

tion is reduced when the dimer is formed. Thus, the destabilization of the EC anion radical would be reflected in the larger observed equilibrium constant.

Conclusion

This work may represent the first successful attempt at fitting two experimental parameters to digitally simulated working curves. The preequilibrium mechanism that has been invoked explains concentration results that were hitherto ambiguous. A mechanism of this type is necessary to explain $\Delta \log t_f/\Delta \log C$ data obtained experimentally. Of course, other mechanisms may be invoked that result in fractional reaction orders (5). However, this mechanism accounts for the experimental data better than any pure first or second order mechanism. This work also provides an operational definition of reaction order in the study of homogeneous electrochemical kinetics (Eq. [17]). This may prove to be useful in future kinetic studies.

Acknowledgment

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The Electrochromic Process at WO_3 Electrodes Prepared by Vacuum Evaporation and Anodic Oxidation of W

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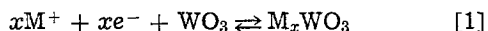
ABSTRACT

The kinetics of the electrochromic process and the stability with different WO_3 electrodes (evaporated film, electrodes obtained by anodic oxidation of W, polycrystalline, and single crystal) were studied. Cyclic voltammetry and chronoamperometry, together with optical absorption measurements in the electrochromic region were carried out. Impedance measurements at different frequencies of the WO_3 - H_2SO_4 (aq) interface were also made to compare the evaporated film and anodic oxide electrodes. These measurements showed that the electrochromic reaction at the WO_3 anodic film was much faster than that at the evaporated film electrode (by about two to three orders of magnitude). This difference in the reaction rates reflects the difference in the rate of diffusion of H^+ in the films. Infrared spectroscopic measurements of the films were carried out to obtain information about the water content of the films. The differences in the kinetic behavior of the electrochromic process at the two electrodes were attributed to differences in porosity and water content of these two films. The stability of the WO_3 film toward dissolution in aqueous solution was also shown to depend on the quantity of water in the film. In addition electrochemical behavior in the electrochromic region was studied in several other systems, including systems which contain H_2SO_4 as the electrolyte but with nonaqueous solvents and systems which contain Li^+ , replacing H^+ , in nonaqueous solvents. The solvent and the cation both affect the kinetics of the electrochromic process and the stability of the amorphous films. The electrochromic process at single crystal and polycrystalline WO_3 was also studied and compared to the behavior of the amorphous film electrodes.

There have been numerous studies of the electrochromic process at the WO_3 electrode; these have been concerned with the fundamental nature of the coloration process and the practical aspects (color and bleach rate, stability) of interest in the construction of WO_3 film display devices (1-11). Most studies have

been performed with amorphous films prepared by vacuum evaporation on conducting glass substrates. We represent this material as WO_3 , although the actual films usually are defect compounds of the type WO_{3-y} , where y is of the order of 0.03 or less (1). The electrochromic process is believed to occur according to the following reaction

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where M is usually hydrogen ion, but may also be a metal ion, e.g., Li^+ . Several mechanisms have been proposed for the optical absorption that produces the blue color in the tungsten bronze, M_xWO_3 . Deb (1) proposed that electrons trapped at the oxygen vacancies in the WO_3 lattice are responsible for the absorption, while Faughnan *et al.* (2, 12) prefer inter-valence (IV) transitions, $W^{+5} \rightarrow W^{+6}$, for the observed color. Recent investigations, involving ESCA measurements (3) of the colored films and optical absorption spectra studies at various crystalline forms of colored WO_3 films (4, 13) suggest that the electrons trapped in the WO_3 which are responsible for the optical absorption in the amorphous colored film are localized on the tungsten ions, and IV transitions or small polaron transitions were proposed as the reason for the blue coloration. For polycrystalline WO_3 films, these measurements (3-4, 13) suggest that the electrons trapped in the WO_3 film during the coloration process are delocalized and the blue color observed is the result of metal-like transitions of these electrons similar to the transition found in single crystal tungsten bronzes (14). Other recent optical and conductivity measurements at WO_3 polycrystalline films (10) indicate that at high concentrations of M^+ the transitions in the colored films are metallic while at low x the transitions are of the localized type from donors in the grain boundaries to the conduction band.

While the nature of the reduced WO_3 and the processes giving rise to the optical absorption now appear to be well understood, the factors which control the kinetics of the coloring and the bleaching processes as well as the stability of the WO_3 film electrodes, which are vital to the construction of practical, display devices, have not been elucidated. Most of the previous efforts toward using the WO_3 film in display devices have used aqueous acid electrolyte solutions. Although thermodynamically, WO_3 is reported to be stable in aqueous acid solution (15), the amorphous WO_3 film dissolves and the lifetime of the device based on these systems is short. The nature of this dissolution reaction is not yet clear, and this problem must be overcome to use this system for practical devices. Other electrolytic solutions were used to replace the acid aqueous solution. Several nonaqueous solvents with acid or other cations like Li^+ (16-19) were tried but problems of irreversibility or slow kinetics were found with these systems. Display devices based on solid electrolytes (10, 20, 21) have been proposed but have not yet been used for practical devices, probably because of very slow coloring and bleaching with these.

The kinetics of the electrochromic process and the factors that control it have been the subject of several studies but a quantitative model of the process has not yet been described. Different amorphous films show quite different kinetic behavior (6, 11), even when the method of preparation of the films was similar. Difficulties in reproducing kinetic results in the case of chemical reduction of WO_3 by hydrogen was also mentioned by Benson *et al.* (22). Information about the mechanism of the electrocoloration reaction and proposed rate-determining steps (rds) have been given by Crandall and Faughnan and co-workers (6-8, 23). From the rate of decay of the current, i , in a two-electrode cell, they concluded that the rate of coloration of an amorphous WO_3 film in acid aqueous solution is controlled at low voltage by the rate of transfer of H^+ through the WO_3 -electrolyte interface. The current decrease was attributed to a "back EMF" formed as the hydrogen activity inside the film increased. At high voltages the rate was said to be controlled by H^+ diffusion in solution or in the film (7, 23). A similar dependence of i on t ($i \propto t^{-1/2}$) in the coloring process was also observed by Chang *et al.*

(9) and was attributed to H^+ diffusion in solution as the rds. The bleaching current, according to Faughnan *et al.* (6), is controlled for some films by the transport of H^+ in the film and is limited by the proton space charge region; however other films which did not behave according to this model were also found (6). Exchange currents (i_0) and symmetry factors (β) for the electrocoloration process were reported by Arnoldussen (24) but no mechanism to which these quantities apply was proposed.

