

Nanogravimetric studies of tungsten oxide thin films obtained by the polymeric precursor method

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Abstract

In this work, the intercalation/de-intercalation process of Li⁺ ions in the tungsten oxide matrix was investigated. The reaction mechanism involved was also investigated. The WO₃ films, prepared by the polymeric precursor method, were deposited on a Pt covered quartz crystal using the dip-coating technique. The electrolyte was 0.1 mol L⁻¹ LiClO₄ in acetonitrile. The morphology and structure of the deposit was accomplished by scanning electron microscopy and X-ray diffraction, respectively. In the electrochemical quartz crystal nanobalance results, it was observed that the mass transport as well as the kinetic processes involved are facilitated in the films cycled at lower potential sweep-rates. The mass variation data as a function of the charge variations in the anodic and cathodic regions indicate the participation of solvent molecules (acetonitrile) during the Li⁺ ion intercalation/de-intercalation process. This was confirmed by the development of a model of the species flux as a function of the potential.

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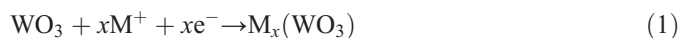
Keywords: Polymeric precursor method; EQCN; WO₃ thin films; Electrochromism

1. Introduction

Interest in WO₃ films is derived from their capacity of changing their optical properties when an electrical field is applied (electrochromism) [1–3]. WO₃ films have attracted considerable attention because of their potential application in certain devices such as displays, high-density memories, sensors, car mirrors and so on [4].

The electro-optical behavior of the electrochromic layer is widely accepted as being caused by the reversible reduction/oxidation of the W atom (W⁶⁺ ↔ W⁵⁺). These reactions involve

the double injection/extraction of electrons and ions in the solid WO₃ to maintain the overall charge neutrality, according to:



where M⁺ usually stands for H⁺ or Li⁺ [2,3].

Lithium ion insertion in thin oxide films is an important physical phenomenon and most researchers in the last decade [3] have concluded that there is a correlation between the oxide structure and the kinetics of lithium ion insertion. It is known that the morphology and structure are highly dependent on the method of synthesis that is used [5,6]. A greater interaction between the host and guest during the intercalation/de-intercalation process is observed for crystalline compounds.

Quantitative parameters of the electrochromic properties of tungsten oxide (efficiency, reversibility and kinetics of coloration–bleaching process) strongly depend on its structural,

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morphological and compositional characteristics and, therefore on the deposition techniques and deposition parameters. As an example, one of these important deposition parameters is the film thickness. In this case, it has been discussed that the coloration efficiency of WO_3 samples at the optimum voltage can be linearly improved by increasing the film thickness at a constant wavelength [7]. Besides, the optical bandgap energy of the oxide shows an increase as the film thickness decreases.

These films are typically made using several physical and chemical methods, such as reactive sputtering [8], thermal evaporation [9], anodization [10] and sol–gel [11]. The sol–gel technique presents many advantages, such as high homogeneity and low cost, nevertheless when using the sol–gel route based in alkoxides we must take into account that this method can be sensitive to the presence of water. The polymeric precursor method presented here consists of the formation of polyester in which the metallic ions are homogeneously distributed in the polymeric chain. The resulting film is not sensitive to the presence of water.

The techniques commonly used to study the electrochemical and optical behavior of WO_3 thin films are: cyclic voltammetry [12], chronoamperometry [13], electrochemical impedance [14], spectroscopic measurements [15–17] and ellipsometry [18].

Another technique that can be used to enhance the understanding of the electrochemical behavior of WO_3 thin films is the electrochemical quartz crystal nanobalance technique [11,19–21]. The EQCN technique is based on inertial effects impressed by an electrodic film on the measured resonant oscillation frequency of a piezoelectric quartz crystal thin wafer electrode [22]. This technique offers an exceptional sensitivity and is well suitable for studies of a variety of phenomena occurring in the interfaces of electrodes and solutions [23–26]. For WO_3 thin films the main discussion from the results obtained using EQCN technique is related to lithium ions intercalation/deintercalation into the oxide matrix and the role of the anions during the process. In this sense, the procedure here adopted for the flux of the lithium ions and acetonitrile species during the WO_3 reduction and oxidation cycles using the EQCN technique has not been described before.

