

César O. Avellaneda · Luis O.S. Bulhões

Electrochromic properties of WO₃ and WO₃:P thin films

Received: 10 June 2002 / Accepted: 11 June 2002 / Published online: 7 August 2002
© Springer-Verlag 2002

Abstract WO₃ and WO₃:P (5 mol% H₃PO₄) thin films were prepared using the sol-gel route and the electrochromic properties of the films were investigated using in situ spectroelectrochemical methods. The measurements were performed in propylene carbonate solution with 0.1 M LiClO₄ as electrolyte. During the cathodic polarization at -0.8 V a blue coloration is observed with a reversible variation between 14% and 84% of the transmittance at $\lambda=633$ nm. The kinetics for the bleaching process is faster for the WO₃:P film than for the undoped WO₃ film.

Keywords Electrochromism · Tungsten oxide · Sol-gel

Introduction

Certain materials, referred to as electrochromic materials, are known to change their optical properties in response to the application of an electric current or an electric potential. This property has been used to produce electrochromic devices which can be controlled to transmit optical energy selectively. Such electrochromic devices typically have a structure consisting of sequential layers including an electrically conducting material, an active electrode formed by an electrochromic material, an ionic conductive layer, a counter electrode film and another electrically conductive layer.

Electrochromism in transition metal oxides and electrochromic devices (ECD) have been extensively investigated since their discovery by Deb [1] in 1973. Tungsten trioxide (WO₃) film is the most investigated

electrochromic material and it is considered a viable material for use in electrochromic devices, such as smart windows, sunroofs, rear and side view mirrors [2, 3, 4]. Several papers have described the fabrication of tungsten oxide thin films for electrochromic applications. These films are typically made by evaporation [5], sputtering [6], anodization [7] and the sol-gel method [8, 9, 10, 11, 12, 13, 14, 15, 16], the latter methodology being very attractive owing to its low cost and to the formation of homogenous films.

Several sol-gel routes have been developed for the fabrication of WO₃ thin films, and the earliest alternative to produce sol-gel WO₃ films was the acidification of sodium tungstate [8, 9]. The major advantage of this method is the formation of WO₃ at room temperature; however, the stability of the solution, which is an important parameter for industrial production, was not found to be adequate. The second method is by means of peroxopolytungstic acid [10, 11], in which tungsten and tungsten carbide powders are dissolved in an aqueous solution of hydrogen peroxide. Another route uses tungsten alkoxide [12], the classical sol-gel route, but this method is expensive and consequently is not useful for industrial applications. The reaction of tungsten oxychloride (WOCLO₄) with isopropanol, proposed by Livage [13], produces a sol that is stable for several months and the process is inexpensive. Finally, two interesting results about the improvement of WO₃ film production have been published. Cronin et al. [14, 15] patented the preparation of a WO₃ electrochromic coating solution by reacting metallic tungsten with hydrogen peroxide and acetic acid. The resulting product, a tungsten peroxy acid, was then esterified by reacting it with alcohol to produce a tungsten peroxy ester derivative (PTE). Denesuk et al. [16] proposed a novel methodology for the synthesis of WO₃ thin films. The precursor sol was prepared using the route proposed by Cronin et al. [14] and to the final solution a 32 mol% solution of dehydrated oxalic acid was added. These films displayed a homogeneous amorphous/crystalline hybrid structure.

C.O. Avellaneda · L.O.S. Bulhões (✉)
LIEC – Laboratório Interdisciplinar de Eletroquímica e Cerâmica,
Departamento de Química,
Universidade Federal de São Carlos,
C.P. 676, CEP 13565-905,
São Carlos-SP, Brazil
E-mail: dlob@power.ufscar.br
Tel.: (55) (16) 2608214
Fax: (55) (16) 2615215

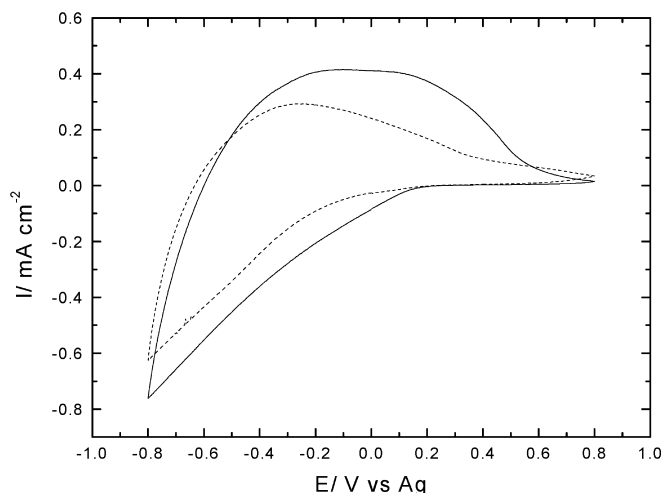


Fig. 1 Cyclic voltammograms for WO_3 (dotted line) and $\text{WO}_3\text{:P}$ (solid line); 0.1 M LiClO_4 dissolved in propylene carbonate at a potential scan rate of 50 mV/s