There have been numerous investigations of the reduction of WO_3 to the blue hydrogen tungsten bronze by chemical reduction of WO_3 by H_2 (22, 25, 26). This reaction occurs at room temperature only if platinum is present and water is preabsorbed on the mixture; the rate of the reaction is determined by the rate of penetration of the hydrogen atoms below the surface of WO_3 into the lattice. Recently it has been observed that water is present in the evaporated thin films of WO_3 obtained under different conditions and that its presence is an important factor in the rate of electrochemical coloration of the film (11, 19, 27-29). There have also been a number of studies of the formation of anodic films on tungsten electrodes and the reduction of these (30). In this paper we describe studies of the kinetics of the electrochromic process and the stability of WO_3 films for different types of WO_3 electrodes including films prepared by vacuum evaporation and anodic oxidation of W, as well as single crystal and polycrystalline materials. The rates of the reactions and the stabilities of these materials are compared and new information about the role of the film structure and the amount water in the films in both the kinetics of the electrochromic processes and the stability of the film is presented.

Experimental

The electrochemical measurements were made with a three-electrode system with a PAR potentiostat (Model 173) which was supplied with voltage from Model 174 universal programmer. The reference electrode was $Hg/Hg_2SO_4/1M H_2SO_4$ (+0.67V vs. NHE) or an evaporated WO_3 film on SnO_2 glass, and the counterelectrode was a Pt wire.

The evaporated WO_3 film electrodes were prepared by heating WO_3 powder (99.9%, Apache Chemical Incorporated) from a W boat in a vacuum bell ($\sim 10^{-5}$ Torr) onto glass covered with SnO_2 (treated before deposition by immersion in a KOH-ethanol mixture for several hours, than in concentrated H_2SO_4 , then rinsed with distilled water, and dried in oven at $\sim 120^\circ C$). The thickness of the film and the rate of deposition (~ 10 A/sec) was monitored by quartz crystal thickness monitor (Sloan Company) or by weighing the sample. The electrical contact to the SnO_2 was made with silver epoxy cement. The anodic WO_3 was usually prepared by oxidizing W metal wire or disks, which were cut from 13 mm diameter W rods (Alfa Products), at +75V vs. a Pt counterelectrode in H_2SO_4 solution with a d-c power supply. The electrical contact to the W was made with silver solder. The electrode areas were: wire, 0.25 cm²; disk, 1.3 cm².

Combined electrochemical-optical measurements were done with a Cary Model 14 spectrophotometer. The cell for these measurements was a glass (or quartz) cell constructed with two flat glass (or quartz) windows. A-C impedance measurements were done with PAR Model HR-8 Lock-in amplifier. The sine wave voltage was supplied to the input of the potentiostat and to reference input of the lock-in amplifier from the same output of the oscillator, but it was attenuated by an operational amplifier adder circuit before connecting it to the input of the potentiostat to yield a modulation amplitude of 2-10 mV. The phase was calibrated at every frequency used with a known resistor and capacitor. The uncompen-

sated iR , caused by solution and electrode resistance was corrected with the positive feedback circuit of the potentiostat.

Infrared measurements were made with a Beckman Model IR9 spectrophotometer. The electrode, after removal from the solution, was rinsed in water and the drop of water left on the electrode was removed by shaking the electrode and with tissue paper. The electrode was then heated for ~ 2 min with a heat gun held far from the electrode. The WO_3 films were scraped from the substrates and pellets with KBr were made with a 0.5% concentration in WO_3 .

Solutions of $LiClO_4$ and tetra-*n*-butylammonium perchlorate (TBAP) in acetonitrile (ACN) were prepared in a He atmosphere in a glove box. The TBAP, polarographic grade (Southwestern Analytical Chemicals, Austin, Texas), was dried under vacuum at 100° - $110^\circ C$ for 3 days. The salts were then stored in the glove box. The ACN used was purified and distilled under vacuum as previously reported (31). The electrical connection to the single crystal WO_3 was made by In first electrodeposited on one face of the crystal and silver epoxy cement was used to connect a Cu wire to the In face.

Results and Discussion

Cyclic voltammetric, chronoamperometric, and coloration behavior.—The WO_3 film obtained by vacuum evaporation is amorphous, as can be observed by x-ray examination of this film. A typical current-potential (i - E) curve of the WO_3 amorphous film electrode ($\sim 1 \mu m$ thick) in $1M H_2SO_4$ solution is shown in Fig. 1 together with the optical absorption of the film recorded simultaneously. The cathodic current which starts at about $+0.55V$ vs. NHE is associated with the coloring process and the anodic current following scan reversal is connected with the bleaching process. The coloration process is optically reversible, i.e., all color formed in the cathodic cycle is bleached in the anodic one. The reversal of the coloration process is relatively slow at the scan rate used. After the direction of the scan was reversed, the current remained cathodic and the color increased, only ~ 200 mV after the direction was reversed did the bleaching process start to take place. In cyclic voltammetry the electro-

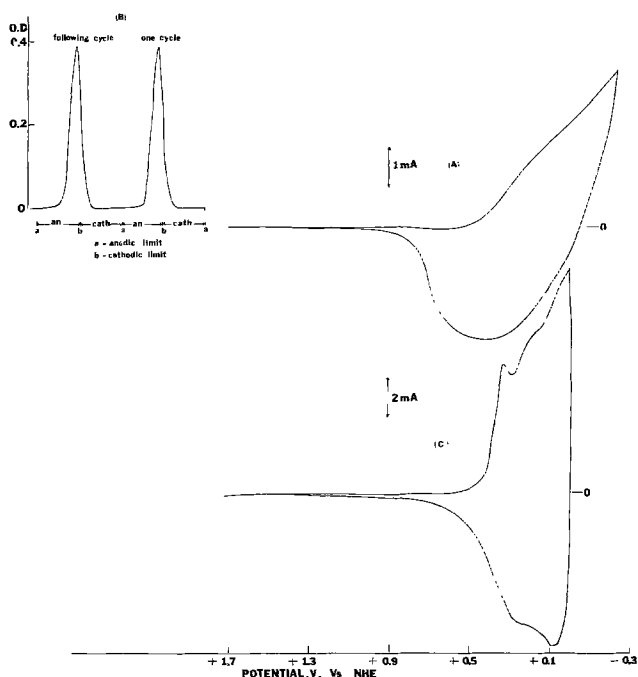


Fig. 1. Cyclic voltammogram (A) and optical absorption at 650 nm (B) measured simultaneously ($\sim 1 \mu m$ thick, $\sim 1 cm^2$ area) at WO_3 evaporated film electrode (100 mV/sec). (C) Cyclic voltammogram at WO_3 anodic film electrode (100 mV/sec, disk).

chromic current at a given E (more negative than $+0.4V$ vs. NHE) was proportional to $v^{1/2}$ at lower scan rates (1-50 mV/sec), as can be seen in Fig. 2(a) for a $1.8 \mu m$ thick film, and showed a somewhat smaller dependence at higher scan rates. This zone of proportionality of i with $v^{1/2}$ was different with different electrodes. This dependence implies that the electrochromic process at the WO_3 amorphous film is diffusion controlled at the lower scan rates.

Figure 3 shows the current (a) and light absorption (b) response at the same electrode during potential steps within the electrochromic region. Again all of the color accumulated in the cathodic step is bleached in the anodic one. Usually 50-100 sec was required to complete the coloring of the film in this potential region and then to bleach it completely for a $1 \mu m$ thick film.

