EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

Experiment Report Form

	Experiment title: Understanding Charge Transfer and Redox Cascade Phenomena in Photoelectrode Architectures by in-operando XAS: a BAG proposal. ROUND 2	**Experiment number**: 08-01-1004
Beamline:	**Date of experiment**: from: 14/06/2016 to: 21/06/2016	**Date of report**: 17/10/2016 *Received at ESRF:*
Shifts: 18	**Local contact(s)**: Francesco d'Acapito	

Names and affiliations of applicants (* indicates experimentalists):

Alessandro Minguzzi*
Tomasz Baran
Cristina Locatelli
Alberto Visibile
Alberto Vertova
Alberto Naldoni
Sara Morandi
Sandra Rondinini
Itai Panas
Elisabetta Achilli*
Martina Fracchia*
Paolo Ghigna
Elisabet Ahlberg
Francesco Malara*

Report:

As proposed in the BAG project and after the encouraging results obtained in previous experiments on α-Fe_2O_3/IrO_x photoanodes (CH-4209) and in the first round of the present BAG proposal, we continue the spetro-photoelectrochemical investigation of photoelectrodes made of one or more components (architectures).

In this second round, we focussed our attention onto $Ni(OH)_2/NiO(OH)$ electrocatalysts for oxygen evolution reaction in alkaline media and on its use as overlayer for an hematite (α-Fe_2O_3) n-type semiconductor.

The (photo-) electrochemical cell coincides with the one adopted in the round-1 experiment and all experiments are carried out in 0.1 M aqueous NaOH. 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:

1) Hematite semiconductor, prepared as reported in reference 1. The support is a 10mm X 20 mm X 1 mm glass covered by a fluorine doped tin oxide film (FTO, purchased by Solaronix)
2) $Ni(OH)_2$ layers electrodeposited onto FTO by applying 16 mA/cm^2 for 10 s.
3) A composite photoanode made by electrodeposition of the $Ni(OH)_2$ layer onto the hematite/FTO photoelectrode.

The aims of the present experiments were:

1) Study the hematite photoanode, i.e. detecting any oxidation state or local structure variation occurring in the hematite film in dependence on the applied potential and/or after illumination with 400 nm light.

2) Study the electrochemical behavior of the $Ni(OH)_2$ electrode, a system previously studied by operando electrochemial XAS[2-4] but only in the framework of supercapacitors, thus not considering potentials at which water is oxidized to O_2. The results and the conclusions will serve for the interpretation of the results obtained in 3).
3) Study the complete system, thus detecting any sharge state or local structure modification of Ni when hematite is excited by 400 nm light.

Part 1 didn't lead to any observation of Fe charge state or local structure modification under illumination or under different applied potentials on hematite/FTO photoelectrodes. This is likely due to the fact that Fe surface/bulk atoms ratio is quite low (crystallytes are about 50 nm in size[1]) and photogenerated holes likely localize at the surface. On the other hand, part 2 and 3 were successful.

