The optical and electrochromic properties of tungsten oxide thin layer: the effect of deposition time

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Abstract
Tungsten oxide (WO₃) thin layers were prepared on Fluorine Tin Oxide glass using the electrodeposition method. WO₃ layers were evaluated as a function of the deposition time (480 s, 600 s, 660 s and 720 s). SEM results showed that by increasing the deposition time, a gradual decrement in cracks on their surface occurred. The electrochromic properties of the WO₃ thin layers were investigated in a nonaqueous LiClO₄–PC electrolyte by means of optical transmittance, cyclic voltammogram (CV) measurements. The WO₃ thin layer with the deposition of time 600 s exhibited a noticeable electrochromic performance with the variation of transmittance being up to 58.26% at 633 nm. The CV measurements also revealed that the WO₃ thin layer with the deposition time of 600 s had a high electrochemical reaction activity and reversibility due to its highly porous structure.

Keywords: tungsten oxide, electrochromic properties, electrodeposition, cyclic voltammogram

1. Introduction
Electrochromic (EC) materials modulate their optical properties depending on charge (electrons and ions) insertion/extraction in the EC materials [1,2]. The optical modulation of EC materials in the visible and infrared regions has received much attention since 1980, both in the science and industry. Tungsten oxide (WO₃) is one of the most promising materials for the spacecraft thermal control or the military camouflage against IR sensors due to its chemical stability and UV radiation resistance [3]. EC device is comprised of an EC active layer, an electrolyte, and an ion storage layer. EC active layer is an active layer inserting or extracting ions, resulting in the coloration and bleaching. WO₃ is an EC material which has been widely investigated as an active EC electrode (working electrode). Ions like H⁺ or Li⁺ in the electrolyte are intercalated into the WO₃ thin layer to reduce WO₃ to MₓWO₃, a blue colored state, when a negative electric field is applied. Under positive electrical field, i.e., oxidation state, the reduced MₓWO₃ is oxidized and returned to the WO₃ original form, which is as follows [4, 5].

\[
\text{WO}_3 + x\text{Li}^+ + xe \rightleftharpoons \text{Li}_x\text{WO}_3 \quad (1)
\]

Clear → Dark blue

EC devices can be used for transmittance modulation, reflectance, thermal emittance and scattering, thus opening new venues for applications in optical technology, including smart windows for energy efficient building [6]. The advantages of EC materials include their open circuit memory, high coloration efficiency and low electric power [7]. WO₃ thin layers have been synthesized using several methods such as sol–gel [8], electrodeposition synthesis [9, 10], template method [11], anodic oxidation [12], chemical vapor deposition [13], electro spinning [14], electron beam evaporation [15], hydrothermal oxidation [16], atmospheric pressure plasma jet [17], etc. In this work, electrodeposition method was employed to prepare WO₃ thin layers with high porous and high surfaces. Our aim was to investigate the EC properties of electrodeposited WO₃ thin layers as a function of the deposition time (480 s, 600 s, 660 s, 720 s) in order to study the morphology of these thin layers, as well as their optical and electrochemical properties.

2. Experimental details
2.1. Deposition of the WO₃ thin layer
To prepare the peroxtungstic acid solution, 3.25 gr of tungsten metal powder (99% pure) was dissolved in 20 ml 30% H₂O₂ (Qualigen) and 2 ml distilled water to obtain a clear solution. This solvent was kept at a low temperature (2°C) for 8 days. The solution was then mixed with the same amount of anhydrous ethanol at room temperature under continuous
stirring. The liquid was heated to 60°C for 30 min before deposition. The solution was then changed to a bright yellow liquid.

The layers were deposited under potentiostatic conditions in a three-electrode electrochemical cell with a fluorine thin oxide (FTO) coated on the glass substrate with the dimensions 2.5×2.5 cm² as the working electrode, a Saturated Calomel Electrode (SCE) as the reference electrode, and a platinum sheet serving as the counter electrode. The working electrode was subjected to a constant cathodic potential of -493 mV for different times (480 s, 600 s, 660 s, 720 s) at the room temperature.

3. Deposition of the NiO thin layer
NiO thin layer was prepared using the Chemical Bath Deposition (CBD) method. The solution for CBD was obtained by mixing 40 ml of 1 M nickel sulfate, 30 ml of 0.25 M potassium persulfate and 10 ml of aqueous ammonia at the room temperature. FTO coated on glass substrates was masked with a polyimide tape to prevent deposition on the nonconductive sides. The FTO samples were placed in the freshly made solution and kept at 20°C for 60 min to deposit the precursor layer under constant stirring. Then they were washed with deionized water. After removing the tape masks, the coated samples were dried at 75°C and annealed at the temperature of 300°C in air for 1.5 h.