The i - E behavior of a WO_3 film obtained by anodization of W is shown in Fig. 1(c). This is a typical characteristic obtained after ~ 20 hr of cycling in the potential region shown. The anodic film was obtained by oxidizing the W metal in the same solution at $+75V$ vs. Pt until a film of $\sim 1 \mu m$ thickness was obtained. A comparison of the i - E curve seen in Fig. 1(c) with that of the evaporated WO_3 electrode [Fig. 1(a)] shows that the coloring process starts at about the same potential in both films, but the shape of the i - E characteristic in the electrochromic process region is different. The electrochromic current at the W- WO_3 electrode is more structured and some current peaks are observed. Moreover the electrochromic process in the W- WO_3 case is faster than for the WO_3 evaporated film. The current in the electrochromic region changes sign and the bleaching anodic current starts almost

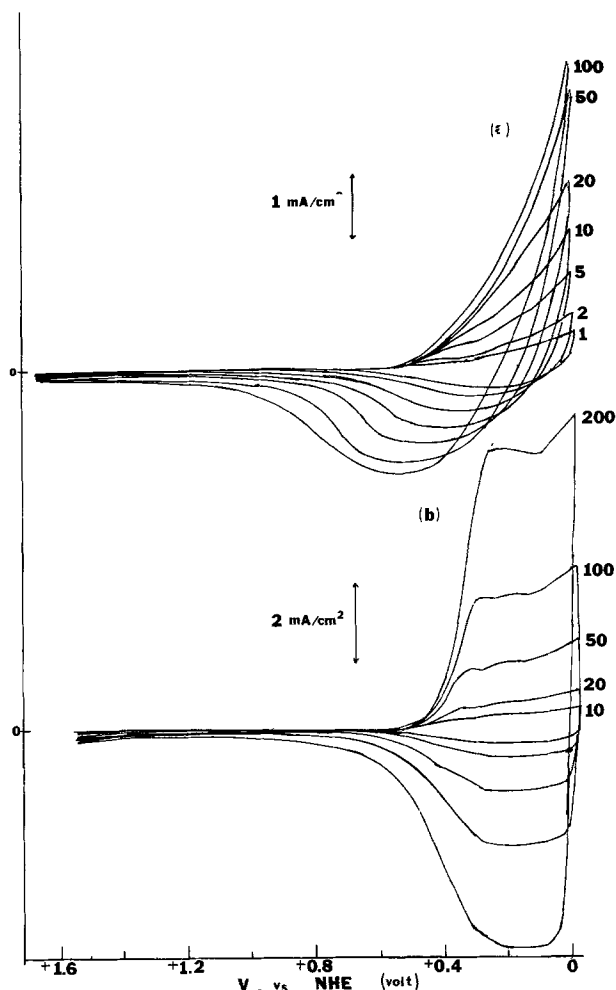


Fig. 2. Cyclic voltammogram recorded at different scan rates at (a) WO_3 evaporated film electrode ($1.85 \mu m$ thick, $0.15 cm^2$ area) and (b) anodic film electrode (disk). The numbers on the curves are scan rates in mV/sec.

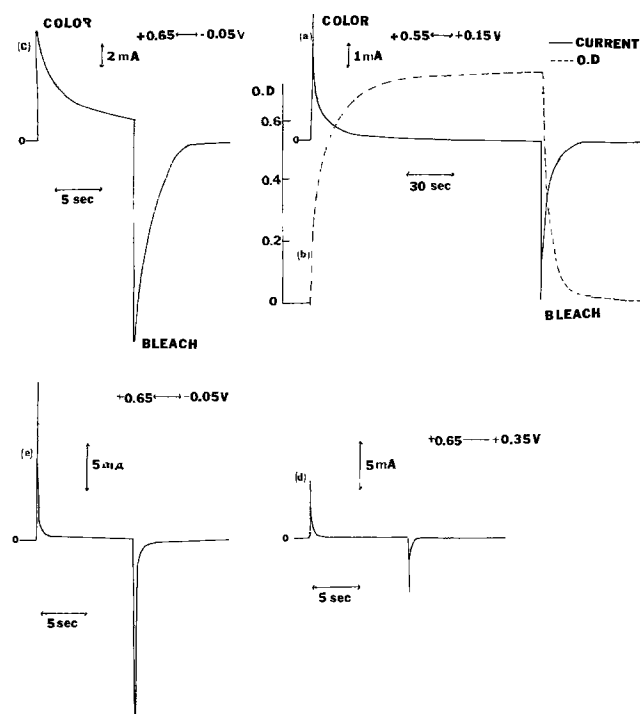


Fig. 3. (a) Current and (b) optical absorption change at 650 nm at WO_3 evaporated film ($\sim 1 \mu$ thick, $\sim 1 \text{ cm}^2$ area), recorded simultaneously during potential steps in the coloration region between $+0.65 \leftrightarrow +0.15\text{V}$; (c) current change at the same electrode during potential steps, $+0.65 \leftrightarrow -0.05\text{V}$; (d) current change at WO_3 anodic film electrode during potential steps in the coloration region between $+0.65 \leftrightarrow +0.35\text{V}$; (e) $+0.65 \leftrightarrow -0.05\text{V}$ (wire).

immediately as soon as the direction of the voltage scan is reversed. The fact that the electrochromic reaction is faster in the W- WO_3 case than in the WO_3 evaporated film is seen by comparison of the $i-t$ curves (d) and (e) vs. (a) and (c) in Fig. 3. The current decay in the W- WO_3 case in response to potential steps in the electrochromic region is faster, and only 0.1-0.5 sec is required to color and bleach a 1μ thick film completely. The dependence of the current in the electrochromic region on the scan rate is also different in both cases, as can be seen by comparing (a) and (b) of Fig. 2. In the W- WO_3 case the current is proportional to v (rather than to $v^{1/2}$ as seen with the evaporated film electrode). The proportionality of the current to v occurs until scan rates of 2 V/sec; above this scan rate the current tends toward $v^{1/2}$ dependence, or even smaller.

