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Electrochromic properties of polycrystalline thin films of tungsten trioxide prepared by chemical vapour deposition

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The electrochromic properties of polycrystalline thin films of tungsten trioxide prepared by chemical vapour deposition were studied using cyclic voltametry and chronoamperometry measurements. Two kinds of films were investigated depending on the conditions of preparation. Although the composition of the layers obtained after pyrolysis of $W(CO)_6$ is influenced by the presence of oxygen flow, the final annealing of these products leads to the same polycrystalline structure. Electrochromic properties have been investigated in acid and hydro-organic electrolytes. Cyclic voltametry shows that both colouration and bleaching of the films are associated with electrochemical reactions. The optical efficiencies and the response times were studied in both media and compared with amorphous WO_3 thin films prepared by vacuum evaporation. Best results have been obtained in acid electrolyte for films prepared by pyrolysis of $W(CO)_6$ in the presence of oxygen flow. We also observed that cycling greatly enhanced the response time. Current injection during colouration was found to depend strongly on time and to be mainly controlled by the resistance of the electrolyte at short times ($t < 200$ ms).

1. Introduction

There have been numerous studies on the electrochromic properties of amorphous WO_3 thin films for application in both display devices [1–11] and 'smart windows' [12–15]. These films were generally obtained either by vacuum evaporation techniques [4–7, 9, 10] or by anodic oxidation of W sheets [2, 16, 17]. However, there have been very few reports concerning the electrochromic properties of crystalline WO_3 films [18–21].

In this paper, results on the electrochromism of WO_3 prepared by chemical vapour deposition (CVD) are described and discussed. Two kinds of WO_3 thin films are investigated: one obtained by annealing in air 'black tungsten' (BW) and the other by annealing in air 'reflective tungsten' (RW). The structure of the films, the electrochromic response time in both acid and hydro-organic electrolytes, and the colouration efficiencies of these oxides are reported. The results of cyclic voltametry and chronoamperometry measurements are discussed and compared with those obtained with amorphous tungsten oxide thin films.

2. Experimental details

Tungsten oxide WO_3 thin films were prepared by chemical vapour deposition of tungsten hexacarbonyl $W(CO)_6$. Pyrolysis at 400° C of $W(CO)_6$ with or without oxygen flow in a radiatively heated quartz chamber leads to the formation of 'black tungsten' (BW) or 'reflective tungsten' (RW) layers, respectively. After deposition, these layers were annealed at 500° C in air until the samples turned transparent [20, 22, 23]. The film thickness was measured by an optical method and was of the order of 500–1500 Å.

WO_3 was deposited onto fused quartz substrates for its structure determination. For electrochromic (EC) measurements, samples were deposited onto SnO_2-coated Pyrex substrates. The sheet resistance of the SnO_2 transparent conductive layer was about $10\,\Omega/\square$.

X-ray diffraction patterns were obtained with a Philips diffractometer using a monochromatized CuK_α incident radiation. The current and power used were 20 mA and 800 W, respectively.

The EC measurements were carried out in two ways: with cyclic voltametry and chronoamperometry techniques. They were made using a Princeton Applied Research (PAR) electrochemical instrumentation (173 potentiostat and 176 current follower) and a classical three-electrode cell. The EC performances of the films: colouring and bleaching times, current density, injected charge, optical density, were deter-

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mined *in situ*. The variations of both the electrical and optical parameters were obtained simultaneously in the electrochemical cell through a Commodore computer control, as described elsewhere [24]. The changes of the optical densities of the film were carried out with an He–Ne laser ($\lambda = 633$ nm). Cyclic voltametry was performed at $100\,\mathrm{mV\,s^{-1}}$ scan rate.

The counter electrode was a platinum plate, much larger than the electrochromic electrode. The acid electrolyte was a normal aqueous H_2SO_4 solution and the reference electrode a saturated sulfate electrode $Hg/Hg_2SO_4/sat.K_2SO_4$ (SSE). The hydro-organic electrolyte was made of 1 M $LiClO_4$ dissolved in a mixed solvent: propylene carbonate (PC)–1% in weight of bi-distilled water. The reference electrode was, in this case, $Ag/AgClO_4(0.01\,M)$ in PC. Previous studies [9, 24] have shown that such an electrolyte gives a fast response time and keeps WO_3 film stable. All the experiments were performed under N_2 atmosphere to avoid both the electrochemical reduction of dissolved oxygen and the oxidation of hydrogen tungsten bronze.

