

# Study of electrochromism in Ti:WO<sub>3</sub> films by sol-gel process

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## ABSTRACT

Electrochromism in sol-gel deposited WO<sub>3</sub> films containing TiO<sub>2</sub> has been observed. The films are deposited by spin coating from peroxo-polytungstic acid and titanium isopropoxide precursors. The films were fabricated on quartz and SnO<sub>2</sub>:F coated glass substrates. Films were heat treated at 150 °C. Morphology of the films was examined by scanning electron microscopy, which indicated that the films were smooth and had a pore free surface.

Results will be presented detailing the optical switching during electrochemical lithium intercalation. These results will be used to compare the performance of the Ti doped WO<sub>3</sub> films with other electrochromics. The Ti:WO<sub>3</sub> films all color cathodically, and the color state is a neutral grayish blue color, while the bleached state is transparent and colorless. Results of the cyclic stability will also be presented. The neutral color of the Ti:WO<sub>3</sub> films means that electrochromic windows based on Ti:WO<sub>3</sub> may have significant advantages over WO<sub>3</sub> - based windows.

A detailed analysis of the optical properties of the bleached and colored states of the films will be presented. The dynamics of coloration for these films is also under investigation, and preliminary results will be presented.

**Key Words:** electrochromism, Ti:WO<sub>3</sub>, sol-gel deposition, electrochemistry

## 1. INTRODUCTION

Over the past decade, numerous transition metal oxides have been extensively investigated for their use in electrochromic switching devices (ECD).<sup>1</sup> The most commonly used electrochromic material in ECD has been amorphous tungsten oxide WO<sub>3</sub>.<sup>2-3</sup> Its advantages are high coloration efficiency and reasonable cyclic stability. Recent emphasis in the development of ECD has been focused to the degradation of tungsten oxide films during lithium ion insertion and extraction. Recent structural and electrochemical investigations have shown that the electrochromic stability of WO<sub>3</sub> films improved by adding TiO<sub>2</sub>.<sup>4-6</sup>

Electrochromic WO<sub>3</sub> films are usually prepared by conventional deposition techniques including sputtering<sup>5</sup> vacuum evaporation,<sup>7-8</sup> and e-beam evaporation.<sup>9</sup> The sol-gel process are used to prepare electrochromic films on a variety of substrates.<sup>10-12</sup> The sol-gel process is based on hydrolysis and condensation of molecular precursors such as metal alkoxides or hydroxylated metal ions in a suitable organic solvent.<sup>13</sup> In this process molecular precursors are transferred into an oxide network by inorganic polymerization reactions. Sol-gel deposition is performed at room temperature and presents many advantages for its simplicity, high productivity and ability to coat large areas. In addition, the sol-gel process is well suited to the deposition of mixed metal oxides as the stoichiometry can be readily varied.

In this paper, we report synthesis and electrochromic characteristics of titanium doped tungsten oxide Ti: WO<sub>3</sub> films. The effect of the dopant concentration on the primary electrochromic parameters was investigated. X-ray diffractometry (XRD), scanning electron microscopy (SEM), optical spectroscopy, and cyclic voltammetry were the principal techniques used to study the properties.

## 2. EXPERIMENTAL

### 2.1 Synthesis of the coating solutions

Tungsten oxide coating solutions were synthesized from peroxo-polytungstate precursors. Preparation of the



WO<sub>3</sub> coating solutions have already been described in detail elsewhere<sup>14-15</sup> and so will only be briefly described here. Stable tungsten oxide coating solution were synthesized using a route based on dissolution of metallic W (1.0-1.3  $\mu\text{m}$  in particle size) powder in a 30% hydrogen peroxide H<sub>2</sub>O<sub>2</sub> aqueous solution. It was dried in a rotary evaporator at 25 °C after removing excess H<sub>2</sub>O<sub>2</sub> catalytically with a platinized Pt net. An amorphous yellowish powder (solid peroxotungstic ester, W-IPA) was obtained. The coating solutions were prepared immediately before use by dissolving W-IPA into ethanol EtOH in the ratio of 2 mol (in terms of total metal) to 1:1. The variation in titania content was achieved by simply adding titanium ethoxide Ti(O-Et)<sub>4</sub> with stirring. The doping concentration Ti/W mole ratio as a percentage was varied from 0-20 % in the solution. The resulting solutions were remarkably stable for 3 weeks, whereby the addition of Ti(O-Et)<sub>4</sub> even seemed to increase the stability. Figure 1 shows the flow chart of the experimental procedure followed to produce Ti:WO<sub>3</sub> films.

