray at energy (E_0) can excite both of them, when E_0 is higher than the binding energy of the core-level electrons excited in the initial state, as shown in Fig. 4A. We used a wavelength-dispersive spectrometer [56] based on a Von Hamos geometry and a position sensitive detector (PSD) which further eliminates the need to scan the emission spectrum (*i.e.* to scan crystals analyzer and detector positions), unlike commonly used spectrometers based on scanning geometries.

We investigated the effect of adding a second element, Ni, to a MnO_x -based bifunctional catalyst (MnNiO_x) active for ORR as well as OER. Wavelength-dispersive XES was employed using the $\text{K}\beta_{1,3}$ emission line, which is sensitive to the oxidation and spin states of the metal centers [57]. A schematic representation of the XES setup used is shown in Fig. 4B. The emitted radiation from the sample is diffracted and focused on to the PSD by crystal analyzers which are cylindrically bent $110 \times 25 \text{ mm}^2$ crystals with a curvature radius of 500 mm. Emission signal from Mn was collected using 12 Si(440) crystals whereas 4 Si(551) crystals were used to focus the Ni signal on to a second PSD. We measured the $\text{K}\beta_{1,3}$ and $\text{K}\beta'$ emission spectra of Mn and Ni of the MnNiO_x catalyst at different potentials between 0.4 V and 1.8 V *vs* RHE, while increasing the potential stepwise (0.2 V steps). A summary of the XES data is shown in Fig. 5, where part A shows the emission spectra of Mn and part B shows the Ni emission spectra. It is important to note that the sharp decrease in the intensity of Mn XES spectra around 6470 eV is an artifact originating from the binning edge effects of PSD. The emission spectrum collected at 0.4 V was subtracted from the spectra collected at higher potentials and the difference spectra are shown in the bottom part of the figure for Mn and Ni. To make the changes more obvious, integrated absolute difference (IAD) values were calculated from the difference spectra and are indicated against the corresponding traces. By comparing the sample spectra with some reference compounds, it was concluded that under ORR relevant potentials (0.6 V *vs* RHE), Mn existed as a combination of Mn^{3+} and Mn^{4+} : the high energy side of $\text{K}\beta_{1,3}$ peak of ORR phase was aligned with that of $\alpha\text{-Mn}_2\text{O}_3$ whereas the low energy side of it extended slightly further towards lower energies as compared to $\alpha\text{-Mn}_2\text{O}_3$, indicating the presence of a small fraction of Mn^{4+} . Upon increasing the potential, oxidation state of Mn gradually increased after 1.0 V, as indicated by a shift of the emission spectra towards lower energies accompanied with the decrease in the intensity of $\text{K}\beta'$ satellite around 6475 eV. A decrease in the intensity of $\text{K}\beta'$ occurs due to the lower probability of 3p/3d spin exchange interaction resulting from decrease in 3d electrons in Mn with higher oxidation states. Under

OER conditions (1.8 V vs RHE) the overall oxidation state of Mn was determined to be +4 as the XES spectrum was similar to that of β -Mn^{IV}O₂. Simultaneously, Ni existed as a mixture of Ni²⁺ and Ni³⁺ under ORR conditions as the XES spectrum was in between those of Ni^{II}(OH)₂ and β -Ni^{III}OOH, and got oxidized to an average oxidation state of +3.7 when the potential was increased to OER conditions, as suggested by the close similarity of the spectrum with that of γ -Ni^{III,IV}OOH. The evolution of oxidation states of Mn and Ni can be easily followed by plotting the IAD values against the corresponding potentials, as shown in Fig. 5C, where an increase in IAD value represents an increase in oxidation state. It appears that a gradual increase in oxidation state of Mn starts after 0.8 V whereas in the case of Ni it begins after 1.0 V. This sequential phase transition has been described by a schematic representation in Fig. 5D.

