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Heat treatment of amorphous electrochromic WO_3 thin films deposited onto indium–tin oxide substrates

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Electrochromic tungsten oxide thin films, obtained by vacuum evaporation, were studied before and after heat treatment between 25 and 250° C for 2 h in air. Electrochromic properties were investigated in acid electrolyte by simultaneous measurements of the electrical and optical parameters. A.c. complex impedance techniques and voltammetry were used to characterize the films from an electrical point of view. We observed an enhancement of the electrochromic response times during both coloration and bleaching after heat treatment carried out between 150 and 220° C. This phenomenon was associated with a decrease of the ohmic drop in the electrode and a continuous variation of the impedance diagrams of these electrochromic electrodes. Moreover, we observed that the diffusion coefficient of H^+ ions into WO_3, obtained on colored thin films, increased as the electrochromic kinetics increased.

1. Introduction

In a previous paper [1] we have shown the effect of temperature treatment on the electrochromic properties of thin films of amorphous tungsten trioxide (WO_3) deposited onto a transparent electrode made of indium–tin oxide (ITO). The temperatures investigated were chosen below the crystallization temperature of tungsten trioxide (i.e. 350–370° C). The impedance of the electrochromic electrode was measured in normal sulfuric acid (H_2SO_4) at high frequency (10 kHz).

The main purpose of this paper is to complete this first study. The effect of heat treatment of thin films of tungsten trioxide, over a more restricted range of temperatures, 25–250° C, is investigated more precisely using different independent ways of measurement: a.c. complex impedance techniques, cyclic voltammetry and chronoamperometry.

The impedance diagram method has been used to obtain information on both ITO/WO_3 and WO_3/electrolyte interfaces. The diagrams were obtained either at the equilibrium potential of uncolored electrochromic electrodes or at the equilibrium potential of colored thin films. In the latter case, it was then possible to determine the diffusion coefficient of H^+ ions into WO_3. The effect of heat treatment in air on the coloration–bleaching kinetics of WO_3 thin films and on the slope of the cyclic voltammetry curves during coloration was also investigated. We shall see that a.c. complex impedance may explain the electrochromic behavior of heat treated thin films of WO_3.

2. Experimental details

2.1. *Thin film preparation*

Tungsten trioxide thin films were deposited by vacuum evaporation of *in situ* prebacked WO_3 powder from a tantalum boat onto indium–tin oxide (ITO)-coated glass substrates. These substrates were a commercial product obtained from Balzers A.G. The resistivity of the indium–tin oxide (known as Z20) was $7.5 \times 10^{-4}\,\Omega\,\mathrm{cm}$ ($300\,\Omega/\square$) and the thickness was 250 Å. A thin film of SiO_2 was deposited between the glass and the oxide to prevent the diffusion of Na^+ ions from the glass substrate. ITO was heat treated at 470° C, for 30 min before use to prevent any change of conductivity during the heat treatment. This material is unavailable for practical use in an electrochromic display because of its very low conductivity. For this reason, WO_3 thin films have also been deposited onto graphite substrates in order to detect any influence of this high resistive material on the results.

The pressure during the evaporation was 10^{-5} Torr and the rate of evaporation was $50\,\text{Å}\,\mathrm{min}^{-1}$. WO_3 film thicknesses of 3600 ± 100 Å onto ITO and 3800 ± 100 Å onto graphite were determined using a Taylor Hobson talystep. These values were chosen in consideration of the maximum speed of the electrochromic effect [2].

X-ray diffraction spectra of the films, before and after heat treatment in air for 2 h, were obtained with a Siemens diffractometer using monochromatized CuK_α incident radiation. These spectra clearly show that crystallization of tungsten trioxide occurs between 300 and 400° C (Fig. 1). The crystallization temperature of evaporated WO_3 thin films occurs at 350–370° C.

2.2. *Cyclic voltammetry and chronoamperometric measurements*

The experimental set-up is shown in Fig. 2. The electrical measurements were carried out using a PAR electrochemical instrumentation (Model 173 potentio-

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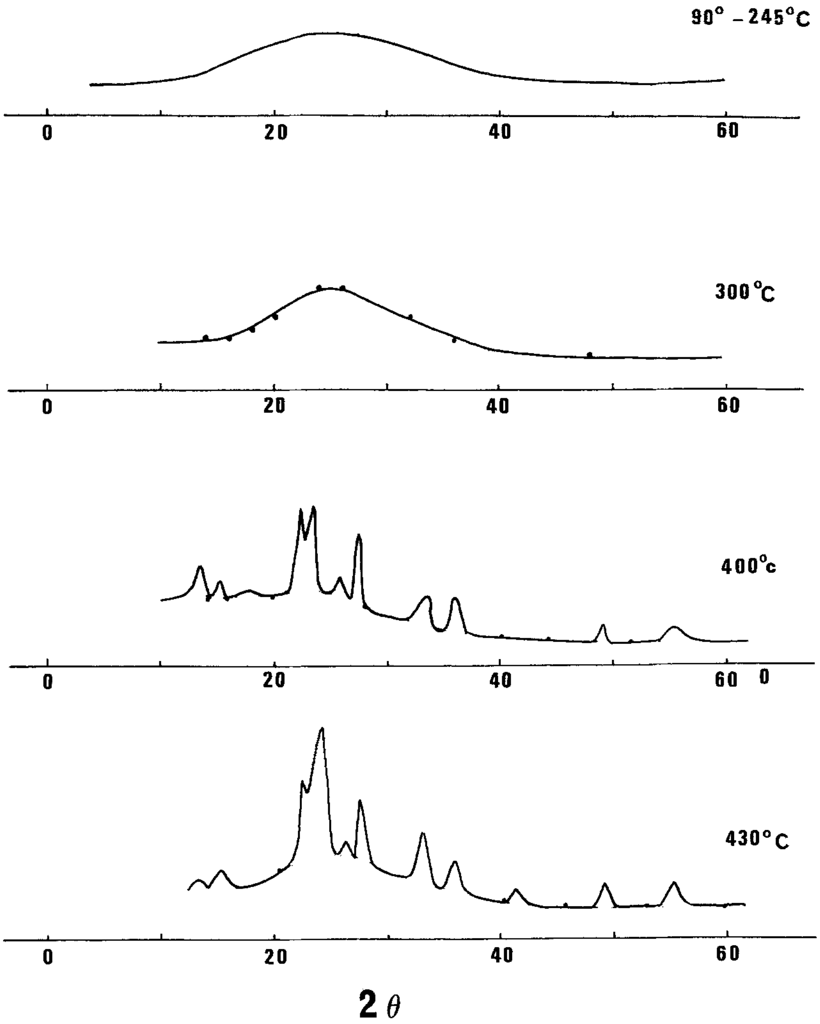


