



	Experiment title: Photoelectrochemical activity of Co-Fe Prussian Blue water oxidation catalyst: operando XAFS.	Experiment number: CH-6417
Beamline: BM-08 LISA	Date of experiment: from: 15/11/2022 to: 21/11/2022	Date of report: 17/02/2023
Shifts: 18	Local contact(s): Alessandro Puri	<i>Received at ESRF:</i>

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Report:

The experiment CH-6417 was performed at beamline LISA BM-08 from November 15th to 21st 2022. The main goal of the experiment was to determine the structural properties of CoFe-Prussian Blue co-catalyst in a fully operating photoelectrochemical (PEC) cell. The operando setup was developed for a previously approved beamtime (CH-6248) and further optimized to allow for full integration of the photoelectrochemical cell with the beamline facilities (Figure 1). The resulting apparatus allowed for remote control of the light stimulus (white LED source), the current-potential regime (potentiostat), and the electrolyte flow (a custom pulse-less peristaltic pump), enhancing mass transport and removing gaseous product from the electrode's surface.

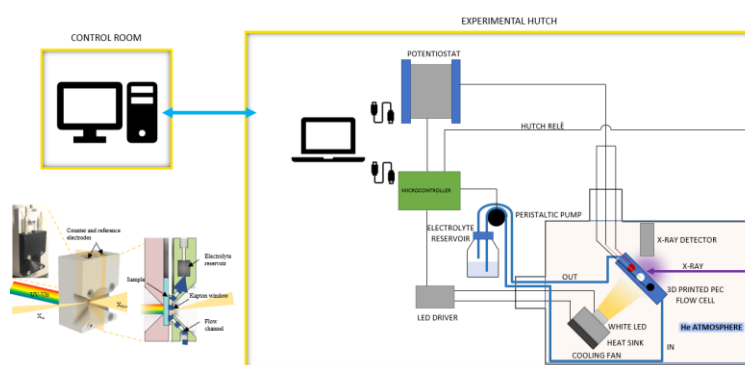


Figure 1: Experimental apparatus for the operando PEC-XAFS analysis, implemented at LISA BM-08.

The samples investigated with the aforementioned setup consisted in $\text{WO}_3/\text{BiVO}_4$ nanostructured photoanodes coated with a thin layer ($\sim 2\text{nm}$) of a mixed Co-Fe Prussian Blue analogue co-catalyst. Ex-situ EXAFS analysis on the Co K-edge of the catalyst exhibits good matching with the simulated spectrum of the canonic Co-Fe Prussian Blue structure, confirming that the catalyst is effectively deposited in the desired phase. A comparison of the Co K-edge ex-situ XAFS spectra with the ones registered in operando conditions (Figure 2a, Borate buffer 0.25M in absence of light, at different potentials) display a blue-shift and a strong alteration of the fine structure as soon as the electrode is in contact with the electrolyte. The XANES region of the operando spectra is highly consistent with the one previously reported for Co-based co-catalysts (J.A.C.S. 2009,

9 (131), 6937). This is pointing out an immediate alteration of the catalyst upon exposure to the electrolyte solution.

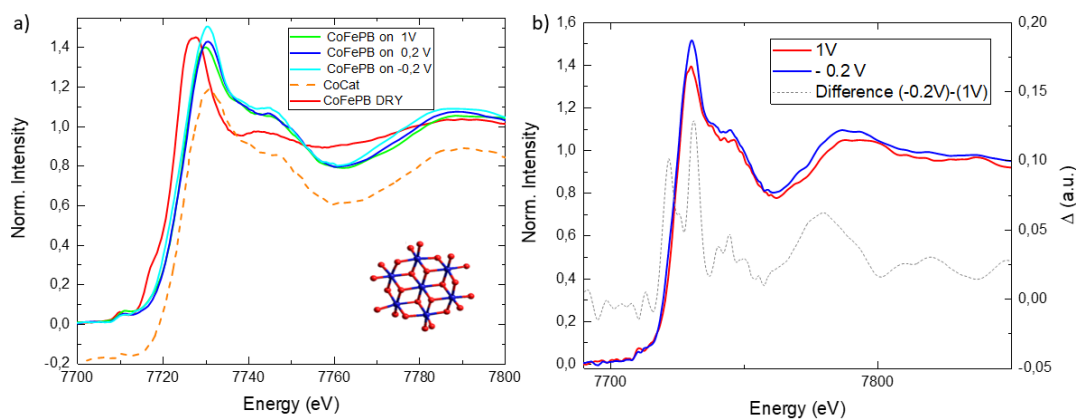


Figure 2: a) XANES spectra of CoFe-PB registered in the PEC cell at different potentials, compared to the one registered ex-situ and the literature-based XANES spectrum for analogue Co-oxo cubane structures (inset). b) detail of XANES spectra at different potentials and difference spectrum.

