

N	species flux, moles/cm ² -sec
R	gas constant, 8.314 J/gmole-deg
Re	$\rho v d_p / \mu$ Reynolds number, dimensionless
Sc	$\mu / \rho D$ Schmidt number, dimensionless
T	temperature, °K
v	mass average velocity, cm/sec
V	volumetric flow rate, cm ³ /min
y	distance along electrode, cm
Y	y/l distance along electrode, dimensionless
z_i	symbol of electronic charge of species i
Greek Characters	
α	anodic transfer coefficient
β	cathodic transfer coefficient
ϵ	void fraction, cm ³ void space/cm ³ reactor volume
Γ	$aknF^{2l^2}c^0/\kappa RT$, mass transfer coefficient, dimensionless
ζ	vl/D , velocity, dimensionless
κ	electrolyte conductivity, (Ω -cm) ⁻¹
μ	viscosity, g/cm sec
λ	species concentration, dimensionless
ρ	density, g/cm ³
ξ	$i_0 a l^2 F / \kappa RT$, electrochemical reaction rate constant, dimensionless
ϕ	potential, V
Φ	potential, dimensionless
Φ_a	applied potential, dimensionless
χ	$i_0 a l^2 / n F D c^0$, mass transfer resistance parameter, dimensionless

Superscripts

l	value at reactor outlet
o	value at reactor inlet
s	surface value

Subscripts

i	species i
r	reference value

REFERENCES

- R. M. Gould, Ph.D. Dissertation, University of Illinois at Urbana-Champaign, Illinois (1979).
- R. de Levie, *Adv. Electrochem. Electrochem. Eng.*, **6**, 329 (1967).
- J. S. Newman and W. Tiedemann, *AIChE J.*, **21**, 25 (1975).
- J. S. Newman and W. Tiedemann, *Adv. Electrochem. Electrochem. Eng.*, **11**, 353 (1978).
- R. W. Houghton and A. T. Kuhn, *J. Appl. Electrochem.*, **4**, 173 (1974).
- R. Alkire and R. Gould, *This Journal*, **123**, 1842 (1976).
- B. G. Ateya, *J. Electroanal. Chem. Interfacial Electrochem.*, **76**, 315 (1977).
- B. G. Ateya and L. G. Austin, *This Journal*, **124**, 1540 (1977).
- J. A. Trainham and J. S. Newman, *ibid.*, **124**, 1528 (1977).
- Y. Volkman, *J. Appl. Electrochem.*, **8**, 374 (1978).
- J. A. Trainham and J. S. Newman, *This Journal*, **125**, 58 (1978).
- R. Alkire and A. Mirarefi, *ibid.*, **124**, 1214 (1977).
- G. M. Cook and C. Portal, Paper 28 presented at the Electrochemical Society Meeting, Las Vegas, Nevada, Oct. 17-22, 1976.
- L. E. Vaaler, *This Journal*, **125**, 204 (1978).
- R. Alkire and B. Gracon, *ibid.*, **122**, 1594 (1975).
- J. C. Armour and J. N. Cannon, *AIChE J.*, **14**, 415 (1968).
- A. E. Harvey, J. A. Smart, and E. S. Amis, *Anal. Chem.*, **27**, 26 (1955).
- J. S. Newman, *Ind. Eng. Chem. Fundam.*, **7**, 514 (1968).
- D. A. G. Bruggemann, *Ann. Phys. (N.Y.)*, **24**, 636 (1935).
- D. N. Bennion and J. S. Newman, *J. Appl. Electrochem.*, **2**, 113 (1972).
- G. W. Vinal and D. N. Craig, *Bur. Stand. J. Res.*, **10**, 781 (1933).
- M. G. Fouad and G. H. Sedhamed, *Electrochim. Acta*, **20**, 615 (1975).
- C. N. Satterfield and D. H. Cortez, *IEC Fundam.*, **9**, 613 (1970).
- L. N. Klatt and W. J. Blaedel, *Anal. Chem.*, **39**, 1065 (1967).
- A. J. Arvia and J. C. Bazan, *Electrochim. Acta*, **9**, 17 (1964); *ibid.*, **11**, 881 (1966).
- R. Caban and T. W. Chapman, *This Journal*, **124**, 1371 (1977).
- "Handbook of Chemistry," 10th ed., p. 1678, McGraw Hill, New York (1967).
- "Handbook of Chemistry," 10th ed., p. 1175, McGraw Hill, New York (1967).
- M. A. Zhamagortsyants, A. A. Yavich, and A. T. Vagramyan, *Elektrokhimiya*, **11** (1), 103 (1975).

Semiconductor Electrodes

XXII. Electrochromism and Photoelectrochemistry at WO₃ Layers

Prepared by Thermal and Anodic Oxidation of W

Benjamin Reichman and Allen J. Bard*

Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712

ABSTRACT

Electrochromism was studied with WO₃ layers prepared by thermal oxidation of W, and compared to the electrochromic behavior of other WO₃ electrodes (anodic, amorphous, and annealed films). Although the WO₃ layers obtained by thermal oxidation of W are crystalline, the electrochromic performance with this electrode is comparable to that of the evaporated amorphous WO₃ electrode. The photoelectrochemical behavior of these electrodes, and in particular the effect of a pretreatment of repeated color-bleaching cycles, was also studied. Repeated color-bleaching cycles resulted in a significant improvement in the photoelectrolytic behavior of the WO₃ layers. The photocurrent increased and the spectral distribution of the photocurrent shifted to longer wavelengths. The repeated color-bleaching cycles also cause a great improvement in the electrochromic behavior of the WO₃ electrode as compared to that of the initially prepared electrode.