Fig. 1. X-ray diffraction spectra of evaporated thin films of WO_3, heat treated for 2 h in air.

stat, Model 176 current follower) controlled by a 8096 Commodore computer. A three-electrode cell was used with the electrochromic electrode as working electrode, a saturated sulfate electrode (SSE) as reference electrode and a platinum plate ($s = 2\,cm^2$) as counter electrode. The three electrodes were in a one-compartment cell but the distance between the counter electrode and the working electrode was about 2 cm to prevent any O_2 diffusion from the counter electrode during the coloration process. In fact, we observed, experimentally that reoxidation of H_2 adsorbed onto Pt occurs during the coloration reaction instead of O_2 evolution. The electrolyte was H_2SO_4 (N) deaerated by N_2 gas bubbling. The variations of the optical density of the electrochromic film were measured with an He–Ne laser ($\lambda = 633\,nm$). The laser beam crossed the electrochemical cell and the intensity of the transmitted light was measured through a photocell.

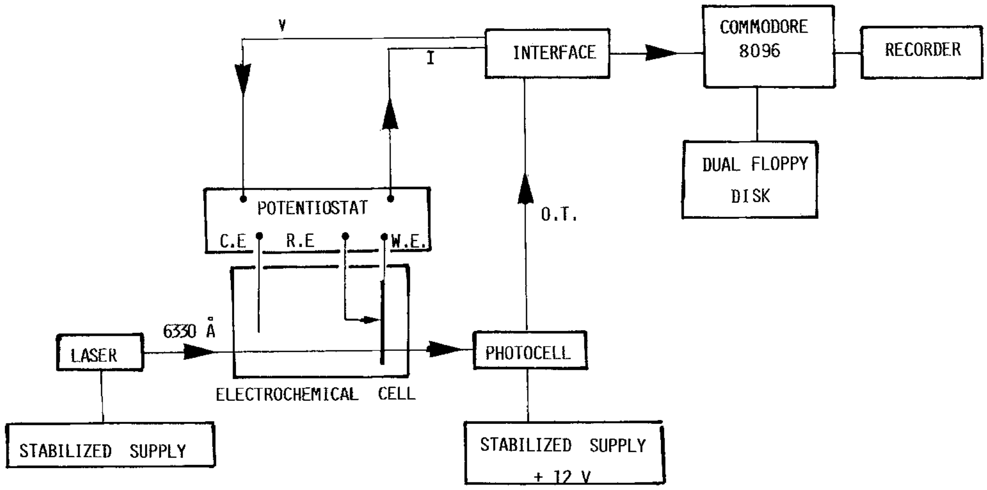


Fig. 2. Computer controlled set-up for simultaneous electrochemical and optical data acquisition.

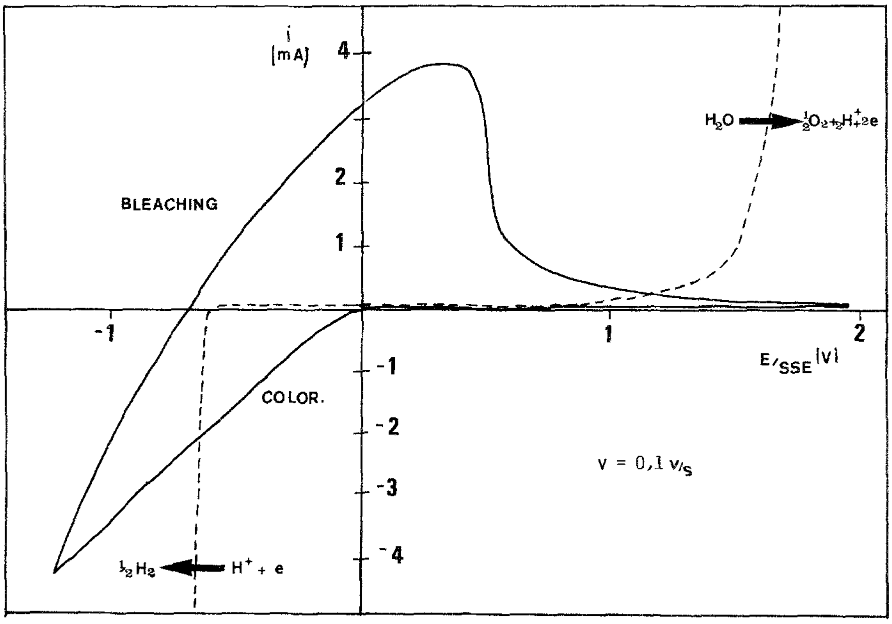


Fig. 3. Voltammograms of ITO/WO_3 electrode in H_2SO_4 (N) (full line) and of a rotating disk Pt electrode in H_2SO_4 (N) (dashed line).