This paper aims to study the process of the intercalation/deintercalation of Li^+ ions in WO_3 thin films obtained by the polymeric precursor method (this kind of film has not been prepared before with this route) using the EQCN technique. In this technique, the mass and charge variations are evaluated in order to give insight into the mechanism of the reaction and provide a model of the fluxes of the species generated during the processes.

2. Experimental details

A one-compartment, three-electrode electrochemical cell made of Pyrex[®] glass was used. The working electrode was a Pt covered AT-cut quartz crystal of 9 MHz fundamental frequency. The WO_3 film was prepared by the polymeric precursor method [27]. In this investigation the precursor solution was prepared by dissolving $(\text{NH}_4)_6\text{W}_{12}\text{O}_{39} \cdot x\text{H}_2\text{O}$ (ammonium metatungstate hydrate) in water under stirring at 70 °C with the addition of

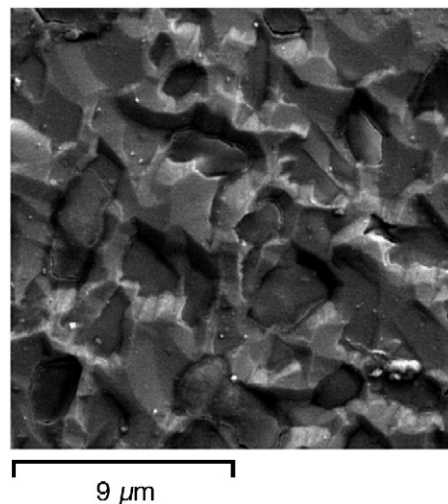


Fig. 1. Scanning electron microscopy micrograph of the WO_3 thin film deposited on Pt covered quartz crystal at 350 °C for 240 min. Secondary electron image (SEM voltage=10 kV).

citric acid (CA) to the solution at a molar ratio of 4:1 (CA:W). Ethylene glycol (EG) was added at a mass proportion of 40% (EG) to 60% (CA). After the total dissolution of the salts, the solution was stirred at 90 °C for one hour. The precursor solution was applied to a Pt/quartz crystal (geometric area=0.2 cm²) by dip coating (withdrawal speed of 10 cm min⁻¹) and it was then thermally pre-treated at 130 °C for 30 min to promote the polymerization of the precursor. Finally, the film was calcinated at 350 °C for 240 min at a heating rate of 10 °C min⁻¹. The film was characterized using X-ray diffraction analysis (diffractometer Rigaku, model Dmax 2500PC) using $\text{CuK}\alpha$ radiation ($\lambda=1.5406$ Å). The lattice parameter was calculated using silicon as the internal standard. The morphology of the film was investigated by scanning electron microscopy (SEM) (ZEISS microscope model DSM 940A) with a secondary electron image (SEM voltage=10 kV).

The sensitivity factor for the EQCN was determined following the method previously described [28]. The value of the sensitivity factor ($\Delta f/\Delta m$) thus obtained was 800 Hz μg^{-1} .

The electrochemical characterization was accomplished using a potentiostat–galvanostat (EG&G PARC, model 263 A) coupled to a quartz crystal analyzer (Seiko EG&G PARC, model QCA917), both managed by a computer (EG&G PARC, M270 software). The voltammetric and mass curves were measured in 0.1 mol L⁻¹ LiClO_4 in acetonitrile solution in the potential range from 0.5 to -0.55 V. A platinum foil was used as an auxiliary electrode. The quasi reference electrode used is a silver wire in which the redox process is the reduction of Ag^+ to Ag^0 . This electrode is suitable for non-aqueous electrochemistry presenting low impedance. Prior to the experiments, the solutions were deaired with N_2 for 30 min.

3. Results and discussion

Fig. 1 presents a micrograph of the WO_3 thin film deposited over the Pt covered quartz crystal electrode at 350 °C for

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