EUROPEAN SYNCHROTRON RADIATION FACILITY

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ESRF

Experiment Report Form

ESRF	**Experiment title:** Understanding Charge Transfer and Redox Cascade Phenomena in Photoelectrode Architectures by in-operando XAS: a BAG proposal. ROUND 3	**Experiment number**: 08-01-1004
Beamline:	**Date of experiment**: from: 29/09/2016 to: 05/10/2016	**Date of report**: 20/03/2017
Shifts: 18	**Local contact(s):** Francesco d'Acapito	*Received at ESRF:*

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Report:

The third round of the BAG proposal is focused on the study of overlayers of Cu_2O, the latter being one of the most promising photocathodes for photoelectrochemical water splitting for its high activity, ease of preparation, absorption in the visible spectra and low cost if compared to many other proposed materials (GaAsP, InP etc). The main drawback of this material is its poor stability. For this reason, it has to be covered with a stable and likely catalytic material that isolates it from the electrolyte still guaranteeing electron transfer. In particular, here we studied α- and γ- FeO(OH) (*gohetite* and *lepidocrocite*, respectively), i.e. the phases present on steel surface during industrial hydrogen evolution reaction (HER)[1].

The (photo-) electrochemical cell coincides with the one adopted in the round-1 and 2 experiments and all experiments are carried out in Na_2SO_4 0.2M+ NaOH 0.1M (pH 11). A Pt wire and a AgCl/Ag (in 1M KCl) were used as the counter and reference electrode. 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.

All experiments were carried out in the fluorescent mode using a 13-elements detector.

The materials under investigation were:

A) α- and γ- FeO(OH) layers electrodeposited on fluorine doped tin oxide (FTO) adopting the conditions reported in reference 2.

B) composite α- and γ- FeO(OH)/Cu_2O photocathodes

The aims of the present experiments were:
1) Study α- and γ- FeO(OH) at the Fe-K edge and their phase transitions in a wide range of potential, including the condition of water reduction to H_2 (HER).
2) Study the composite materials at both the Cu-K and the Fe-K edges.

In part 1, we carried out fixed energy X-ray absorption voltammetry (FEXRAV[3]) to evidence the potentials at which phase transitions occurred for both deposits.
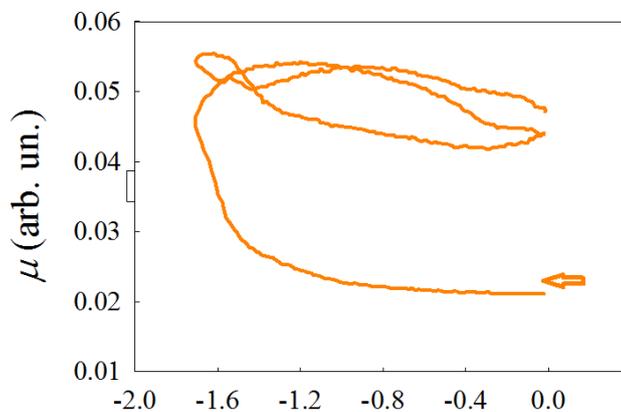

Figure 1. FEXRAV of α-FeO(OH) at 7125 eV
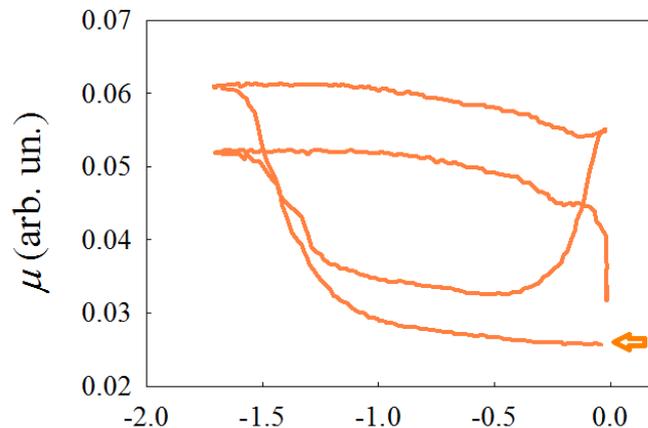
Figure 2. FEXRAV of γ-FeO(OH) at 7125 eV