This experimental set-up could be used either for cyclic voltammetry, $i = f(V)$, or chronoamperometry, $i = f(t)$. It could give, in the same experiment, the kinetics of the electrochemical reactions (i), the electrical charge crossing the cell (Q), the variations of the optical density of the electrochromic film (OD) and the speed of the coloration and of the bleaching phenomena ($d(OD)/dt$). The optical density, to obtain a good contrast, was determined to be 0.3. The times of coloration and bleaching mentioned in this paper were then related to such an optical density variation.

2.3. *Impedance measurements*

The impedance diagrams were obtained with a Solartron Schlumberger frequency response analyser (Model 1172) with an electrochemical interface 1186 and a Wavetek 452.01 filter. The automatized measurements were controlled by an Apple IIe microcomputer. The applied a.c. voltage was 10 mV RMS in all experiments. The Nyquist plots were drawn with a Hewlett-Packard plotter.

2.4. *Electrochromic electrodes preparation*

All the electrodes were cut from the same plate of ITO/WO_3 ($s = 5 \times 3\,cm^2$). A copper wire was solded onto silver paint applied to the ITO. A polymeric non-conductive paint covered all the electrode except for a small window with a surface varying from 0.5 to 1 cm^2 in contact with the electrolyte.

2.5. *Heat treatment*

The furnace was an electrical ADAMEL furnace and the temperature was measured with a chromel–alumel thermocouple. The time of the treatment in air was 2 h. The variation of the temperature was less than 1° C during this period of time.

3. Results

3.1. *Cyclic voltammetry, high frequency impedance and kinetics of the electrochromic phenomenon*

The cyclic voltammogram of the electrochromic electrode shown in Fig. 3 exibits a pseudolinear behavior in the reduction region corresponding to the coloration of the ITO/WO_3 electrode. The slope of this part

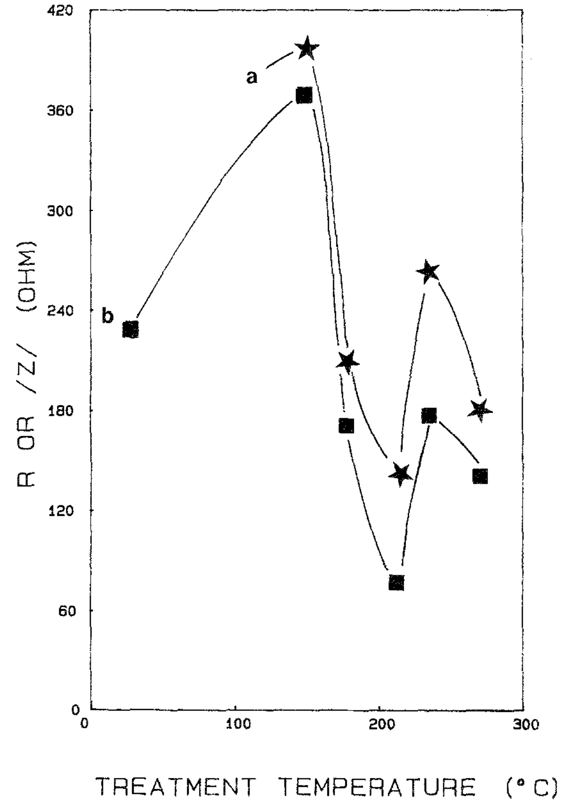


Fig. 4. Influence of heat treatment on ITO/WO_3 thin film electrodes: (a) inverse of the slope of the cathodic curve of the voltammogram dE/dI; (b) a.c. impedance module at 10 kHz, measured at the equilibrium potential of the electrochromic electrode.

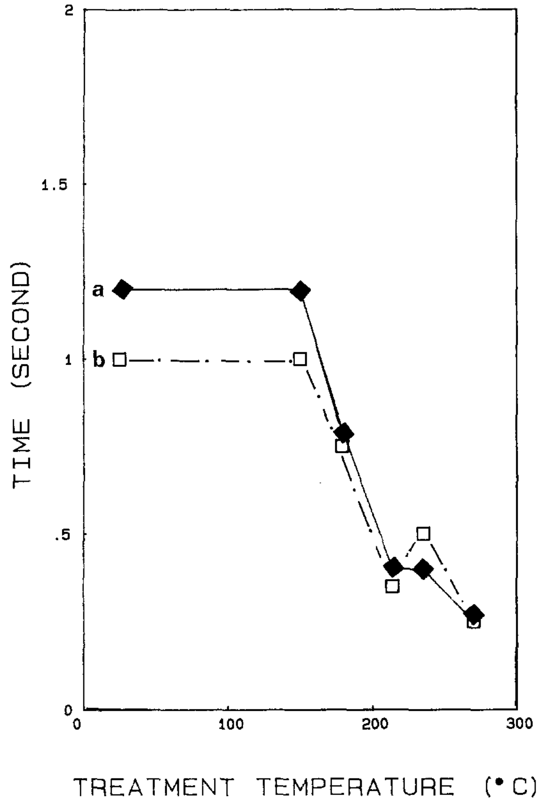


Fig. 5. Influence of heat treatment on ITO/WO_3 thin film electrodes: treatment temperature dependence on the response time for: (a) coloration; (b) bleaching.

of the voltammetric curve has the same unit as the inverse of resistance. The variations of the inverse of this slope with the heat treatment temperatures are shown in Fig. 4 (curve a). Impedance diagrams were produced for the same samples at the equilibrium potential of the electrochromic electrode. The variations of the module of the impedance of these electrodes, measured at 10 kHz, are also shown in Fig. 4 (curve b). We observe a similar effect of the temperature treatment on the behavior of these two curves: a hump is observed between 210 and 230° C.

