EUROPEAN SYNCHROTRON RADIATION FACILITY
INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

Experiment Report Form

	Experiment title: Ag as electrocatalyst for the electro-reduction of organic halides: an in-situ XAS investigation on the sequence of electron transfer and chemical steps	**Experiment number**: CH-3932
Beamline:	**Date of experiment**: from: 25/11/2013 to: 03/12/2013	**Date of report**:
Shifts: 18	**Local contact(s)**: Francesco d'Acapito	*Received at ESRF:*

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Report:

In a previous experiment ad BM08 (CH-3511), some of us developed a new technique, the Fixed Energy X-Ray Absorption Voltammetry (FEXRAV) that allows to perform conventional electrochemical methods while following the oxidation state transitions occurring at the element under consideration, likely the main component of the working electrode. This allowed to study Ir-based electrodes and to attain a better understanding of their role as catalyst for the oxygen evolution reaction. In the present experiment the goal was, on one side, to extend the new technique capabilities and, on the other, to study another interesting electrochemical phenomena, i.e. the electrochemical reduction of organica halides, one of the most hazardous class of water and air pollutants. In the present experiment we performed in-situ XAS measurements on electrodes of Ag nanoparticles (NP) as electrode material for fundamental electrochemical studies.

This is due to the exceptional catalytic activity of silver toward the C-Cl bond breaking that resulted in a deep interest also in terms of the mechanistic point of view. In particular, very recently, some of us showed the electrochemical evidence of the adsorption of the organic halide mojeties onto the Ag surface that is likely at the bases of the observed electrocatalytic capability. This experiment aims therefore to confirm and better describe the nature of this adsorption thanks to the complementary information given by conventional *in-situ* XAS and FEXRAV.

As a preliminary study, we carried out experiment in aqueous electrolyte in the presence of halide ions, (Cl^-, Br^- and I^-) to better underline the potentialities offered by FEXRAV in following the formation/destruction of the corresponding Ag halides.

The experiment CH-3932 allowed us to:

1-design and test an improved electrochemical cell that allows electrochemical *in-situ* XAS measurements in transmission and fluorescence modes and allows to contain a low amount of solution (about 2 ml)
2-perform *in-situ* XANES, EXAFS and FEXRAV in the presence of a low amount of organic halide both in aqueous and non-aqueous environments
3- perform *in-situ* XANES, EXAFS and FEXRAV in the presence of specifically adsorbing halides.
All experiments are carried out at the Ag-k edge (fluorescence mode).

Fig 1 shows images of the cell used during the experiment inside the BM-08 hutch.

