

Experiment Report Form



	Experiment title: Operando XAS on a bio-inspired molecular photocathode: observing the behavior of the Co-complex catalyst	Experiment number: CH-5491
Beamline: ID-26	Date of experiment: from: 05/06/2018 to: 12/06/2018	Date of report: 24/02/2020
Shifts: 18	Local contact(s): David Degler	<i>Received at ESRF:</i>
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Report:

Aim of this proposal was to perform operando XAS measurements on bio-inspired molecular photocathodes for photoelectrochemical (PEC) water splitting, aiming at a better understanding of their working principles. It is worth to state that this XAS investigation is the first ever carried out on a multicomponent semiconductor-dye-catalyst photoelectrode capable of generating a negative photocurrent, corresponding to H₂ evolution, with no use of noble metals. In particular, the present proposal focuses on directly observing the oxidation state and local structure of the terminal Co-based complex.

Reaction [1]



occurs thanks to a smart combination of an organic dye, that absorbs visible light and reaches an excited state, followed by an electron transfer to the Co-complex catalyst. The circuit is closed by the recovery of the fundamental state of the dye through the acceptance of an electron coming from an inorganic semiconductor. The high dilution of Co in the system, together with the need of adopting hard X-rays for working under operative condition (i.e. in the presence of a liquid electrolyte) required the use of a high-energy resolved fluorescence detector to allow the analysis of the Co-K pre-edge and thus to have a direct observation of the *d* states of Co. The (photo-)electrochemical cell coincides with the one successfully adopted previous experiments carried out at the ESRF (e.g. 08-01 1004 and CH-4654) and was filled with 0.1M MES (2-(N-Morpholino)ethanesulfonic) buffer. A Pt wire and a AgCl/Ag (in 1M KCl) were used as the counter and reference electrode. The visible light source was a 520 nm green LED. We recorded both XAS spectra and RIXS maps.

XAS spectra in different operative conditions (e.g. in dark, under 505 nm LED irradiation and at different potentials) are compared in **Figure 1**. In order to study the cobalt oxidation state the XAS spectra of the standards (CoO, Co₃O₄, CoOOH) are also shown. Going to more reductive potentials (*vs.* Ag/AgCl), a shift of the edge energy position towards lower energies is observed, indicating a lower mean oxidation state of Co. Instead, little to no differences were found comparing light and dark spectra at the same potential.

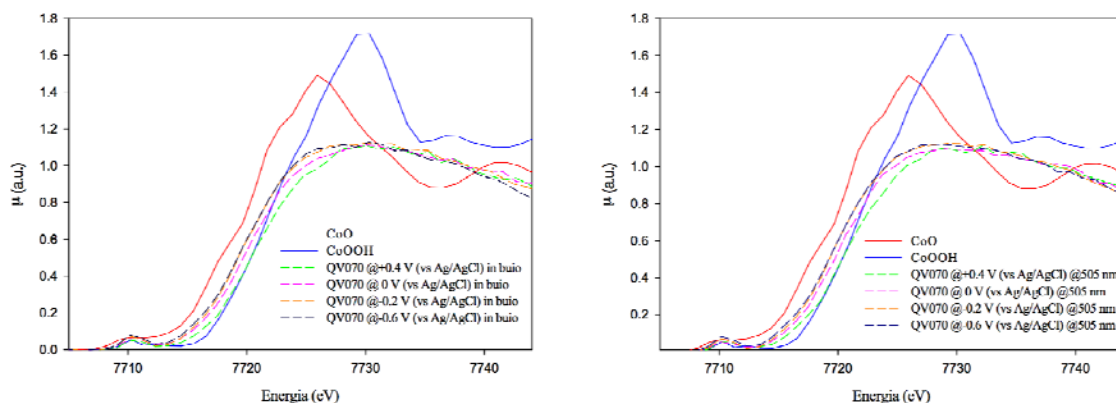


Figure 1. Comparison between XAS spectra of the standards and the XAS spectra for QV070 photocathode at various potentials in dark (left) and under 505 nm LED irradiation (right).

The analysis of the experimental RIXS maps required a different approach. In order to explain the variations observed in the experimental maps, simulations have been carried out using the Quanty4RIXS interface. Different cobalt oxidation states and different coordination geometry were tested. Going to more reduced cobalt species (*i.e.* from Co(III) to Co(II) to Co(I)), the peak in the calculated RIXS map shifted towards lower incident energies. Also, the calculated RIXS intensity decreased as the cobalt oxidation state decreased. That is due to the filling of Co 3d orbitals, thus decreasing the number of final state allowed for the transition. Different geometries, on the contrary, showed changes in the shape, intensity and position of the peak. That is due to a different splitting of the cobalt 3d orbitals and allows distinguishing different coordination geometries. An example of experimental *vs* calculated RIX spectra is reported in **Figure 2**.

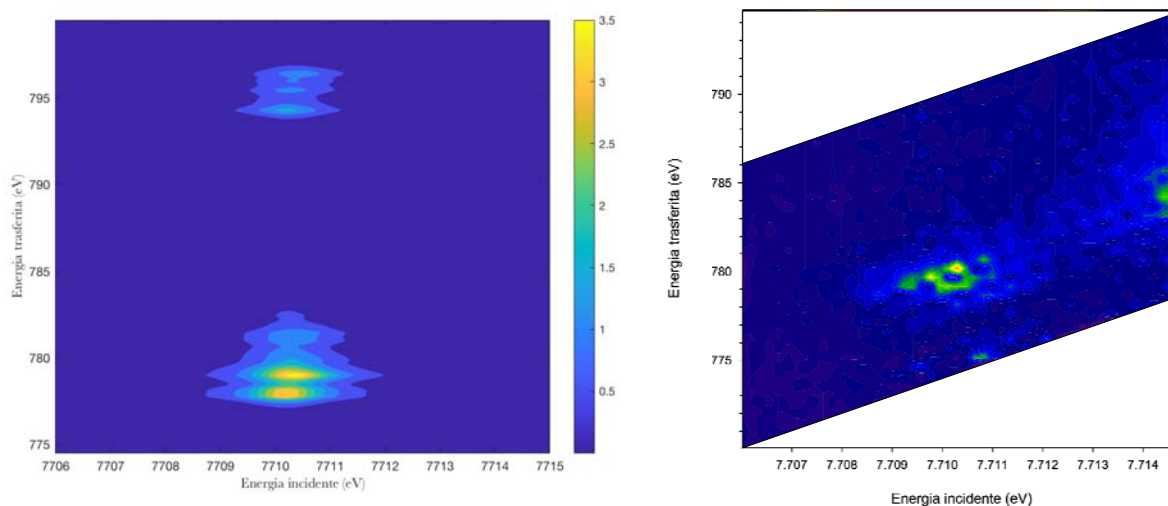


Figure 2. Calculated RIXS map for the H₂O₂ evolving catalytic cycle (left). Experimental RIXS map for the QV070 photocathode at 0 V vs Ag/AgCl under 505 nm LED irradiation (right).

The experimental RIXS maps allow for some initial considerations: while going to more negative potentials the edge position shifts towards lower energies, indicating a lower mean cobalt oxidation state. That is pointed by the intensity increase in the 7714 eV region; the pre-edge intensity became lower under LED irradiation. This is due to the filling of cobalt 3d orbitals upon illumination; going to more negative potentials, the region between 7709 and 7710 eV gains intensity, showing the formation of more Co(II) species. This increase is more important in dark conditions, because irradiation promotes the formation of Co(I) species, with little to no intensity in that region.