On the same electrodes, we have determined the times of both coloration and bleaching. The results are presented in Fig. 5 for both coloration and bleaching. The coloration pulse was − 3 V (SSE) and the bleaching pulse + 1.5 V (SSE). The same behavior as previously mentioned is observed on the electrochromic kinetics: a hump between 210 and 230° C on both curves.

The results of impedance module measurements show a variation of the ohmic drop in the films with the heat treatment and, therefore, may explain the variations of the coloration and bleaching kinetics. A 'critical' temperature appears at 217° C. At this temperature, the values of R and $|Z|$ are reduced six-fold and the coloration time four-fold. For a treatment temperature higher than this 'critical' temperature, the values of R and $|Z|$ increase and, consequently, the electrochromic kinetics decrease.

3.2. *Impedance diagrams*

The impedance diagrams were obtained at the equilibrium potential of the electrochromic electrode in H_2SO_4 (N). The equilibrium potential of the untreated electrode was −0.195 V (SSE). For the heat treated samples, it varies from −0.135 to −0.221 V (SSE). The frequency range investigated was 0.1–9999 Hz (the maximum frequency possible with the AFT 1172).

3.2.1. Untreated electrode. The impedance diagram, plotted in the complex plane, for the untreated sample deposited onto ITO substrate, is shown in Fig. 6. It is composed of three parts: (i) in the high and (ii) in the intermediate frequency ranges, two semicircles, and (iii) in the low frequency range, a vertical straight line. The center of the second semicircle lies below the real axis. An angle of 7° appears between the radius of this semicircle and the real axis.

The equivalent circuit (Scheme 1) made of resistances and capacitances only, can be proposed for this untreated electrode.

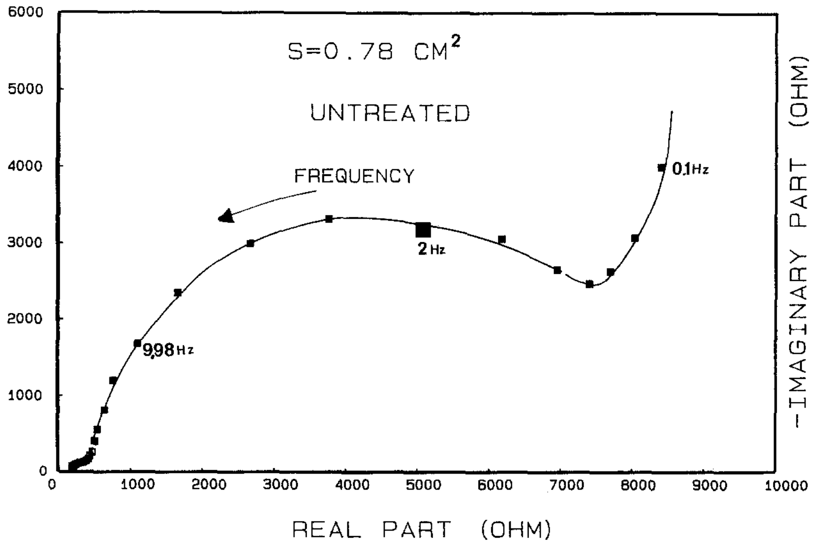
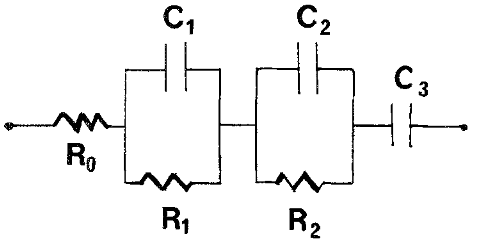


Fig. 6. Nyquist plot of the a.c. impedance diagram of the untreated ITO(Z20)/WO_3 electrode, at the equilibrium potential. Electrolyte: H_2SO_4 (N).

Table 1. R in Ωcm^2; C in $\mu F cm^{-2}$.

T (°C)	R_0	R_1	C_1	R_2	C_2	C_3
170	186	22680	1.40	≃30000	-	173
199	134	2360	0.22	≃3400	0.91	200
217	144	230	0.46	≃560	-	226
230	209	8820	4.50	10000	-	172



Scheme 1.

The values of the components are:

$$R_0\,(\Omega cm^2) = 117$$

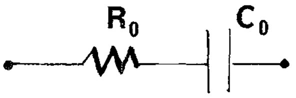
$$R_1\,(\Omega cm^2) = 374 \quad C_1\,(\mu F cm^{-2}) = 1.69$$

$$R_2\,(\Omega cm^2) = 6240 \quad C_2\,(\mu F cm^{-2}) = 12.75$$

$$C_3\,(\mu F cm^{-2}) = 510$$

These values are commonly obtained with WO_3 electrodes evaporated into ITO substrates.

The presence of two semicircles in Fig. 6 may be attributed to the nature of the substrate. When other substrates, such as graphite, tungsten or more conductive ITO thin films are used the impedance diagrams are more simple. With a graphite substrate, the impedance diagram can be described by the following equivalent circuit (Scheme 2).



Scheme 2.

The values of the components are:

$$R_0\,(\Omega cm^2) = 2.4 \quad C_0\,(\mu F cm^{-2}) = 300$$

3.2.2. Heat treated samples.

3.2.2.1. ITO/WO_3 electrode. The temperatures investigated were 170, 199, 217 and 230°C. The Z20/WO_3 electrode impedance diagrams are shown in Figs 7, 8 and 9(a, b) for 170, 199 and 217°C treatment temperatures, respectively. The effect of the heat treatment is important. However, these diagrams exhibit the same features as for the untreated sample: a distorted loop which can be decomposed into two semicircles in the high and intermediate frequency ranges, and a straight line in the low frequency range. The same equivalent circuit, as proposed for untreated samples, can then be considered. Table 1 summarizes the values of the different components of this circuit, depending on the temperature treatment.