Electrochromism of WO₃ electrodes has been the subject of intensive investigation during the last few

years in connection with its use in display devices (1-5). A major problem with the WO₃ evaporated film which is commonly used as the display electrode, is the fact that it dissolves in the H₂SO₄-aqueous solution,

* Electrochemical Society Active Member.
Key words: electrode, electrolyte.

which is usually used as the electrolytic solution in the device (6-8). Several methods have been attempted to circumvent this problem [e.g., nonaqueous solvents with sulfuric acid or Li^+ as the electrolyte (6, 7, 9-11)]. In some solutions the WO_3 evaporated film electrode was found to be more stable than in aqueous solutions, but in these cases the response times for the color-bleach process were longer (6, 7). Display systems based on solid electrolytes have also been studied (12-14). Display devices based on dielectric materials which absorb water to replace the liquid electrolyte also failed to show satisfactory performance (15-18). As opposed to the amorphous WO_3 evaporated film (which is obtained by vacuum evaporation), polycrystalline WO_3 formed by heating the evaporated film to 400°C was found to be more stable in aqueous sulfuric acid solution; the electrochromic performance of such electrodes was very poor, however (1, 7, 13-21).

In this paper, we describe the electrochromic process with WO_3 electrodes obtained by thermal oxidation of tungsten metal. These WO_3 layers are crystalline, but as opposed to the crystalline WO_3 which is obtained by annealing the amorphous evaporated WO_3 films, they show good electrochromic behavior and with a performance similar to that of the amorphous WO_3 evaporated film. On the other hand, the stability of the WO_3 obtained by thermal oxidation of W is also high and therefore these WO_3 layers or modification of them seem to be promising materials for electrochromic display devices.

Because WO_3 is an n-type semiconductor, it has recently attracted attention in photoelectrochemical applications. Photooxidation of water was studied using WO_3 single crystals (22-23) and polycrystalline WO_3 prepared by several methods (24-28). In most of these electrodes, photoanodic current is generated only under irradiation with light of wavelength below 400-480 nm. Several methods have been tried to extend the response of wide bandgap semiconductor electrodes to longer wavelengths. We show here that treatment of the thermally oxidized WO_3 electrode by repetitive color-bleaching cycles leads to a marked extension of the photoelectrochemical response. This change in the spectral distribution of the photocurrent suggests that the repeated color-bleaching cycles cause the creation of new electronic states in the WO_3 lattice which are located at energies within the bandgap of the semiconductor.

Experimental

The thermally oxidized WO_3 electrodes were prepared by heating W disks in air in a furnace at about 750°C for 30 min. The WO_3 layers obtained were yellow in color with usual thicknesses of about $25\ \mu\text{m}$ [as estimated by weighing before and after oxidation taking a WO_3 density of $7.16\ \text{g}/\text{cm}^3$ (1)]. Part of the WO_3 was scraped off and electrical contact to the underlying W was made with silver epoxy cement. The WO_3 anodic film was prepared as described earlier (7). The area of the electrodes was $\sim 1.3\ \text{cm}^2$.

Electrochemical measurements were performed with a Princeton Applied Research (PAR) potentiostat (Model 173) which was supplied with voltage from a PAR Model 174 universal programmer. The reference electrode was $\text{Hg}/\text{Hg}_2\text{SO}_4/1\text{M}\ \text{H}_2\text{SO}_4$ ($+0.67\text{V}$ vs. NHE) and the counterelectrode was a Pt wire. The uncompensated IR, caused by solution and electrode resistance, was corrected with the positive feedback circuit of the potentiostat. An Oriel 450-W xenon lamp and Model 7240 grating monochromator were used to illuminate the electrodes. The radiant power was measured with Model 550-1 Radiometer/photometer (E.G.&G., Salem, Massachusetts). The semiconductor electrodes were irradiated through a flat Pyrex window. X-ray diffraction spectra were determined with a Philips Norelco x-ray diffractometer. IR spectra were taken with Beckman IR spectrophotometer IR5A. For these measurements, the WO_3 was scraped from the electrode and a pellet with KBr was made (0.5%).

Results

Electrochromic behavior.—Typical current-voltage curves, in the dark, of the $25\ \mu\text{m}$ layer of WO_3 obtained by thermal oxidation of W in air are shown in Fig. 1(a). The cathodic current which starts at $\sim +0.55\text{V}$ is associated with coloration of the WO_3 . The potential where the coloration starts is similar to that for the evaporated and anodic WO_3 films (7, 32). The shape of the current-voltage wave, however, is more like that of the evaporated WO_3 film, i.e., the anodic (bleaching) current starts $\sim 200\ \text{mV}$ after reversal of the potential scan. The variation of electrochromic current with scan rate, v , (Fig. 2) is close to $v^{1/2}$ dependence, as previously found for the evaporated WO_3 film (7, 32). As we discussed previously (7, 32), this dependence demonstrates that the electrochromic current is controlled by diffusion of hydrogen through the film, rather than by the nernstian (thin layer) response shown by the anodic film. This behavior has been reproduced by a digital simulation model and will be discussed elsewhere (38). The response time for the color-bleaching process is of the order of one second, as shown by potential-step experiments [Fig. 1(b)]. X-ray diffraction measurements made with these WO_3 layers show that they are crystalline. It has previously been reported that the crystalline WO_3 film obtained by annealing a WO_3 evaporated film at 400°C was not electrochromic (1, 7, 20-21). However, WO_3 crystalline layers formed by annealing the evaporated film have a monoclinic structure [Fig. 3(b)] (6, 20, 33) while the WO_3 layers obtained by thermal oxidation of W has a triclinic structure [Fig. 3(a)] (26, 33). The difference in the crystal structure of these two forms of WO_3 is clear from comparison of Fig. 3(a) and 3(b). The peak at $d = 3.84$, which is characteristic of triclinic structure (33), appears only in the x-ray pattern of the WO_3 obtained by thermal oxidation of W [Fig. 3(a)]. This peak never appears in the pattern of the monoclinic structure (33). Another distinct difference between the pattern of Fig. 3(a) and (b) is the pair of peaks at $d = 2.64$, and $d = 2.66$ which are characteristic of the triclinic structure (33) while in the monoclinic structure only the one in $d = 2.62$ appears. In both cases, there is some deviation from complete randomization of the crystallites and preference for some planes exists.