3. Results and discussion

3.1. *Structure of the film*

X-ray diffraction spectra of WO_3 film, prepared by annealing a 'BW' layer at 500° C in air, are shown in Fig. 1. We recall that 'black tungsten' is mainly composed of $W_{18}O_{49}$ [22]. Figure 1a is relative to a layer deposited on to a fused quartz substrate and Fig. 1b to a layer deposited on to a SnO_2-coated substrate. The WO_3 films then obtained crystallized in the monoclinic system with a preferential orientation, the (001) planes oriented parallel to the substrate. In Fig. 1b, the peaks of both the monoclinic WO_3 and the SnO_2 electrode can be observed.

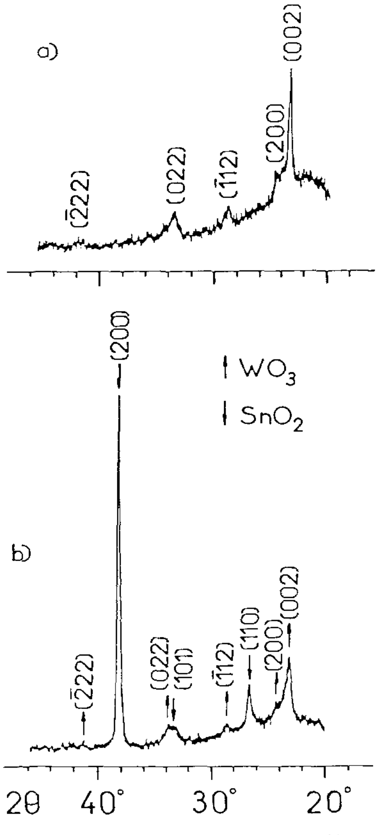

Fig. 1. X-ray diffraction spectra of two WO_3 films prepared by annealing 'RW' films at 500° C in air deposited on to fused quartz substrate (a) and SnO_2-coated glass (b).

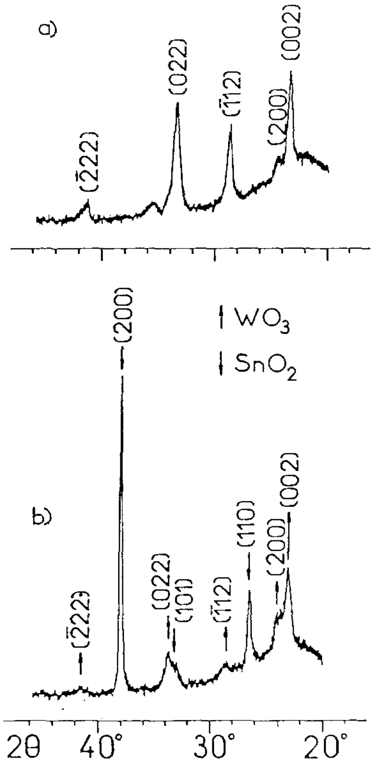

Fig. 2. X-ray diffraction spectra of two WO_3 films prepared by annealing 'RW' films at 500°C in air deposited on to fused quartz substrate (a) and SnO_2-coated glass (b).

Figure 2 shows the X-ray diffraction patterns of WO_3 film prepared by oxidation, at 500° C in air, of an 'RW' layer deposited on to fused quartz substrate (Fig. 2a) and SnO_2-coated transparent electrode (Fig. 2b). The 'reflective tungsten' is made of WO_xC_y ($x = 0.15$, $y = 0.2$) [22]. Despite the difference in composition between 'BW' and 'RW' layers, the oxidation leads to the same polycrystalline structure, the monoclinic form of WO_3.

3.2. *Electrochromic properties in acid electrolyte*

3.2.1. Cyclic voltametry. Cyclic voltamograms are shown in Fig. 3 for oxidized 'BW' films. The numbers (1 or 37) on the curves represent the number of colouration–bleaching cycles. The speed of the electrochemical reactions is presented in Fig. 3a as a classical J–V curve; the corresponding colouration of the film is shown in Fig. 3c and the speed of this optical effect is reported in Fig. 3b. A low current density associated with a low colouration of the WO_3 film can be observed during the first cycle. Both current and colouration increase as the sweeps are repeated. Such behaviour may be caused by a modification of the oxide during cycling or by the hydration of the film in contact to the electrolyte.