The parameters of the first relaxation, R_1 and C_1, can be determined with good precision. The first relaxation resistance, R_1, varies considerably (by a factor of 10^2) when the temperature of the treatment varies from 170 to 217°C (Fig. 10). The effect of heat treatment can also be observed on the second relaxation resistance, R_2, and on the low frequency capacitance, C_3, as shown in Fig. 11.

3.2.2.2. Graphite/WO_3 electrode. The same heat treatments were carried out on WO_3 deposited onto graphite substrates. The impedance diagrams, obtained in H_2SO_4 (N) at the equilibrium potential of the electrode, reveal a particular behavior at 217°C, as previously mentioned for ITO/WO_3. This behavior can then be attributed to the oxide or to the interface substrate/WO_3 and not to the low conductive material ITO [3]. Table 2 summarizes these results.

3.2.3. Colored thin films (H_xWO_3). The diffusion coefficient of H^+ ions into the electrochromic thin film

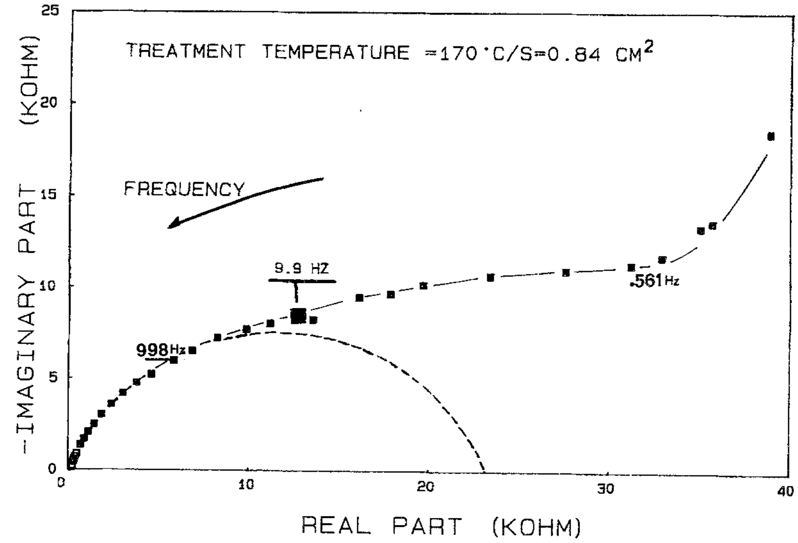


Fig. 7. Nyquist plot of the a.c. impedance diagram (at the equilibrium potential) of the ITO(Z20)/WO_3 electrode treated in air at 170°C for 2h. Electrolyte: H_2SO_4 (N).

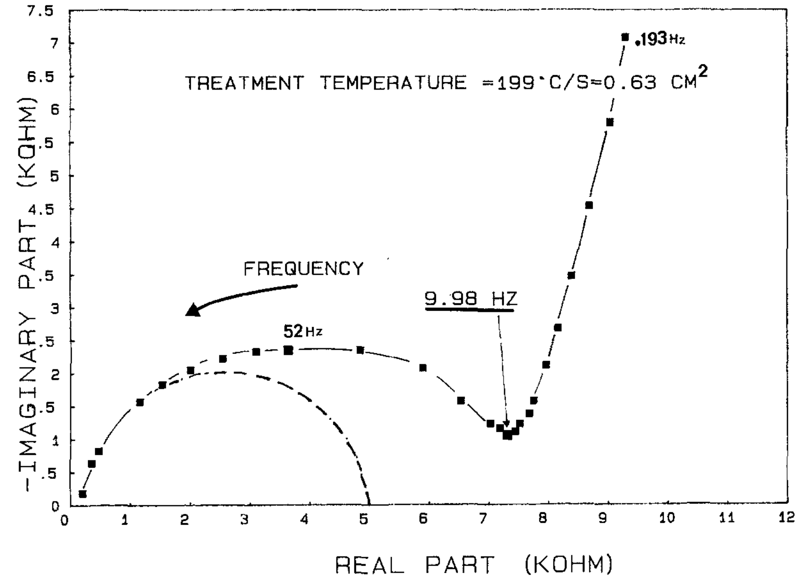


Fig. 8. Nyquist plot of the a.c. impedance diagram (at the equilibrium potential) of the ITO(Z20)/WO_3 electrode treated in air at 199° C for 2 h. Electrolyte: H_2SO_4 (N).

can be calculated from the results of the impedance measurements on colored samples. The impedance diagrams are obtained at the equilibrium potential of the colored electrode in H_2SO_4 (N).

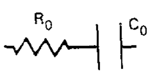
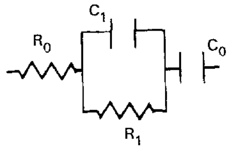
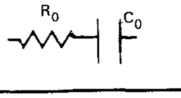
The method of calculation was described by Ho *et al.* [4]. It was used by many workers for WO_3 and for other electrochromic materials [5–7] and recently for polymeric thin films [8]. The impedance diagrams of the colored thin films in the complex plane exhibit two straight lines. The first straight line can be related to a diffusion process. Indeed, a 45° angle appears between this straight line and the real axis. In the low frequency range, a vertical straight line can be observed which is characteristic of the finite thickness of the oxide film. All the diagrams obtained with the heat treated samples are identical to the diagram shown in Fig. 12. The diffusion coefficient of H^+ ions, $\tilde{D}$, is obtained from the following formula:

$$|Z| = \frac{V_M (dE/dy)_y}{zF\tilde{D}^{1/2} a} \omega^{-1/2}$$

where z and F are the valence number and the Faraday number, respectively, V_M is the molar volume of WO_3 ($d = 5.5\,\mathrm{g\,cm^{-3}}$), $(dE/dy)_y$, the slope of the coulometric titration curve at the insertion rate y, and a is the electrode area (cm^2). The calculation is made from the diffusion part of the diagrams. Table 3 gives the values of $\tilde{D}$ for the different heat treatment temperatures. dE is the variation of the equilibrium potential for the uncolored state to the colored state when a charge dq is injected into the electrochromic film. (dq/dE) is then a differential capacitance.