XES results were further corroborated by *in situ* XAS measurements on MnNiO_x catalyst under ORR and OER relevant potentials (data not shown). The edge position of the Mn spectrum corresponding to ORR phase was found to be close to that of birnessite which has an average oxidation state of +3.6. Under OER conditions, the Mn edge position was close to that of λ -Mn^{IV}O₂. Similarly, the edge position of Ni under ORR relevant potential is in between those of Ni^{II}(OH)₂ and β -Ni^{III}OOH confirming that oxidation state of Ni is between +2 and +3. Under OER conditions, the Ni spectrum was similar to that of γ -Ni^{III,IV}OOH indicating an average oxidation state close to +3.7. Structural information obtained from XAS (particularly EXAFS) revealed that Mn and Ni are not mixed at the atomic scale but exist as nanocrystalline domains of Mn-rich and Ni-rich regions. Pure MnO_x prepared under similar conditions was also investigated and it was observed that although Mn has a similar oxidation state under ORR conditions in both catalysts, the presence of Ni facilitates the access of Mn to a higher oxidation state under OER potentials. This finding suggests that nickel ions serve as a reservoir for oxidizing equivalents, while the chemical platform for bond formation would be the manganese ions. The methodology used for this study is general and can be applied to study the reaction kinetics of materials consisting of multiple elements to follow the dynamics of catalytic and electron transfer reactions [58].

6. Future directions

In situ/Operando X-ray spectroscopies have shown their potential in describing the local and electronic structure of OER and HER electrocatalysts under functioning conditions. More progresses can be expected from these techniques, in particular concerning the role of light elements. Another energy-related reaction that will benefit from such studies is the reduction of CO₂ (CO₂ reduction Reaction, CO₂RR). Only a handful of *operando* studies have been performed so far on CO₂RRs [59], but it is already clear that this reaction should be considered differently than the above-mentioned ones, since it produces a much wider range of molecules. Hence, several classes of catalysts are currently under study from nano-structured metals [60–62] to amorphous chalcogenides [63] and transition metal molecular complexes [64–66]. The reaction itself also differs from OER or HER because several different bonds have to be formed or broken, resulting in several intermediate states and products. Mechanistic information can therefore be obtained by probing the catalyst, but also the substrate and products. Given the nature of the bonds involved (C=O, C—O, C—C),

vibrational spectroscopies will clearly be useful, as already shown [67,68]. X-ray based spectroscopies capable of probing the ligands directly (metal K-pre-edge and ligand K-edge XAS, X-ray Raman) or their binding mode with the metal (XAS, $K\beta_{2,5}/K\beta''$ XES) will very likely play a crucial role. Such advanced techniques, which allow probing ligands or metal-ligand interactions, will likely become methods of choice to better understand the effects of light elements in catalysis. This might require further technological development to meet more demanding requirements, since the edges of light elements can only be observed in the tender (S, P, Cl) or soft (B, C, N, O) X-ray energy range and thus have to be adapted to vacuum environments. Examples of such experiments have been described [69] but remain challenging, particularly in the soft X-ray range. X-ray Raman (also known as Inelastic X-ray Scattering, IXS), however, can probe light elements using hard X-rays by a photon in – photon out energy-loss process [70]. This allows performing demanding *operando* experiments under ambient pressure, which is a major technical advantage. Such an experimental setup also allows for performing Resonant Inelastic X-ray scattering measurements, which provides a more complete picture on localized and delocalized electronic states of a material [20,71].

Finally, it is worth indicating that efficient OER catalysts based on binary, ternary, and quinary combinations of metal oxides have been reported from combinatorial approaches [31,71]. Understanding the chemistry of such materials with the aim to attribute a specific role to each element will require specific *in situ/operando* techniques. The example of multicolor X-ray emission spectroscopy we described above should certainly be useful for application to such complex materials.

7. Concluding remarks

We have described several electrochemical systems for OER, ORR and HER catalysis, which we have studied using *in situ* and *operando* X-ray spectroscopies. Experimental setups are now well controlled for the hard x-ray energy range, but still require improvements in the soft X-ray range to be more widely applied. With this technique, structural phases of amorphous materials as well as their overall oxidation state have been determined, as a function of the applied electrochemical potential. This information has been used in turn to propose mechanistic hypotheses and stress the strength and weaknesses of a catalyst. Although time-resolved *operando* X-ray spectroscopy has not been established yet for electrochemical reactions, kinetic information can nevertheless be extracted from steady state measurements, provided they are combined with other analytical methods. Advanced techniques such as HERFD-XANES, XES or RIXS (Resonant Inelastic X-ray Scattering) have been applied in a handful of cases, but they should become more wide-spread in the future if one is to distinguish the various species that coexist during an electrocatalytic experiment and attribute a specific function to each of them. Although *in situ/operando* X-ray spectroscopy is a very powerful tool, it cannot be applied to all OER or HER-active materials routinely because of the difficulties in obtaining X-ray beamtime in a timely manner. It is probably more important to focus on fundamental studies that provide experimental evidence to conclude about general mechanistic hypotheses, such as the influence of a given ligand, of a specific oxidation state or a binding mode on the catalytic efficiency of a class of materials.

