



Experiment title: **Exploring the Core@Shell Electro-catalyst Preparation: Kinetics of the Underpotential Deposition of Cu on Supported Au Nanoparticles by Dispersive XAS**

Experiment number:
CH-4409

Beamline: ID24	Date of experiment: from: 08/04/2015 to: 14/04/2015	Date of report: 20/02/2016 <i>Received at ESRF:</i>
Shifts: 18	Local contact(s): Giovanni Agostini	

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Report:

Background Gold-copper based materials as (photo-)electrodes for (photo-)electrochemical processes are fundamental in the field of energy conversion being actively studied materials for low temperature fuel cells or photoelectrochemical water splitting. The Au-Cu system is also gaining lot of attention because of the promising features of electrodeposited Cu_2O as photocathode for hydrogen production in photoelectrochemical water splitting. Cu_2O photocathodes electrodeposition is a complex process that, for unknown reasons, leads to high performance photoelectrodes only if carried out on Au. Attempts on deposition on other supports like FTO or Ti lead to unactive Cu_2O layers. This is likely due to different nucleation of the oxide on the different materials, a process that occurs on the initial few ms of the process. This is at the bases of the need of a time resolved and in-situ XAS investigation on the electrodeposition of Cu_2O on Au and FTO.

Aim We started an investigation on kinetics of the electrodeposition and electro-dissolution of copper by energy dispersive XAS aiming at shading light on the different mechanism of the electrochemical reactions. This is intended to be the first step of a deeper investigation of the reactions involved in preparation of the electrocatalysts.

Experimental description.

In order to perform *in operando* XAS measurements a spectroelectrochemical cell was designed and built by the present experimental team. Fig. 1A schematically shows the main components of the electrochemical device. This consists of two parts: a polycarbonate disc (1) and a Teflon hollow cylinder (21 mm diameter, 6 mm thickness, and 7 mm cavity, 2). The working electrode is held between the main body of the

polycarbonate cell (through the use of an o-ring) and the Teflon plate that also includes a hole for the X-Rays beam. The cell can contain the electrolyte solution and can provide the best conditions to perform measurements during the applications of specific electrochemical programs. Indeed, it can host a Pt foil counter electrode and AgCl/Ag reference electrode. The reference electrode can be separated from the solution by means of a salt bridge made of a glass pipette filled with agar containing 0.2 M aqueous KClO_4 . Fig. 1.B provides an image of the electrochemical cell with the three-electrodes set up mounted in the experimental hutch of beamline ID24. Thanks to this stable architecture, it is possible to obtain the best conditions to perform spectro-electrochemical measurements.

Results Figure 2 shows an example of a chronoamperometric experiment carried out in aqueous 20 mM CuSO_4 and H_2SO_4 0.5 M by applying a constant potential equal to $-0.05 \text{ V vs. Ag/AgCl}$. In this condition Cu(II) is not stable in solution and the XANES spectra reveal a gradual transition from the spectral shape of the Cu(II) hydrated ion to metallic copper. Indeed, the spectral structure at ca. 8885 eV, that can be attributed to the Fermi level of metallic copper, increases monotonically, while the structure at ca. 8900, that is attributed to the WL of hydrated Cu(II) , decreases monotonically with increasing time. This result is a direct indication that the reduction reaction of hydrated Cu(II) to give metallic Cu is a bi-electronic process.

As an additional example, the stability of Cu(II) in basic solutions has been investigated. The results are shown in Fig. 3, where the results of a linear voltammetry carried out in 76 mM Cu(II) lactate at pH 12 are illustrated. It is quite apparent that copper lactate is stable in solution for applied potentials larger than 0.4 V, while at lower potential the deposition of Cu_2O (that is clearly marked by the increase of the spectral structure at ca. 8885 eV) takes place.

Conclusion By applying different electrochemical programs to different Cu(II) solutions in different conditions, we could detect different pathways for the reduction of hydrated Cu(II) . While further investigation and further data processing for better determining the pertinent kinetics and mechanisms of the processes involved is required, the data obtained in this experiment may represent a solid basis for a better understanding of the electrodeposition of metallic copper on different substrates.

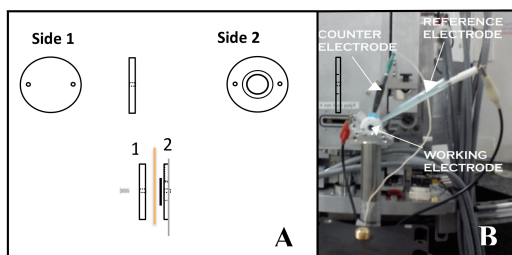


Fig.1

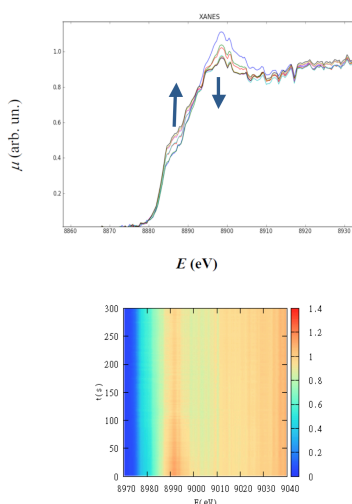


Fig. 2

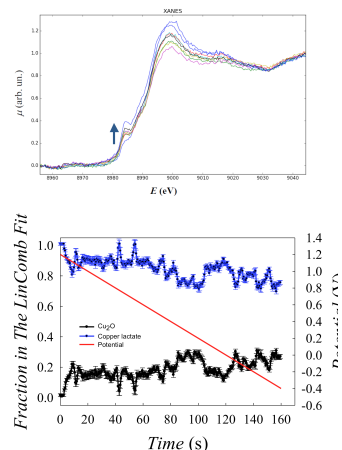


Fig. 3