The difference in the cyclic voltammetric behavior of the two different films in the scan rate range described above implies that the electrochromic process is much faster at the anodic film. In this time regime the coloring process in the evaporated film is limited by diffusion while at the anodic film it is controlled by the conversion of the film in a Nernstian manner with a behavior typical of thin or adsorbed layers. More information about the rate-determining processes was obtained by a detailed analysis of the current-time curves obtained in the potential step experiments; typical results are shown in Fig. 4. Both films show generally similar behavior (for the cathodic and anodic regions), although the appropriate time regimes differ by a factor of 1000. There is a region for both films where the current decays with a $t^{-1/2}$ dependence (solid lines). This is the region of mass transfer control. At shorter times (corresponding to high scan rates) the current deviates from the $t^{-1/2}$ line in a direction suggesting limitation by kinetic control of a chemical or surface process. At longer times the deviation is in the direction in ac-

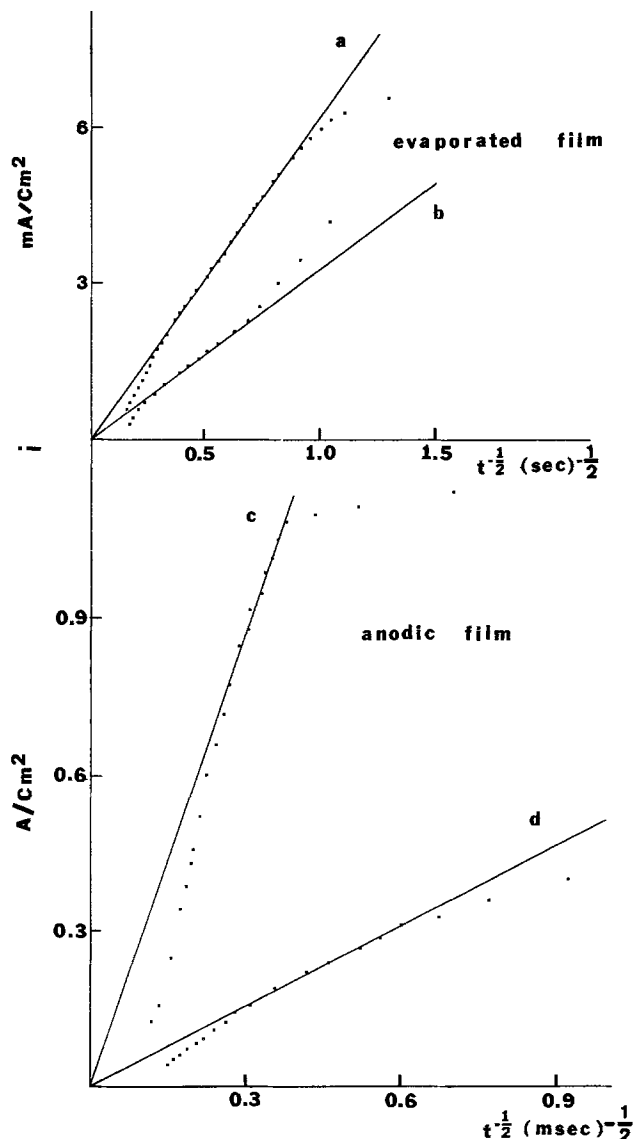


Fig. 4. Dependence of current on $t^{-1/2}$ at WO_3 evaporated film electrode (a) coloring at $+0.65 \leftrightarrow 0\text{V}$ steps, (b) bleaching at $+0.65 \leftrightarrow +0.15\text{V}$ steps; and at WO_3 anodic film electrode, (c) coloring at $+0.65 \leftrightarrow 0\text{V}$ steps, (d) bleaching at $+0.65 \leftrightarrow +0.25\text{V}$ steps.

cord with bulk modification of the film and the onset of thin layer behavior.

An estimate of the diffusion coefficient of the species in the film governing the current (proton or hydrogen atoms) in the diffusion-controlled region can be obtained by assuming a negligible contribution of migration and noting at what time the current begins to deviate from the $t^{-1/2}$ behavior. This occurs roughly when the diffusing species reaches the solid wall side of the film and is approximately given by a time, τ , of $0.3 l^2/D$ (32, 33), where l is the thickness of the film and D is the diffusion coefficient. From Fig. 4 (a and b) this occurs with the 1.8μ evaporated film at 10 sec, corresponding to a D of $1 \times 10^{-9} \text{ cm}^2/\text{sec}$. For the 1μ anodic film [Fig. 4 (c and d)] this occurs at 10 msec, yielding a D of $3 \times 10^{-7} \text{ cm}^2/\text{sec}$. These D values are generally in the range previously reported for diffusion of protons in WO_3 films (9). The time required to complete coloration of the film is about 10τ .

It should be pointed out that the diffusion coefficient (of H^+ in the evaporated film) calculated for the experiments, described under Fig. 4 (a and b) is a typical one. With the evaporated films, diffusion coefficients generally in the range of 8×10^{-9} - $1 \times 10^{-10} \text{ cm}^2/\text{sec}$ were found. Moreover, in some cases, in the

bleaching current with the evaporated film, a $t^{-1/2}$ region was not observed and instead other exponents of t , rather than -0.5 (-0.6 , -0.75 , for example) were observed in the middle range of the decay, indicating a migration contribution to the bleaching current in these cases (6, 34).

The behavior of polycrystalline and single crystal WO_3 in the electrochromic process was also examined. Polycrystalline WO_3 films were obtained from the amorphous evaporated films by annealing at 400°C for about 3 hr in air or under a nitrogen atmosphere. X-ray analysis shows that the film obtained is polycrystalline with a monoclinic structure. As shown previously (1, 11), the coloration of the polycrystalline WO_3 film was very difficult. The currents observed in cyclic voltammetry for film reduction were small and coloration required very negative potentials (i.e., in the hydrogen evolution region). Moreover, the electrochromic process was very irreversible. Similarly the electrochromic process with a WO_3 single crystal was much slower than that at the amorphous WO_3 film.

Impedance measurements at WO_3 -1M H_2SO_4 interface.—Further information about the kinetics of the electrochromic process at WO_3 was obtained by a-c current measurements at the WO_3 -1M H_2SO_4 interface in the electrochromic region. The in-phase and out-of-phase a-c currents as a function of voltage for scans of the d-c potentials within the electrochromic region at the WO_3 evaporated film electrode (with 30 Hz modulation frequency) are shown in Fig. 5. Similar results for the anodic WO_3 film are given in Fig. 6. These measurements were made with different modulation frequencies, the admittances in the equivalent parallel circuit, R_p^{-1} and ωC_p , were calculated for each frequency, and plots of $(\omega R_p)^{-1}$ vs. C_p (a Cole-Cole plot) (35) were drawn. Figure 7 is a Cole-Cole plot drawn for the electrochromic process at the WO_3 evaporated film (a) and at the anodic WO_3 film at two different d-c potentials (b and c). The relaxation frequency for the electrochromic process at the WO_3 evaporated film is lower than the lowest frequency used (i.e., <5 Hz) (and therefore a full semicircle cannot be observed). The shape of the plot at the frequencies shown is in accordance with the voltammetric behavior where there is a deviation from $v^{1/2}$ dependence of the current at high scan rates, as well as deviation from $t^{-1/2}$ dependence at short times. On the other hand, the relaxation frequency for the elec-

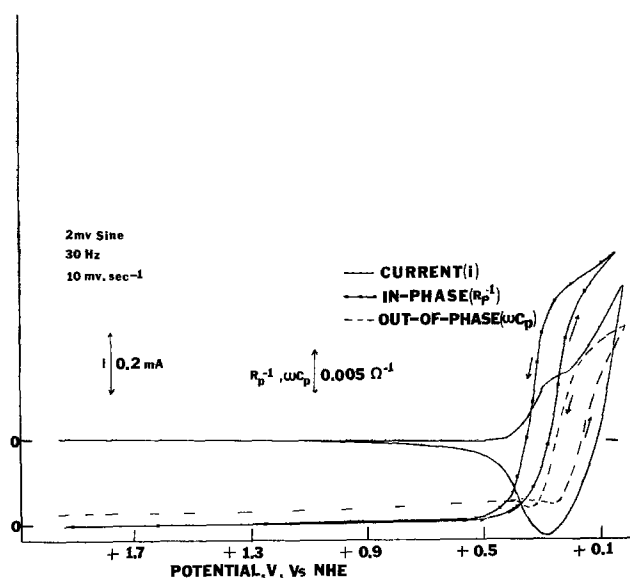


Fig. 5. A-C currents (in and out-of-phase) at the WO_3 evaporated film, 1M H_2SO_4 (30 Hz), and the cyclic voltammogram recorded simultaneously.

