EUROPEAN SYNCHROTRON RADIATION FACILITY

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ESRF

Experiment Report Form

	Experiment title: Understanding Charge Transfer and Redox Cascade Phenomena in Photoelectrode Architectures by in-operando XAS	**Experiment number**: CH-4654
Beamline:	**Date of experiment**: from: 09/06/2016 to: 14/06/2016	**Date of report**: 28/09/2017
Shifts: 18	**Local contact(s)**: Giovanni Lepore	*Received at ESRF:*

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Report:

The request of beamtime for the present experiment came after the encouraging results obtained in previous experiments on Fe_2O_3/IrO_x photoanodes (CH-4209), when we underwent a deep spetro-photoelectrochemical investigation of photoelectrodes made of one or more components (architectures). The aim was to further study under operative conditions the semiconductor alone and its interactions (charge transfers) with overlayers, that are added to improve the performances by optimizing its density of states distribution, limiting charge recombination and improving the interface reaction kinetics. In the present experimental setup, the photoelectrode was mounted in a cell properly designed to be highly transparent to both UV-Vis and X-ray photons. The cell allows the lodging of a Pt counter electrode and a glass tube that hosts a Ag/AgCl reference electrode. The electrolyte solution was aqueous 0.1 M K_2HPO_4 (pH 9.1) or 0.5 M NaH_2PO_4 + 0.5 M NaOH (pH=11.1).

The visible light source was a 400 nm LED that can be controlled through the beamline software for precise timing and synchronization with the X-ray absorption acquisition system.

Unfortunately, the initial scope of the experiment failed for a too difficult maintainence of visible and X-ray beams convergence. Therefore, we decided to partially drift the subject of the experiment.

In more details, we considered studying IrO_2-SnO_2 composites, a system of great interest in electrochemistry and photoelectrochemistry for the high activity and stability as catalyst for the oxygen evolution reaction (OER) conditions. In fact, IrO_2 is worldwide recognized as the most active material catalyst for this reaction but its high cost and poor abundance requires its dilution into a stable, low-cost matrix. One of the most studied and industrially adopted materials, SnO_2, is an n-type semiconductor stable in acidic/neutral media and appears to synergically add activity and stability to IrO_2.[1,2] In this work, we used a SnO_2-IrO_2 powder (containing 15%mol IrO_2) prepared by a sol-gel technique followed by impregnation and heat treatment at

450°C [2]. The powder was deposited onto a dispensable carbon electrode and studied in 0.5 M H_2SO_4 in a spectroelectrochemical cell described in reference [1].

The first experiment consisted in recording the FEXRAV[3] signal as recorded by fixing the energy of the impinging beam at 11222.1 eV, that corresponds to the maximum absorption at the Ir-L_{III} edge of IrO_2. It is apparent that μ increases up to applied potentials equal to ca. 1 V, then remains approximately constant and starts to decrease when the potential decreases below 1 V.

As a consequence, full XAS spectra have been recorded by applying selected potential values as follows: 0.3, 1, 1.3, 1.4 and 1.5 V vs the reversible Hydrogen Electrode (RHE). The spectra are shown in Fig. 1, together with the spectra of $IrCl_3$ and IrO_2 that are used as standards for Ir(III) and Ir(IV), respectively. The corresponding derivatives spectra are also shown for better reference.

