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 $\Delta \log t/t' \Delta \log C$ 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.

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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$_3$-HSO$_4$ (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$_2$SO$_4$ 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$_{3-x}$, 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.
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, MₓWO₃. Deb (1) proposed that electrons trapped at the oxygen vacancies in the WO₃ lattice are responsible for the absorption, while Faughnan et al. (2, 12) prefer inter-valence (IV) transitions, W⁺⁺ → W⁺⁺, for the observed color. Recent investigations, involving ESCA, x-ray photoelectron spectroscopy (XPS) of the coloration absorption spectra studies at various crystalline forms of colored WO₃ films (4, 13) suggest that the electrons trapped in the WO₃ 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 of polycrystalline WO₃ films. These measurements (3-4, 13) suggest that the electrons trapped in the WO₃ 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 WO₃ polycrystalline films suggest 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 WO₃ 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 WO₃ film electrodes, which are vital to the construction of practical, display devices, have not been elucidated. Most of the previous efforts toward using the WO₃ film in display devices have used aqueous acid electrolyte solutions. Although thermodynamically, WO₃ is reported to be stable in aqueous acid solution (15), the amorphous WO₃ 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 and chemical reduction of WO₃ by hydrogen were 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 the amorphous WO₃ film by hydrogen absorption is controlled at low voltage by the rate of transfer of H⁺ through the WO₃-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 on the 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 (8). Exchange currents (iₑ) 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 WO₃ to the blue hydrogen tungsten bronze by chemical reduction of WO₃ by H₂ (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 WO₃ into the lattice. Recently it has been observed that water is present in the evaporated thin films of WO₃ 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 WO₃ films for different types of WO₃ 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/Hg₂SO₄/1M H₂SO₄ (+0.67V vs. NHE) or an evaporated WO₃ film on SnO₂ glass, and the counterelectrode was a Pt wire. The evaporated electrodes were prepared by heating WO₃ powder (99.8%, Apache Chemical Incorporated) from a W boat in a vacuum bell (~10⁻⁵ Torr) onto glass covered with SnO₂ (treated before deposition by immersion in a KOH-ethanol mixture for several hours, then in concentrated H₂SO₄, then rinsed with distilled water, and dried in oven at ~120°C). The thickness of the film and the rate of deposition (~10 A/sec) were determined from the crystal thickness monitor (Sloan Company) or by weighing the sample. The electrical contact to the SnO₂ was made with silver epoxy cement. The anodic WO₃ 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 H₂SO₄ solution with a d-c power supply. The electrical contact to 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. 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°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 electrolyte was prepared in a He atmosphere in a glove box. The TBAP, perchlorate (TBAP) in acetonitrile (ACN) were prepared in a He atmosphere in a glove box. 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 (~1 μm thick) in 1M H$_2$SO$_4$ solution is shown in Fig. 1 together with the optical absorption of the film recorded simultaneously. The film coloration is optically reversible, i.e., all color formed in the cathodic step is bleached in the anodic step. The detection 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 +0.5V vs. Pt until a film of ~1 μm 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...
immediately as soon as the direction of the voltage scan is reversed. The fact that the electrochromic reaction is faster in the W-WO₃ case than in the WO₃ 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-WO₃ 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 1 μm 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-WO₃ case the current is proportional to v (rather than to v¹/² 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 v¹/² dependence, or even smaller.

A dependence of current on τ⁻¹/² at WO₃ evaporated film electrode (a) coloring at +0.65 ↔ 0 V steps; (b) bleaching at +0.65 ↔ -0.15V steps; and at WO₃ anodic film electrode, (c) coloring at +0.65 ↔ 0 V steps, (d) bleaching at +0.65 ↔ -0.05V (wire).

Fig. 4. Dependence of current on τ⁻¹/² at WO₃ evaporated film electrode (a) coloring at +0.65 ↔ 0 V steps; (b) bleaching at +0.65 ↔ -0.15V steps; and at WO₃ anodic film electrode, (c) coloring at +0.65 ↔ 0 V steps, (d) bleaching at +0.65 ↔ -0.05V (wire).