The effect of the applied potential to the photoanode (dark conditions) is reported in Fig. 2b, where an edge shift towards lower energy is observed as the potential is swept to potentials more negative than the open circuit potential (~ 0.2 V vs Ag/AgCl). Thus, in the positive potential region the steady state oxidation state is not differing from the one expected for the pristine catalyst (Co^{III}), whereas a shift towards lower oxidation state is observed by decreasing the potential (Co^{II}). The role of the photoinduced charges on the co-catalyst was investigated by comparing the XAFS spectrum at a fixed potential in absence/presence of light stimulus (Fig. 3a). Only in the spectra acquired at 0.2V a slight modification of the XAFS signal was observed, in particular related to the white line intensity. This small but non negligible photoinduced modification of the spectrum was investigated by Fixed Energy X-ray Absorption Voltammetry (FEXRAV), namely a continuous acquisition of the attenuation coefficient at a single energy, sweeping the potential within the desired electrochemical window (Fig. 3b). A maximum $\Delta\mu$ is observed where the potential is swept to negative potentials, consistent to a red-shift of the edge peak or an increased white line magnitude, corresponding to increased density of states, resulting from a partial reduction of Co^{III} to Co^{II} . Strikingly, the same measurement upon sample illumination provides the same $\Delta\mu$ trend, but the potential window where this process occurs is enlarged to more positive potentials, suggesting a decrease in the thermodynamic requirements for the reduction process, that may be related to a fast co-catalyst reduction process from the photoinduced charges.

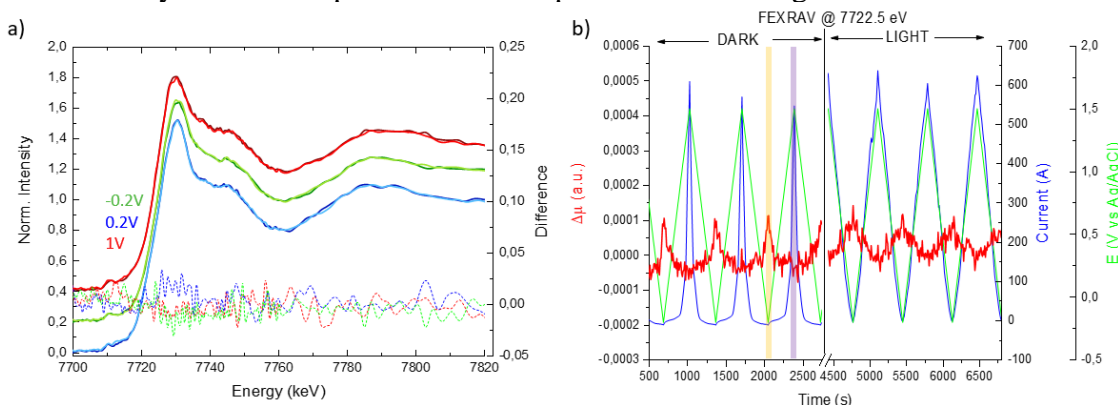


Figure 3: a) Comparison of XAFS spectra of CoFe-PB registered in the PEC cell at different potentials in absence and presence of light stimulus. b) FEXRAV plot for CoFe-PB upon potential sweep from 1.5V to -0.2V, in dark and light conditions. Potential and Current are superimposed, extracted from the cyclic voltammeteries.

During the beamtime we also measured the operando XAFS response of an analogue cocatalyst, Cobalt-Iron Oxide (CoFeOx), which is another promising catalyst for water oxidation in PEC cells. An unexpected opposite trend in the FEXRAV analysis was observed upon illumination, suggesting that this analytical technique might be able to efficiently discern different photocatalytic pathways.

As future outlook, we foresee the operando investigation of the Fe K-edge of the same samples, and performing time-resolved experiments, to investigate the transient co-catalyst structure in the positive potential regime, where the actual water oxidation process occurs.