ESRF	**Experiment title:** Photoelectrochemical activity of novel Cu-macrocyclic water oxidation catalyst: operando XAFS.	**Experiment number**: CH-6248
Beamline: BM-08 LISA	**Date of experiment**: from: 14/06/2022 to: 20/06/2022	**Date of report**: 23/02/2023
Shifts: 18	**Local contact(s)**: Francesco d'Acapito	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

- Dr. Raffaello Mazzaro*, University of Bologna Department of Physics and Astronomy viale C. Berti Pichat 6/2 IT - 40127 BOLOGNA
- Prof. Federico Boscherini, University of Bologna Department of Physics and Astronomy viale C. Berti Pichat 6/2 IT - 40127 BOLOGNA
- Prof. Luca Pasquini, University of Bologna Department of Physics and Astronomy viale C. Berti Pichat 6/2 IT - 40127 BOLOGNA
- Dr. Alberto Piccioni*, University of Bologna Department of Physics and Astronomy viale C. Berti Pichat 6/2 IT - 40127 BOLOGNA
- Dr. Pierpaolo Vecchi*, University of Bologna Department of Physics and Astronomy viale C. Berti Pichat 6/2 IT - 40127 BOLOGNA

The experiment CH-6248 was performed at beamline LISA BM-08 from June 14th to 20st 2022. The main goal of the experiment was to study the structure and the stability of metal-based catalysts, like Fe-based macrocycle molecules and CoFe based thin films deposited on $WO_3/BiVO_4$ photoanodes. We performed also operando measurements with a custom 3D-printed PEC cell, which allows X-ray fluorescence detection under bias and light stimulation.

Concerning Fe-based macrocycle molecules, we measured Fe K-edge XAFS of the sample before and after the electrochemical process, to check the structural changes around the Fe atom. We measured spectra of samples deposited on carbon paper after 15 minutes of working time in an electrochemical cell and we compared it to the fresh sample. The results for the *$[Fe(L3)]^{2-}$* catalyst are reported in Figure 1. It is apparent that the spectra are quite similar, suggesting that the macrocycle does not undergo major structural changes during the electrochemical process.

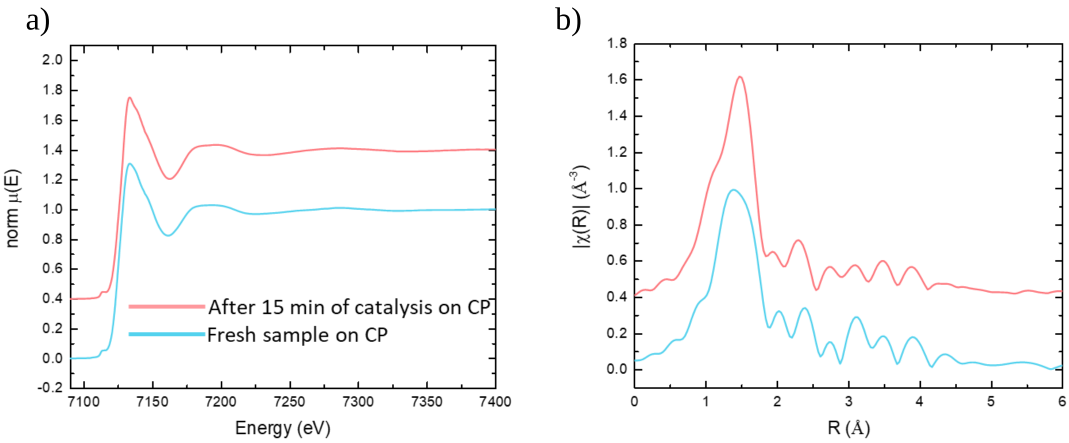

Figure 1: a) normalized Fe K-edge EXAFS of fresh and used sample; b) experimental Fourier transforms of k^2-weighted EXAFS.

Regarding operando measurements on CoFe catalyst thin film deposited on $WO_3/BiVO_4$ photoanodes, we developed an experimental setup to be fully integrated with the LISA beamline. The scheme is reported in Figure 2. This setup allows to control several experimental conditions for operando XAFS directly from the control room of the beamline. Thanks to the potentiostat we control the PEC cell, i.e. the voltage applied to photoanodes, but also the illumination of the sample provided by a white LED source and the flux of the electrolyte in the cell for enhancing mass transport and removing gaseous product from the electrode's surface.