## 2.2 Fabrication of electrochromic films

Precleaned quartz and transparent conducting Tec 15 glass substrate (14.5 $\Omega/\text{cm}^2$  fluorine doped tin oxide, Libbey-Owens-Ford Corporation) were used as substrates. The coatings were fabricated by spin coating on a custom-made spin coater. Ti:WO<sub>3</sub> films were produced under ambient atmosphere with a spinning rate of 1200 rpm. The films were fired in a circulating air oven to a temperature of 150 °C at a rate of 1 °C/min for one hour. The average fired thickness of the single layer Ti:WO<sub>3</sub> films was determined to be 0.25-0.27  $\mu\text{m}$  depending on the titanium concentration. A slight increase of the film thickness with increasing titanium content was observed. All coatings were uniform and continuous.

## 2.3 Characterization of coatings

The deposited films were analyzed using various characterization techniques. The film thickness was measured using Alpha-Step 200 surface profiler (Tencor Instruments). Structural investigation was performed by X-ray diffraction. XRD spectra were collected for doped and undoped WO<sub>3</sub> films deposited on soda-lime glass. A Philips Model PW 1710 diffractometer with a Ni-filtered CuK $\alpha$  ( $\lambda = 1.542 \text{ \AA}$ ) source was used for XRD examinations. Step scans with a step size of  $2\theta = 0.02^\circ$  were performed in the range  $5 < 2\theta < 90^\circ$ . The surface morphologies of the films were observed by a Jeol Model JSM 6400 scanning electron microscope. A gold coating was deposited on the samples to avoid charging the surface. The in-situ spectroelectrochemical measurements were carried out using Shimadzu Model UV 3100 double beam spectrophotometer in the 0.3-1  $\mu\text{m}$  wavelength range. Electrochemical experiments were performed in a three electrode cell. The films were cycled in a non-aqueous 1M LiClO<sub>4</sub>/propylene carbonate solution at room temperature. Cycling was carried out galvanostatically. A Pt foil was used as the counter electrode and Ag/AgCl as a reference electrode. The area of the film/electrolyte interface was 2 cm<sup>2</sup>. The voltammetric and chronoamperometric measurements were accomplished in a Solatron 1286 electrochemical interface analyzer. Cyclic voltammetry was performed at the voltages between -1.5 and 0.5 V relative to Ag/AgCl with a scan rate of 10 mV/s. Current was recorded during 10, 100, and 500 cycles under the conditions described above.

## 3. RESULTS AND DISCUSSION

The films were smooth, highly uniform, and showed good adhesion to the substrate. They also showed long term stability with respect to their optical and electrochemical properties. Films of various thicknesses were obtained by varying the amount of doping material. By observing the surface morphology and optical transparency, it was found that a heat treatment of 150 °C was necessary.

X-ray diffraction studies were carried out on doped WO<sub>3</sub> films heat treated in the 150-450 °C temperature range. In Figure 2, XRD patterns are presented for the Ti: WO<sub>3</sub> films. All Ti doped WO<sub>3</sub> films heat treated below 300 °C were completely amorphous without any significant diffraction peaks of TiO<sub>2</sub> and WO<sub>3</sub> films. After firing the films at 400 °C a set of peaks appeared which belongs to TiO<sub>2</sub> and WO<sub>3</sub>. Analysis of XRD spectra on the crystalline Ti:WO<sub>3</sub> films showed TiO<sub>2</sub> peak due to (101) plane in the anatase phase and WO<sub>3</sub> peaks due to (111) and (021) planes in the hexagonal lattice.

Surface morphologies of 5 mole % Ti doped WO<sub>3</sub> films heat treated at 150 °C are shown in Figure 3. It is observed that in all cases films are relatively smooth with few pinholes or microcracks throughout the film. SEM cross sectional morphology of the films show that both undoped and Ti doped WO<sub>3</sub> films are very uniform. It is seen from the cross sectional examinations that surface roughness increases with increasing titanium concentration from 5-20 mole %. However, non-uniformity is not observed even in the 20 % Ti doped film.