At 7125 eV, the increase in intensity accounts for a reduction from Fe(III) to Fe(II). From FEXRAV, the different behaviour of the two deposits is evident: when a decreasing potential is applied to α-FeO(OH) there is a reduction to Fe(II), but after the re-oxidation the starting phase is not fully restored (Figure 1). On the other hand, in the case of γ-FeO(OH) (Figure 2) the starting phase is almost completely obtained after the re-oxidation, so the electrode shows a good reversibility.

The characteristic phases that were identified by FEXRAV can be finely studied by means of XANES spectra recorded at constant potential. The results obtained for α-FeO(OH) are shown in Fig. 3, while the spectra obtained for γ-FeO(OH) are shown in figure 4:
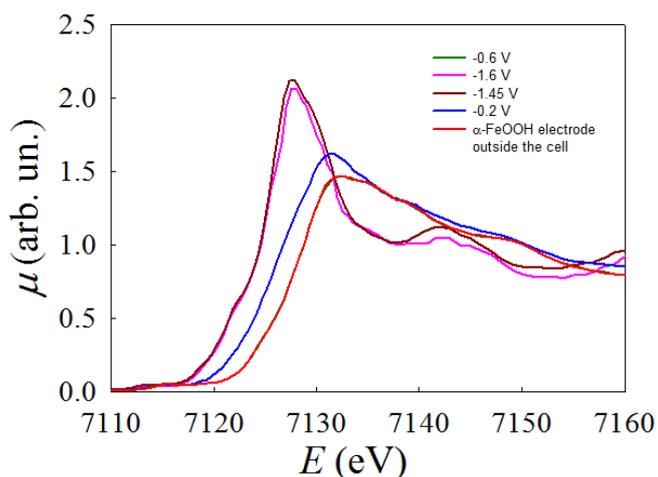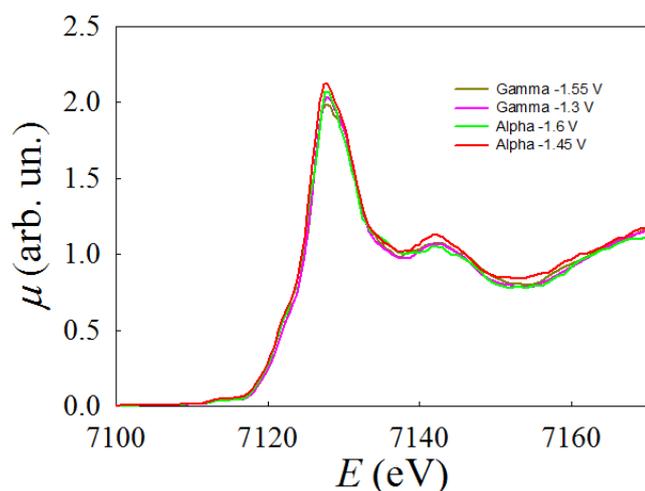

**Figure 3.** XANES spectra of α-FeO(OH) at various applied potentials
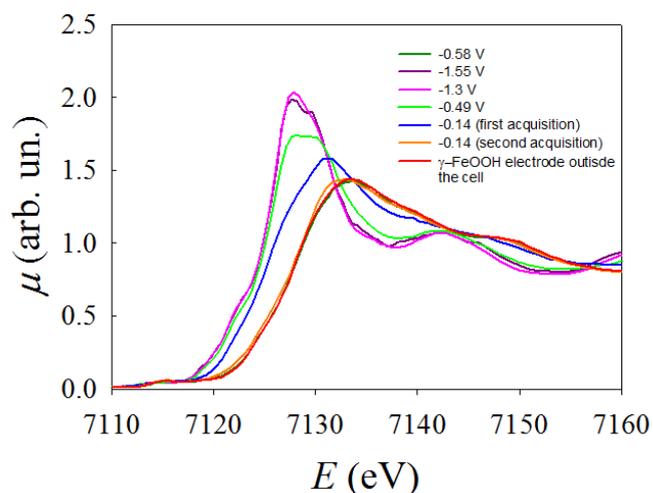
Figure 4. XANES spectra of γ- FeO(OH) at various applied potentials