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References

1. Lewis NS, Nocera DG. *Proc Natl Acad Sci USA*. 2006; 103:15729–15735. [PubMed: 17043226]
2. Armaroli N, Balzani V. *Angew Chemie Int Ed*. 2007; 46:52–66.
3. Zandi O, Hamann TW. *Nat Chem*. 2016; 8:778–783. [PubMed: 27442283]
4. Louie MW, Bell AT. *J Am Chem Soc*. 2013; 135:12329–12337. [PubMed: 23859025]
5. Grunwaldt JD, Kimmmerle B, Baiker A, Boye P, Schroer CG, Glatzel P, Borca CN, Beckmann F. *Catal Today*. 2009; 145:267–278.
6. Scott FJ, Roth C, Ramaker DE. *J Phys Chem C*. 2007; 111:11403–11413.
7. Grady WEO, Pandya KI, Swider KE, Corrigan DA. *J Electrochem Soc*. 1996; 143:1613–1616.
8. Velasco-Velez JJ, Wu CH, Pascal TA, Wan LF, Guo J, Prendergast D, Salmeron M. *Science*. 2014; 346:831–834. [PubMed: 25342657]
9. Gorlin Y, Lassalle-Kaiser B, Benck JD, Gul S, Webb SM, Yachandra VK, Yano J, Jaramillo TF. *J Am Chem Soc*. 2013; 135:8525–8534. [PubMed: 23758050]
10. Klingan K, Ringleb F, Zaharieva I, Heidkamp J, Chernev P, Gonzalez-Flores D, Risch M, Fischer A, Dau H. *Chem Sus Chem*. 2014; 7:1301–1310.
11. Najafpour MM, Ehrenberg T, Wiechen M, Kurz P. *Angew Chemie Int Ed*. 2010; 49:2233–2237.
12. Gorlin Y, Jaramillo TF. *J Am Chem Soc*. 2010; 132:13612–13614. [PubMed: 20839797]
13. Kanan MW, Nocera DG. *Science*. 2008; 321:1072–1075. [PubMed: 18669820]
14. Jiao F, Frei H. *Angew Chemie Int Ed*. 2009; 48:1841–1844.
15. Dinca M, Surendranath Y, Nocera DG. *Proc Natl Acad Sci USA*. 2010; 107:10337–10341. [PubMed: 20457931]
16. Trotochaud L, Young SL, Ranney JK, Boettcher SW. *J Am Chem Soc*. 2014; 136:6744–6753. [PubMed: 24779732]
17. Kanan MW, Yano J, Surendranath Y, Dinca M, Yachandra VK, Nocera DG. *J Am Chem Soc*. 2010; 132:13692–13701. [PubMed: 20839862]
18. Bediako DK, Lassalle-Kaiser B, Surendranath Y, Yano J, Yachandra VK, Nocera DG. *J Am Chem Soc*. 2012; 134:6801–6809. [PubMed: 22417283]
19. Risch M, Ringleb F, Kohlhoff M, Bogdanoff P, Chernev P, Zaharieva I, Dau H. *Energy Environ Sci*. 2015; 8:661–674.
20. Friebe D, Bajdich M, Yeo BS, Louie MW, Miller DJ, Casalongue HS, Mbuga F, Weng TC, Nordlund D, Sokaras D, Alonso-Mori R, Bell AT, Nilsson A. *Phys Chem Chem Phys*. 2013; 15:17460–17467. [PubMed: 24026021]
21. Delaplane RG, Ibers JA, Ferraro JR, Rush JJ. *J Chem Phys*. 1969; 50:1920.
22. Risch M, Klingan K, Ringleb F, Chernev P, Zaharieva I, Fischer A, Dau H. *ChemSusChem*. 2012; 5:542–549. [PubMed: 22323319]
23. Farrow CL, Bediako DK, Surendranath Y, Nocera DG, Billinge SJL. *J Am Chem Soc*. 2013; 135:6403–6406. [PubMed: 23547707]
24. Du P, Kokhan O, Chapman KW, Chupas PJ, Tiede DM. *J Am Chem Soc*. 2012; 134:11096–11099. [PubMed: 22720737]
25. Koroidov S, Anderlund MF, Styring S, Thapper A, Messinger J. *Energy Environ Sci*. 2015; 8:2492–2503.
26. Zhang M, de Respinis M, Frei H. *Nat Chem*. 2014; 6:362–367. [PubMed: 24651205]
27. Pham HH, Cheng MJ, Frei H, Wang LW. *ACS Catal*. 2016; 6:5610–5617.