Coloration of films was carried out in a nitrogen-purged three electrode cell. Cyclic voltammetry was used for lithium insertion reaction. Cyclic voltammograms (CV) for four different compositions are shown in Figure 4. The shape of the voltammograms for films with < 5 mole % Ti are essentially similar as for WO<sub>3</sub> films. Films with Ti content below 5 mole % had similar current density as undoped WO<sub>3</sub> films. Films with Ti content above 5 mole % had lower charge density and therefore a lower absorption. Voltammograms for films with a Ti content above 5 mole % had a noticeable dependence on Ti doping. Generally, current and charge densities decreases with increasing Ti content. The CV of 5 mole % Ti doped film is shown in Figure 5. Anodic peaks on the bleaching cycle are observed at about -0.7 V vs Ag/AgN<sub>3</sub> and associated with Li<sup>+</sup> extraction. Figure 6 shows the transmittance spectra of 5 mole % Ti doped WO<sub>3</sub> films polarized at the -1.5 and 0.5 V vs Ag/AgCl. Spectral behavior was quite similar to the undoped WO<sub>3</sub> films. A further increase in Ti content resulted in a slight decrease in colored state transmittance. The coloration efficiency (CE) of Ti:WO<sub>3</sub> films was determined spectroscopically using an in-situ galvanostatic ramp. Electrochromic coloration efficiency ( $\eta$ ) calculated using optical density ( $\Delta OD$ ) values ( $\Delta OD = \log(T_b/T_c)$  where b: bleached, c: colored)  $\eta$  defined as  $\Delta OD$  per unit charge injected ( $\eta = \Delta OD/Q$ ). Coloration efficiency recorded at a wavelength of 685 nm. It decreases with increasing titanium content (5-20 mole %). Refractive index of the Ti:WO<sub>3</sub> films were determined from transmittance measurements by evaluating interference minima and maxima in the wavelength range 800-1000 nm.<sup>17</sup> For all samples the refraction index increases with Ti-doping. The results of the electrochromic properties of films are listed in Table 1.

Table 1. Optical characteristics of Ti:WO<sub>3</sub> films after reduction at -1.5 V vs Ag/AgCl.

Ti/W (mole %)	Film thick. (nm)	CE (Color) cm <sup>2</sup> /C	n (800-1000 nm)
0	250	40	1.87
1	253	41	1.88
5	262	46	1.88
10	263	42	1.89
15	265	36	1.90
20	268	33	1.91

Figure 7 shows the transmittance response of Ti:WO<sub>3</sub> films. On application of -1.5 V vs Ag/AgCl to the films, the coloration process begins. In the bleaching process, WO<sub>3</sub> film returns to the original clear state in 30 s. In contrast, Ti:WO<sub>3</sub> film bleaches in 65 s. As shown in Figure 7, the coloration process is considerably slower than bleaching in the WO<sub>3</sub> films. It is noted that Ti:WO<sub>3</sub> films demonstrate perfect reversibility of coloration bleaching cycles within the given potential range. The films were found stable over 1000 cycles.

#### 4. CONCLUSION

Titanium doped tungsten oxide films deposited from peroxo-polytungstate precursors were investigated by using electrochemical and physical analysis methods. The sol-gel process with spin coating deposition was found to be an effective way for producing Ti:WO<sub>3</sub> films with good optical quality. Additions of the titanium dopant to the tungsten oxide coating solutions lead to an increased solution stability and improved coating qualities. Ti:WO<sub>3</sub>(1-5 mole %) films showed improved electrochromic property under Li<sup>+</sup> insertion/extraction. The titanium doped film with the best overall property was about 5 mole % Ti:WO<sub>3</sub>. The results led us to undertake a more detailed study of amorphous Ti:WO<sub>3</sub> films, which at present seem to be very promising for ECD applications.

#### 5. ACKNOWLEDGEMENTS

In the early part of this work, we benefited greatly from discussions with Dr. Anoop Agrawal and Dr. Carl Lampert; we would like to thank them for their assistance. We would like to thank Dr. Yalcin Tanes for use of the structural characterization facility in the Arcelik Research Laboratory. This work was supported by the I.U Research Foundation under Contract No. O-2 57-97.