We previously studied an anodically formed WO_3 film (7, 32) which exhibited very good electrochromic behavior and was amorphous. Recently, an electrochromic WO_3 anodic film prepared under constant current conditions, which is crystalline was described (34). The crystal structure of these anodic films from the x-ray spectra shown in Ref. (34) also appears to be triclinic. Although the electrochromic behavior of the crystalline WO_3 obtained by thermal oxidation of W in the initially prepared form was poor, it improved on repeated cycling through a number of color-bleaching cycles. As shown in Fig. 4, the electrochromic current was low initially but increased gradually upon cycling. The current increased markedly during the first few scans, finally resulting in a steady-state i - E curve after about 20 hr of cycling at $100\ \text{mV}/\text{sec}$. Together with the observed increase in cathodic current, there was an increase in the depth of coloration. Although initially the coloration was weak, very good coloration was eventually attained by cycling. After this treatment, the i - E curves remained constant over a long period of time (i.e., for at least two months of continuous cycling in the aqueous sulfuric acid), implying good stability of the electrode. One can show that the higher stability of this electrode is not connected with the fact that the WO_3 layer here is thick compared to that usually used with the evaporated film electrode ($\sim 1\ \mu\text{m}$). Neither is it connected with the fact that for the same amount of charge penetrating into the lattice, the concentration of charge in the thicker film is lower. As the digital simulation model clearly shows (38), in the time scale used in these experiments, the hydrogen does not

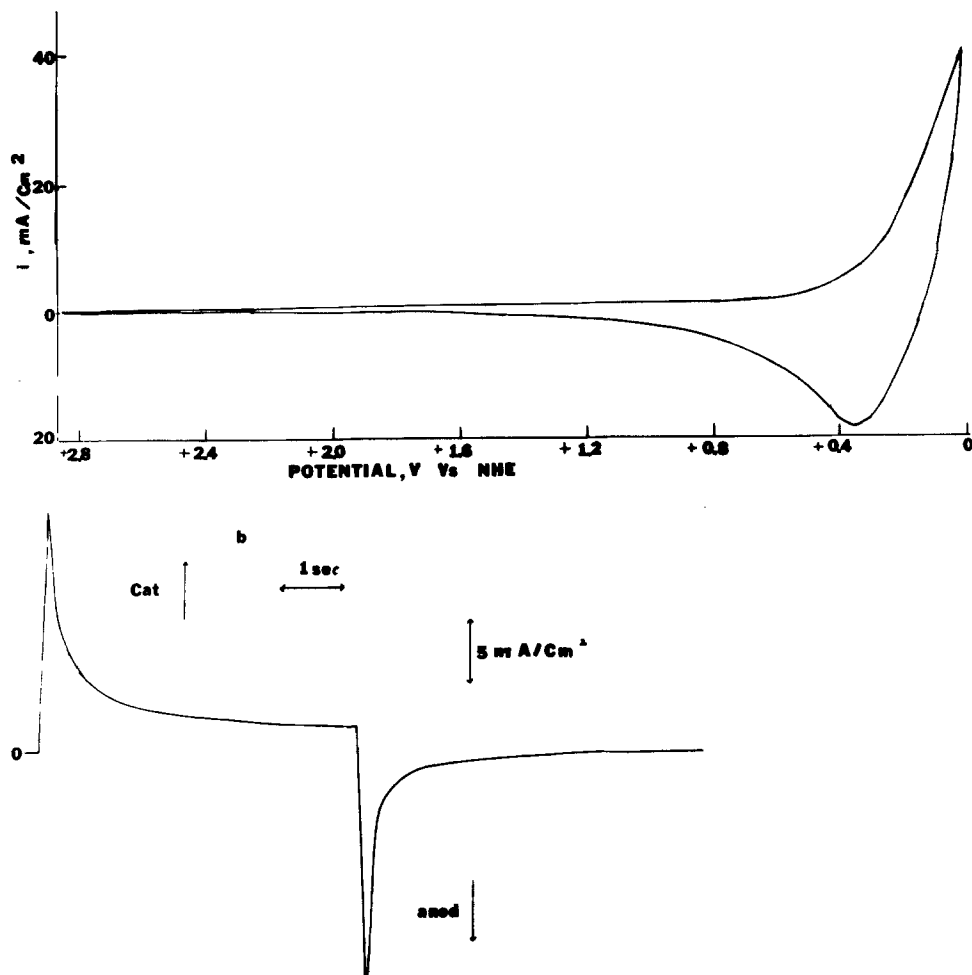


Fig. 1. (a) Current-voltage curve, in the dark, at $25 \mu\text{m}$ WO_3 layers obtained by thermal oxidation of W, recorded at scan rate of 100 mV/sec ; (b) Current change at the WO_3 layers, recorded during potential steps in the coloration region between $0-0.9\text{V}$. These curves were obtained with electrode after cycling in the color-bleach region for $\sim 20 \text{ hr}$.

penetrate very deeply into the lattice and most of the charge at these times is concentrated in the first $1 \mu\text{m}$. Thicker films were used in these experiments simply to produce WO_3 layers which are yellow in color in the bleached form. The apparent stability of the electrode

can also not be attributed to further oxidation of the W substrate with continuous replenishment of oxide, as we have shown happened in the case of the WO_3 anodic film (7). The fact that we observe equal amounts of charge during the cathodic and the anodic