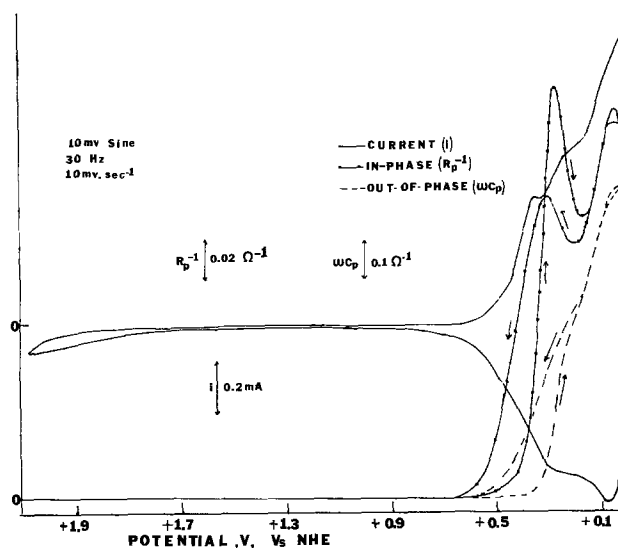


Fig. 6. A-C currents (in and out-of-phase) at the WO_3 (anodic film, wire) 1M H_2SO_4 (30 Hz), and the cyclic voltammogram recorded simultaneously.

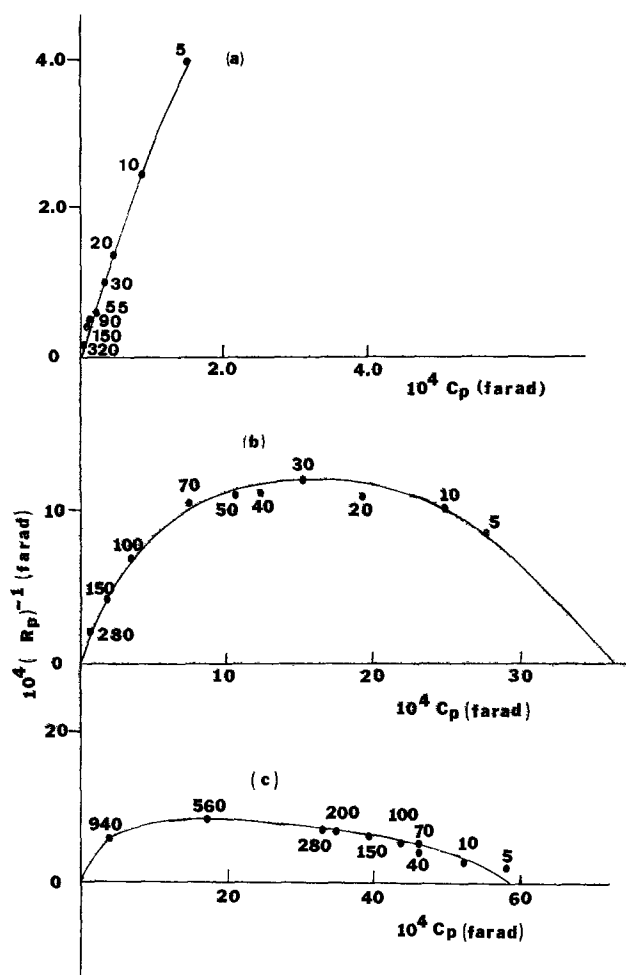


Fig. 7. Results of complex plane analysis (Cole-Cole plots) for the impedances measured at the WO_3 -1M H_2SO_4 interface. The numbers written on the plots are the frequencies in Hz. (a) WO_3 evaporated film electrode at $+0.17\text{V}$, (b) WO_3 anodic film electrode at $+0.23\text{V}$, (c) WO_3 anodic film electrode at $+0.01\text{V}$, (wire).

trochromic process at the WO_3 anodic film in 1M H_2SO_4 is much higher and a complete Cole-Cole plot could be drawn for this case as can be seen from Fig. 7 (b and c). For the process occurring at the more negative potential, the relaxation frequency is ~ 30 Hz (b) while at more negative potentials the re-

laxation frequency is even higher (~ 500 Hz). The shape of the Cole-Cole plot in Fig. 7 (b and c) indicates that the electrochromic process in this case is controlled by both activation and diffusion. Note that in the case of the W-WO₃ electrode structure occurs in the a-c currents in the electrochromic region which have different relaxation frequencies. Such structure is also observed in the cyclic voltammetric *i*-*E* curves. The probable reason for this is discussed later.

The studies described in the above sections show very clearly that the rates of the electrochromic process at the two WO₃ electrodes are different and suggest significant differences in the film structure.

Effect of water and porosity on the rate of the electrochromic process and stability of the film.—Anodic films are often hydrated and porous (36-39) and the water content of evaporated WO₃ films was recently examined (11, 19, 27-29). Since the observed differences in the rate of the electrochromic process could be associated with differences in water content, a study correlating these was undertaken. The water content of the films was measured from the infrared spectra of the films. A typical infrared spectrum of WO₃ films (Fig. 8) clearly shows the presence of the water. The sharp peak at 1650 cm⁻¹ and the peak at 3500 cm⁻¹ are characteristic of water with hydrogen bonding [the peaks at ~ 1650 and 3500 cm⁻¹ are associated with the O-H stretch and the H-O-H bend, respectively (27)]. There is a direct relationship between the water content of the films and their kinetic behavior. The difference in the infrared spectra of the WO₃ evaporated film electrodes [Fig. 8 (a and b)] shows a difference in water content. Fresh electrodes whose infrared spectra show a larger water content show larger currents in the electrochromic region and thus a more rapid coloring process. A direct relation between the amount of water in the evaporated film and its kinetic behavior is demonstrated by the experiments of Fig. 9(a). In this figure continuous cyclic voltammograms of the evaporated WO₃ film, whose infrared spectrum is shown in Fig. 8(a), are shown. The electrochromic current increases on cycling and the bleaching occurs more rapidly on scan reversal. These changes are accompanied by an increase in the color intensity as can be seen by simultaneous optical measurements (as in Fig. 1) and even by eye. Thus the rate of the electrochromic process becomes faster during continuous cycling in this region. The increase in the current is fast at the beginning and then becomes slower until the current reaches a maximum level after which it does not change for some time. If the cycling is continued for longer periods, the current starts to decrease gradually with time. Infrared examination of the WO₃ film from this series before performing the cycling process described above and after continuous cycling revealed that the amount of