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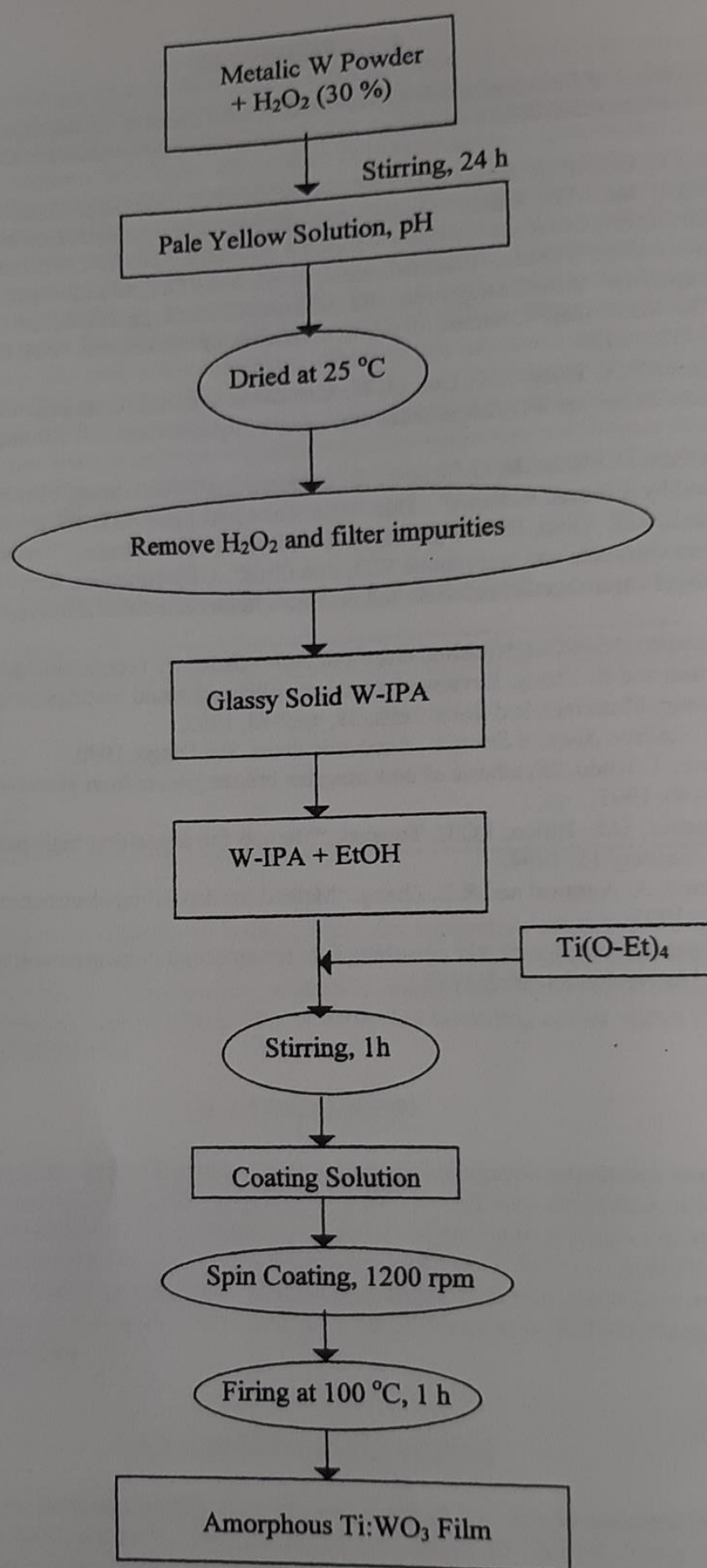


Fig. 1: Process flowchart for the synthesis of Ti:WO<sub>3</sub> precursor and film.



