Electrodeposition of WO_3 Thin Films

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Cathodic electrodeposition is a promising alternative route for electrochromic WO_3 thin film deposition. Unfortunately, the methods reported in the literature are very time consuming and the precursor solution used is poorly stable.

We present a new, simple and fast method for preparing the deposition solution [1]. The starting tungsten species is a salt, Na_2WO_4, which is mixed to H_2O_2 prior to be acidified at pH 1.2 by perchloric acid addition. This solution is remarkably stable. The films are deposited between 0.06 and 0.34 V versus NHE at room temperature. They are smooth and well-covering. They are amorphous by X-ray diffraction study. Voltammograms typical of WO_3 amorphous films have been recorded in H_2SO_4 and $LiClO_4$-PC. The coloration efficiencies measured at a wavelength of 633 nm for H^+ and Li^+ intercalation range between 62 and 66 $cm^2.C^{-1}$ and are similar to the results obtained with evaporated films.

The deposition process has been studied by X-ray absorption spectroscopy from a high intensity synchrotron source (ESRF-Grenoble). A large variety of samples (summarized in table 1), from the deposition solution to crystallised WO_3 and electrodeposited WO_3 thin film cycled or not in $LiClO_4$-PC medium have been investigated. It appears that the condensation process can be followed by means of the white line height (WLH) of the tungsten L_3 absorption edge. We propose an arbitrary scale reflecting this parameter and which gives rise to a linear relationship with the WHL (Fig.1). The XANES results have been correlated with Raman and EXAFS analysis which shows in particular dramatic structural changes in the electrodeposited WO_3 films induced by the first cyclings in $LiClO_4$-PC medium.

[1] Th. Pauporté, *J. Electrochem. Soc.*, **149,** C539-545 (2002).

Sample	N°	Condensation degree[a]	W L_3 WL heigth
- WO_3 crystallized	1		3.04
- ed-WO_3[b] cycled in Li-PC	3	6	3.01
- sp.-WO_3[c] cycled in Li-PC	4		3.02
- Aged deposition solution	5	3	3.34
- ed- WO_3[b].	6	2	3.41
- sp.-WO_3[c]	7		3.41
- solubilized Na_2WO_4 .	8		3.58
- fresh deposition solution	9	1	3.53
- deposition sol. stored 2 days	10		3.55

[a] Scale arbitrarily set from 1 to 6

[b] Electrodeposited film, [c] film deposited by sputtering.

Table 1: Set of samples investigated.

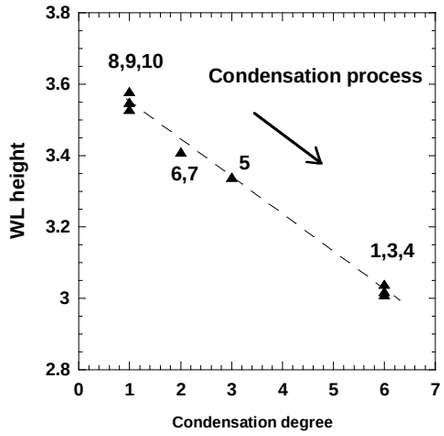

Figure 1: Variation of the white line height of the W L_3 edge with the condensation processes induced electrochemically (label: sample N°).