The heat treatments give no significant variation of the diffusion coefficient $\tilde{D}$. However, we observe that $\tilde{D}$ increases slightly with the heat treatment for a temperature smaller than 220° C. On the other hand, for a higher temperature (i.e. 230° C), $\tilde{D}$ decreases. This result may be compared to the results previously obtained on uncolored heat treated films and shown in Figs 10 and 11. A change in the variations of the first relaxation resistance and in the low frequency capacitance can be observed around 220° C.

Table 2. R in Ωcm^2; C in $\mu F cm^{-2}$.

T (° C)	Equivalent circuit	R_0	R_1	C_1	C_0
170		1.7	–	–	464
217		0.49	480	670	5216
230		5	–	–	564

4. Discussion

Our results clearly show that WO_3, heat treated between 150 and 220° C, gives enhanced electrochromic kinetics for coloration and bleaching. This phenomenon is associated with a decrease of the ohmic drop in the electrode, shown in both the voltammograms and the impedance module measurements at high frequency (10 kHz). Moreover, a continuous variation in the impedance diagrams of these electrodes is observed.

These results can be compared to those obtained by the DTA technique on this evaporated material [1]

Table 3.

T (° C)	a (cm^2)	$\tilde{D}$ ($cm^2 s^{-1}$)	dE (V)	dq/dE (μF)	dq (mC)
170	0.84	3.7×10^{-10}	0.229	28515	6.53
199	0.80	4.3×10^{-10}	0.199	35920	7.15
217	0.96	6.5×10^{-10}	0.243	41152	10
230	0.84	3.9×10^{-11}	0.244	40983	10

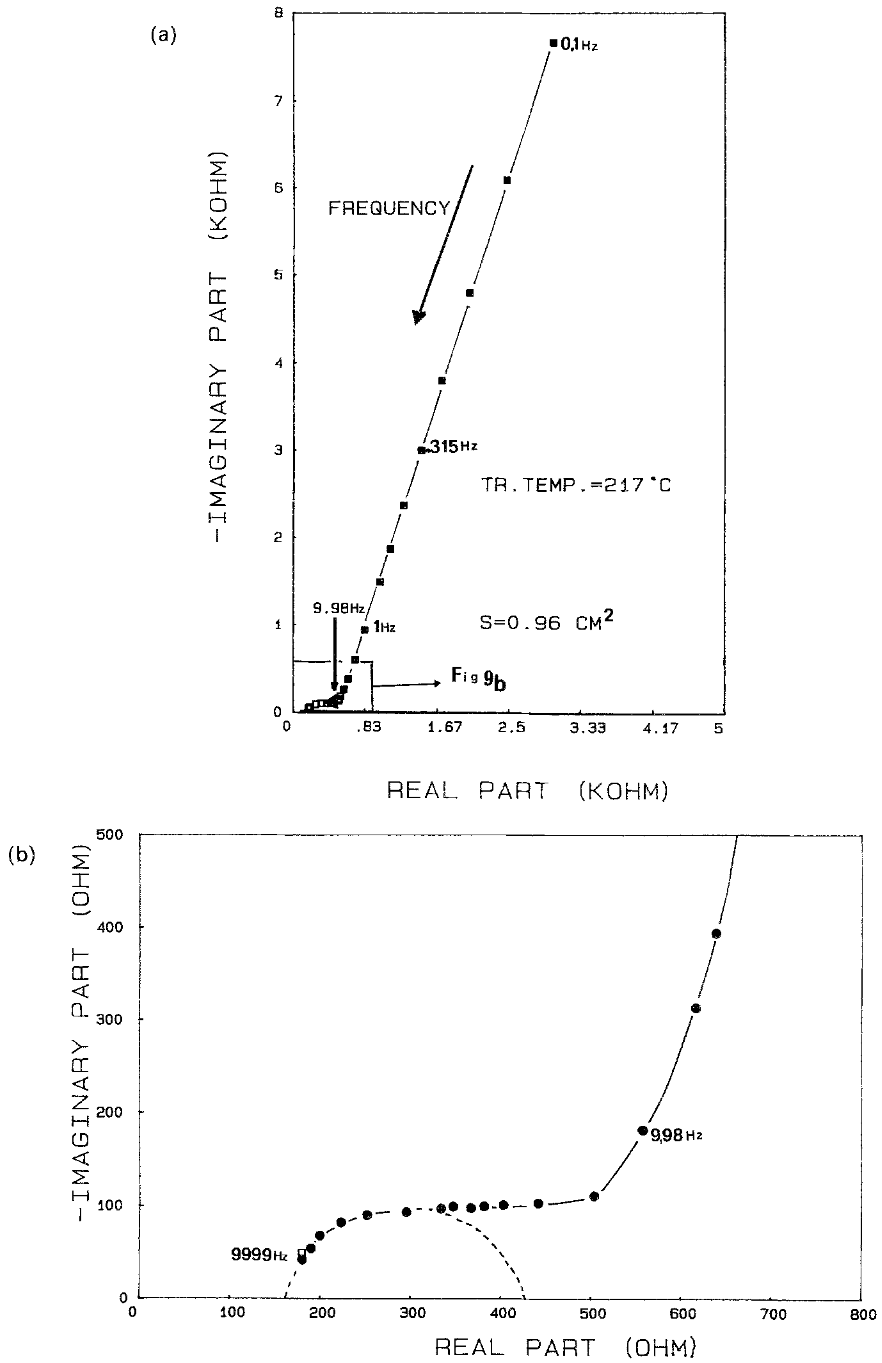


Fig. 9. (a) Nyquist plot of the a.c. impedance diagram (at the equilibrium potential) of the ITO(Z20)/WO_3 electrode treated in air at 217° C for 2 h. Electrolyte: H_2SO_4 (N). (b) Enlarged high frequency diagram.