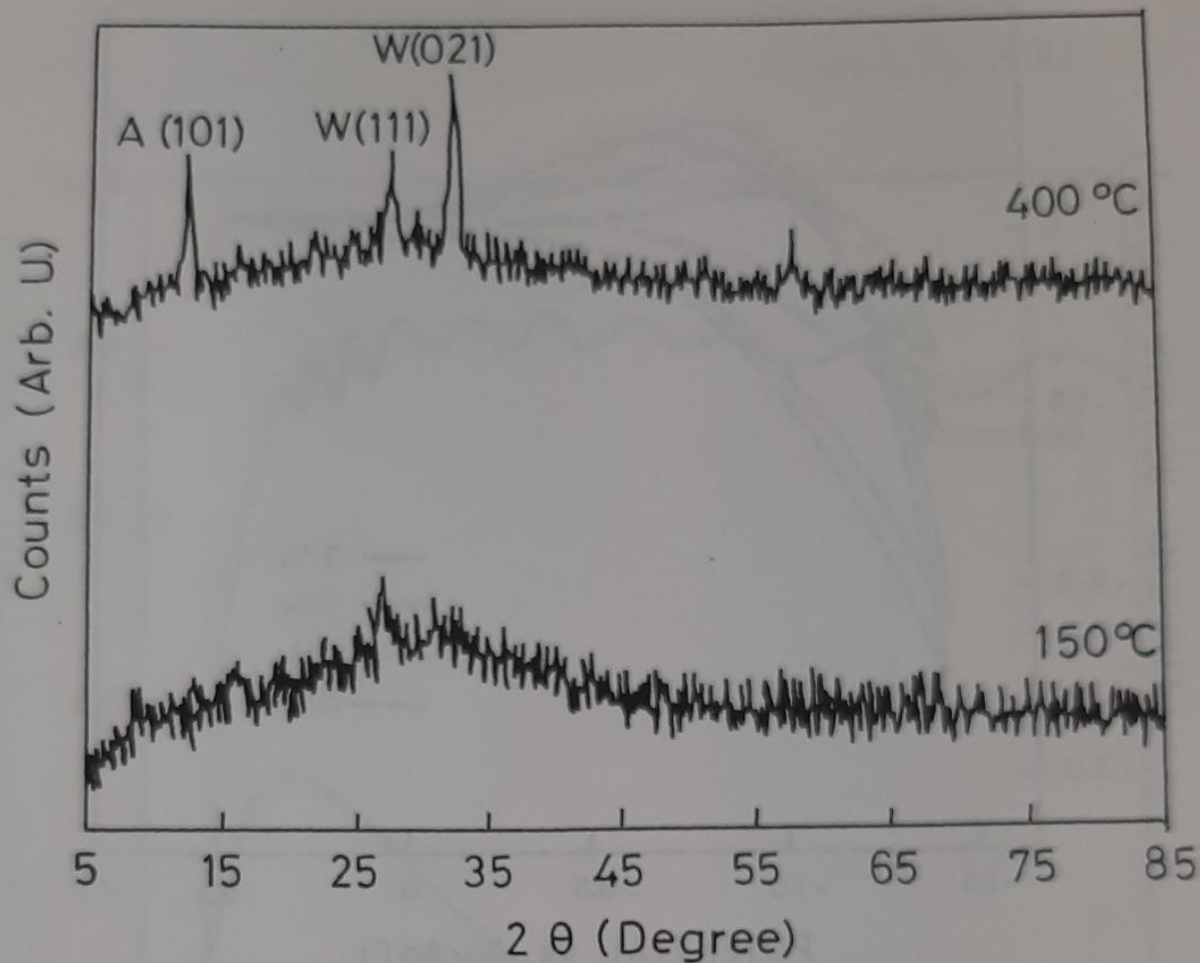


Fig. 2. XRD spectra of Ti:WO<sub>3</sub> films deposited on soda-lime glass substrates.



Fig. 3. SEM micrograph of a 0.26 μm thick of 5 mole % Ti doped WO<sub>3</sub> film deposited on a quartz substrate.

