
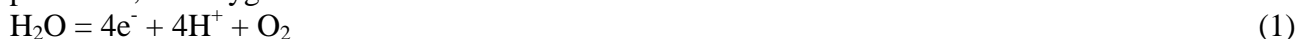


## Experiment Report Form

	<b>Experiment title:</b> In-situ X-Ray absorption spectroscopy measurements of IrO <sub>2</sub> -based materials under oxygen evolution/reduction conditions	<b>Experiment number:</b> CH-3511
<b>Beamline:</b>	<b>Date of experiment:</b> from: 14/11/2012 to: 20/11/2012	<b>Date of report:</b>
<b>Shifts:</b> 6	<b>Local contact(s):</b> Francesco d'Acapito	<i>Received at ESRF:</i>
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### Report:

This experiment goal was to perform in-situ XAS measurements on iridium oxide (IrO<sub>x</sub>) layers as electrocatalysts for electrochemical processes that are fundamental in the field of energy conversion. In particular, the oxygen evolution reaction was considered:

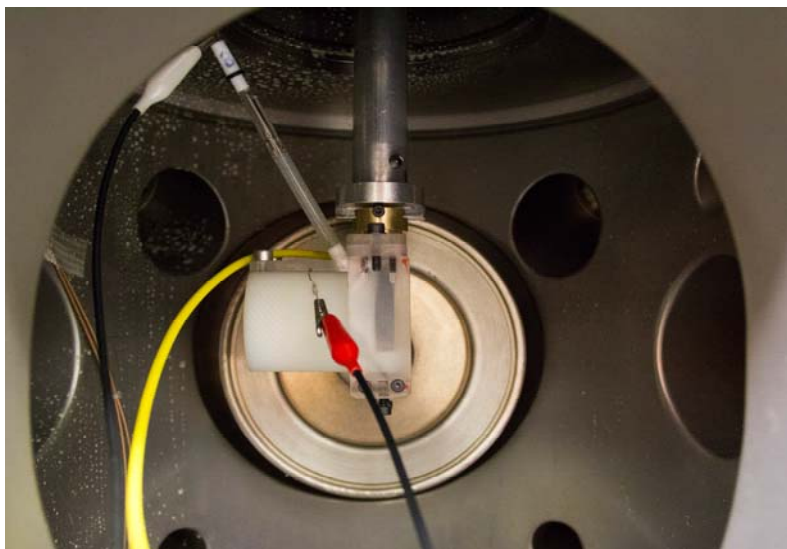


Iridium oxide is well known for its high performances as electrocatalytic material for the OER in acidic environment and its properties are likely extendable as a promoting agent in photoelectrochemical water splitting devices. However, most of the details on the reaction mechanisms and on the origin of IrO<sub>2</sub> activity are still lacking. In particular, changes in the oxidation state and structural modifications of iridium oxide during the oxygen evolution process are still not completely understood.

The experiment CH-3511 allowed us to:

- 1-design and test a spectroelectrochemical cell that allows electrochemical *in-situ* XAS measurements
  - 2-Understand the possibilities and the limits offered by electrochemical *in-situ* XAS
  - 3-Development of a new method for rapid evaluation of oxidation state in dependence on the potential applied to the electrode
  - 4-perform XANES, EXAFS and qEXAFS *in-situ* to shine light on the reaction mechanism
- All experiments are carried out at the Ir-L3 edge (fluorescence mode).

Fig 1 shows an image of the cell used during the experiment inside the BM-08 hutch.

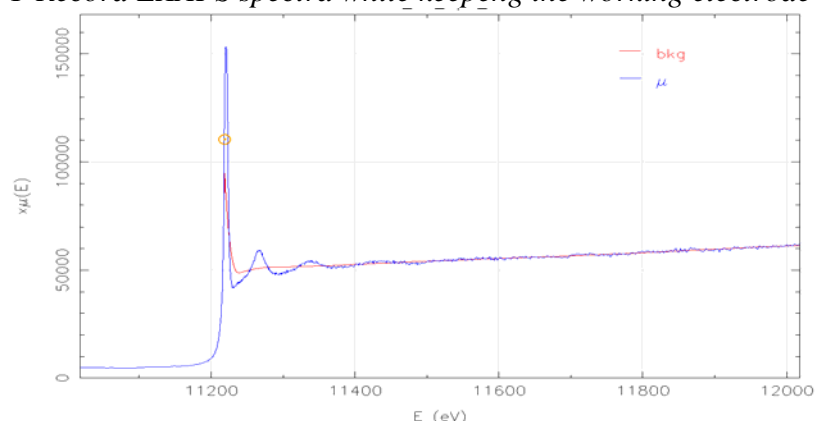


**Figure 1** Picture of the spectroelectrochemical cell in the XAS hutch

The spectro-electrochemical cell shown in Fig.1 allows to use a three-electrodes configuration and contains the electrolyte solution. A hole in the frontal part allows the X-Rays to hit the sample and the fluorescence radiation to reach the detector.

The working electrode is made of a dispensable screen printed electrode made of carbon on which IrO<sub>x</sub> is deposited. The experiments were conducted controlling the electrochemical instrumentation (CH Instrument 633D potentiostat/galvanostat) from the control room. Three main different types of experiments were carried out:

*1- Record EXAFS spectra while keepeng the working electrode at a fixed potential value.*



**Figure 2** An example of EXAFS spectrum.

The data are still under elaboration but it is already clear that the potential strongly influences both the position of the white line and the EXAFS signal.

*2- Record qEXAFS spectra while the potential is varied following a stair-step potential profile.*

In this case the energy corresponding to the white line peak was mainly considered. qEXAFS allows to quickly record spectra relatively to a high number of potential values. Preliminar results are in agreement to those obtained by EXAFS.

*3- Record the fluorescence signal at a fixed X-Ray energy as a function of the applied potential*

This represents a novel method to rapidly screen the X-Ray absorption features of the electrode material in a desired potential window. The energy is selected according to the white line peak as recorded for an IrO<sub>2</sub> reference sample. Any deviation from the maximum of the fluorescence (located at about 1.0 V) indicates the averaged transition of Ir sites oxidation state from (IV) to other values: e.g. (III) or (>IV).