The scope of this paper is to discuss the fabrication and characterization of the WO_3 and $\text{WO}_3\text{:P}$ (5 mol% H_3PO_4) thin films, which were produced by the sol-gel method in combination with the dip-coating technique. In order to improve the electrochromic properties of tungsten oxide we have studied the effect of phosphorus insertion on the electrochromic behavior of the film. It is well known that a mixture of W^{6+} and P^{5+} ions in the oxide matrix gives rise to the formation of different heteropolyanions [17].

Experimental

Preparation of the sol

In the present paper, the route proposed by Cronin et al. [14] was used for the preparation of the WO_3 sol, in which metallic tungsten reacts with hydrogen peroxide (30%) and acetic acid, keeping the

solution temperature between 0 and 12 °C during 24 h. Then the product was filtered and evaporated to dryness, resulting in a transition metal-peroxy acid powder that reacts at room temperature with ethanol to form a transition metal-peroxy ester derivative; 5 mol% H_3PO_4 was added to the final solution [18, 19].

Preparation of the films

The films were deposited by the dip-coating method on glass slides covered with an indium-doped SnO_2 film (ITO, Donnelly, 14 Ω/\square), previously cleaned and rinsed with bi-distilled water, ethanol, and then dried at room temperature. The ITO substrates were withdrawn from the solution in ambient atmosphere (RH < 60%) at a rate of 10 cm/min, with the samples being subsequently dried in air at room temperature and then thermally treated at 120 °C for 1 h. The resulting coatings after one dip were transparent and homogeneous, without any visual cracks.

Measurement technique

Cyclic voltammetry and chronoamperometry experiments were performed with an EG&G PAR model 273 computer-controlled potentiostat galvanostat, driven by 270 Electrochemical Analysis software. A conventional three-electrode cell was used; the counter-electrode was a platinum foil of 1 cm^2 area and the quasi reference electrode was a silver wire. The electrolyte was 0.1 M LiClO_4 dissolved in propylene carbonate (PC). The cell was previously purged with dry N_2 gas. Visible spectra of the films were recorded in situ with a model 5G Varian spectrophotometer, by placing the coated substrate in a special electrochemical cell with two flat glass windows.

Results and discussion

The cyclic voltammograms for doped and undoped WO_3 samples, obtained by sweeping the potential in the range from -0.8 V to +0.8 V, are depicted in Fig. 1. Initially, the two samples were almost transparent; when a more negative potential was applied, an increase in the cathodic current and a blue color can be observed, which is associated with WO_3 oxide reduction and simultaneous Li^+ insertion. Changing the potential sweep

Fig. 2 In situ visible transmittance measurements of (a) WO_3 and (b) $\text{WO}_3\text{:P}$: as deposited (solid line), colored (dashed line), and bleached (dotted line)