and also to those obtained by Zeller and Beyeler [9]: the differential calorimetric spectra showed a large endothermic band between 150 and 230° C on evaporated WO_3 films before and after heat treatment at 150° C for 16 h. Zeller and Beyeler explained this experimental result by a loss of H_2O (0.5 mol. of H_2O per W atom). Indeed, the presence of H_2O molecules in evaporated WO_3 thin films is now an undoubted fact [10, 11]. Moreover, we found a decrease of the thickness of the films after heat treatment: a 3800 Å thick film at 25° C becomes 3710 Å thick after 150° C heat treatment and 3640 Å thick at 250° C [14]. It is also well established that this evaporated material is oxygen deficient. We determined a stoichiometric coefficient (O/W) of 2.7 before heat treatment [12]. The arrangement in the film is a network composed of groups such as WO_2, W_2O_5 and WO_3 with bridges of H_2O [13]. We also determined a variation in the optical properties of these films. The refractive index, at $\lambda = 5000$ Å, which is constant and equal to 2.00 between 25 and 150° C heat treatment, varies from 2.03 for film treated at 230° C to 2.06 for film treated at 300° C [14]. These experimental results show that heat treatment gives rise to a loss of H_2O as well as to a variation in the stoichiometry of the oxide. The treatment may also give rise to a change in the porosity of the material.

The a.c. complex impedance measurements show a variation of the interface substrate/WO_3. Indeed, this technique is a way of characterizing the interface between ITO and WO_3 and between WO_3 and the electrolyte. Yoshika *et al.* have also chosen this way of

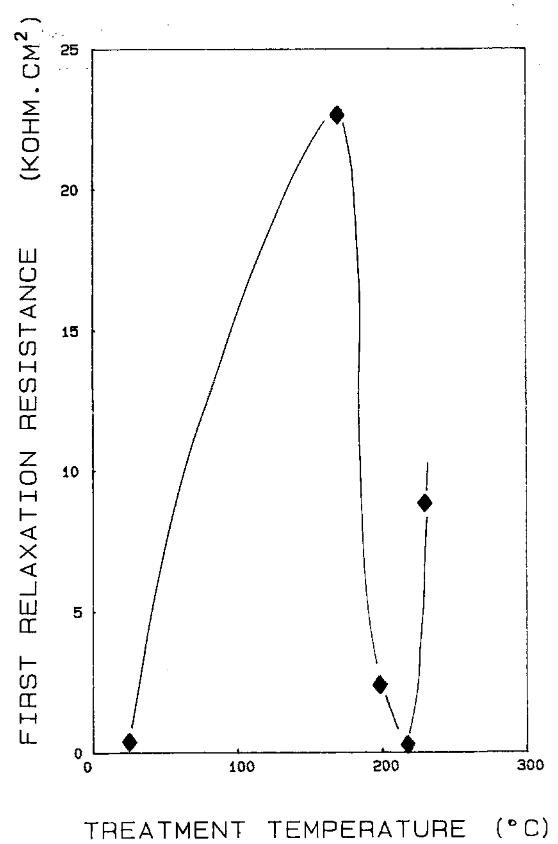


Fig. 10. Effect of the heat treatment on the first relaxation resistance R_1 (high frequency semicircle) of the ITO/WO_3 electrode in H_2SO_4 (N).

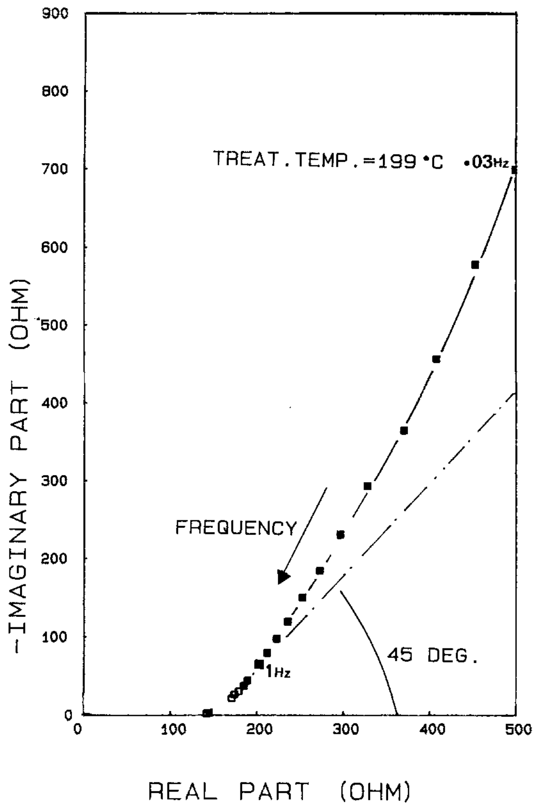


Fig. 12. Nyquist plot of the a.c. impedance diagram of a colored ITO/WO_3 electrode. Q_{col} = 9.15 mC, a = 0.63 cm^2.

characterization [15]. The resistance R_0 is, without doubt, related to the resistance of both the electrolyte and ITO. The two relaxation circuits R_1C_1 and R_2C_2 are in relation because of the similar effect of the treatment on both. The low frequency capacitance, C_3, is characteristic of the WO_3/electrolyte interface. From the results of heat treatment, we observe that the higher the temperature treatment, the better the contact between the WO_3 and the ITO substrate as shown by the decrease of the two resistances R_1 and R_2 (Table 1). This better contact gives rise to faster electrochromic kinetics (Fig. 5). The variation of the interface, shown by a continuous variation of the distorted loop in the complex impedance diagrams (Figs 7–9), may be described by a system of varying sublayers. The first assumption, which is related to the presence of pores in the oxide, would be the formation of a composite layer of the electrolyte introduced into the pores of the tungsten oxide. The second assumption would be the formation of a new layer at the interface ITO/WO_3. A reaction between ITO and WO_3 during heat treatment may give rise to a sublayer in this electrode.