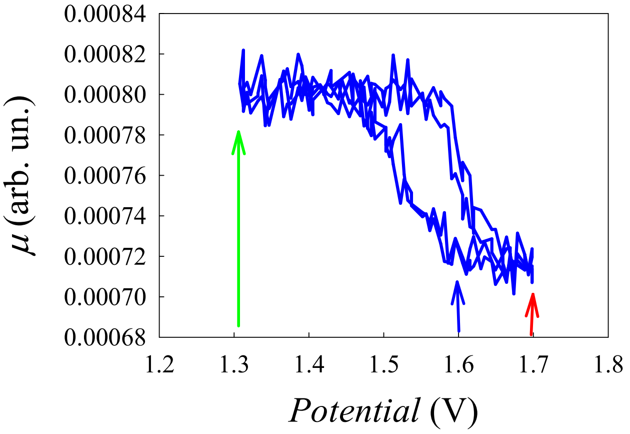

Figure 1. *FEXRAV of NiOOH/FTO at 8350.49 eV*

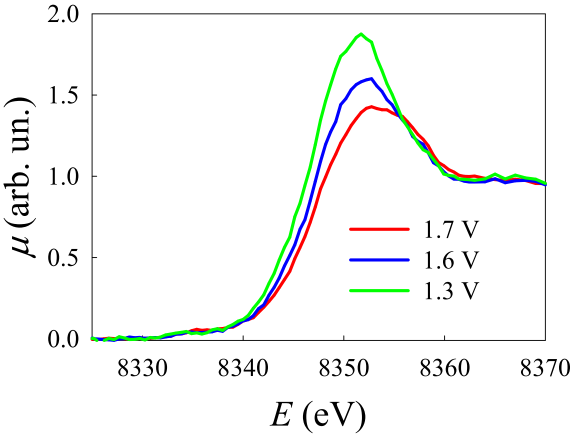

Figure 2. *XANES of NiOOH/FTO at three selected potential values*

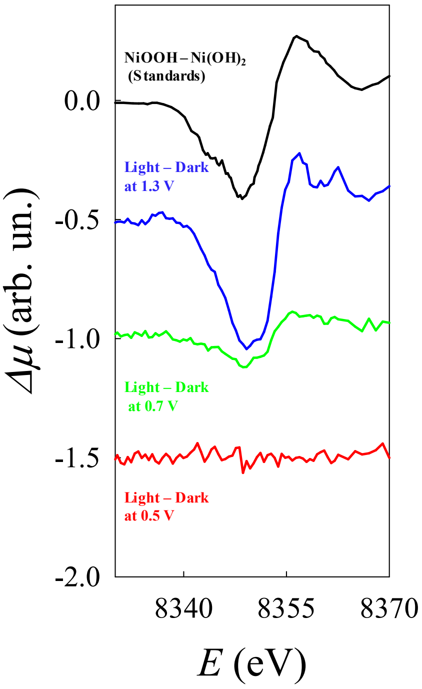

Figure 3. *differential XANES spectra of NiOOH/* α-Fe_2O_3/FTO

Experiments on $Ni(OH)_2$/FTO clearly highlighted a strong dependence on the Ni-K edge energy on the applied potential. Preliminary experiments were carried out using fixed energy X-ray absorption voltammetry[5] at an energy correspondent to the maximum of the $Ni(OH)_2$ spectrum, Figure 1, which highlighted a significant modification between 1.5 and 1.7 V vs. the reversible hydrogen electrode (RHE).

Moreover, the electrochemically induced transition of $Ni(OH)_2$ to NiO(OH) is clearly apparent as reported in Fig.2. Interestingly, the spectra at 1.6 V is significantly different from that at 1.7V, the latter condition corresponding to the observation of high currents due to water oxydation.

In part 3, spectra of $Ni(OH)_2$/ α-Fe_2O_3/FTO composites were recorded under different applied potentials (namely, 0.5, 0.7 and 1.3 V vs RHE, i.e. the potentials indicated in Fig.1 by arrows) in the dark and under 400 nm light.

The results, reported in Fig. 3, clearly show that at 0.5 V the illumination of hematite has no influence on the Ni oxidation state, while at increasing potential a progressive oxydation of $Ni(OH)_2$ into NiO(OH) is clearly detected.

1. F. Malara, A. Minguzzi, et al. ACS Catal. 2015, 5, 5292-5300
2. K. I. Pandya, R. W. Hoffman, et al. J. Electrochem. Soc., 1990, 137, 383
3. J. McBreen, W.E. O'Grady, et al. Langmuir. 1987, 3, 428–433
4. Y. Hu, I.T. Bae, et al. Can. J. Chem. 1997, 75, 1721–1729.
5. A. Minguzzi, O. Lugaresi, et al. Anal. Chem. 2013, 85, 7009-7013