28. Bergmann A, Martinez-Moreno E, Teschner D, Chernev P, Gliech M, de Araujo JF, Reier T, Dau H, Strasser P. *Nat Commun.* 2015; 6:8625. [PubMed: 26456525]
29. Goerlin M, Gliech M, de Araujo JF, Dresch S, Bergmann A, Strasser P. *Catal Today.* 2016; 262:65–73.
30. Yang J, Cooper JK, Toma FM, Walczak KA, Favaro M, Beeman JW, Hess LH, Wang C, Zhu C, Gul S, Yano J, Kisielowski C, Schwartzberg A, Sharp ID. *Nat Mater.* 2017; 16
31. Haber JA, Cai Y, Jung S, Xiang C, Mitrovic S, Jin J, Bell AT, Gregoire JM. *Energy Environ Sci.* 2014; 7:682–688.
32. Friebe D, Louie MW, Bajdich M, Sanwald KE, Cai Y, Wise AM, Cheng MJ, Sokaras D, Weng TC, Alonso-Mori R, Davis RC, Bargar JR, Norskov JK, Nilsson A, Bell AT. *J Am Chem Soc.* 2015; 137:1305–1313. [PubMed: 25562406]
33. Goerlin M, Chernev P, de Araujo JF, Reier T, Dresch S, Paul B, Kraehnert R, Dau H, Strasser P. *J Am Chem Soc.* 2016; 138:5603–5614. [PubMed: 27031737]
34. Merki D, Hu X. *Energy Environ Sci.* 2011; 4:3878–3888.
35. Popczun EJ, McKone JR, Read CG, Biacchi AJ, Wiltrout AM, Lewis NS, Schaak RE. *J Am Chem Soc.* 2013; 135:9267–9270. [PubMed: 23763295]
36. Meyer S, Nikiforov AV, Petrushina IM, Koehler K, Christensen E, Jensen JO, Bjerrum NJ. *Int J Hydrogen Energy.* 2015; 40:2905–2911.
37. Zeng M, Wang H, Zhao C, Wei J, Qi K, Wang W, Bai X. *Chem Cat Chem.* 2016; 8:708–712.
38. Masa J, Weide P, Peeters D, Sinev I, Xia W, Sun Z, Somsen C, Muhler M, Schuhmann W. *Adv Energy Mater.* 2016; 6
39. Eijssbouts S, Mayo SW, Fujita K. *Appl Catal A.* 2007; 322:58–66.
40. Jaramillo TF, Jorgensen KP, Bonde J, Nielsen JH, Horch S, Chorkendorff I. *Science.* 2007; 317:100–102. [PubMed: 17615351]
41. Tang ML, Grauer DC, Lassalle-Kaiser B, Yachandra VK, Amirav L, Long JR, Yano J, Alivisatos AP. *Angew Chemie Int Ed.* 2011; 50:10203–10207.
42. Merki D, Fierro S, Vrubel H, Hu X. *Chem Sci.* 2011; 2:1262–1267.
43. Vrubel H, Merki D, Hu X. *Energy Environ Sci.* 2012; 5:6136–6144.
44. Lassalle-Kaiser B, Merki D, Vrubel H, Gul S, Yachandra VK, Hu X, Yano J. *J Am Chem Soc.* 2015; 137:314–321. [PubMed: 25427231]
45. Vrubel H, Hu X. *ACS Catal.* 2013; 3:2002–2011.
46. Sun Y, Liu C, Grauer DC, Yano J, Long JR, Yang P, Chang CJ. *J Am Chem Soc.* 2013; 135:17699–17702. [PubMed: 24219808]
47. Kornienko N, Resasco J, Becknell N, Jian CM, Liu YS, Nie K, Sun X, Guo J, Leone SR, Yang P. *J Am Chem Soc.* 2015; 137:7448–7455. [PubMed: 26051104]
48. Kibsgaard J, Chen Z, Reinecke BN, Jaramillo TF. *Nat Mater.* 2012; 11:963–969. [PubMed: 23042413]
49. Kibsgaard J, Jaramillo TF, Besenbacher F. *Nat Chem.* 2014; 6:248–253. [PubMed: 24557141]
50. Popczun EJ, Read CG, Roske CW, Lewis NS, Schaak RE. *Angew Chemie Int Ed.* 2014; 53:5427–5430.
51. Chen X, Wang D, Wang Z, Zhou P, Wu Z, Jiang F. *Chem Commun.* 2014; 50:11683–11685.
52. Xiao P, Sk MA, Thia L, Ge X, Lim RJ, Wang JY, Lim KH, Wang X. *Energy Environ Sci.* 2014; 7:2624–2629.
53. Zhang B, Zheng X, Voznyy O, Comin R, Bajdich M, Garcia-Melchor M, Han L, Xu J, Liu M, Zheng L, de Arquer FPG, Dinh CT, Fan F, Yuan M, Yassitepe E, Chen N, Regier T, Liu P, Li Y, De Luna P, Janmohamed A, Xin HL, Yang H, Vojvodica A, Sargent EH. *Science.* 2016; 352:333–337. [PubMed: 27013427]
54. Seitz LC, Dickens CF, Nishio K, Hikita Y, Montoya J, Doyle A, Kirk C, Vojvodica A, Hwang HY, Norskov JK, Jaramillo TF. *Science.* 2016; 353:1011–1014. [PubMed: 27701108]
55. Gul S, Ng JWD, Alonso-Mori R, Kern J, Sokaras D, Anzenberg E, Lassalle-Kaiser B, Gorlin Y, Weng TC, Zwart PH, Zhang JZ, Bergmann U, Yachandra VK, Jaramillo TF, Yano J. *Phys Chem Chem Phys.* 2015; 17:8901–8912. [PubMed: 25747045]