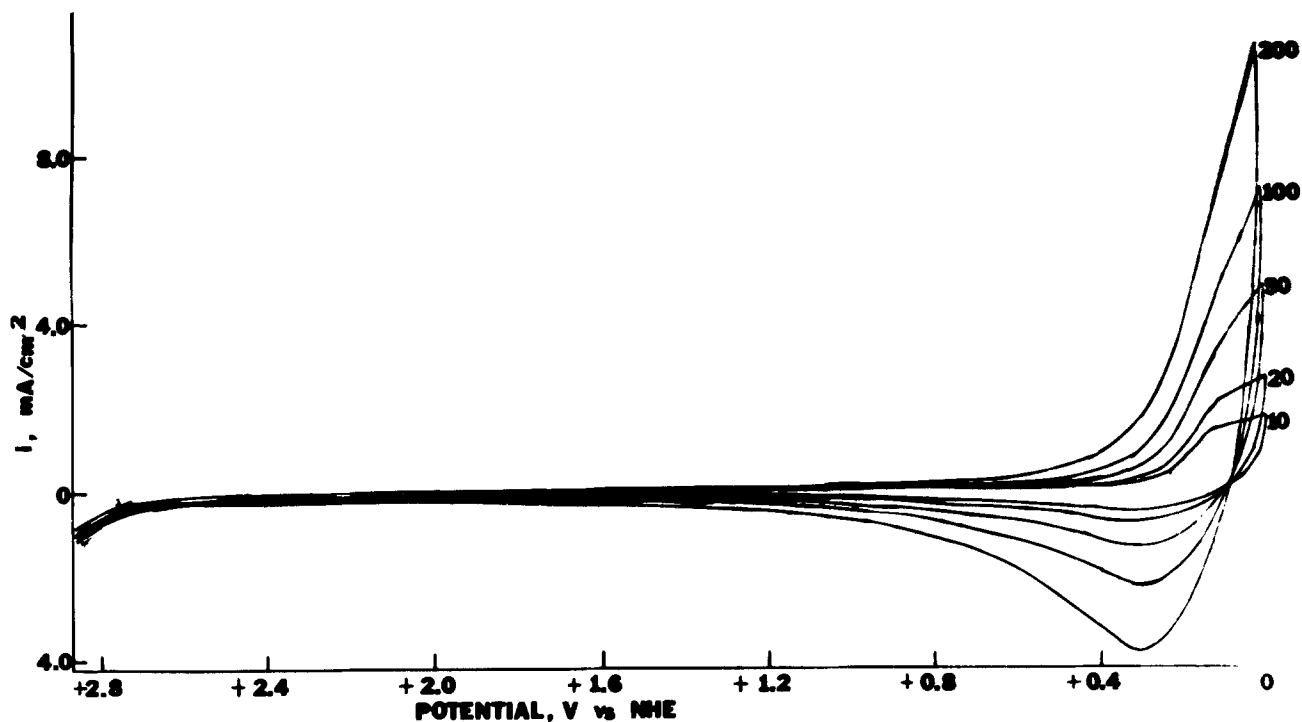


Fig. 2. Cyclic voltammograms recorded at different scan rates at WO_3 layers prepared as in Fig. 1. The numbers on the curves are scan rates in mV/sec .

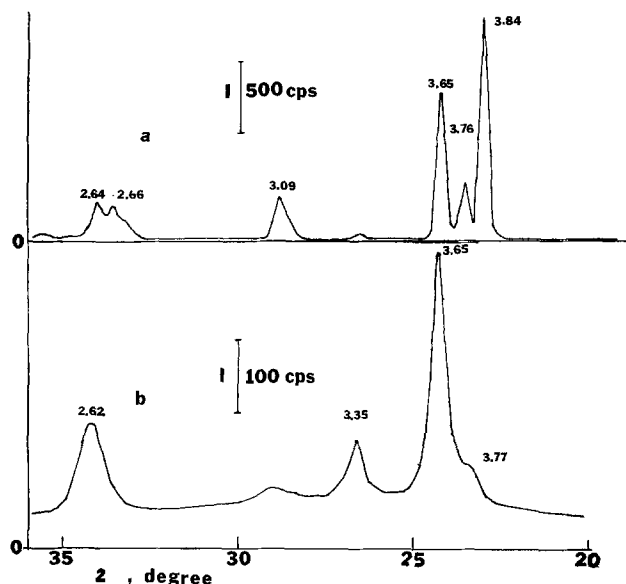


Fig. 3. X-ray diffraction pattern recorded for (a) WO_3 layers obtained by thermal oxidation of W; (b) WO_3 film obtained by annealing to 400°C , the evaporated film on glass. The d spacing associated with the different peaks is marked in the figures.

processes during cycling eliminates this possibility. Moreover, further oxidation of the W can probably not occur with such thick oxide films at the low positive polarizations ($\sim +2\text{V}$) used in these experiments; usually $\sim 100\text{V}$ is needed to grow $1\ \mu\text{m}$ of WO_3 anodically (7). Thus, the stability of the WO_3 layers ob-

tained by thermal oxidation of W must be inherent in the material itself. During the repeated color-bleach cycling, no change in the degree of porosity of the film was found as can be judged from the scanning electron microscope pictures shown in Fig. 5(a, b). This is in contrast to the more porous WO_3 anodic film electrode (7) in which the degree of porosity increased during repeated color-bleach cycling [Fig. 5(c, d)]. Moreover, IR-spectroscopic measurements of pellets prepared with WO_3 scraped from the electrode show that the amount of water in the thermally oxidized film, which is initially small, does not increase during this color-bleaching process in contrast to the behavior of the anodic and evaporated film electrodes (7). In Fig. 6, IR spectra taken with (a) a typical anodic film electrode after cycling for several hours, (b) an evaporated film electrode, and (c) an electrode of WO_3 obtained by thermal oxidation are shown for comparison. The peaks at 1650 and $3500\ \text{cm}^{-1}$ which are the characteristic IR peaks of water, are largest for the anodic film electrode which show that these films contain the highest amounts of water. They are smaller in the evaporated film electrode and are negligible for the WO_3 obtained by thermal oxidation, showing that these latter films are "dry." In the previous paper (7), we have shown that the amount of water in the anodic film and also in the evaporated film electrodes increases during continuous color-bleaching cycles and the rate of coloration is related to this amount of water. For the WO_3 layer obtained by thermal oxidation, the spectrum shown in (c) is typical for both a virgin layer or for a layer which was cycled many times in the color-bleach region. An IR spectrum similar to (c) was also obtained for evaporated films which were annealed at 400°C for 3 hr [x-ray pattern in Fig. 3(b)].