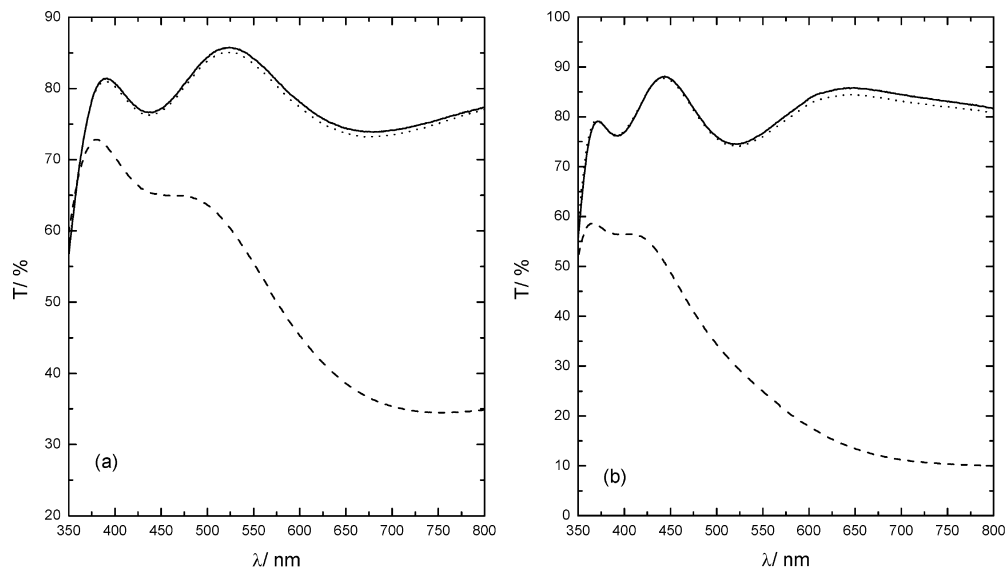


Fig. 3 Kinetics measurements measured at 633 nm: (a) WO_3 and (b) $\text{WO}_3\text{:P}$, using -0.8 V (colored) and $+0.8$ V (bleached) during 15 s

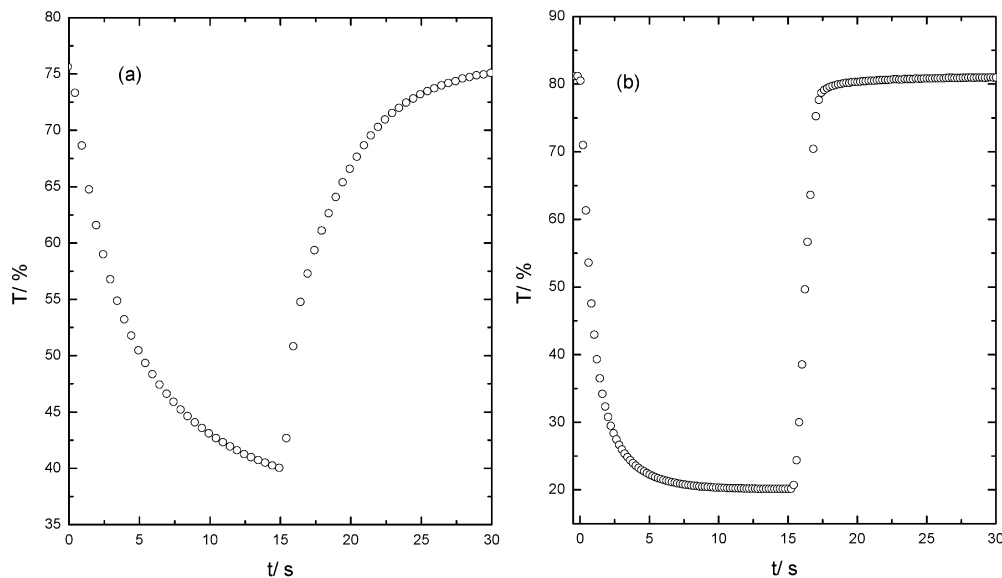
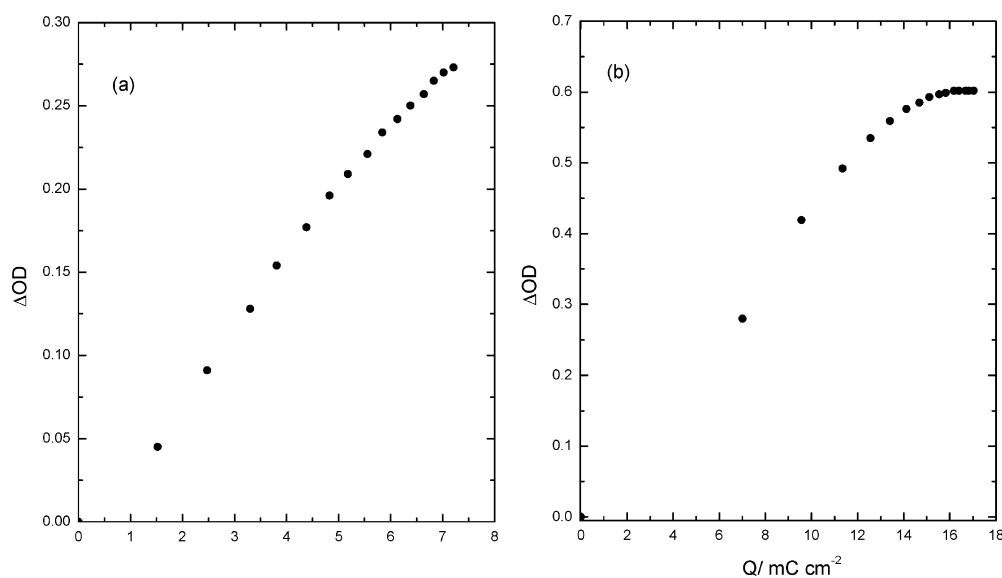