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 agreement 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 l²/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 1.8 μm evaporated film at 10 sec, corresponding to a D of 1 x 10⁻⁹ cm²/sec. For the 1 μm anodic film [Fig. 4 (c and d)] this occurs at 10 msec, yielding a D of 3 x 10⁻⁷ cm²/sec. These values are generally in the range previously reported for diffusion of protons in WO₃ 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 x 10⁻¹⁰-1 x 10⁻¹⁰ cm²/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$_2$SO$_4$ 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$_2$SO$_4$ 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, $R_P$ and $C_P$ 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 $t^{1/2}$ 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 electrochromic process at the WO$_3$ anodic film in 1M H$_2$SO$_4$ 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 $\sim$30 Hz (b) while at more negative potentials the relaxation frequency is $\sim$5 Hz (c).
The relaxation 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 WWO3 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 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 H\(_2\)SO\(_4\) 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 H\(_3\)O\(^+\) 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

![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.](image_url)
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 WO₃ 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 WO₃ anodic film electrodes on continuous cycling in H₂SO₄ solution is different than that found with the WO₃ 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 R. 

The first cycle looks small and irreversible, and resembles the i-E curve at the WO₃ evaporated film. For the first few cycles at the scan rate used, the current remained cathodic (coloring) after the direction of the voltage sweep 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 WO₃ lattice. Examination of these films by infrared spectroscopy after 30 min of cycling shows that the film contains more water than the WO₃ evaporated films.

Continuous growth of the oxide film on the W electrode initially requires anodization at very positive potentials. Oxidation at potentials of +2 V 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 +1.9 V 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. This anodic current after repeated coloring-bleaching...
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 WO3. 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 WO3 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 films electrodes as compared to the evaporated film then accounts for the difference in the 1ds for the electrochromic reaction at these two electrodes, leading to a much higher rate at the anodic film electrode.

Stability of WO3 electrodes. — Both the single crystal and polycrystalline WO3 films 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 WO3 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 WO3 electrodes in acidified nonaqueous solutions [methanol, acetonitrile (ACN), ethylene glycol, and glycerol containing 1M H2SO4] was also investigated. The electrochromic process was slower in all of these solvents than with the acid, aerous solvents) probably is caused by much slower transport of the solvated proton and the slower dissolution 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 H2SO4/glycerol) was excellent. More than 5 million color-bleaching steps were performed with this electrode by cycling continuously (± 3V) between two identical electrodes at 0.5 Hz for a period of about 6 months and the WO3 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 LiClO4 and tetra-n-butylammonium perchlorate (TBA +), no coloring was observed at the WO3 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 WO3 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 MoO3 and other chalcogenides with differ-

![Fig. 11. (a) Cyclic voltammogram (100 mV/sec) and (b) change of current during potential steps in the coloring region at WO3 evaporated film electrode in H2SO4-glycerol solution.](image)

![Fig. 12. Comparison of cyclic voltammogram at WO3 anodic film electrode (100 mV/sec) in (a) H2SO4-water solution and (b) H2SO4-glycerol solution, disk electrode.](image)
ent cations. Hersh et al. (19) mention "aging" effects in the reduction and oxidation of WO₃ 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

$$\text{WO}_3 + XH^+ + \text{H}_2\text{O} + \text{X}^- \rightarrow \text{H}_x(\text{H}_2\text{O})_y\text{WO}_3 \quad [2]$$

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., WO₃·H₂O (37, 39) and WO₃·2H₂O); these hydrates are known to be more than WO₃ itself. WO₃ is insoluble in acid solution (15) and WO₃·2H₂O dissolves more readily than WO₃·H₂O. There is also (37-39, 48) the possibility that the hydrated WO₃ dissolves in acid solution as WO₃X⁻.

The irreproducible behavior sometimes found (e.g., by Faughnan et al. (61) in the kinetic behavior of different amorphous evaporated WO₃ 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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