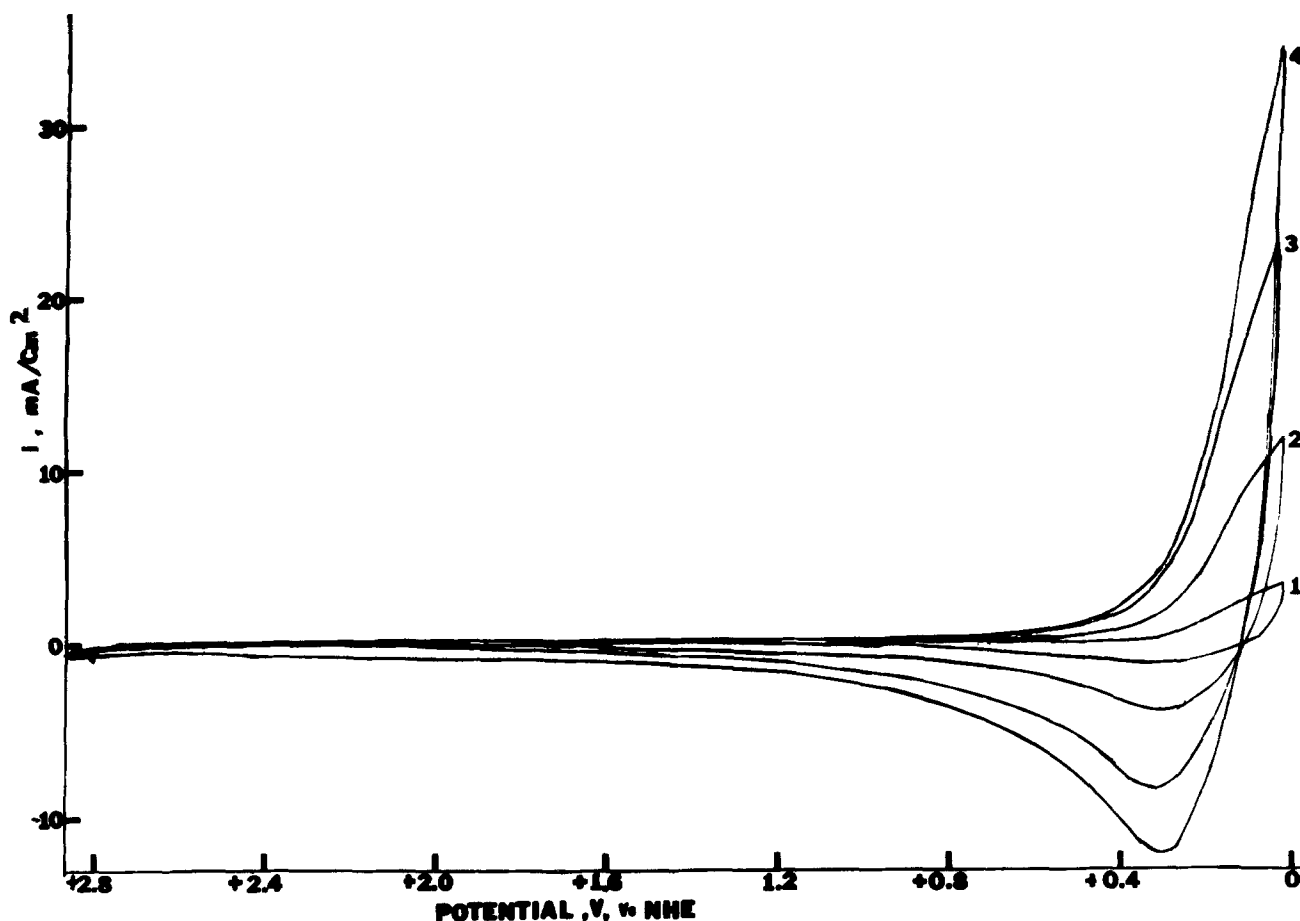


Fig. 4. Change of current during repeated color-bleach cycling at the WO_3 electrode prepared by thermal oxidation of W. The numbers in the figures represent voltammograms recorded at different times during the repeated color-bleaching process: curve 1, first cycle; curve 2, after 2 hr of color-bleaching steps between 0 and $+2.8\text{V}$ at 2 Hz frequency; curve 3, after additional 15 hr cycling at $100\ \text{mV/sec}$ within the potential limits shown in Fig. 1; curve 4, after additional $3\frac{1}{2}$ hr color-bleaching steps as in No. 2.