The surface morphology was observed by field emission scanning electron microscopy (FESEM; Hitachi S-4160). To measure the layers optical transmittance the UV spectrum was performed using a UV-1800 PC Shimadzu spectrophotometer. Transmission spectra were recorded for the colored and bleached thin layers in the 300-1100 nm wavelength range with respect to air. The Cyclic Voltammogram (CV) was used to measure the EC properties of the thin layers. The measurements were performed in a three-electrode electrochemical cell between -1.5 and +1.5 V, where a WO₃ thin layer was deposited on the FTO coated glass substrate was used as the working electrode. SCE was selected as the reference electrode and the Pt foil was used as the auxiliary electrode. In this research, lithium perchlorate in propylene carbonate with the 1M density (1M LiClO4-PC) was used as an electrolyte solution with the scan rates of 50 mv/s (BEHPAOOH, BHP2063+).

4. Results and discussion
4.1. Surface morphology of the layers
Figure 1. depicts the SEM micrograph of the surface of layers deposited with different deposition times (480 s, 600 s, 660 s, 720 s). The surfaces of the layers were fairly uniform with only a few large aggregates of WO₃ particles on them. SEM results showed that by increasing the deposition times, a gradual decrease in the cracks appeared and there was an increase in the aggregates of WO₃ particles on their surface. Therefore, the layer deposited with time 480 s, in contrast to the layers deposited for longer times, showed a better open structure.

4.2. Optical properties of the layers
Figure 2. shows the optical transmittance spectra within the
6. Electrochromic performance of the layers

Figure 3 shows CV for different WO₃ thin layers with different deposition times (480 s, 600 s, 660 s, 720 s). All data presented here were obtained with the same sweep rate of 50 mV/s after 9 consecutive coloration-bleaching cycles using the electrolyte solution 1 M LiClO₄-PC. The coloration current, an indicator of the speed of Li⁺ intercalation in the thin layers, was higher with the deposition time of 480 s and 600 s, respectively; this was lower for the layers with other deposition times. It is usual for a structure with more cracks to allow better penetration of lithium ions. The visible transmittance of the layer with the deposition time of 480 s was ∼62.4 %, which dropped to ∼50% in the solar region due to an increase in the reflectance from the underlying FTO substrate near the infrared region. This value was higher than the reported AT values for WO₃ thin layers deposited by cathodic electrophotocatalytic deposition using a peroxotungstate deposition bath of the Na₂WO₄·2H₂O salt (that was a complex in distilled water with concentrated hydrogen peroxide added), exhibiting a ΔT =58.7% at λ=700 nm [18]. The high transmittance (T ≈ 63%) in the visible range was retained for WO₃ thin layers deposited by sol-gel and it was dropped to ∼42-44% in the solar region due to an increase in the reflectance from the underlying FTO substrate near the infrared region [19]. Electrochemical measurements on WO₃ thermal evaporation layers of tungsten trioxide powder exhibited a ΔTVIS = 34.5% [20].

The WO₃ thin layers were successfully prepared by the cathodic electrodeposition, such as A.J. MORE et al [21], T. Pauporte et al (CE=62-66 cm² C⁻¹) [22], and M Deep et al. [23] (CE=70 cm² C⁻¹).

It was obvious that the thin layer deposited with the time of 600 s offered the best changes for transmission modulation, absorption in the colored state, and coloration efficiency.

7. Conclusion

The WO₃ thin layers were successfully prepared by the electrodeposition technique. The CE of the layers was found to be considerable, making them suitable in the production of...
WO₃-based EC devices. The open structure of the layer with the deposition time 600 s showed high transmission modulation (ΔT ∼58.26%) and coloration efficiency (CE = 98.4 cm² C⁻¹ at λ = 638 nm). The poor performance of the layers deposited with the time of 660 s and 720 s was related to the dense structure. Therefore, the electrochemical reversibility for the redox processes involving the insertion and extraction of lithium ions was attained only for the layer with the deposition time of 600 s. This layer also exhibited an excellent transmittance modulation effect in the visible region. The surface morphology of the layers was investigated. The results indicated that the layer with the deposition time of 600 s had remarkable reversible EC properties and its EC reversibility was also very good in the visible region.

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