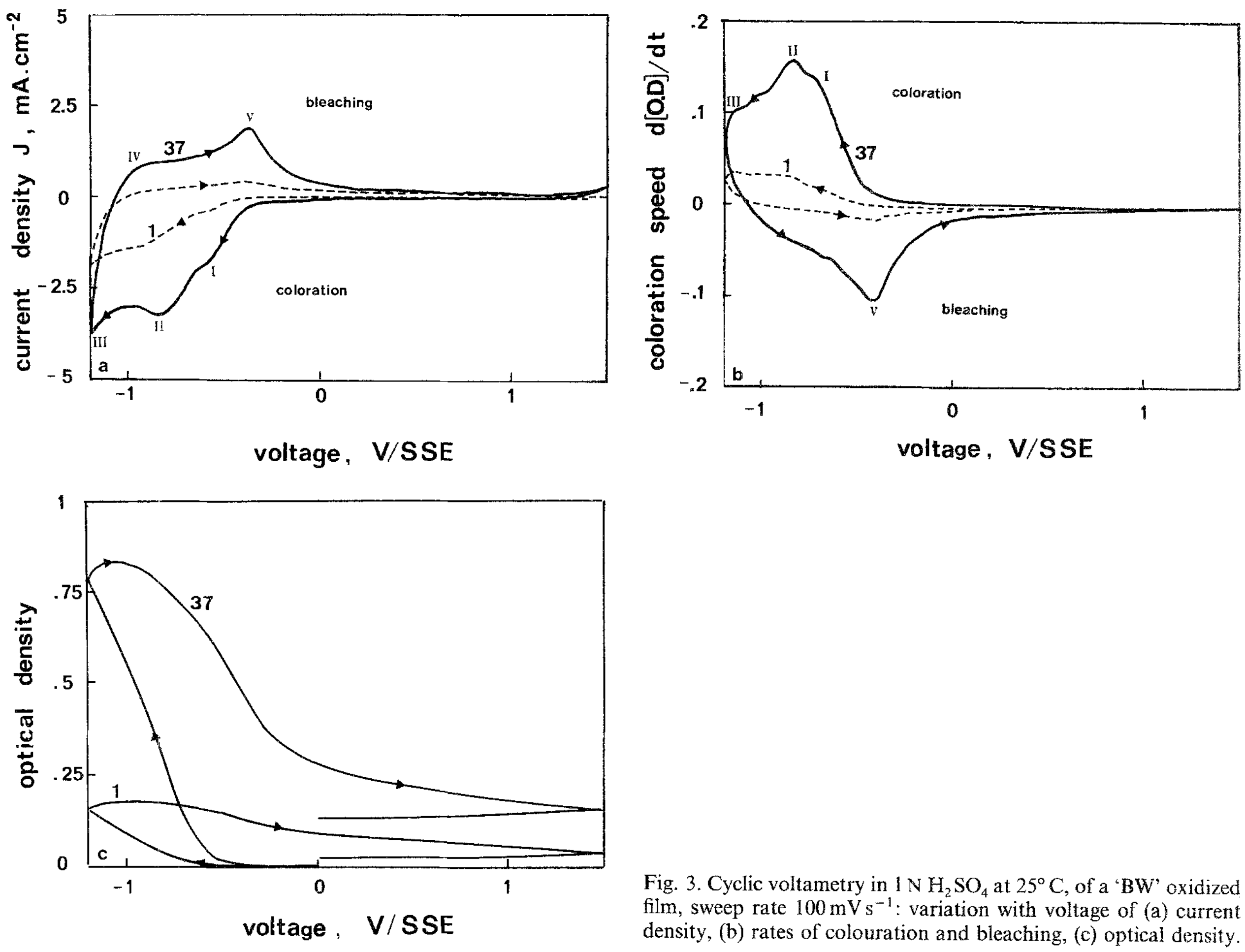

Fig. 3. Cyclic voltametry in 1 N H_2SO_4 at 25° C, of a 'BW' oxidized film, sweep rate $100\,mV\,s^{-1}$: variation with voltage of (a) current density, (b) rates of colouration and bleaching, (c) optical density.

