

## Electron Microscopy and Electrochemical Studies of WO<sub>3</sub> Thin Films Deposited by Pneumatic Spray Pyrolysis

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Smart windows are recognized as a promising technology to reduce building energy consumption, however a major challenge in electrochromic materials with application directed to smart windows is to ensure their durability and stability for at least 20 years [1]. Electrochromic materials have gained considerable interest during the last decades [1] because of their interesting properties that make them capable of a reversible change evocation in their optical properties through an applied voltage pulse, due to the insertion and extraction of charges in the material [2].

This kind of material is of great interest since it can be used for several potential applications in devices such as large area information displays [3], rear-view mirrors for automobiles [4], and smart windows [5]. WO<sub>3</sub> was deposited on the SnO<sub>2</sub>:F substrates by pneumatic spray pyrolysis at 500°C from a solution of 0.01M of WCl<sub>6</sub> in 50ml of N-dimethylformamide (DMF) with a carrier gas flow of 5 ml/min. Estimated sheet resistances of deposited FTO coatings were in between 8 and 15 Ω/□. The film was prepared immediately after the synthesis of the precursor solution.

Morphological and structural studies in pristine films and in those that were under electrochemical treatment were performed with X-rays diffraction and SEM and TEM conventional observation techniques. From XRD studies, peaks triplet at 2θ = 23.24, 23.52, 24.33° and corresponding interplanar spacing d = 3.84, 3.76 and 3.64 Å, and two minor intensity peaks at 2θ = 28.87, 41.85°, indicating monoclinic crystal structure of WO<sub>3</sub> in accordance with JCPDS-ICDD card # 41-1445. From SEM micrographs displayed in Figures 1 and 2 it can be observed noticeable differences in surface morphology: After the electrochemical experiment the surface of the WO<sub>3</sub> looks eroded after 15,000 cycling number and as a consequence of charges injection and extraction process. Electrochromic behaviors of the crystalline WO<sub>3</sub> thin films were studied in a potentiostat/gavanostat (GillAC system) using a three electrodes electrochemical cell, using 0.001 M sulfuric acid ([H<sub>2</sub>SO<sub>4</sub>], Baker) aqueous solution as electrolyte. Platinum wires were used as pseudo reference and counter electrodes.

To analyze the electrochemical behavior of the WO<sub>3</sub> thin films, Cyclic Voltammetry measurements were performed with a potential window of 2500mV to -1500 mV at 66 mV/s scan rate, the experiment was performed in 0.001 M H<sub>2</sub>SO<sub>4</sub> electrolyte, using WO<sub>3</sub> film as a work electrode, and platinum wires as reference and counter electrode. The resulting parameters of cyclic voltammetry studies were analyzed with the Randles Scevichik equation and are presumed in Table I. When the potential is carried in the cathodic direction, WO<sub>3</sub> film electrodes shown a progressive increase in blue coloration with decreasing the potential to negative values, during the cathodic scan around 1500 to 250 mV the current density stays almost unchanged until we get close to negatives values of potential when start decreasing and attains a maximum negative value at the potential of -1500 mV, at this potential we have the most intense colored state, as a result of the reduction of W<sup>6+</sup> to W<sup>5+</sup> associated with the insertion of electrons and H<sup>+</sup> ions into the WO<sub>3</sub> films. After the cathodic scan finished we can observe that we have the

absence of a well-defined “cathodic” peak, this is attributed to the back electromotive force formed within the tungsten bronze during ion insertion.

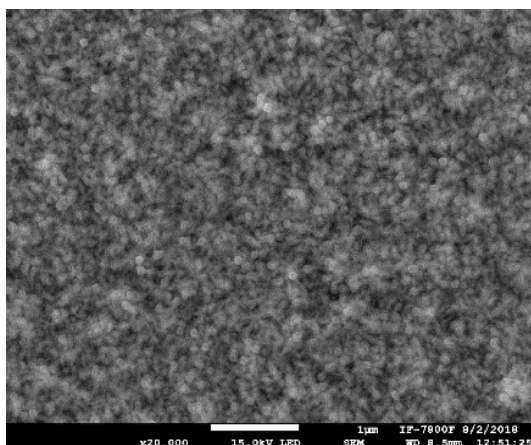


Figure 1. SEM micrograph of an as deposited film

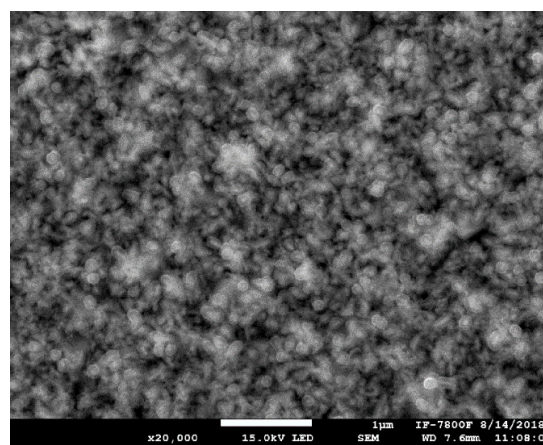


Figure 2. SEM micrograph of a film after 15,000 charges Insertion/extraction cycles

Table I

Cycle	$ip_c$ (mA/cm <sup>2</sup> )	$D_{inset}$ (cm <sup>2</sup> /s)	$V_a$ (mV)	$ip_a$ (mA/cm <sup>2</sup> )	$D_{extract}$ (cm <sup>2</sup> /s)
1	-0.9528	$1.8869 \times 10^{-4}$	-358.846	0.4394	$4.0129 \times 10^{-5}$
1000	-1.3056	$3.5429 \times 10^{-4}$	155.076	0.8473	$1.4921 \times 10^{-4}$
5000	-1.7323	$6.2372 \times 10^{-4}$	113.4179	0.6355	$8.3941 \times 10^{-5}$
10000	-2.2727	$1.0735 \times 10^{-3}$	-10.9233	0.4833	$4.8549 \times 10^{-5}$
15000	-2.505	$1.3042 \times 10^{-3}$	-37.1986	0.4257	$3.7666 \times 10^{-5}$

Table I gives the diffusion coefficient values for WO<sub>3</sub> thin film at different cycle number, reported diffusion coefficients for H<sup>+</sup> range from  $5.20 \times 10^{-12}$  to  $3.28 \times 10^{-8}$  (cm<sup>2</sup>/s) for crystalline WO<sub>3</sub> [5-7] however the values obtained in this work are higher in at least three or more magnitude orders, which indicates that our films have a great insertion–extraction capacity,

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