

## Experiment Report Form



	<b>Experiment title:</b> In-situ observation of halogenated species adsorption onto Ag electrode by XANES, EXAFS and FEXRAV at the Ag-k and Br-k edges	<b>Experiment number:</b> CH-4208
<b>Beamline:</b>	<b>Date of experiment:</b> from: 23/02/2015 to: 03/03/2015	<b>Date of report:</b>
<b>Shifts:</b> 18	<b>Local contact(s):</b> Francesco d'Acapito	<i>Received at ESRF:</i>
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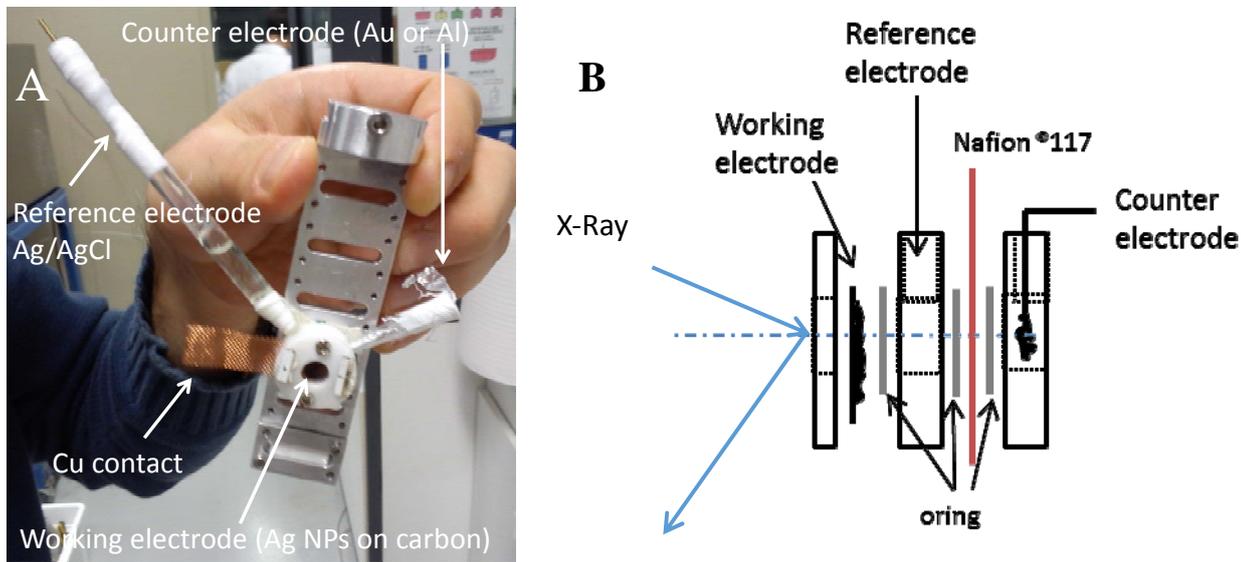
### Report:

In a previous experiment ad BM08 (CH-3932), we were able to study Ag nanoparticles deposited onto glassy carbon electrodes. In more detail, we were able to prove the adsorption of Trichloromethane,  $\text{CHCl}_3$ , a test molecule representative of volatile organic halide, one of the most harmful classes of airborne and wastewater pollutants. Proving the adsorption of  $\text{CHCl}_3$  on Ag is very relevant in the framework of the study of the exceptional catalytic activity of Ag for the electrochemical hydrodehalogenation reaction that in the particular case leads to  $\text{CH}_4$ . The experiment also leads to further proving the effectiveness and reliability of *Fixed Energy X-Ray Absorption Voltammetry* (FEXRAV), a technique recently developed by us that consists in fixing the value of X-ray energy while scanning the electrode potential at will. In the present case, this allowed to study Ag nanoparticles in a broad potential windows and in the presence of specifically adsorbing ions, namely  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$ .

During the present experiment the goal was the study of adsorption phenomena occurring on Ag nanoparticles of both ions and molecules. Moreover, we worked at the Br edge in order to investigate these phenomena from the adsorbate "point of view". The goals of the experiment include the understanding of the orientation of organic halides when adsorbed on Ag. In particular, o-, m- and p-bromophenols were considered.