The electrochemical reductions I and II (Fig. 3a) are associated with a deep colouration of the film (Fig. 3c), the colouration speed (Fig. 3b) following the electrochemical reactions speed. A maximum is found on both curves 3a and 3b at $-850\,mV$ (SSE). These two reductions correspond to the hydrogen tungsten bronze formation:

$$WO_3\ (\text{transparent}) + xH^+ + xe^- \longrightarrow H_xWO_3\ (\text{blue})$$

The presence of two peaks during reduction has also been observed with WO_3 prepared by anodic oxidation of W [2]. It has been attributed to the insertion of two different H^+ ions into WO_3: hydrated H^+ ions adsorbed onto WO_3 surface or enclosed into the pores of the oxide and hydrated H^+ ions coming from the bulk of the electrolyte. However, further studies are necessary to confirm this assumption in the case of CVD oxide films.

The reaction III, which is not totally associated with a colouration, as shown in Figs 3a and 3b, corresponds to the hydrogen evolution. It occurs around $-1\,V$ (SSE) according to the reaction:

$$H^+ + e^- \longrightarrow \tfrac{1}{2}H_2\uparrow$$

The atom of hydrogen may either form a hydrogen molecule H_2 or insert into WO_3 to form hydrogen tungsten bronze and then colour the film. This behav-

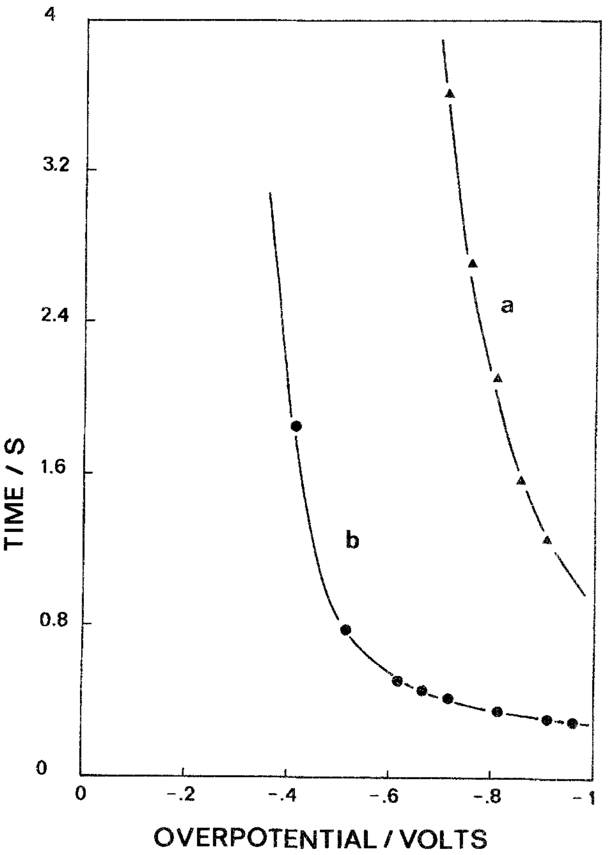

Fig. 4. Colouration time versus overpotential for an optical density of 0.3 in 1 N H_2SO_4 of (a) 'RW' oxidized film and (b) 'BW' oxidized film.

iour may explain the form of the curve of Fig. 3b around −1.1 V (SSE).

During oxidation, two electrochemical reactions are detected: the first one (IV) corresponds to the oxidation of adsorbed hydrogen on the electrode surface and the second one (V) to the oxidation of the tungsten bronze and to the bleaching of the film, according to the reaction:

$$H_xWO_3\,(\text{blue}) \longrightarrow xH^+ + xe^- + WO_3\,(\text{transparent})$$

The electrochemical oxidation that has to be avoided during electrochemical experiments is the oxygen evolution occurring at +1.8 V (SSE). During a cycle, we can observe in Fig. 3c that the electrochromic phenomenon is not totally reversible. This is due to the fact that bleaching occurs more slowly than colouration. However, we shall see later that reversibility can be obtained under other operating conditions.

The same sweep ramp made on oxidized 'RW' film shows a very low colouration response of this material. Indeed, a maximum optical density of 0.07 is obtained with 'RW' film instead of 0.80 with 'BW' film.