Fig. 4 Optical density of (a) WO_3 and (b) $\text{WO}_3\text{:P}$



direction, the lithium de-insertion occurs close to -0.6 V, where the oxidation process begins, followed by a peak at $E = -0.2$ V. The charge capacities (Q in mC/cm^2), cathodic (q_c) and anodic (q_a) charging were obtained from the cyclic voltammograms; the q_a/q_c ratios of the films were 0.9 and 1.0 for WO_3 and $\text{WO}_3\text{:P}$, respectively.

The color changes for doped (5 mol% H_3PO_4) and undoped WO_3 thin films were accompanied by in situ visible measurements from 350 nm to 800 nm (Fig. 2). The results show that the films exhibit different spectral transmission patterns, in which the doped film exhibits much higher electrochromic reversibility, yielding at $\lambda = 633$ nm a transmittance of 14% for the colored state and 84% for the bleached state, against the undoped film with 40% for the colored and 75% for the bleached states at the same wavelength.

The electrochromic responses for the doped and undoped WO_3 films were recorded by spectral transmittance at $\lambda = 633$ nm and are shown in Fig. 3; the measurements were performed at a constant potential, determined from previous sweep voltammetric measurements, which was -0.8 V (colored state) or $+0.8$ V (bleached state), applied for 15 s. The bleaching process for both doped and undoped WO_3 films are complete, with the doped film bleaching faster than the undoped film. The slope of the transmission variation curves ($\Delta T\%/\Delta t$) for the extraction process were 3.1 s^{-1} and 11.8 s^{-1} for the undoped and doped WO_3 films, respectively. These changes are accompanied by chronocoulometric measurements, yielding for the best film a charge density of $18 \text{ mC}/\text{cm}^2$ and $8 \text{ mC}/\text{cm}^2$ for doped and undoped films, respectively.

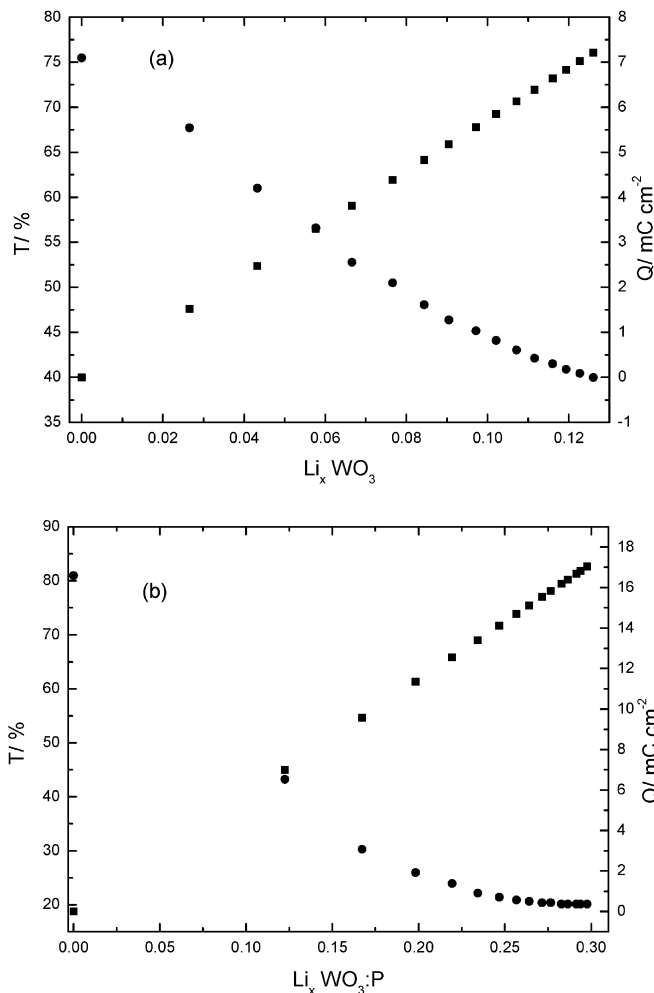


Fig. 5 Transmittance (*circles*) and charge density (*squares*) versus lithium concentration x for (a) WO_3 and (b) $\text{WO}_3\text{:P}$