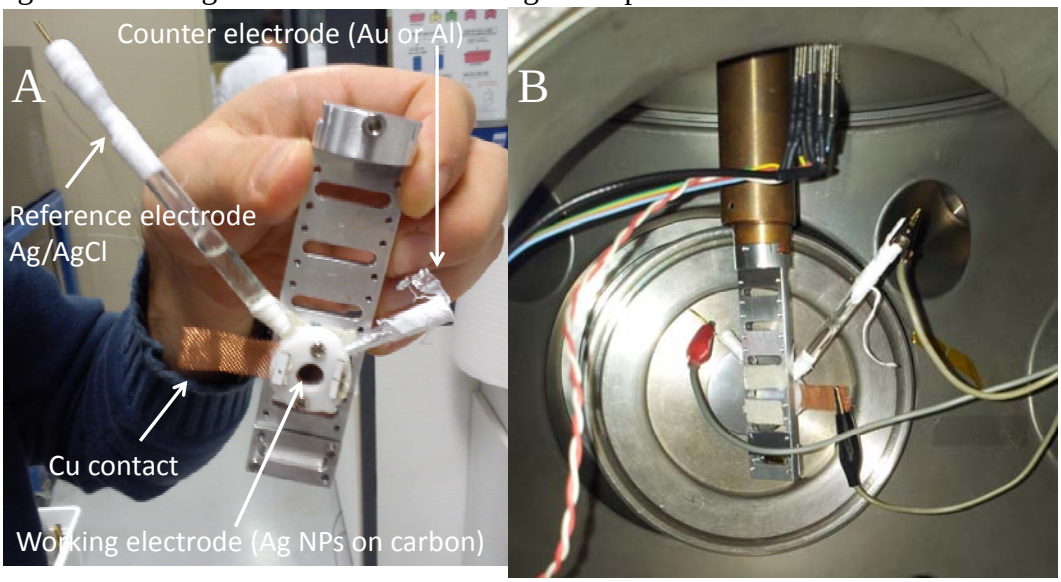

Figure 1 (A) Picture and description of the spectroelectrochemical cell mounted (B) in the XAS hutch

The spectro-electrochemical cell shown in Fig.1 allows to use a three-electrodes configuration and contains the electrolyte solution. A hole in the frontal part allows the X-Rays to hit the sample and the fluorescence radiation to reach the detector.
The working electrode is made of Ag nanoparticles (by different preparations, having avg. *d* between 10-100 nm) previously (before our arrival at ESRF) deposited on Glassy Carbon (1mm thick). The experiments were conducted controlling the electrochemical instrumentation (CH Instrument 633D potentiostat/galvanostat) from the control room.
The data are under elaboration but both XANES/EXAFS analysis and FEXRAV clearly shows the change of Ag chemical surroundings and of the relevant changes of oxidation state in dependance on the applied potential. Figure 2 and 3 show the case of AgCl formation/destruction.

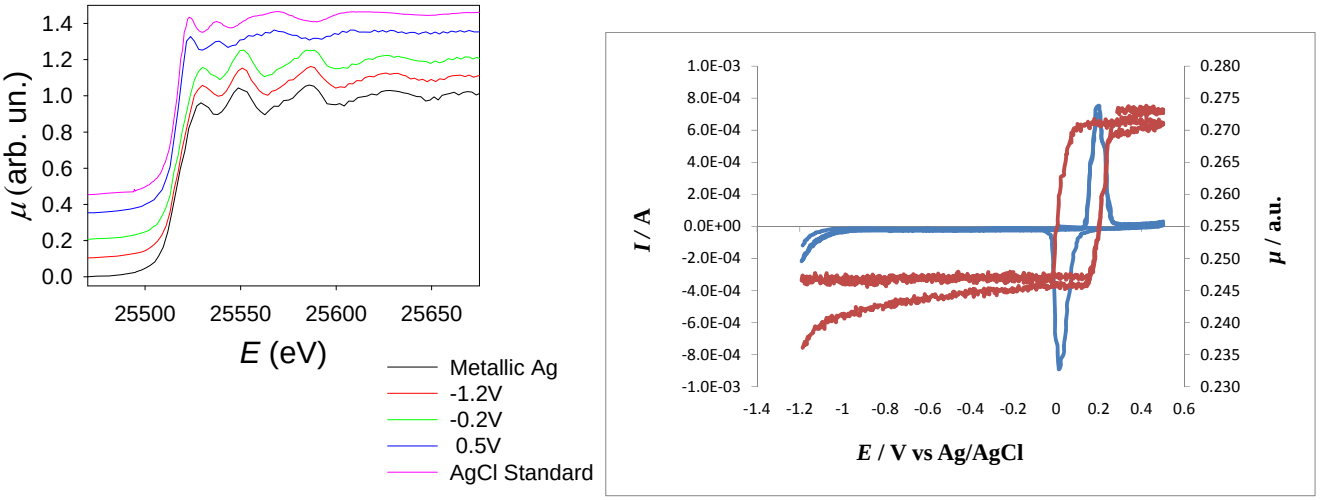

Figure 2 (A) EXAFS spectra at different applied potential; (B) FEXRAV (red line) and conventional CV (blue line) of Ag NPs recorded in KCl 0.1M