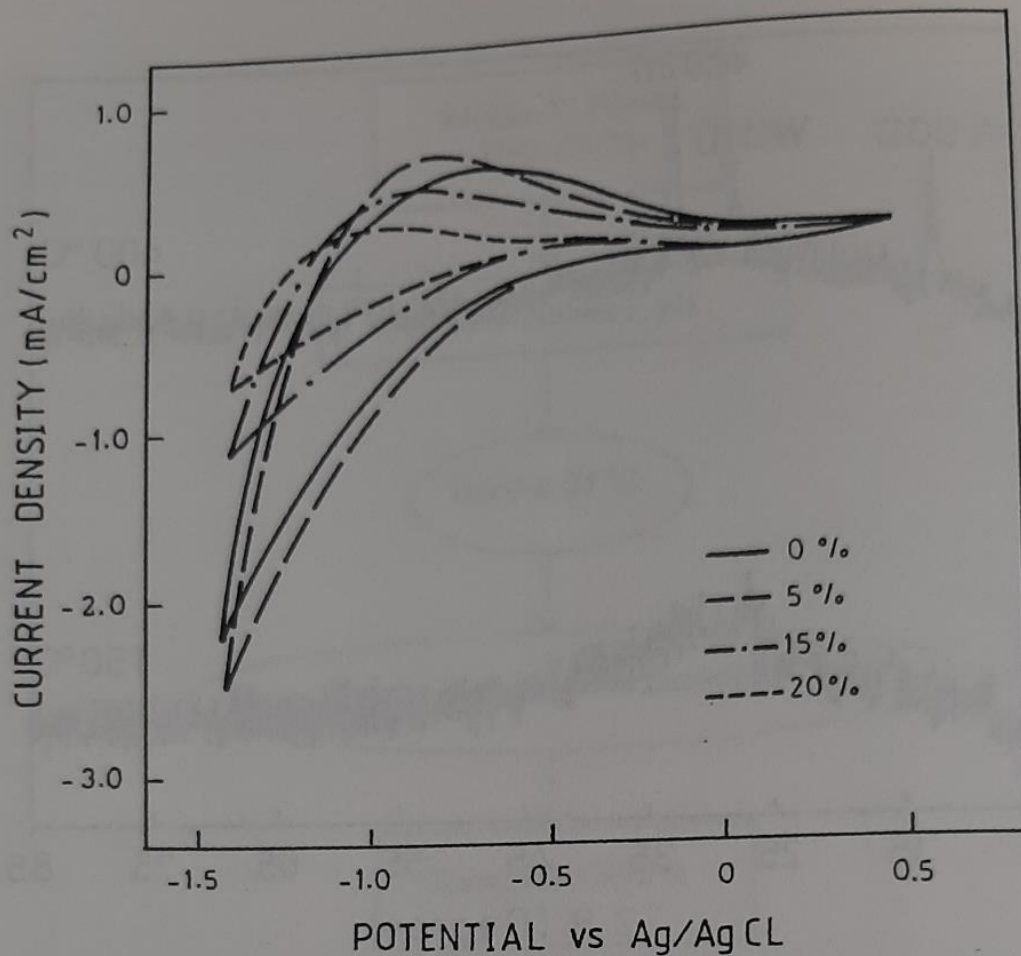


Fig. 4. Cyclic voltammograms of amorphous  $\text{Ti:WO}_3$  films in  $0.5 \text{ M LiClO}_4/\text{PC}$  Solution for different compositions.

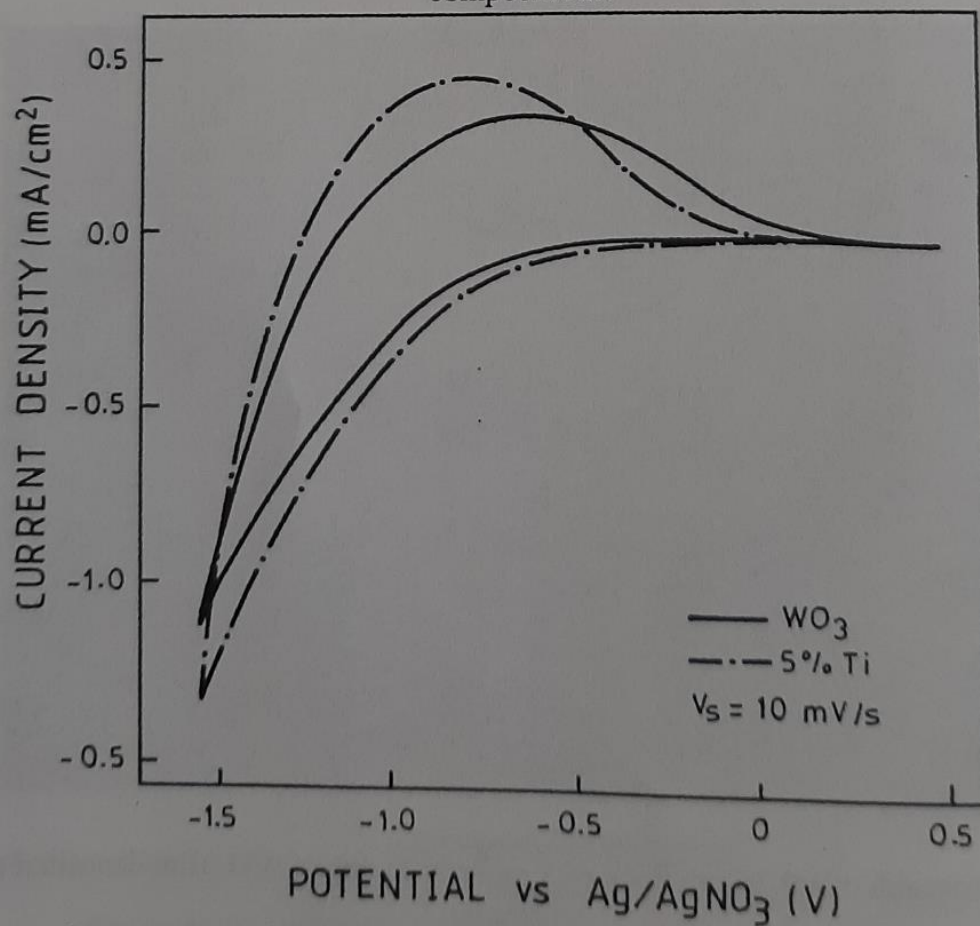


Fig. 5. Cyclic voltammograms of 5 mole % Ti doped  $\text{WO}_3$  films in  $0.5 \text{ M LiClO}_4/\text{PC}$  solution for different scan rates.

