

Report on the experiment CH992 performed on beamline ID26, October 3rd to 8th 2001.

Experiment title : XAS Measurements at Controlled Electrochemical State for the Study of Lithium Electroinsertion in Tungsten Trioxide. T. Pauporté, Y. Soldo-Olivier and R. Faure.

3 papers have been published in relation to these experiments :

- *XAS Study of Amorphous WO₃ Formation from a Peroxo-Tungstate Solution (Published in J. Phys. Chem. B, 107 (2003) 8861)*

Electrodeposition is a low cost method for WO₃ thin film preparation. The starting dissolved tungsten precursor is a peroxo-compound which can be prepared by an equimolar mixing of sodium tungstate and hydrogen peroxide. The precursor preparation as well as the electrodeposition and precursor solution ageing processes have been studied by X-ray absorption spectroscopy (XAS) at the W L₃-edge. By extended X-ray absorption fine structure (EXAFS) analysis, the local structure of the first oxygen octahedral shell around the W absorber has been characterized both in the colloidal oxide formed after deposition solution ageing and in electrodeposited films. The colloidal compound could be fitted with the same procedure as that successfully used with a monoclinic WO₃ reference and involving two different W-O interatomic distances. The ageing product is identified as amorphous WO₃. If the spectra of as-electrodeposited films could not be fitted by the same procedure, the structural parameters of those cycled electrochemically in a lithium ion containing organic medium have been determined. If compared to crystallized WO₃, the mean W-O distances in amorphous WO₃ (films and colloids) are found significantly shorter, whereas the Debye-Waller factors are much larger. The condensation process has been investigated by analyzing the variation of the x-ray absorption near edge structure (XANES) spectra. We show that the white line height of the W L₃-edge is a good indicator of the condensation state of the matter during the deposition. According to this parameter, the electrodeposited WO₃ films would undergo a dramatic reorganization process during the first potential cyclings in the lithium ion containing organic medium. The same behavior is observed with electrochromic films deposited by sputtering, a more classical method.

- *Structural Changes in Electrochromic WO₃ Thin Films Induced by the first Electrochemical Cycles (J. Electrochem. Soc. (2003) in press).*

We have investigated the effect of the very first electrochemical cycles on the local structure and bonding for two different amorphous transparent electrochromic WO₃ thin films, namely a sputtered film and an electrodeposited film. The cycles are performed at constant potential scan rate between 0.65 and -0.55 V vs NHE in a 0.3M LiClO₄ / propylene carbonate solution. We show that this treatment has a weak influence on the short range order in sputtered film. On the contrary, dramatic changes are found in electrodeposited ones. Both Raman spectroscopy and extended X-ray absorption fine structure (EXAFS) data show that the initial electrodeposited oxide films are highly disordered with a highly asymmetric structure. The Fourier transforms of the EXAFS spectra of these films show four different W-O distances in the first oxygen shell with values ranging between 1.5 and 2.4 Å (after phase correction). After the electrochemical treatment, the radial distribution of the oxygen atoms is changed. The structure becomes similar to that classically reported for amorphous WO₃ films and can be fitted assuming two different main distances. Raman spectroscopy and EXAFS reveal a larger W-O distance distribution in the two different amorphous films compared to a

monoclinic WO₃ reference sample. They show a higher dispersion of the W-O distances in cycled electrodeposited films, compared to the cycled sputtered ones.

- *In Situ X-Ray Absorption Spectroscopy Study of Lithium Insertion into Sputtered WO₃ Thin Films (J. Electroanal. Chem. (2003) in press).*

We have performed an *in situ* X-ray absorption spectroscopy (XAS) study of the effect of Li⁺ electroinsertion into amorphous sputtered WO₃ thin films. Three different potentials have been investigated, which are +0.66 V, -0.84 V and -1.04 V vs SHE. We have estimated by electrochemical and chemical titration that they correspond in Li_xWO₃ to *x* equal to 0, *ca.* 0.32 and *ca.* 0.45 respectively. Shifts of the tungsten L_I and L_{III}-edge positions towards lower energies are observed with lithiation and attributed to the decrease of W oxidation state. Significant modifications are also observed on the extended X-ray fine structure (EXAFS) spectra. The analysis of first oxygen shells clearly shows an increase of the mean W-O interatomic distance upon lithiation which is not due to a crystallization process induced by the cathodic reaction.