When the applied potential is equal to 1 V, the Ir-L_{III} XANES of the material is virtually identical to that of IrO_2, in agreement with our previous investigations [4]. However, at 0.3 V, only a fraction of Ir is converted to Ir(III). The amount of Ir(III) can be estimated by fitting the XANES at this potential with a linear combination of the spectra of $IrCl_3$ and IrO_2, as shown in Fig. 2A, and is equal to ca. 5(1) % (atomic ratio). This is in striking contrast with what we previously reported [4]. When the applied potential is increased above 1 V, Ir retains the Ir(IV) oxidation state up to 1.4 V. At this potential, some Ir in a high oxidation state is formed. This is better evidenced in Fig. 2B, where the difference between the spectrum at this potential and that of IrO_2 is shown as a red line. The difference clearly demonstrates the presence of a high energy tail of the WL with respect to IrO_2. The energy position (ca. 11225 eV) of the maximum in the difference may be consistent with the presence of Ir(VI).
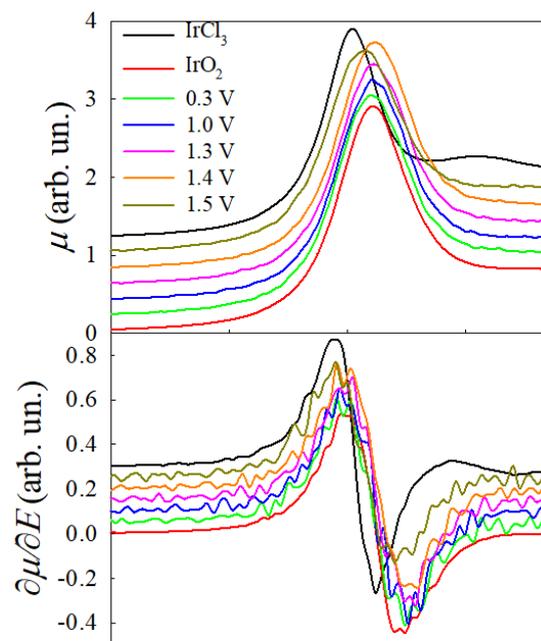
Figure 1. XANES spectra (and relevant derivatives) of the SnO_2-IrO_2 powder at various potentials in 0.5 M H_2SO_4

However, it should be noted that the amount of Ir in this high oxidation state is quite small, amounting to few percent.

A further increase of the applied potential to 1.5 V has a dramatic effect on the Ir-L_{III} XANES (Fig. 2C). Indeed, not only the small high energy tail disappears, but the whole spectrum is shifted towards *low* energy, indicating the presence of Ir in a low oxidation state. This is further confirmed by the fit reported in Fig. 3C, obtained with a linear combination of the spectra of $IrCl_3$ and IrO_2: the amount of Ir(III) obtained by the fit is 47(1) % (atomic fraction).
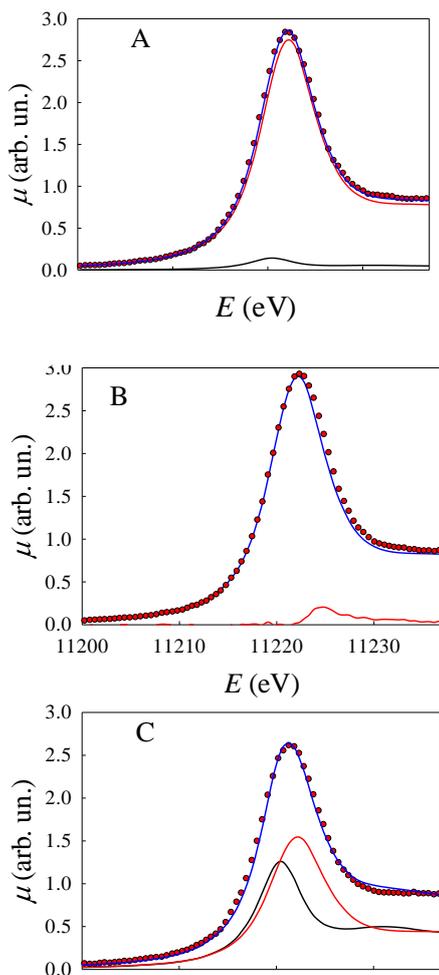
Figure 2. *fit of single XANES spectra by means of linear combinations of standar spectra as described in the text*

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[2] Minguzzi A., Locatelli C.,Cappelletti, G., Bianchi C.L., Vertova A., Ardizzone S., Rondinini S. *J. Mater. Chem.*, 2012, 22, 8896
[3] Minguzzi A., Lugaresi O., Locatelli C., Rondinini S., d'Acapito F., Achilli E., Ghigna P. *Anal. Chem.* 2013, 85, 7009
[4] Minguzzi A., Lugaresi O., Achilli E., Locatelli C., Vertova A., Ghigna P., Rondinini S., *Chem. Sci.*, 2014, 5, 3591