3.2.2. Chronoamperometry. Figure 4 shows the relationship between the colouration time of 'RW' (a) and 'BW' (b) oxidized films and the over potential applied to the film during chronoamperometry experiments. In normal sulfuric acid, the equilibrium potential of both 'RW' and 'BW' films is −400 mV (SSE). The colouration time reported in Fig. 4 is relative to a colouration of the film up to a 0.3 optical density. Colouration times as fast as 250 ms, at 25° C for a charge density of 7.4 mC cm^{-2}, were obtained for 'BW' film and 1.25 s for 'RW' film, under the same experimental conditions. As can be seen, the response time is strongly dependent on the preparation procedure used to obtain electrochromic film. This may be due to the presence of oxygen during pyrolysis but also to other parameters relative to the oxide such as composition and degree of crystallization.

Figure 5 shows the relationship between the optical density of the electrochromic film and the injected charge for 'RW' (a) and 'BW' (b) oxidized films. The slopes of the straight lines obtained give the colouring efficiencies of the electrochromic films. These values have been obtained from a linear regression calculus. They are found to be 38 cm^2 C^{-1} (correlation coefficient = 99.67%) and 41 cm^2 C^{-1} (correlation coefficient = 99.75%) for 'RW' and 'BW', respectively, in transmission mode. The efficiency obtained with vacuum evaporated WO_3 electrode (Fig. 5c) is included for comparison. It is 60 cm^2 C^{-1} with a correlation coefficient of 99.96%. The lower efficiency obtained with CVD film may be attributed to the polycrystalline nature of these oxides.

In the case of chronoamperometry measurements, we observed a good reversibility of the electrochromic effect over tens of cycles even if the decolouration time is long, of the order of 30–60 s.

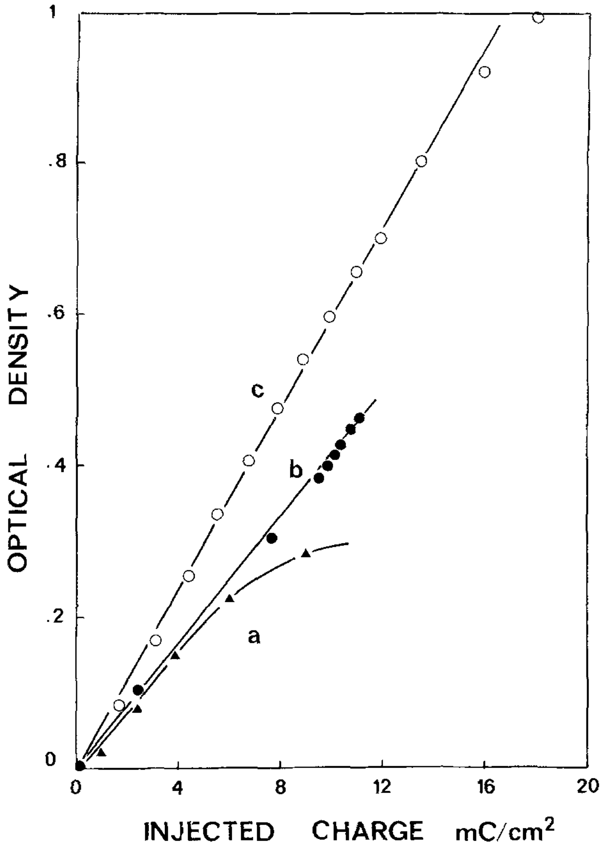

Fig. 5. Optical density of the electrochromic films versus injected charge in 1 N H_2SO_4: (a) 'RW' oxidized film, (b) 'BW' oxidized film, (c) vacuum evaporated WO_3 film.

3.3. *Electrochromic properties in hydro-organic electrolyte*

The electrochromic effect has also been measured in hydro-organic electrolyte for 'BW' oxidized film only. As in acid electrolyte, the electrochemical reduction and oxidation are associated with film colouration and decolouration, respectively. However, bleaching occurs even more slowly as compared to the colouring process. Moreover, colouration time, for a variation of the optical density of 0.3, is longer than in acid electrolyte and is of the order of seconds, as shown in Fig. 6.