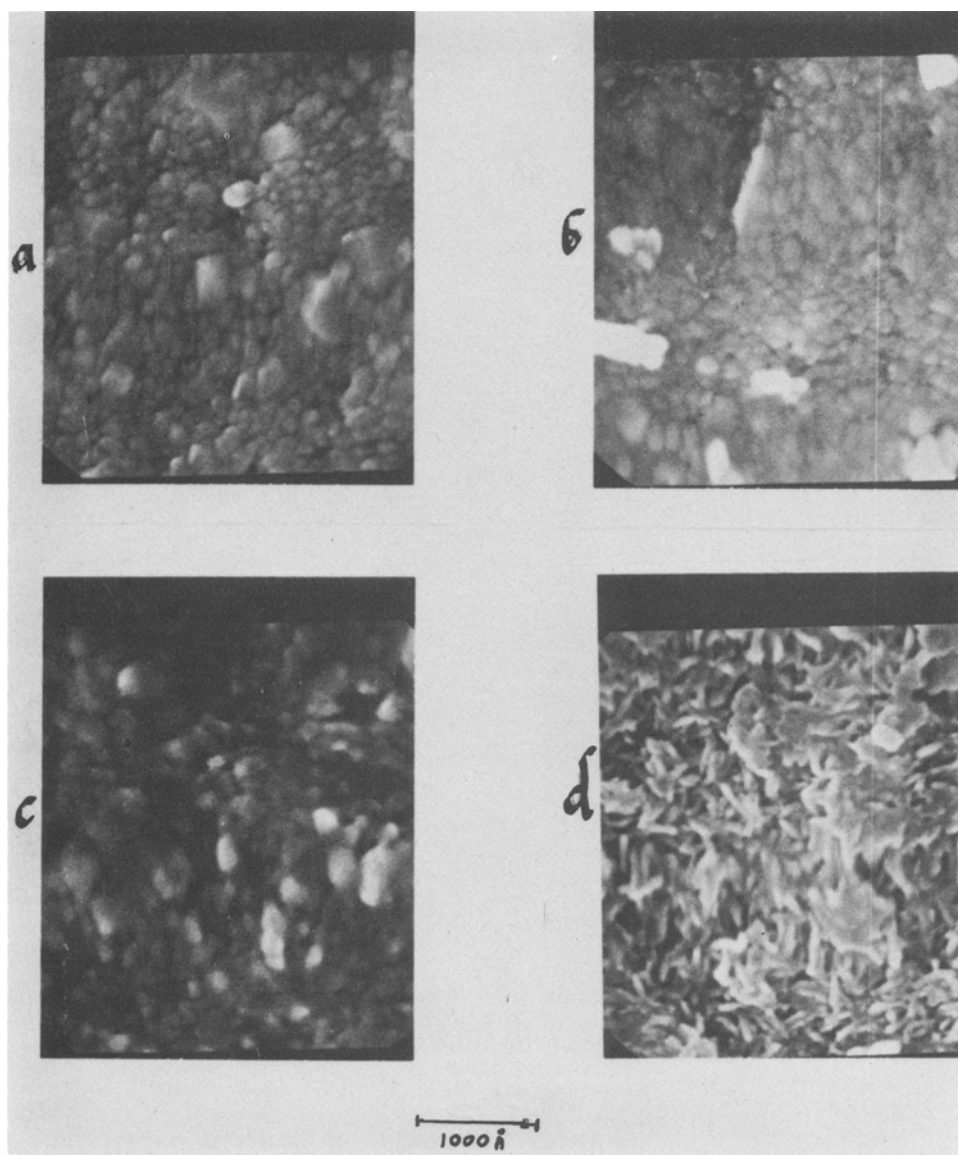


Fig. 5. Electron microscope picture of WO_3 obtained by thermal oxidation and anodic oxidation of W: (a) "as prepared" WO_3 thermally oxidized WO_3 ; (b) after cycling it in the color-bleaching region for about 20 hr; (c) "as prepared" anodic WO_3 film; (d) after cycling it in the color-bleaching region for about 20 hr.

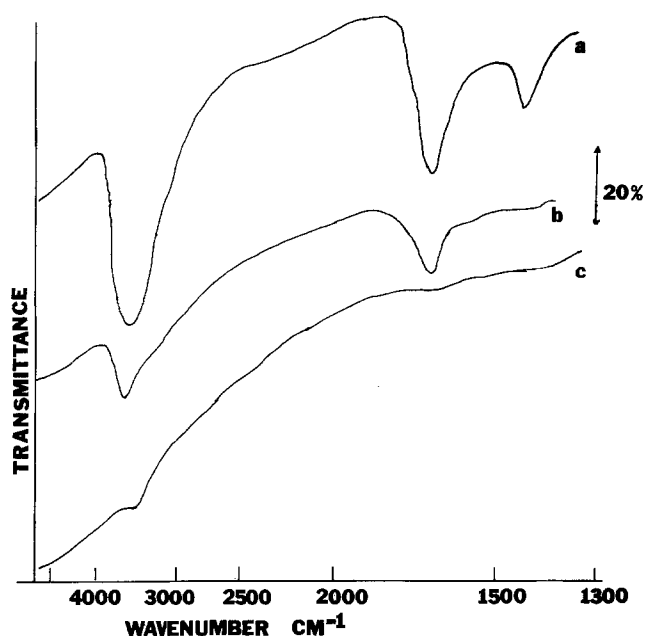


Fig. 6. IR spectra of (a) WO_3 anodic film electrode after cycling for 20 hr; (b) WO_3 evaporated film electrode after cycling for 7 hr; (c) WO_3 layer obtained by thermal oxidation of W metal, either fresh or after cycling.

Photoelectrochemical behavior of thermally oxidized WO_3 electrode and effect of cycling.—We also found, as described below, that these changes in the thermally oxidized WO_3 upon cycling also cause an improvement in the photoelectrochemical behavior of the electrode. The steady-state photocurrent-potential curves in 1M H_2SO_4 of the thermally oxidized WO_3 electrode after cycling through the color-bleach process for different times, with illumination of the electrode by the full power of 450-W xenon lamp is shown in Fig. 7. The photocurrent increased gradually as a result of the continuous cycling, paralleling the increase in the current for the electrochromic process. At the same time a small decrease in the dark current for the oxidation of water occurred. Continuous cycling finally resulted in the establishment of a maximum photocurrent; cycling beyond this point through the color-bleach process caused a small gradual decrease in the photocurrent. A similar phenomenon was also observed recently with TiO_2 (35). The increase in the photocurrent upon cycling is at least partially attributable to changes in the spectral distribution of the anodic photocurrent (Fig. 8). With the fresh electrode, the photocurrent started at about 400 nm. However, with continuous cycling through the color-bleach process the current response shifted to longer wavelengths with a peak in the photocurrent appearing at about 450 nm. This change in the spectral distribution of the photocurrent suggests that cycling causes the creation of new states

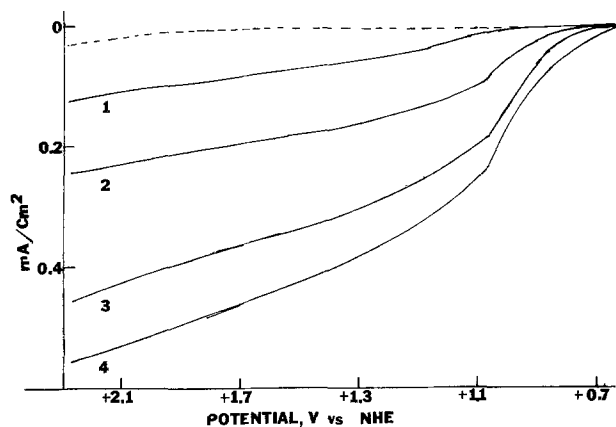


Fig. 7. Steady-state anodic photocurrent at the WO_3 electrode, obtained by thermal oxidation of W at different times during a continuous color-bleaching process in $1\text{M H}_2\text{SO}_4$ solution. The numbers represent the times as in Fig. 4.