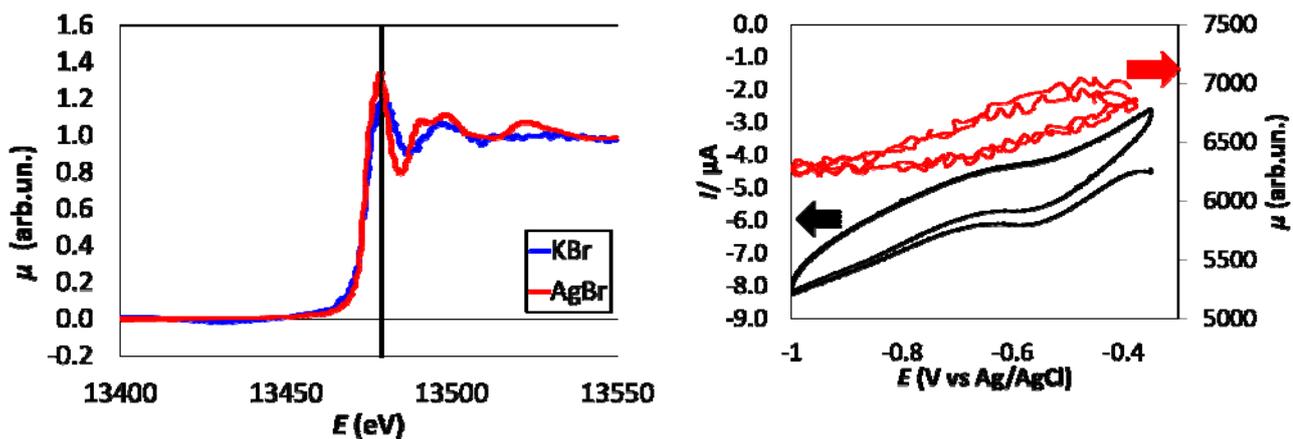
The setup was rather similar to the one used in CH-3932 and consists in a teflon cell that can host the counter and the reference electrode. Ag nanoparticles (NanoComposix Inc<sup>®</sup>), are deposited by drop-casting on a custom-made carbon screen printed electrode (DRP-P-C11XX, Dropsense) that includes a Ag track for the external electrical connection. X-rays are shined from the electrode back, in the fluorescence mode. The cell can contain the electrolyte, aqueous  $\text{KClO}_4$  0.1M.

Fig 1 shows an image and a scheme (cross-section) of the cell used during the experiment.



**Figure 1** (A) Picture and description of the spectroelectrochemical cell mounted on an holder (B) schematic cross-section of the cell .

The experiment consisted in recording the XAS spectra of standards (AgBr, KBr, solutions of bromophenols) to address the best energy for perform FEXRAV. An example is reported in Fig. 2.



**Figure 2:** a) XANES spectra of AgBr and KBr. The vertical line indicates the energy at which the FEXRAV was recorded , b) FEXRAV in 150  $\mu\text{M}$  KBr +  $\text{KClO}_4$  0.1M. Potential scan rate:  $1 \text{ mV s}^{-1}$ ; X-ray energy=13480 eV

In Fig 2a, the black line marks the energy adopted for recording FEXRAV. Note that, at this energy, a higher value of the absorption coefficient,  $\mu$ , is observed for AgBr. This evidence is used to interpret the FEXRAV reported in Fig. 2b, where the current trace clearly presents a peak at -0.56V (vs Ag/AgCl) during the cathodic scan in the presence of KBr. In parallel,  $\mu$  decreases. According to Fig.2a this can be attributed to the desorption of  $\text{Br}^-$  from the Ag surface.

This result demonstrates the really good agreement between CV and FEXRAV measurements. The variation of absorption coefficient with the potential can be used to track the adsorption/desorption of  $\text{Br}^-$  on Ag surface.

Similar experiments were carried out using bromophenol instead of  $\text{Br}^-$ . The results point to the adsorption of the molecules at the Ag surface even at open circuit potential. The results are strengthened by the complete XAS spectra recorded after addressing the most significant potential values thanks to preliminary FEXRAV scans.