The relationship between the optical density of the film and the injected charge is shown in Fig. 7. The colouration efficiency of a CVD film was found to be 25.5 cm^2 C^{-1} with a correlation coefficient of 99.77% (Fig. 7a). We also reported, for comparison, the optical density obtained with vacuum evaporated WO_3 film in the same electrolyte (Fig. 7b). A colouration efficiency of 41.2 cm^2 C^{-1} (correlation coefficient = 99.86%) was determined. As in acid electrolyte, a lower colouration efficiency was obtained with CVD film than with vacuum evaporated films. The deviation from linearity observed in Fig. 7a, around 12 mC cm^{-2}, may be attributed to a saturation of inserted species into the oxide.

A reversible electrochromic effect has also been

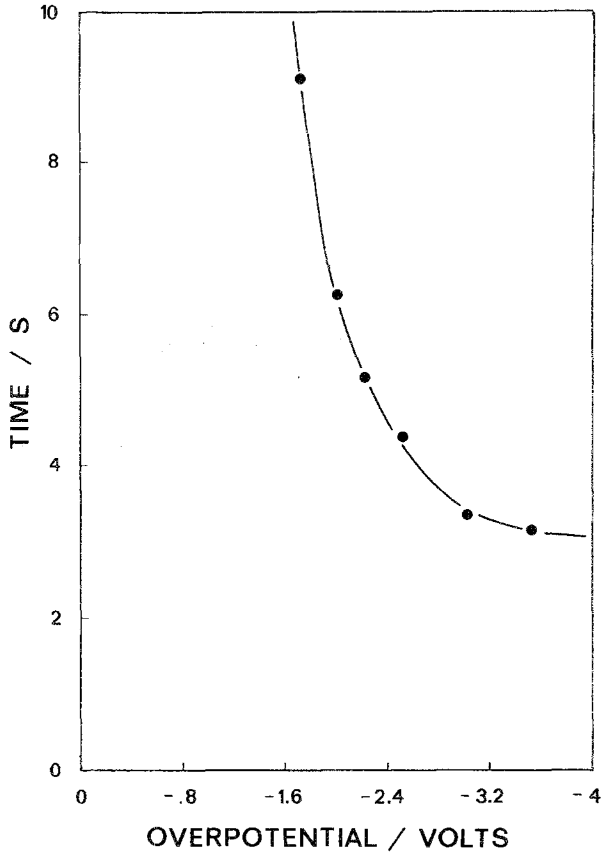

Fig. 6. Colouration time versus over-potential for an optical density of 0.3 in 1 M $LiClO_4$–1% H_2O-PC of a 'BW' oxidized film.

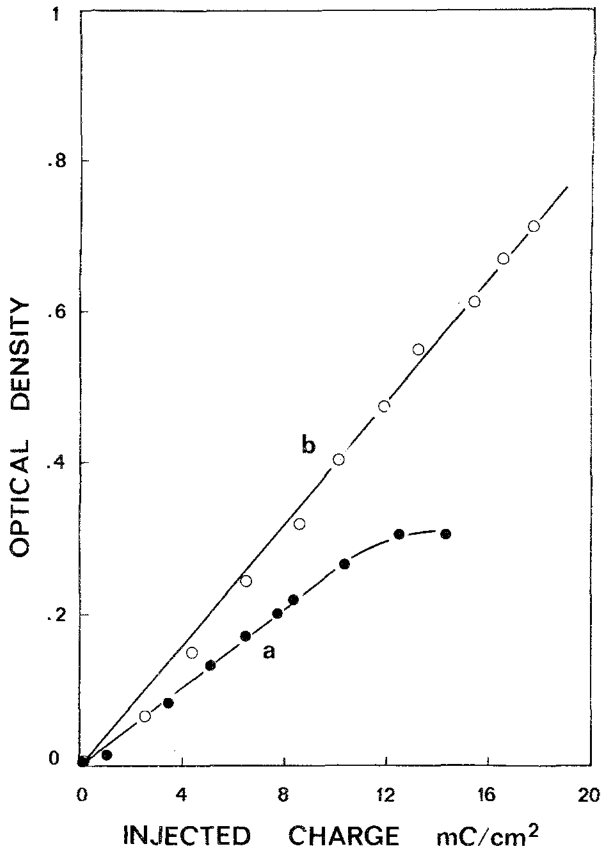

Fig. 7. Optical density versus injected charge in 1 M $LiClO_4$–1% H_2O-PC of: (a) 'BW' oxidized film, (b) vacuum evaporated WO_3 film.

observed in this hydro-organic electrolyte although complete decolouration of a 0.3 optical density film occurred in 60–120 s. However, further studies are necessary to improve electrochromic response and bleaching kinetics in this medium.