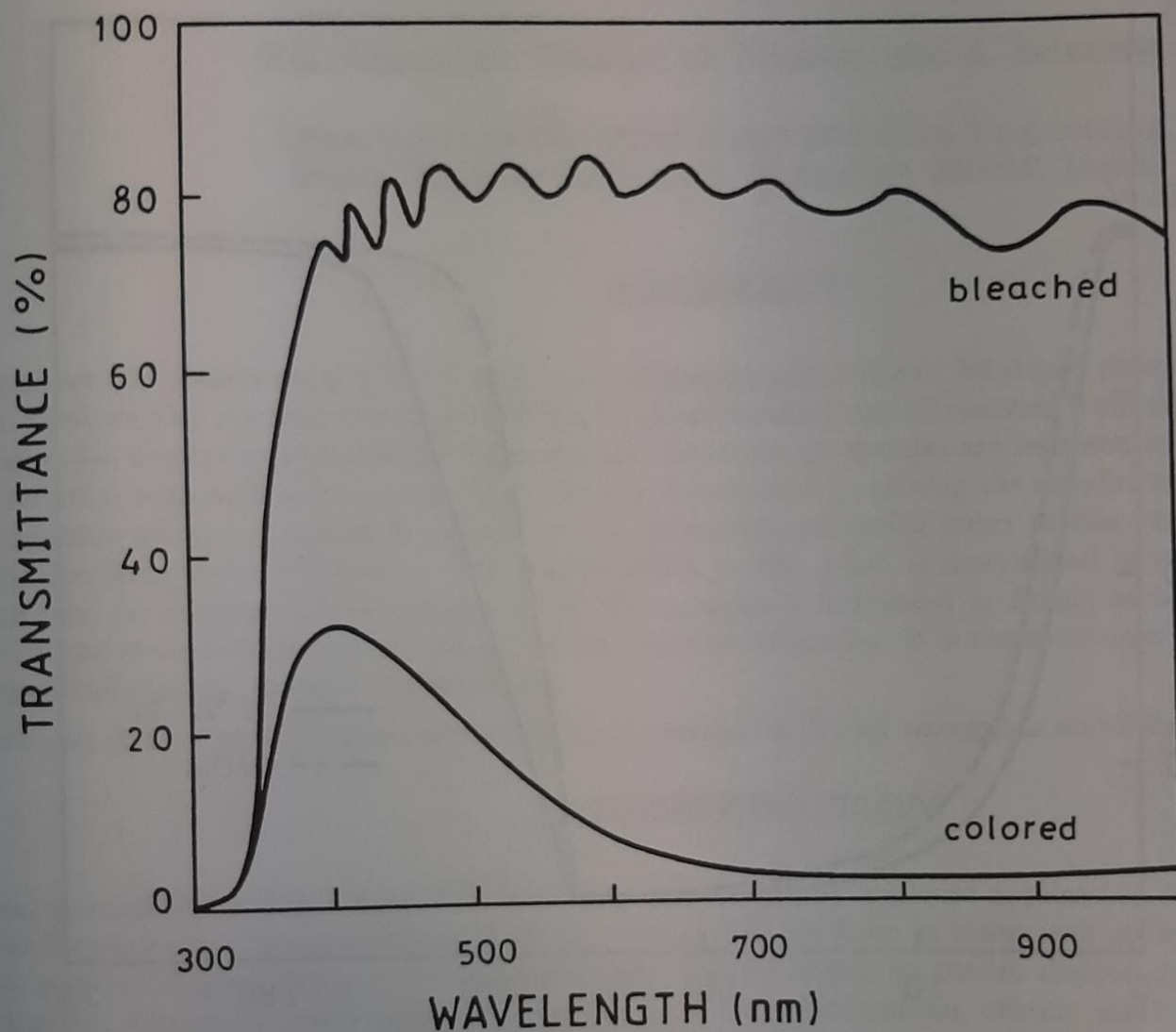


Fig. 6. In-situ UV-Vis spectra of a 0.26 μm thick Ti:WO<sub>3</sub> (5 mole %) film in the reduced (dotted line, colored at -1.5 V) and oxidized (solid line, bleached at 0.5 V) state.



