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X-Ray Reflectometry for electrochromic thin film characterisation: WO₃ as an example.

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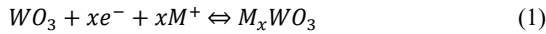
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Abstract—This document is a template for the submission to Journées Plénières GDR NAME 2022 conference.

Electrochromic (EC) materials and devices are able to modify their optical properties under the appliance of a voltage. This technology is recognized as one of the key green technology for sustainability and energy saving. Smart windows in residential and commercial buildings are one of the typical example of applications [1]. Among electrochromic oxides, WO₃ shows a cathodic coloration upon reduction with electrochemical insertion of small cations M⁺ (H⁺, Li⁺, Na⁺) as follow:



The reaction in Eq. (1) is associated with visual change from colourless to dark blue as illustrated in FIGURE 1.

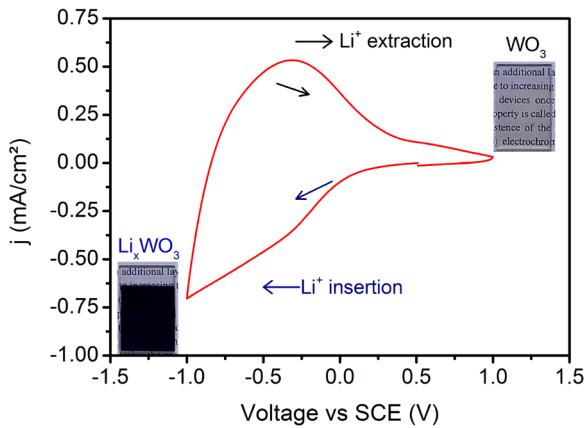


FIGURE 1. Cyclic voltammogram (1st cycle) of WO₃/LiTFSI in EMIMTFSI (1:9%mol.)Pt vs SCE cells recorded at 20 mV.s⁻¹.

The ability of electrochromic materials to maintain their coloured state once the applied voltage is withdrawn associated to its reversibility is called the memory effect. This unusual property on metal oxides allows to reduce power consumption of devices by avoiding to apply a voltage permanently in order to keep the desired colour. WO₃ thin films of ~100 nm were grown by radio-frequency magnetron sputtering using a WO₃ ceramic target in an argon and oxygen atmosphere. The control of sputtering conditions as power density, total pressure and

oxygen partial pressure allows to adjust the memory effect on WO₃ films. By varying the total pressure from 1 Pa to 2 Pa and 4 Pa, WO₃ thin films with an irreversible colouration, a high memory effect or a poor memory effect can be obtained [2]. Hence the presentation will make a focus on WO₃ films deposited at 2 Pa. This memory effect property was characterised by the evolution of the optical transmittance at 550 nm after 48h as shown in FIGURE 2 on a WO₃ film coloured at -1.0 V. The slight increase of 15.8% in transmittance indicates that the Li_xWO₃ is still blue after two days meaning a high persistence of the colour in open-circuit.

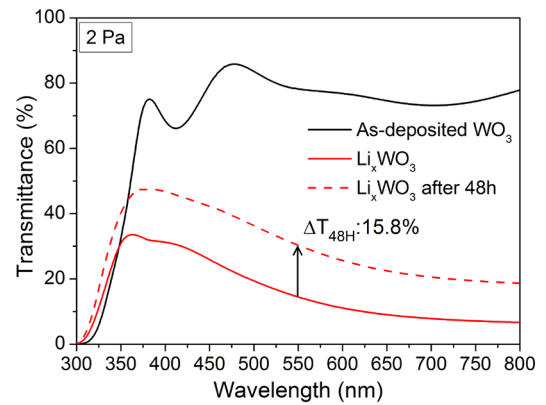


FIGURE 2 Optical transmittance of Li_xWO₃/ITO before and after 48h at 25°C and 50 % R.H.

The origin of the memory effect property lies into the film structure, morphology and composition. The determination of the number of exchanged electrons from Eq. (1) allows to determine the composition with the x value in Li_xWO₃ that can be calculated from:

$$x = \frac{Q \cdot M}{F \cdot \rho \cdot t} \quad (2)$$

where Q (C/cm²) is the electrochemical capacity in reduction calculated from $\frac{\int j \cdot dV}{s}$ on the FIGURE 1, s is the scan rate (20 mV.s⁻¹), M is the molar mass of WO₃ (231.84 g.mol⁻¹), F is the Faraday constant (96 485 C.mol⁻¹), ρ is the density and t is the film thickness.

X-Ray Reflectometry (XRR) is a non-destructive technique which is a useful tool to evaluate thickness and the thin film density, thus the composition. From XRR, density, thickness, surface and interface roughness can be obtained. XRR measurements were performed at the Metrology beamline at SOLEIL synchrotron using CASTOR device [3]. The reflectivity was recorded on a WO₃ thin film deposited on silicon wafer at 8 keV photon energy. Simulation of XRR curves were performed using model based on different layers as substrate, film/substrate interface and thin film. FIGURE 3 presents a XRR curve and the corresponding fitting of a WO₃ thin film of 90 nm deposited on silicon substrate.

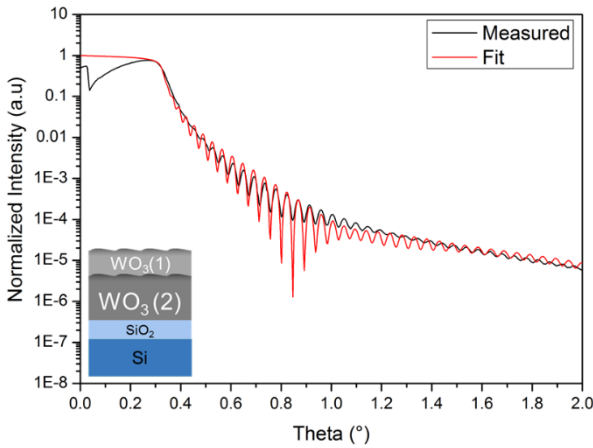


Figure 3 X-Ray Reflectivity of a ~90 nm thick WO₃ film on Silicon substrate with the layer model in inset.

The main fitted parameters and corresponding fitted values are listed in TABLE 1.

Layer	Density (g.cm ⁻³)	Thickness (nm)	Roughness (nm)
WO ₃ (1)	6.00	6.7	1.5
WO ₃ (2)	6.25	84.5	-
SiO ₂	2.65	2.4	-
Si	2.33	-	-

TABLE 1 XRR fitting results

A better fit requires to consider WO₃ thin films as two layers with different electronic densities. A first thin layer about ~7 nm at the surface and a second denser layer of ~84 nm. The determined film density of 6.25 g/cm³ leads to composition of Li_{0.36}WO₃ using Eq. (2).

In this presentation, the control of the deposition conditions leading to WO₃ thin film with a memory effect will be discussed. Then focus will be made on the XRR technique to a better characterisation of electrochromic films.

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