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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.

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 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).

$$2H_2O \rightarrow O_2 + 4e^- + 4H^+ \quad (1)$$

$$4H^+ + 4e^- \rightarrow 2H_2 \quad (2)$$

$$2H_2O \rightarrow O_2 + 2H_2 \quad (3)$$

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.

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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 Kα 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 $L_{2,3}$-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 $Co^{III}O(OH)$ 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

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