When a potential of -0.6 V is applied to α- and γ-FeO(OH), in both cases the obtained spectrum is indistinguishable from the spectrum of the starting electrode.

When the applied potential is sufficiently low, the electrode material is completely reduced. As shown in figure 5, the spectra corresponding to -1.3 V and -1.55 V (for γ-FeO(OH)) and to -1.6 V and -1.45 V (for α-FeO(OH)) exhibit the same features, so it can be stated that, independently from the phase of the starting electrode, the structure which is reached after the reduction is the same. The pre-edge peaks corresponding to the spectra of the reduced phases have been extracted, in order to get information about the oxidation state, the coordination and the spin state of iron.


Figure 5. XANES spectra of α-FeO(OH) and γ-FeO(OH) at various reducing potentials.
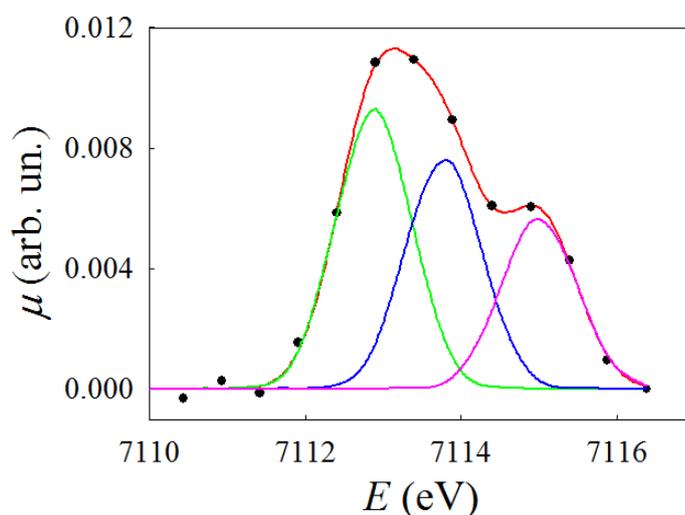
Figure 6. Extraction and fitting of the pre-edge for the spectrum of γ-FeO(OH) at -1.3 V.

The pre-edge peaks were extracted for each spectrum by subtracting the experimental data to a background, which was interpolated by a quadratic polynomial. The resulting signal (shown in Figure 6) is similar for all the spectra, and the position of the centroids confirms that oxidation state of iron is 2+. In addition, the signal has a low intensity, thus indicating that the crystal structure must possess an inversion centre; the most likely coordination for Fe(II) is therefore the octahedral one. The profile of the signal is consistent with an octahedral coordination where the Fe(II) is in a high spin state; the curve can be fitted with three Gaussian functions, which correspond to the three transitions expected for high-spin Fe(II). This result is also consistent with the high intensity of the White Line, which is expected to sensibly increase in case of high spin iron (II) with respect to the low spin state. The exact phase which is formed after the electrochemical reduction is unknown, but both the pre-edge analysis and the fit of the XANES and the EXAFS regions seem to indicate a brucite-like structure, like that of $Fe(OH)_2$ or green rust.
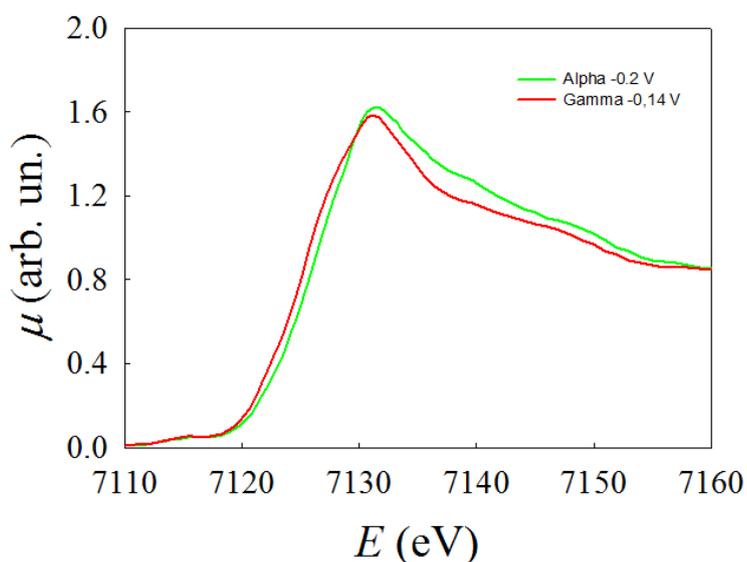