Figure 4 shows the results of optical density versus charge density for the electrochromic behavior of the WO_3 and $\text{WO}_3\text{:P}$ films. At the beginning the transmittance is 75% and 81%; as the charge is inserted there is an initial linear increase in ΔOD , followed by saturation; this phenomenon is more pronounced by the $\text{WO}_3\text{:P}$ film. The linear increase is to be expected from the Beer-Lambert law, and the slope of this characteristic gives the electrochromic efficiency η , which is defined by:

$$\eta = \frac{\Delta\text{OD}}{Q}$$

where Q is the total charge passed through a unit film area for a corresponding change in optical density (ΔOD). The values obtained for the WO_3 and $\text{WO}_3\text{:P}$ films were both $\sim 42 \text{ C/cm}^2$.

The same data are plotted in Fig. 5 against the mole fraction of lithium (x in Li_xWO_3 and $\text{Li}_x\text{WO}_3\text{:P}$), where the level of insertion of Li^+ ions in the investigated films was calculated according to the equation:

$$x = \frac{q_{\text{ins}}M}{\rho_{\text{film}}FdS}$$

where M is the molar weight of WO_3 , q_{ins} is the charge inserted per unit area, ρ is the density of the films ($\rho_{\text{film}} = 5.5 \text{ g/cm}^3$), d is the thickness, and F is Faraday's constant (96,487 C/mol). It can be seen from Fig. 5b that the saturation appears to be connected with a specific molar fraction of lithium due to the presence of phosphorus in the solution. The small- x region (< 0.02 and < 0.05 for the undoped and doped tungsten oxide films) shows a similar linearity in the transmittance, but when $x > 0.02$ and $x > 0.05$ the samples differ, being more pronounced for the doped film.

Conclusions

The sol-gel route using peroxotungstic acid doped with phosphorus was found to be suitable for producing dip-coated tungsten oxide with excellent electrochromic properties, being possible for use in electrochromic devices.

Acknowledgements This research was financially supported by FAPESP, FINEP/PRONEX, and CNPq.

References

1. Deb SK (1973) *Philos Mag* 27:801
2. Granqvist CG (1995) *Handbook of inorganic electrochromic materials*. Elsevier, Amsterdam
3. Monk PMS, Mortimer RJ, Rosseinsky DR (1995) *Electrochromism fundamentals and applications*. VCH, Weinheim
4. Aegerter MA (1996) *Struct Bonding* 85:149
5. Bohnke O, Bohnke C, Robert G, Carquille B (1982) *Solid State Ionics* 6:121
6. Green M, Smith WC, Weiner JA (1976) *J Mater Sci Lett* 38:89
7. Ohtsuka T, Goto N, Sato NJ (1990) *J Electroanal Chem* 287:249
8. Chemseddine A, Morineau R, Livage J (1983) *Solid State Ionics* 9–10:357
9. Xu G, Chen L (1988) *Solid State Ionics* 28–30:1726
10. Yamanaka K (1981) *Jpn J Appl Phys* 20:1307
11. Oi J, Kishimoto A, Kudo T (1992) *J Solid State Chem* 96:13
12. Takase A, Miyakawa K (1991) *Jpn J Appl Phys Part 2* 30:L1508
13. Livage J (1992) *Solid State Ionics* 50:307
14. Cronin JP, Tarico DJ, Agrawal A, Zhang L () *US Pat* 5,277,986
15. Cronin JP, Tarico DJ, Tonazzi JC, Agrawal A, Kennedy SR (1993) *Sol Energy Mater Sol Cells* 29:371
16. Denesuk M, Cronin JP, Kennedy SR, Law KJ, Nielson GF, Uhlman DR (1994) In: *International symposium on optical materials technology for energy efficiency and solar conversion XIII (SPIE 2255)*. SPIE, Bellingham, Wash., USA, p 52
17. Thor H (1983) *Heteropoly and isopoly oxometalates*. Springer, Berlin Heidelberg New York
18. Avellaneda CO, Dahmouche K, Bulhões LOS, Pawlicka A (2000) *J Sol Gel Sci Technol* 19:447
19. Avellaneda CO, Bulhões LOS (2000) *Proc SPIE* 4104:57