56. Alonso-Mori R, Kern J, Sokaras D, Weng TC, Nordlund D, Tran R, Montanez P, Delor J, Yachandra VK, Yano J, Bergmann U. *Rev Sci Instrum.* 2012; 83
57. Glatzel P, Bergmann U. *Coord Chem Rev.* 2005; 249:65–95.
58. Alonso-Mori R, Sokaras D, Zhu D, Kroll T, Chollet M, Feng Y, Glowacki JM, Kern J, Lemke HT, Nordlund D, Robert A, Sikorski M, Song S, Weng TC, Bergmann U. *J Synchrotron Radiat.* 2015; 22:612–620. [PubMed: 25931076]
59. Eilert A, Roberts FS, Friebe D, Nilsson A. *J Phys Chem Lett.* 2016; 7:1466–1470. [PubMed: 27045045]
60. Li CW, Kanan MW. *J Am Chem Soc.* 2012; 134:7231–7234. [PubMed: 22506621]
61. Mistry H, Varela AS, Bonifacio CS, Zegkinoglou I, Sinev I, Choi YW, Kisslinger K, Stach EA, Yang JC, Strasser P, Cuenya BR. *Nat Commun.* 2016; 7
62. Loiudice A, Lobaccaro P, Kamali EA, Thao T, Huang BH, Ager JW, Buonsanti R. *Angew Chemie Int Ed.* 2016; 55:5789–5792.
63. Asadi M, Kumar B, Behranginia A, Rosen BA, Baskin A, Repnin N, Pisasale D, Phillips P, Zhu W, Haasch R, Klie RF, Kral P, Abiad J, Salehi-Khojin A. *Nat Commun.* 2014; 5
64. Grice, KA., Kubiak, CP. *CO2 Chemistry.* Aresta, M., Eldik, R., editors. Elsevier Academic Press; 2014. p. 163-188.
65. Bourrez M, Molton F, Chardon-Noblat S, Deronzier A. *Angew Chemie Int Ed.* 2011; 50:9903–9906.
66. Costentin C, Drouet S, Robert M, Saveant JM. *Science.* 2012; 338:90–94. [PubMed: 23042890]
67. Aldana PAU, Ocampo F, Kobl K, Louis B, Thibault-Starzyk F, Daturi M, Bazin P, Thomas S, Roger AC. *Catal Today.* 2013; 215:201–207.
68. Machan CW, Sampson MD, Chabolla SA, Dang T, Kubiak CP. *Organometallics.* 2014; 33:4550–4559.
69. Braun A, Sivula K, Bora DK, Zhu J, Zhang L, Graetzel M, Guo J, Constable EC. *J Phys Chem C.* 2012; 116:16870–16875.
70. Lelong G, Radtke G, Cormier L, Bricha H, Rueff JP, Ablett JM, Cabaret D, Gelebart F, Shukla A. *Inorg Chem.* 2014; 53:10903–10908. [PubMed: 25275633]
71. Al Samarai M, Delgado-Jaime MU, Ishii H, Hiraoka N, Tsuei K-D, Rueff J-P, Lassalle-Kaiser B, Weckhuysen BM, de Groot FMF. *J Phys Chem C.* 2016; 120:24063–24069. <http://dx.doi.org/10.1021/acs.jpcc.6b06444>.