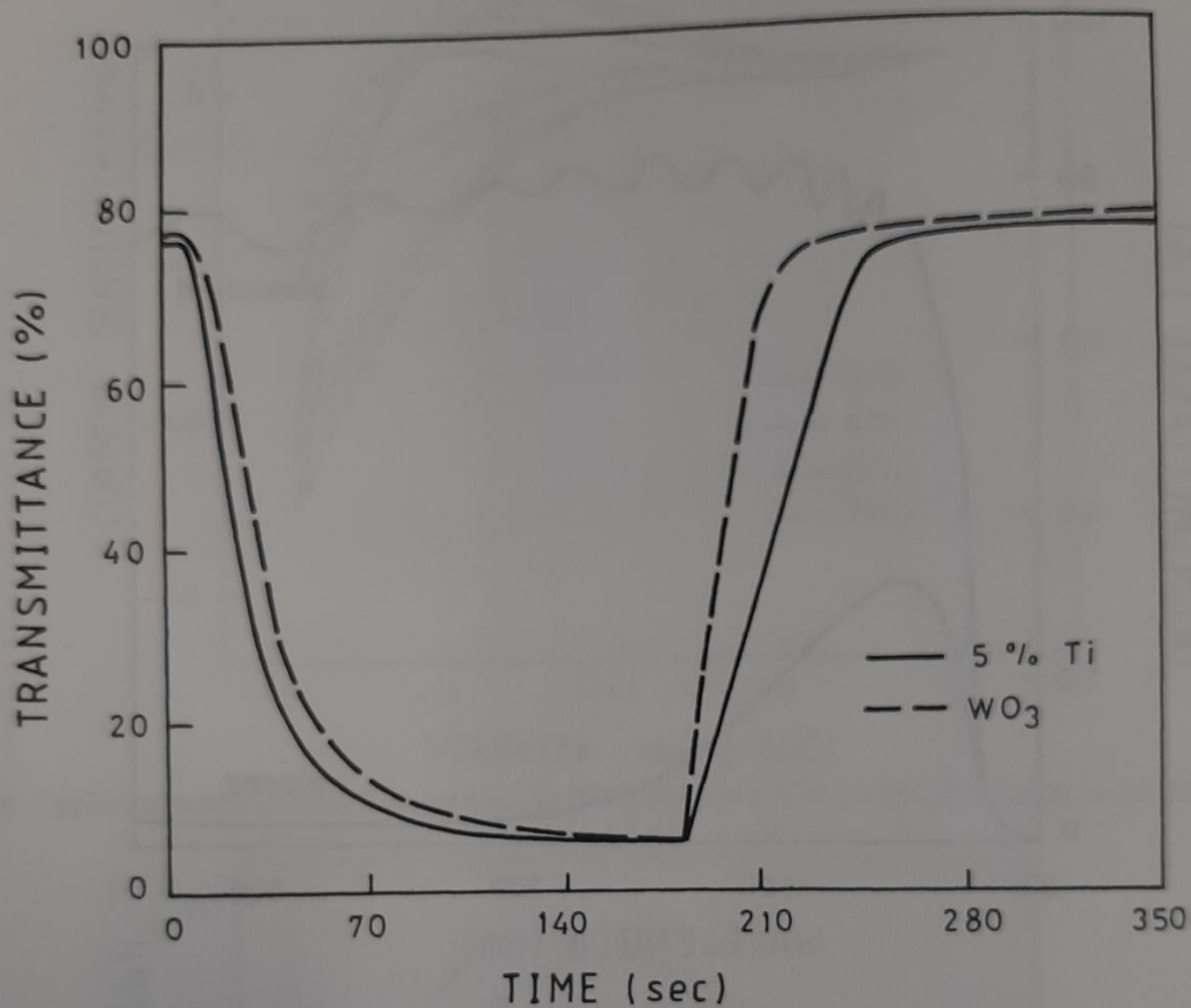


Fig. 7. Optical switching response of 5 mole % Ti doped WO<sub>3</sub> film by the application of square wave potentiostatic pulses between -1.5 and 0.5 V vs Ag/AgCl, recorded at 550 nm.