3.4. *Current injection rate*

Current density–time curves, for colouration of WO_3, are shown in Figs 8 and 9 for acid and hydro-organic electrolytes, respectively, and 'BW' films. In both media, colouration characteristics are similar. At a constant applied voltage, the current drops with time because of the increase in chemical potential of the injected cation with time. The relationship between the applied voltage V_a and the current density J is represented by:

$$V_a = \mu(x)/NF + \eta + RJ$$

where $\mu(x)/NF$ is the change in the chemical potential across the barrier due to the inserted species concentration (x) in the WO_3, N is Avogadro's number, F is Faraday's number, η the overpotential (the potential drop across the Helmholtz double layer HDL when $J = 0$), R a resistance (sum of film resistance, electrolyte resistance, SnO_2 resistance, interface resistances). From Figs 8 and 9, we observe that the kinetics are influenced by the electrolyte conductivity; the higher the electrolyte conductivity, the higher the current density flowing through the cell for a given overpotential, as mentioned by Kamimori *et al.* [7]. However, we do not observe a current injection rate independent of time, as reported by Sun and Holloway [25], Kamimori *et al.* [7] and Haranahalli and Holloway [26], at short times ($t < 1.0$ s).

In Fig. 10, the colouring current density in acid electrolyte, at a given injected charge value (or at a given x value), is plotted with respect to applied potential. The numbers on the curves are the times of polarization in ms. For short times ($t < 200$ ms) the current depends linearly on the applied voltage suggesting that it is controlled by a resistance. The slope of the straight lines gives the value of this resistance:

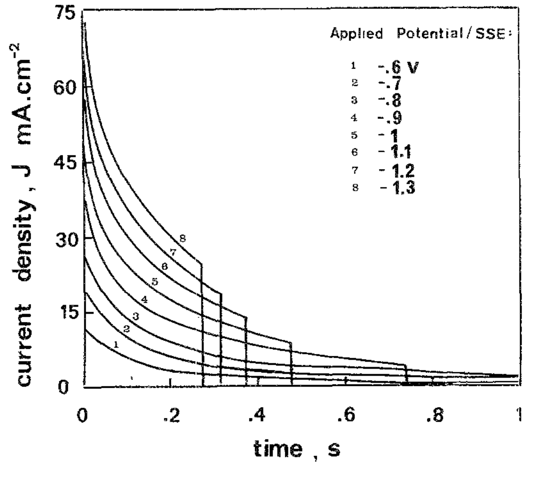

Fig. 8. Chronoamperometric measurements of a 'BW' oxidized film in 1 N H_2SO_4 at 25°C and at different applied potentials (V/SSE).

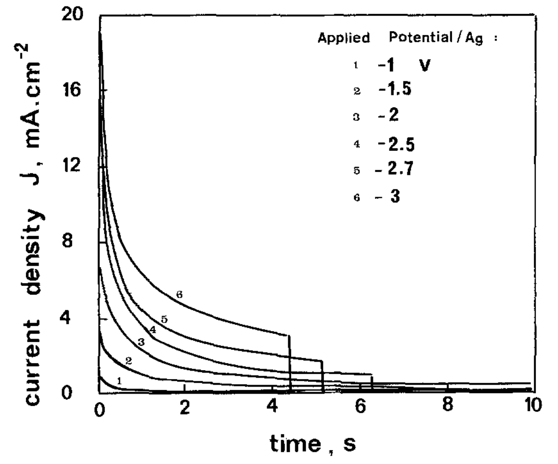

Fig. 9. Chronoamperometric measurements of a 'BW' oxidized film in 1 M $LiClO_4$–1% H_2O–PC at 25° C and at different potentials (V/Ag).