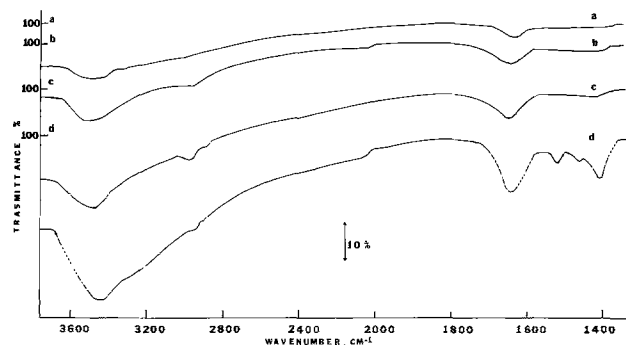


Fig. 8. Infrared spectra of WO₃ films: (a) WO₃ evaporated film which contains a small amount of water, (b) WO₃ evaporated film which contains larger amounts of water, (c) WO₃ anodic film after 1/2 hr cycling, (d) WO₃ anodic film after 20 hr cycling.

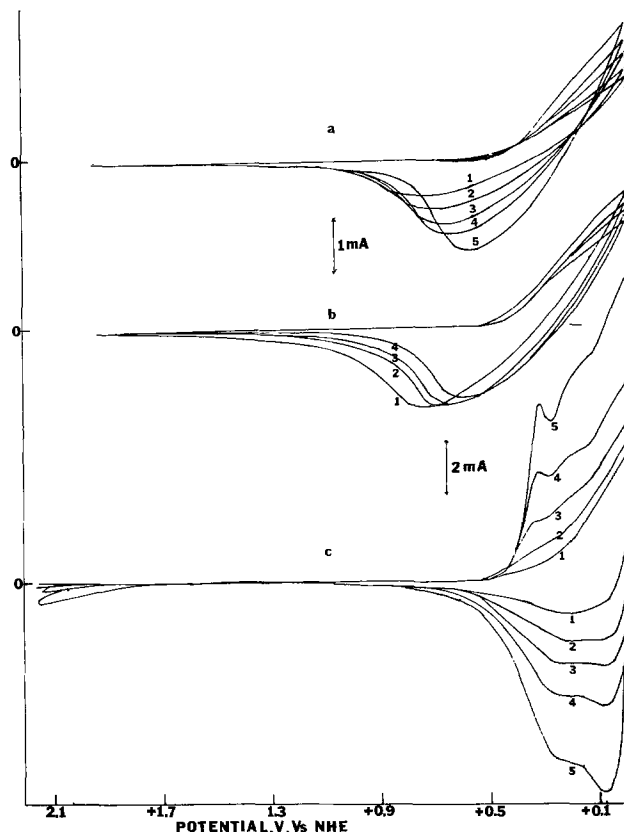


Fig. 9. (a) Change of current during continuous cycling (100 mV/sec, 1M H₂SO₄) of WO₃ evaporated film electrode which contains a small amount of water [Fig. 8(a)], the numbers in the figures represent voltammograms recorded at different times during the cycling process. Curve 1, first cycle; curve 2, after 7 min; curve 3, after 45 min; curve 4, after 2 1/4 hr; curve 5, after 13 1/2 hr. (b) Change of current during continuous cycling (100 mV/sec, 1M H₂SO₄) of WO₃ evaporated film electrode which contains higher amounts of water [Fig. 8(b)]. Curve 1, first cycle; curve 2, after 5 1/4 hr; curve 3, after 11 1/2 hr; curve 4, after resting at open-circuit conditions for additional 11 1/2 hr after curve 3 was recorded. (c) Change of current of the WO₃ anodic film electrode during continuous cycling in the 1M H₂SO₄ solution (100 mV/sec, disk). Curve 1, first cycle; curve 2, after 40 min; curve 3, after 1 1/2 hr; curve 4, after 4 hr; curve 5, after 22 hr.

water in the film increased during the continuous cycling process (i.e., the peaks in the infrared spectra increased). This experiment demonstrates that the increase in the rate of the coloration is associated with an increase of the water content in the film. This increase in the rate of the reaction is probably also associated with an increase in the porosity of the film. As we have shown in the previous section, the coloration process at the WO₃ evaporated film is diffusion controlled, where the diffusion process is probably that of hydrogen ions or atoms in the film. It is unlikely that diffusion of H⁺ in solution, which should be very fast for the 1M H₂SO₄ solutions employed here, can be rate determining. The increase of the amount of porosity and water content of the film probably makes the diffusion process faster, since the film becomes a better ionic conductor [hydrogen ions can be transported via H₃O⁺ by exchange between adjacent water molecules (22)]. In contrast to the changes observed in the film in the series described above, evaporated films which initially contain a larger amount of water [Fig. 8(b)] show different behavior on cycling in the electrochromic region. With these electrodes, the current decreases with time on continuous cycling and this trend starts from the first cycle [Fig. 9(b)]. At the same time the light absorption by the electrode also decreased. When the electrode was left in solution at open-circuit conditions

after being cycled in the electrochromic region for some time and then the cycling process was started again, the initial current after the rest period was lower than it was in the last cycle before the interruption [curve 4 in Fig. 9(b)]. The decrease in current described above is caused by the dissolution of the WO_3 film. The capacity of the film with respect to the coloring charge is dependent on the film thickness. On dissolution the film thickness decreases, the charging capacitance decreases, and, as a result, the current decreases. The difference in the evaporated films used in the experiments described in Fig. 9(a and b) can be attributed to differences in the procedure used in their preparation. The films described in the experiments in Fig. 9(b) were held under vacuum in the vacuum deposition apparatus after evaporation for a shorter time.