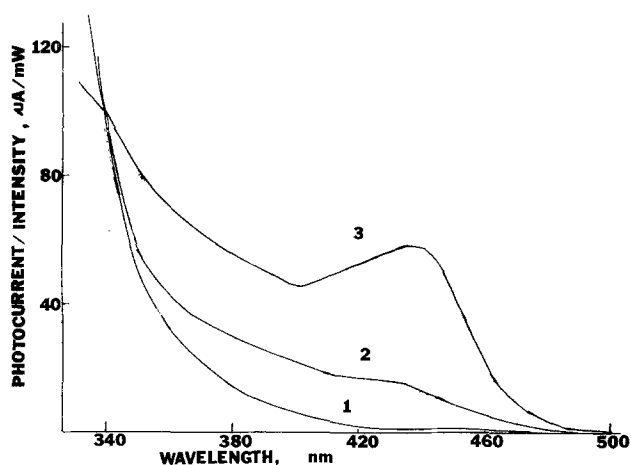


Fig. 8. Spectral distribution of the anodic current measured at $+2.2\text{V}$, at different times during the continuous color-bleaching process: curve 1, "as prepared", curve 2, after 3 hr cycling in the color-bleaching region (100 mV/sec); curve 3, after 20 hr cycling. The spectra were corrected for the power spectra of the lamp.

in the WO_3 lattice, located at energies within the band-gap. The anodic photocurrent in such an activated electrode occurs, not only via the valence band-conduction band transitions, but also through transitions involving these new states. The photocurrent at this activated electrode was very stable for at least 3 hr under illumination. The space charge capacity of the electrode at different stages during the continuous color-bleach cycling could not be measured because a small dark current exists at potentials positive of the flatband potentials.

Photoelectrochemical behavior of anodic film WO_3 electrode and effect of cycling.—An anodic photocurrent could also be observed with the anodic film WO_3 electrode, prepared as previously described (7). The photocurrent observed with these amorphous WO_3 electrodes were 10–100 times smaller than those with the thermally oxidized WO_3 layers described above. The steady-state photocurrent-potential curves at different times after color-bleach cycling are shown in Fig. 9(a). The currents in the electrochromic region at the same times are shown in Fig. 9(b) for comparison. Note that as opposed to the case of the thermally oxidized WO_3 , the photocurrent with the anodic WO_3 film decreased as a result of the cycling, while at the same time the electrochromic current increased.

Discussion

We (7, 32) and others (20) have shown that the existence of water in the WO_3 amorphous film is im-

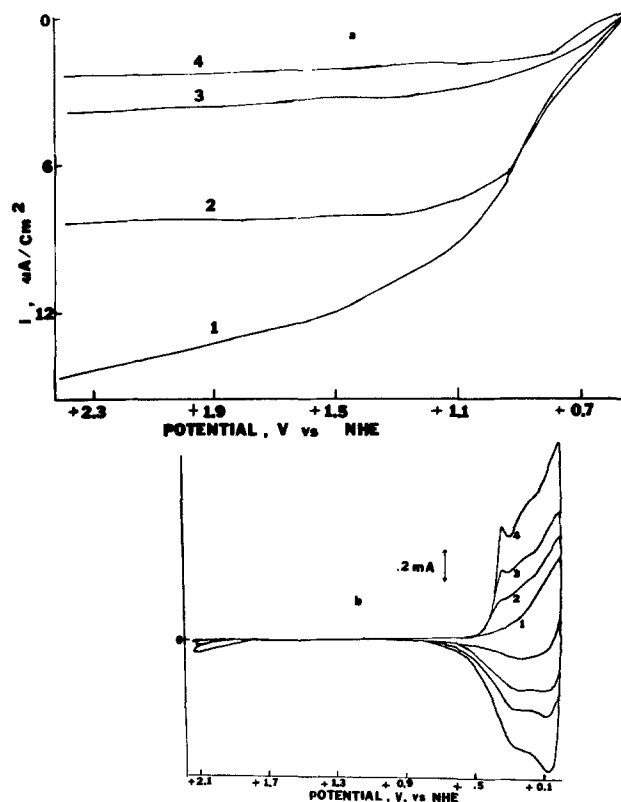


Fig. 9. (a) The anodic photocurrent, and (b) the electrochromic current recorded with WO_3 anodic film at different times during continuous color-bleaching cycles (100 mV/sec): curve 1, "as prepared" electrode; curve 2, after $1\frac{1}{2}$ hr; curve 3, after 6 hr; curve 4, after 20 hr. The area of the electrode, 1.3 cm^2 .