12 Ω cm^2. This result shows clearly that current injection is not controlled by the HDL. Indeed, the situation in which current flow is limited by thermal activation across a barrier is well known and leads to the result that the current depends exponentially on the applied potential [27]. The same linear relationship is found in hydro-organic electrolyte for $t < 200$ ms. In this case, the slope of the straight lines is 84 Ω cm^2. The value of the resistance R is the summation of film resistance, electrolyte resistance, charge transfer resistance, SnO_2 resistance and interface resistances but is mainly due to the electrolyte resistance in our case. This result is in agreement with those of Kamimori *et al.* [7], Rezrazi *et al.* [2] and Falaras [28]. The parallelism of the straight lines is due to the change of $\mu(x)$ with injected charge.

For longer times ($t > 200$ ms), the current does not vary linearly with applied potential. However, a pure exponential variation is not observed suggesting that a more complicated mechanism than a pure HDL control, as mentioned by Faughnan and Crandall [11], is involved.

4. Conclusions

Polycrystalline thin films of tungsten trioxide prepared by chemical vapour deposition show electrochromic effects in both acid and hydro-organic electrolytes. Despite the difference in composition between 'BW' and 'RW' thin films, further oxidation in air leads to the same polycrystalline structure: the monoclinic form of WO_3.

Cyclic voltametry shows that colouration and bleaching of the oxide films were associated with electrochemical reactions. Insertion of protons or lithium ions to form tungsten bronze is involved. The response time was improved by cycling the cell. This effect may be caused by either a modification of the oxide layer or the hydration of the film in contact with the electrolyte. From chronoamperometry measurements, it was found that in acid electrolyte, optical efficiencies were 38 cm^2 C^{-1} and 41 cm^2 C^{-1} for 'RW' and 'BW' layers, respectively, and in hydro-organic electrolyte 25.5 cm^2 C^{-1} for 'BW' films. These low values, as compared with amorphous WO_3 prepared by vacuum evaporation, may be attributed to the polycrystalline nature of the CVD oxides. Moreover, the response times were strongly dependent on the preparation procedure used during pyrolysis of $W(CO)_6$. As a result, for 'BW' films, a colouration time as fast as 250 ms at 25° C for a charge injection of 7.4 mC cm^{-2} was obtained in acid electrolyte. Although reversibility has been observed, bleaching time was found to be longer, of the order of 30–60 s.

The current injection during colouration was found to vary linearly with applied voltage at short times ($t < 200$ ms). This suggests that a resistance controls the kinetics of colouration. It has been found that this

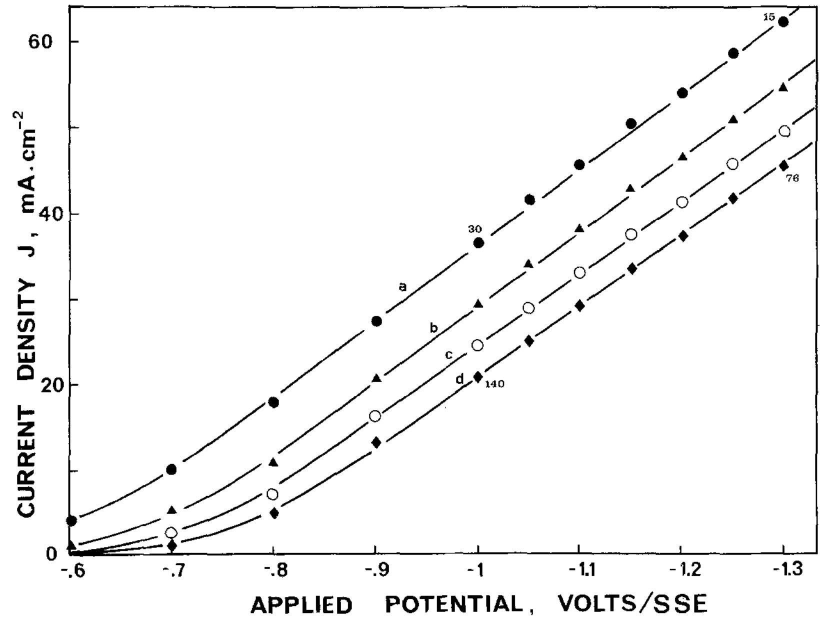

Fig. 10. Current density versus applied potential (V/SSE) in 1 N H_2SO_4 for insertion values Q (mC cm^{-2}) of (a) 1; (b) 2; (c) 3; (d) 4. The electrochromic material is a 'BW' oxidized film.

resistance is mainly due to the electrolyte resistance. Moreover, a strong variation of the current density with time has been observed in both media.

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