Figure 7. XANES spectrum of γ-FeOOH at -0.1.4 V (red line) and of α-FeOOH at -0.2 V (red line)

This phase is metastable, and it shows a "memory effect": the electrode, even when reduced, is able to preserve a memory of the initial crystal structure; in fact, during the re-oxidation, this brucite-like phase shows different behaviour depending on the starting phase. We know from the XANES spectra that both the electrodes form the same structure when reduced; nevertheless, after the electrochemically-driven re-oxidation, the product that is formed is different, and this can be clearly seen by the FEXRAV in figure 1 and 2, which have completely different profiles.

This is also shown in the XANES spectra acquired in the re-oxidation process; an α-FeO(OH) electrode was reduced to -1.6 V and then oxidized to -0.2 V, and the resulting spectrum is shown in figure 7 (green line). The same was done on a γ-FeO(OH), which was reduced to -1.3 V and then re-oxidized to -0.14 V; the resulting spectrum is shown in figure 7 (red line). The two spectra show different features, and this confirms the presence of two different structures in the phase of re-oxidation; this is in agreement with the FEXRAV analysis.

The cycle of reduction and re-oxidation was deeply investigated for γ-FeO(OH); the XANES spectra and the corresponding pre-edge peaks are shown in figure 8.
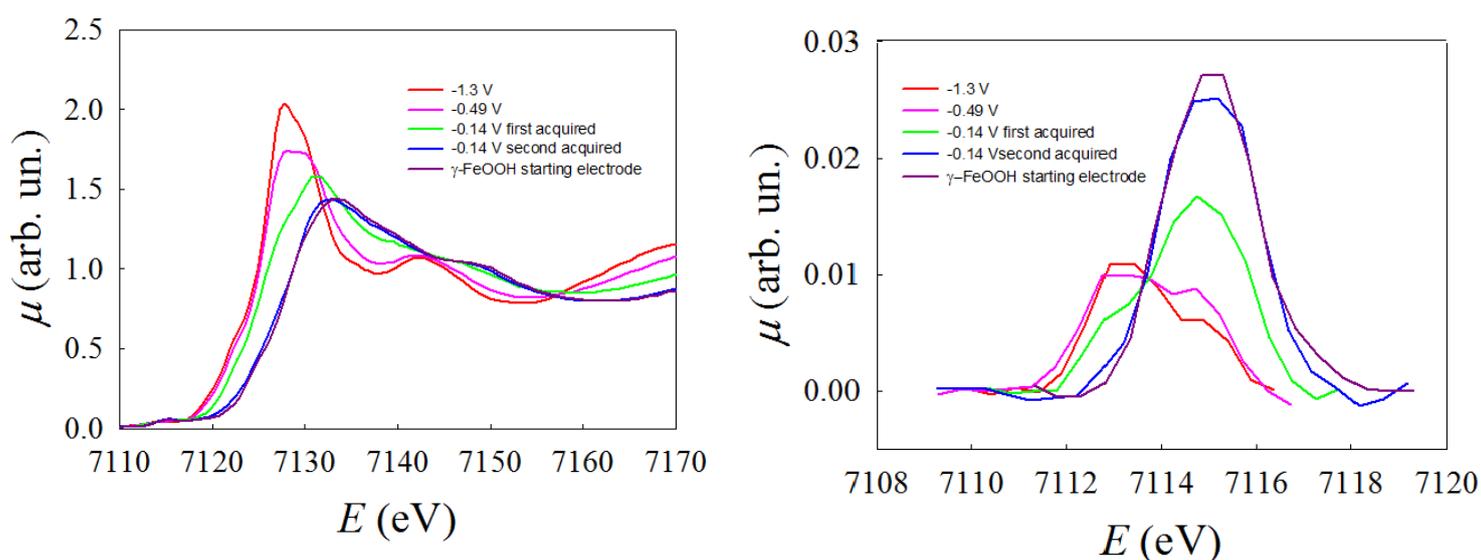