The behavior of WO_3 anodic film electrodes on continuous cycling in H_2SO_4 solution is different than that found with the WO_3 evaporated film electrodes. The i - E curve shown in Fig. 1(c) is characteristic of this electrode after about 20 hr cycling in the potential region shown after the W metal was first oxidized at +75V. The first cycles after the oxidation are shown in Fig. 9(c). Note that a very pronounced change in the i - E behavior occurs on continuous cycling. The first cycle looks small and irreversible, and resembles the i - E curve at the WO_3 evaporated film. For the first few cycles at the scan rate used, the current remained cathodic (coloring) after the direction of the voltage scan was reversed and became anodic (bleaching) only ~ 200 mV after the direction was reversed. On further cycling the current in the electrochromic region increased continuously and the voltage of zero current moves gradually to more negative voltages similar to the behavior shown for the films in Fig. 9(a). On further cycling the current continued to grow and new peaks in the current appeared; at the same time the direct dependency of the current on v became established. These changes in the i - E characteristic reflect changes in the rate of the electrochromic reaction and suggest that during the continuous cycling the electrochromic process at this electrode becomes faster. This and the new peaks which appear in the i - E curve during the cycling probably reflect changes in the WO_3 lattice. Examination of these films by infrared spectroscopy after 30 min of cycling shows that the film contains more water than the WO_3 evaporated films [Fig. 8(c)]. Examination of the films by infrared after 20 hr cycling shows that the quantity of water in the film has increased even more [Fig. 8(d)]. Moreover, not only did the intensity of the usual infrared peaks at 1650 and 3500 cm^{-1} increase, but new peaks appeared at 1400, 1460, and 1520 cm^{-1} in the infrared spectrum. These changes may be associated with the new peaks which appear in the i - E curve and which may be a result of new water phases in the WO_3 lattice (these peaks are approximately located at energies where peaks in the infrared spectrum of evaporated water appear, so that they might represent new phases of water in the WO_3 lattice which are not hydrogen bonded). Thus the results with the anodic WO_3 films again suggest that the change in the rate of the electrochromic process is associated with the change in the quantity of water in the film and that the increase in quantity of water in the lattice is accompanied by increase in rate of the electrochromic process. The infrared experiments with the anodic films and the evaporated films described above along with the i - E curves suggest that the presence of water in the films is important in the kinetics in the electrochromic region. For the WO_3 evaporated film electrode, where the quantity of water in the film is small, the electrochromic process is controlled by the diffusion of hydrogen ions or atoms in the film and the rate of this process increases with the amount of water in the films. For the anodized WO_3 electrode

after prolonged cycling, the water content of the film is sufficiently high for rapid diffusion of H^+ and the electrochromic process is reversible with these films to very high scan rates. Even for the first few cycles with W-WO_3 electrodes, when the i - E curves look irreversible and the infrared spectrum shows that the amount of water in the anodized film is not much higher than that in the evaporated WO_3 film, the current at a given potential is closer to proportionality with scan rate. The porosity of the film may also be a factor in the rate of reaction. The fact that the amount of water increases in the films during cycling for both the evaporated film and the anodized electrodes probably reflects changes occurring in the porosity of these films during the repeated coloring-bleaching cycles, as protons migrate in and out of the film structure. The increasing porosity of the anodic WO_3 film on repeated color-bleach cycles can be seen again from the anodic current which appears during the recording of the i - E curve [Fig. 9(c)].

Continuous growth of the oxide film on the W electrode initially requires anodization at very positive potentials. Oxidation at potentials of +2V shows an anodic current which quickly decays to zero as an insulating film forms on the electrode. Sustained oxidation and film growth only occur during oxygen evolution at extremely positive voltages (30). After about an hour of repeated cycling of the anodized W electrode a small anodic current at about +1.9V appears in the i - E curve as shown in Fig. 9(c). This current increases on further cycling and then starts to decrease, disappearing after several hours of cycling. The magnitude of this current and the number of cycles needed before it starts to appear is very sensitive to the way the initial anodic film was prepared and to its initial thickness. This current appears at more positive potentials, the less negative the cathodic scan limit potential is for cycles in the electrochromic region. Moreover, if after the anodic current appears, the anodic limit of the cycle is brought to a less positive potential, after another few cycles through the electrochromic region the anodic current again appears at the less positive potentials [Fig. 10(a)]. That this anodic current after repeated coloring-bleaching

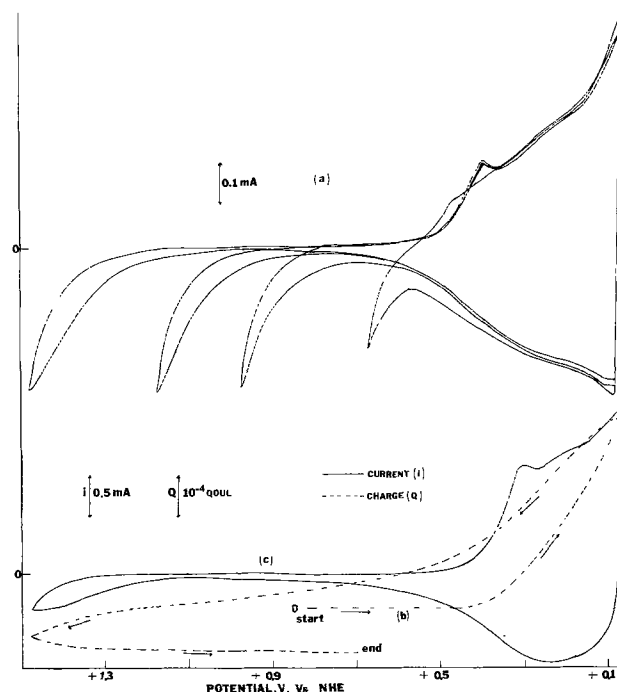


Fig. 10. (a) Current-voltage at WO_3 anodic film electrode recorded at different anodic limit potentials (100 mV/sec). (b) Charge-voltage and (c) current-voltage curves at WO_3 anodic film electrode, recorded simultaneously (100 mV/sec), wire.

cycles is not connected with the bleaching process is seen from the charge-voltage curve [Fig. 10(b)], where all cathodic (coloring) charge is removed before this anodic current starts. More likely it is caused by additional oxidation of the W metal to WO_3 . This further oxidation at such low positive potentials becomes possible because the repeated cycles in the electrochromic region cause some change in the structure of the WO_3 film that makes it a better ionic conductor, probably with a more porous structure to the film. The increase in the porosity of the film can be attributed to repeated expansion of the lattice during the penetration of the solvated hydrogen ion (40-42). If the anodic limit of the scan is brought to more negative potentials, more color-bleach cycles are needed before the oxidation current again appears at lower positive potentials. The greater porosity and higher water content of the anodic film electrodes as compared to the evaporated film then accounts for the difference in the rds for the electrochromic reaction at these two electrodes, leading to a much higher rate at the anodic film electrode.

Stability of WO_3 electrodes.—Both the single crystal and polycrystalline WO_3 electrodes show high stability in the aqueous acid solutions toward dissolution under open-circuit conditions and when the potential is cycled in the electrochromic region (where only very small currents flow). The amorphous film electrodes, on the other hand, dissolve slowly even at open circuit in the aqueous acid solutions. The rate of dissolution appears to be associated with the amount of water in the film. Thus for an evaporated film electrode initially containing a small amount of water the current in the i - E curves attains a maximum value and then begins to decrease [Fig. 9(a)]. Films that contain a larger amount of water [Fig. 9(b)] show a decrease right from the start. This decrease is associated with dissolution of the WO_3 which ultimately leads to failure of the electrode to color and bleach.

