In-operando XAS study of photocatalytic water splitting: state of catalytic sites as a function of irradiation and applied potential. Proposal 30-02-1072

During this run we studied at Co K edge the cobalt species in the oxygen evolution reaction (OER) catalysts, under *operando* conditions, as a function of applied potential and illumination.

In the last years, cobalt-based OER catalysts were widely studied as prospective components of the photocatalytic water splitting systems. Such systems should include a semiconductor (often TiO_2), providing light harvesting and an electron hole-pair generation, and two catalytic phases, namely a hydrogen evolution reaction (HER) catalyst, which might be a noble metal (Pt) and an OER catalyst. Our effort was focused on the properties of the OER cobalt-based phases, known in the literature as CoPi and CoBi. These designations are related to the presence of phosphate (CoPi) and borate (CoBi) species in the amorphous solids, containing otherwise Co(III) and Co(II), oxygen and protons, and structurally resembling the cobalt oxide hydrohide CoOOH.

The experimental setup has been described in previous reports (30-02-1045). In brief, an FTO electrode was immersed into an electrolyte and cobalt-containing solid was deposited onto the FTO surface electrochemically or photoelectriochemically. The measurements were carried on the growing layer of OER catalyst in a cobalt-containing electrolyte. Otherwise, after depositing a known amount of CoPi (CoBi) phase, electrolyte was replaced and a measurement was done on a working catalyst in a steady state conditions. The measurements were performed in the meniscus zone, where FTO is covered by a sufficiently thin electrolyte layer, allowing to collect photons from the surface (several hundreds µm).

The properties of solids deposited in phosphate and borate buffers at different pH have been compared, as a function of the layer thickness, defined by the amount of charge. The solids were deposited onto bare FTO or onto the TiO_2/FTO electrodes prepared on site by electrophoretic adhesion of TiO_2 nanoparticles to the FTO surface. The properties of the solids deposited in dark or under illumination have been compared. We also tried to deposit similar to CoPi and CoBi fluoride-containing phases (described in the literature) but no deposition was obtained in the range of applied anodic potetntial 1.0 – 1.5 V.

The main question to answer was on the nature of CoPi (CoBi) species. We inquired into the structural differences of phosphate and borate-containing solids. The structural differences include chemical environment of cobalt and the degree of disorder, as well as the involvement of anionic species into the structure. The oxidation degree of cobalt is another important parameter as the deposits might contain variable amounts of Co(II)/Co(III) that is supposed to strongly influences their OER activity.

A great number of results have been obtained, which are still under treatment. We can however outline the main conclusions of this study as follows.

The structural properties of CoPi and CoBi solids are very similar and close to those of disordered CoOOH phase, whatever the substrate and the deposition mode. The structural parameters obtained from EXAFS fitting is given in Table 1. Both CoPi and CoBi are very similar to the CoOOH structure and require three shells to obtain a high fidelity fit. Coordination numbers are lower than the theory values partially due to self-adsorption but also due to structural disorder. Indeed, the first coordination number is 4.9 and the second is only 3.6 whereas theory value is 6 for both numbers.

Both CoPi and CoBi shows a well-defined third peak near R= 3.4 (in Fig.1 non-phase corrected, corrected value near 3.1). This peak can be tentatively attributed to Co-O, in an irregular position, probably due to anionic species in the structure.

Table 1. Structural parameters of the CoPi and CoBi phases deposited under similar conditions. The error of fitting is indicated in parentheses, in the units of last significant digits.

Element	R(Å)	N	σ^2 Å^2	ΔE_0 , eV	%R
CoPA130-131 (CoBi)					
O	1.899(5)	4.9(5)	0.0041(8)	-0.5(5)	8
Co	2.839(6)	3.6(6)	0.0049(9)	0.6(4)	
O	3.407(8)	1.0(5)	0.0076(8)	0.5(5)	
CoPA 237-238-239 CoPi					
O	1.907(9)	4.8(5)	0.0049(3)	0.18(10)	9
Co	2.81(2)	3.6(6)	0.0041(5)	-2(1)	
O	3.418(8)	1.2(5)	0.0088(8)	-1.0(8)	

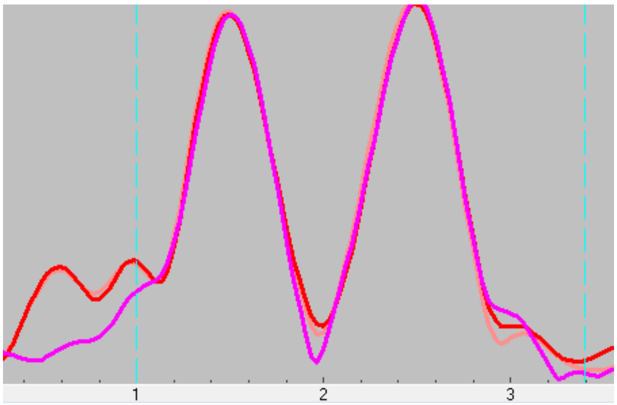
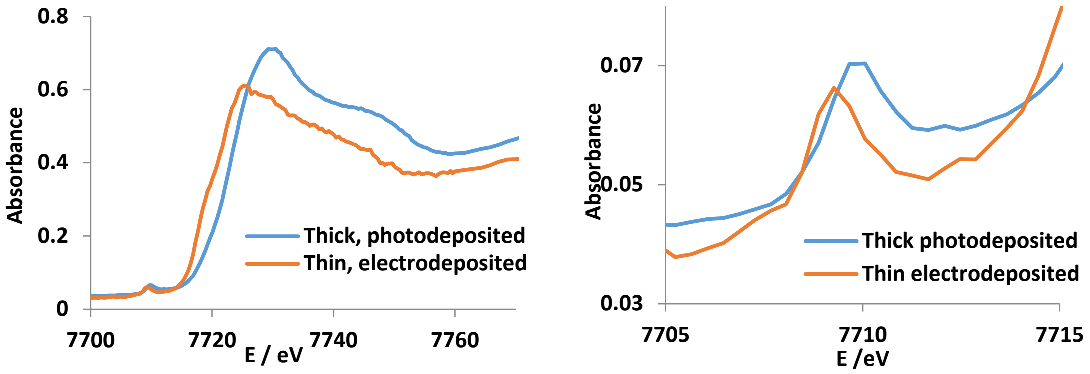


Fig. 1 Fit of the EXAFS spectrum for the CoBi phase in the R-space. Pink line – simulation, red –experimental spectrum.

Unlike the structural parameters of CoPi and CoBi in the thick deposits (necessary to acquire EXAFS), the oxidation degree of cobalt in the growing layers is subjected to strong variations. As a general conclusion, photoassisted layers tend to have much higher proportion of Co(III) than the electrochemically deposited phases (Fig 2). Apparently in the initially formed thin layer, a CoO-like Co(II) phase is formed which is further transformed to CoOOH (Co(III) upon oxidation by electronic holes coming from illuminated titania.



A

B

Fig. 2 Co K XANES profiles (A) and pre-edge features (B) for the thick film of photodeposited CoPi vs. an electrodeposited thin layer.