Figure 8. XANES spectra of γ-FeOOH at various applied potentials (left) and corresponding extracted pre-edge (right)

The electrode was reduced to -1.3 V, and then oxidized to -0.49 V; at this potential the oxidation state of iron is still 2+, but the difference in the XANES spectra demonstrates a change in the structure. Afterwards, the same electrode was oxidized to -0.14 V; the first acquired spectrum shows a partial oxidation from Fe(II) to Fe(III). Another spectrum was acquired subsequently in time: the resulting spectrum is very different from the previous one, thus indicating that the oxidation process is very slow. In this case, the electrode is almost completely oxidized to Fe(III), and the γ-phase is restored.

In part 2, composite semiconductor/overlayer are studied in order to evidence phase transitions of both components as well as to confirm the protective role of FeO(OH). This is well demonstrated by figure 9, that shows the results of a FEXRAV experiment carried out at 8979 eV (Cu-K edge), i.e. at the maximum $\Delta\mu$ of standard Cu_2O and Cu spectra.

In the forward scan (toward less positive potentials), the covered semiconductor undergoes reduction (positive drift of μ) at lower potentials than for pure CuO, thus demonstrating the effective protection role of FeO(OH).
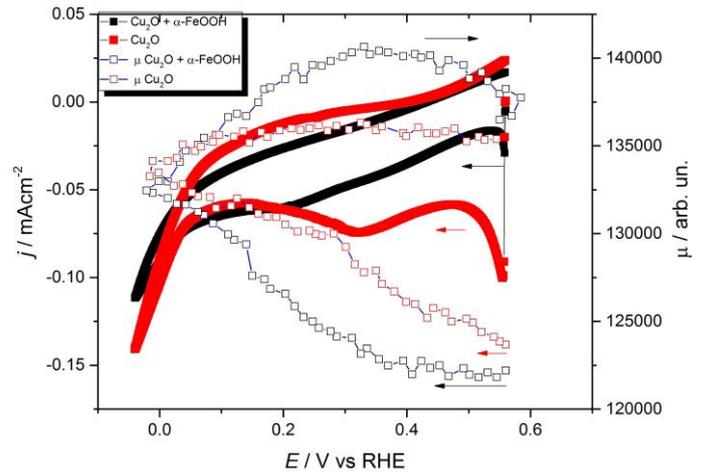
Figure 9. *FEXRAV* spectra of α-FeO(OH)/Cu_2O and Cu_2O photocathodes under illumination at 400 nm

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2. L. Martinez, D. Leinen, F. Martín, M. Gabas, J. R. Ramos-Barrado, E. Quagliata, E. A. Dalchiele, Journal of The Electrochemical Society, 2007, 154, D126-D133
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