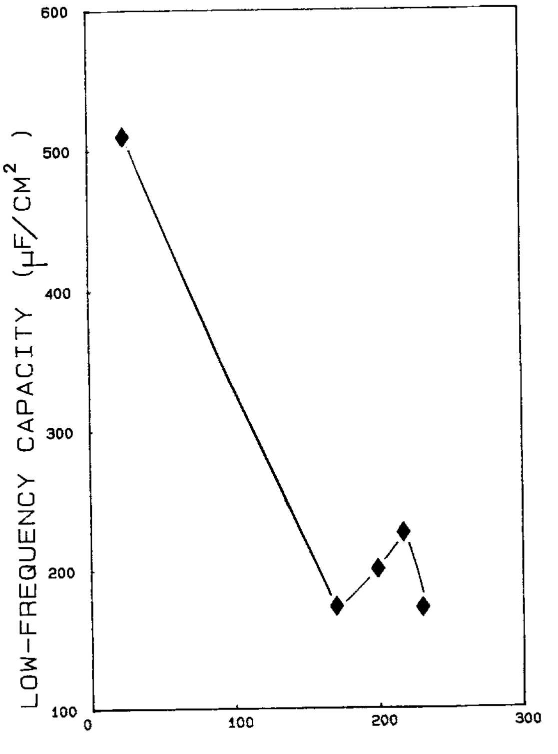


Fig. 11. Effect of heat treatment on the low frequency capacitance C_3 of the ITO/WO_3 electrode in H_2SO_4 (N).

In a recent study, Thevenin and Muller [16] have proposed different electrical models of the metal/surface layer/solution system depending on the structure of the surface layer, for the interpretation of the impedance measurements of lithium electrodes in organic electrolytes. Two of these models can be considered in our case.

The porosity of the WO_3 thin films can be taken into account in the first model; the SPL (solid-polymer layer) model. In this model, the surface layer consists of a composite layer made of solid compounds dispersed into a polymer electrolyte. Porosity can be represented by such a composite medium model. The liquid electrolyte can migrate through the pores of the tungsten oxide and form such a layer. If the time constants of the different processes involved (conduction, charge transfer) are not well separated, the a.c. impedance diagram is a single distorted loop, which can only suggest the existence of several processes. The dispersion of the time constants may also give rise to a distorted loop. Each process is then represented by a pseudo *RC* parallel circuit (Cole and Cole dispersion).

In the second model, the CSL (compact stratified layer) model, the surface layer is considered to be made of two sublayers with different permittivities and conductivities. The equivalent circuit consists of two *RC* parallel circuits in series. When the time constants of the circuits are not well separated, the impedance diagram, in the complex plane, exhibits only one loop. On the other hand, when the time constants are different, the impedance diagram shows two semicircles. Heat treated ITO/WO_3 layers may be modeled by a two-sublayer system. A new layer may be formed during the heat treatment by a reaction between ITO and WO_3. New electrical values can be obtained for this new sublayer. The a.c. impedance diagram is, in this case, a loop which can be decomposed into two semicircles.

The experimental a.c. impedance diagrams shown in Figs 6–8 show either two semicircles (Fig. 6) or a distorted loop (Figs 7 and 8) which can be explained by either one of these two models. Further studies are in progress to clarify this point and to choose between the models.

Between 150 and 220° C, the diffusion coefficient of H^+ ions into WO_3, obtained on colored thin film, increases as the kinetics increase.

When the temperature of heat treatment reaches a value of 220° C, the contact substrate/WO_3 seems to be changed since the values of R_1 and R_2 increase (Table 1), the electrochromic kinetics are modified (Fig. 5) and the diffusion coefficient of H^+ ions decreases (Table 3). No crystallization is detected by X-ray diffraction and DTA measurements.

5. Conclusions

We have shown the effect of heat treatment in air on the electrochromic properties of thin films of WO_3 obtained by vacuum evaporation onto an electronic and transparent conductor currently used in electro-optical devices: ITO. The heat treatment, from 25 to 220° C, gives an enhancement of the electrochromic effect. This phenomenon is associated with a decrease of the ohmic drop in the electrode and with a continuous variation of the complex impedance diagrams of these electrodes. A 'critical' temperature, which may be associated with a thin film rearrangement, is determined as 217° C. The same behavior has been observed with conductive substrates such as graphite. Three techniques of measurements were used: cyclic voltammetry, simultaneous optical and electrical measurements and a.c. complex impedance techniques.

The a.c. impedance diagrams were obtained at the equilibrium potential of the electrochromic electrode, in H_2SO_4 (N). Polymeric/metal interface models have been used in order to explain the a.c. complex diagrams obtained on uncolored heat treated WO_3 electrodes. In the case of heat treated colored films, the diffusion coefficient of H^+ ions into the oxide were obtained from these diagrams. The values of $\tilde{D}$ vary from $3.7 \times 10^{-10} cm^2 s^{-1}$ at 170° C, to $6.5 \times 10^{-10} cm^2 s^{-1}$ at 220° C.

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