Fig. 1. (left) Schematic representation of an *in situ/operando* X-ray spectroelectrochemical cell and (right) simplified energy diagram showing X-ray absorption and K β emission processes for MnO_x . CE, RE and WE stand for counter, reference and working electrodes, respectively. SR and DET stand for synchrotron radiation and detector, respectively.

Fig. 2.

A) XANES spectra at the Co K-edge recorded on the Co-Pi catalyst under resting (0.4 V) and catalytic (1.1 V) conditions. B) Consecutive cyclic voltammograms showing the deposition of NiO_x material on an ITO electrode. The colored zones indicate the electrochemical potential regions at which XAS spectra were recorded. C) XANES spectra at the Ni K-edge recorded on the NiBi catalyst under resting (0.5 V), pre-catalytic (0.8 V) and catalytic (1.05 V). D) Side view of the γ -NiOOH lamellar structure showing intercalating alkali ions and top view of the largest proposed particles of γ -NiOOH (ca. 40 atoms, 2 nm diameter) and CoOOH (ca. 7 atoms, <1 nm) domains. Figure adapted from reference [17,18].

Fig. 3.

A) Sulfur K-edge XAS spectra and B) Molybdenum L₃-edge XAS spectra of the MoS_x material under as prepared, pre-catalytic and catalytic conditions, together with MoS₂, MoS₃ and Mo₃S₄ reference compounds. C) Proposed mechanism for the electrocatalytic reduction of protons into hydrogen by MoS_{2+x}. The *Cat-H* species is putative. D) molecular representations of the MoS₂ structure, and of the chain-like and cluster structures of MoS₃. Figure adapted from reference [44].

Fig. 4.

A) A schematic representation of $K\beta$ energy diagram for two elements that are excited simultaneously with the same incident X-ray energy (E_0). B) Experimental setup for simultaneous collection of emission spectra from two elements using a von Hamos spectrometer. Blue and pink traces represent the pathways of emitted photons from two different elements, Mn and Ni. Figure adapted from reference [55].

Fig. 5.

A) Mn and B) Ni K β emission spectra (top) of MnNiO_x electrocatalyst collected at different potentials. A second order polynomial was used to smooth the Ni XES spectra. Difference spectra (bottom) of A) Mn and B) Ni XES obtained by subtracting the spectrum measured at 0.4 V vs RHE. C) Integrated absolute difference (IAD) values from the bottom panels of A and B plotted against the corresponding potentials. D) Schematic representation of sequential phase evolution of MnNiO_x upon increasing potential. Figure adapted from reference [55].