The effect of solvent on the kinetics and stability.—The behavior of the WO_3 electrodes in acidified non-aqueous solutions [methanol, acetonitrile (ACN), ethylene glycol, and glycerol containing 1M H_2SO_4] was also investigated. The electrochromic process was slower in all of these solvents than with the acid aqueous solution. For methanol and ACN, the current in the electrochromic region was about 5-10 times lower than in the water solution with the evaporated film electrode. The WO_3 electrode in these solutions was also not stable and slow dissolution occurred. The i - E and i - t curves for an evaporated film electrode in glycerol solution (1:10 H_2SO_4 /glycerol) is shown in Fig. 11. The current in the glycerol solution is about 2 or 3 times smaller than the current at the same electrode in the water solution. This is reflected by a decrease in the speed of coloration by about the same factor. The difference between the i - E curve in water

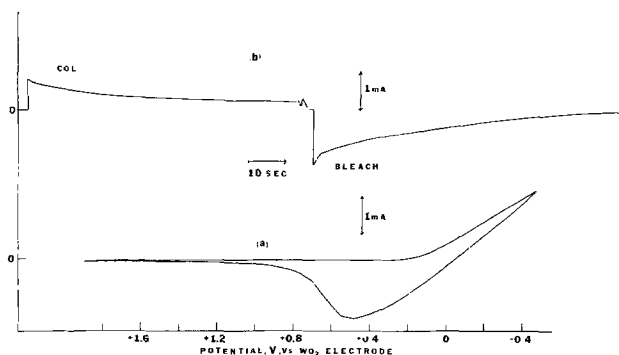


Fig. 11. (a) Cyclic voltammogram (100 mV/sec) and (b) change of current during potential steps in the coloring region at WO_3 evaporated film electrode in H_2SO_4 -glycerol solution.

and glycerol solution is especially pronounced for the anodic film electrode (Fig. 12). Transfer of the electrode from water (where curve a is obtained) to glycerol solution (curve b) causes a large change in the i - E curve. The peaks in the i - E curve seen in water disappear and the i - E curve resembles that of the evaporated film electrode in glycerol or aqueous solution. The current in the glycerol solution decreased for some time with continued cycling after the transfer from the water to the glycerol solution. At low scan rate the current in the glycerol solution varies with $v^{1/2}$, implying diffusion control in this solution. The change in the kinetic behavior and the slower response in the case of glycerol (and the other non-aqueous solvents) probably is caused by much slower transport of the solvated proton and the slower aequation of the film. For the evaporated film, the electrochromic process is still diffusion controlled while for the anodic film the electrochromic reaction, which showed thin layer behavior in the water solution, became diffusion controlled on transfer to the glycerol solution.

The stability of the evaporated film electrode in the glycerol solution (1:10 H_2SO_4 /glycerol) was excellent. More than 5 million color-bleaching steps were performed with this electrode by cycling continuously ($\pm 3V$) between two identical electrodes at 0.5 Hz for a period of about 6 months and the WO_3 electrode still remained stable. The reason for the stability of this electrode in the glycerol solution is probably connected with the fact that the electrode does not continually take up water during the cycling.

The electrochromic behavior with two other cations (rather than hydrogen ion) was also studied by using the salts $LiClO_4$ and tetra-*n*-butylammonium perchlorate (TBAP) in pure ACN. With the large cation TBA^+ , no coloring was observed at the WO_3 evaporated film even at large negative potentials. With Li^+ , this electrode could be colored a deep blue but the reaction was irreversible, and the electrode could not be bleached again, even at very positive potentials. These experiments show that the electrochromic behavior is sensitive to the radius of the ion which must penetrate the WO_3 lattice in the reduction process. For the small hydrogen ion, the electrochromic reaction is much faster and more reversible, while with TBA^+ , the reduction is not possible and with Li^+ , which is smaller than TBA^+ but larger than H^+ , the reduction is slow and irreversible. A similar trend was mentioned by Schöllhorn *et al.* (40, 41) for redox reactions at MoO_3 and other chalcogenides with differ-

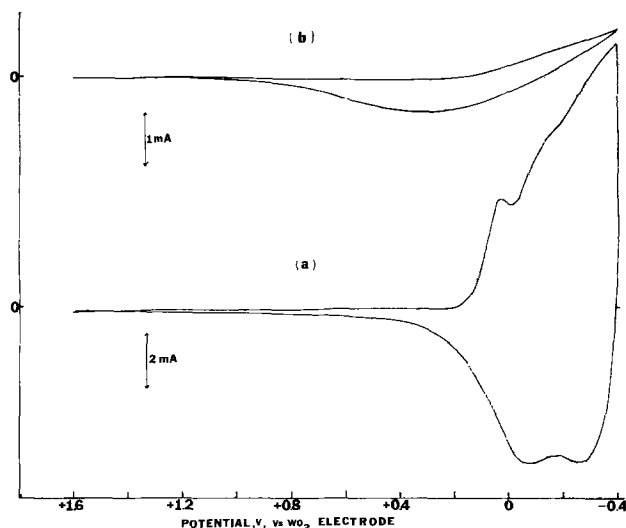


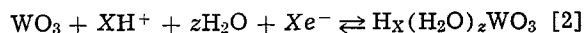
Fig. 12. Comparison of cyclic voltammogram at WO_3 anodic film electrode (100 mV/sec) in (a) H_2SO_4 -water solution and (b) H_2SO_4 -glycerol solution, disk electrode.

ent cations. Hersh *et al.* (19) mention "aging" effects in the reduction and oxidation of WO_3 in the presence of Li^+ in propylene carbonate solutions. In this case the electrode gradually became blue on repeated color-bleaching steps.

Conclusions

The electrochromic reaction is much faster at anodic film than at the evaporated film electrodes. The kinetic behavior depends on the quantity of water in the film and its porosity. The stability of the film toward dissolution in acid aqueous solution is also dependent on the amount of water and the porosity of the film. The higher the porosity and water content of the film is, the higher the rate of the electrochromic process at this film, but at the same time the stability of the film toward dissolution in the acid aqueous solution decreases.

This behavior can be understood, if the over-all reaction mechanism is written as



and one assumes that the mobility of hydrogen ions (or atoms) in the film depends on the amount of water in it. The penetration of water into the film causes expansion of the lattice (40-42) and makes it more porous and available to even greater water penetration. However the higher the water content of the film, the more easily it dissolves. This dissolution may be due to hydrate formation [e.g., $\text{WO}_3 \cdot \text{H}_2\text{O}$ (37, 39) and $\text{WO}_3 \cdot 2\text{H}_2\text{O}$]; these hydrates are known to be more soluble than the WO_3 itself. WO_3 itself is insoluble in acid solution (15) and $\text{WO}_3 \cdot 2\text{H}_2\text{O}$ dissolves more readily than $\text{WO}_3 \cdot \text{H}_2\text{O}$ (43, 44). There is also (37-39, 45) the possibility that the hydrated WO_3 dissolves in acid solution as WO_2^{+2} .

The irreproducible behavior sometimes found [e.g., by Faughnan *et al.* (6)] in the kinetic behavior of different amorphous evaporated WO_3 films can also be understood. Different electrodes, even if they are prepared in a similar manner, may contain different amounts of water or differ in porosity and will thus show different kinetic behavior. They may show different dissolution rates and stabilities for the same reasons.

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