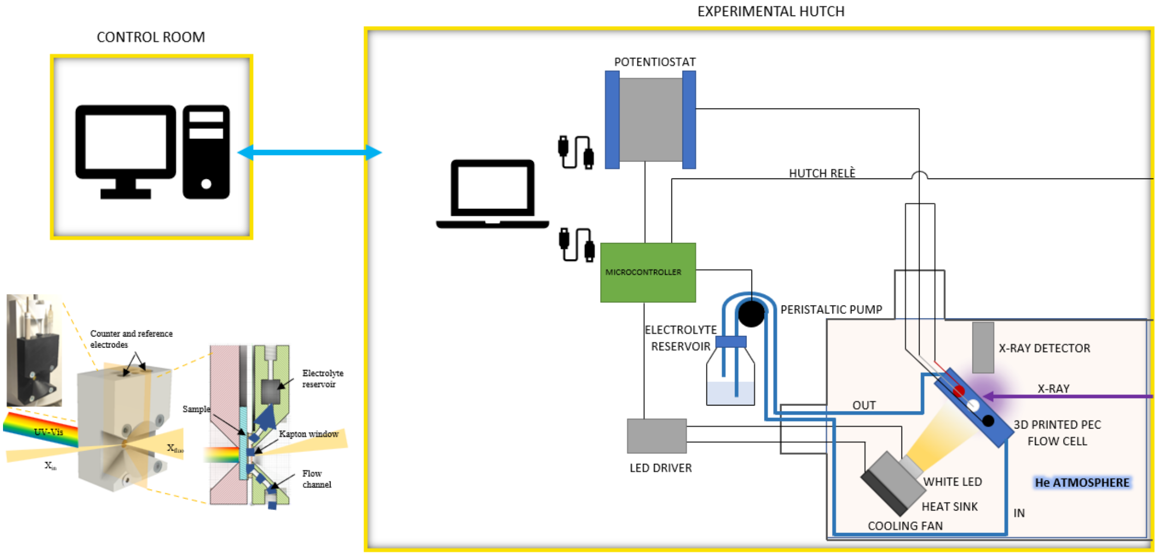

Figure 2: Experimetal setup integrated with LISA Bemline used for operando XAFS.

The 3D printed cell was designed to minimize the thickness of the electrolyte in front of the sample in order to reduce the attenuation of the X ray signal. Figure 3 shows that the presence of the electrolyte reduces only by 20-30% the fluorescence signal, resulting in a S/N ratio which is still accettable for measuring spectra in fluorescence mode.

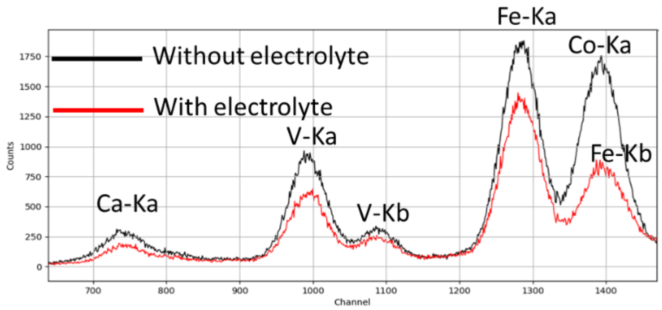

Figure 3: Signal attenuation due to the electrolyte in front of the sample

In order to test the feasibility of operando XAFS with our setup, we mesured the Co K-edge spectra of a CoFe-oxide catalyst deposited on a $WO_3/BiVO_4$ photoanode. The spectra were measured in Open Ciruit Potential condition and during a chronoamperometry (both with light on and off) for 30 minutes each. The spectra measured with the light on show a decrease in the white line upon illumination.. A detailed data analysis is in progress.

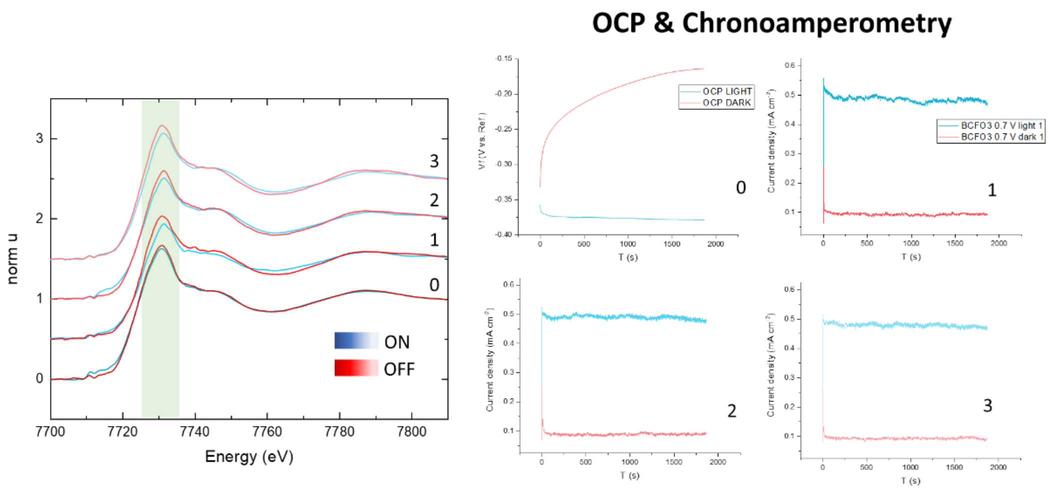

Figure 4: Operando XAFS spectra recorded at Co-K edge of CoFe-oxide catalyst on $WO_3/BiVO_4$ photoanodes with light on and off.