portant for a good electrochromic performance with these films, and that "dry" WO_3 which was obtained by annealing the evaporated film to 400°C was a very poor electrochromic. In the present work, we see that the water in the film, high porosity, and low density are less important factors for good electrochromic behavior, if the WO_3 layer has the right crystal structure. The fact that the WO_3 obtained by thermal oxidation of W is electrochromic, while the WO_3 which is obtained by annealing the evaporated film to 400°C is not, although they are both polycrystalline, must be caused by the difference in the crystal structure of both films. The triclinic structure of the thermally oxidized WO_3 , must allow more rapid transfer of protons or hydrogen atoms within the crystal lattice to form the blue hydrogen tungsten bronze (H_xWO_3) as compared to the monoclinic structure of the annealed evaporated film. That the crystalline form of WO_3 shows electrochromic properties similar to those of the amorphous WO_3 is interesting from a practical point of view, because the crystalline form is much more stable as compared to the amorphous one in the aqueous sulfuric acid used as the electrolyte for display devices. The increase in the electrochromic current as well as the depth of coloration under repeated color-bleach cycling suggests further changes in the crystal lattice as a result of this continuous cycling process. As opposed to the behavior of WO_3 evaporated and anodic films described in a previous paper (7), the improvement in the electrochromic performance in the case of the thermally oxidized WO_3 layer is not associated with changes in the porosity or the amount of water in the film and does not result in qualitative changes in the shape of the current-voltage curves. For the thermally oxidized WO_3 films, the increase in the electrochromic current and the depth of coloration must be mainly due to an increase in the amount of hydrogen which can exist in the WO_3 lattice at equilibrium, rather than to an increase in the rates of reactions (38). The photocurrent measurements sug-

gest that on cycling new electronic levels are produced in the WO_3 which promote photooxidation of water. These new levels may involve defects which may also allow an increase in the amount of hydrogen which can penetrate the WO_3 lattice at equilibrium, and thus improving the electrochromic performance. It is interesting to compare this effect of continuous cycling on the photooxidation behavior with the effect of annealing of WO_3 electrodes obtained by sputtering, found by Gissler and Memming (27). These authors found that the current associated with the photooxidation of water increased upon annealing the sputtered WO_3 layer in an oxygen atmosphere; the longer was the annealing time, the higher was the photocurrent. The highest response was obtained with WO_3 formed by heating tungsten in an oxygen atmosphere to high temperatures ($760^\circ\text{--}780^\circ\text{C}$). These authors also found changes in the spectral distribution of the current on annealing similar to those found here and attributed these effects to the production of intraband bulk states. These findings suggest that the new states produced by Gissler and Memming by annealing the WO_3 samples in an O_2 atmosphere can also be created by continuous electrochemical cycling. Note that while the continuous cycling process causes an improvement in the photoelectrochemical properties for the thermally oxidized WO_3 film, it causes a degradation in the photocurrent for the anodic WO_3 films. This indicates that the nature of the change in the WO_3 lattice for these two films is different. In fact, we have previously shown (7, 32) that, as a result of the repeated color-bleach cycling with the anodic film, the amount of water in these films and its porosity increases. While these changes produce a large improvement in the electrochromic performance, they may well cause a deterioration in the photoelectrochemical behavior. On the other hand, the changes in the case of the thermally oxidized WO_3 layers on cycling, are not associated with changes in the water content or porosity of the film, but rather with the creation of states or defects in the film which lead to an improvement in both electrochromic and photoelectrochemical behavior.

Acknowledgment

The support of this research by Texas Instruments, Incorporated, is gratefully acknowledged.

Manuscript submitted April 23, 1979; revised manuscript received June 12, 1979.

Any discussion of this paper will appear in a Discussion Section to be published in the June 1980 JOURNAL. All discussions for the June 1980 Discussion Section should be submitted by Feb. 1, 1980.

Publication costs of this article were assisted by The University of Texas at Austin.

REFERENCES

- S. K. Deb, *Philos. Mag.*, **27**, 801 (1973).
- B. W. Faughnan, P. S. Crandall, and P. M. Heyman, *RCA Rev.*, **36**, 177 (1975).
- H. N. Hersh, W. E. Kramer, and J. H. McGee, *Appl. Phys. Lett.*, **27**, 646 (1975).
- I. F. Chang, B. L. Gilbert, and T. I. Sun, *This Journal*, **122**, 955 (1975).
- R. S. Crandall and B. W. Faughnan, *Appl. Phys. Lett.*, **28**, 95 (1976).
- J. P. Randin, *J. Electron. Mater.*, **7**, 47 (1978).
- B. Reichman and A. J. Bard, *This Journal*, **126**, 583 (1979).
- T. C. Arnolduseen, Abstract D-2 presented at The 20th Conference on Electronic Materials, University of California, Santa Barbara, California, June 1978.
- T. B. Reddy and E. A. Battistelli, Abstract G-4 presented at The 19th Conference on Electronic Materials, Cornell University, Ithaca, New York, June 1977.
- S. K. Mohapatra, *This Journal*, **125**, 284 (1978).
- T. J. Knowles, H. N. Hersh, and W. Kramer, Abstract I-3 presented at The 19th Conference on Electronic Materials, Cornell University, Ithaca, New York, June 1977.
- M. Green and D. Reichman, *This Solid Films*, **24**, 595 (1974).
- W. C. Dautremont-Smith, M. Green, and K. S. Kang, *Electrochim. Acta*, **22**, 751 (1977).
- G. Barna, *J. Electr. Mater.*, **8**, 153 (1979).
- I. Shimizu, M. Shizukuishi, and E. Inone, Private communication.
- Y. Hajinota, M. Matsushima, and S. Ogura, Abstract B-3 presented at The 20th Conference on Electronic Materials, University of California, Santa Barbara, California, June 1978.
- H. J. Stocker, S. Singa, L. G. VanUitert, and G. Zydrik, Abstract B-4, *ibid.*, 1978.
- A. J. Hughes, P. Lloyd, and R. Hurditch, Abstract I-5 presented at The 19th Conference on Electronic Materials, Cornell University, Ithaca, New York, June 1977.
- H. R. Zeller and H. U. Beyeler, *J. Appl. Phys.*, **13**, 231 (1977).
- R. J. Hurditch, *Electron. Lett.*, **11**, 142 (1975).
- B. W. Faughnan, R. S. Crandall, and M. A. Lampert, *Appl. Phys. Lett.*, **27**, 646 (1975).
- M. A. Butler, R. D. Nasby, and R. K. Quinn, *Solid State Commun.*, **19**, 1011 (1976).
- M. A. Butler, *J. Appl. Phys.*, **48**, 1914 (1977).
- G. Hodes, D. Cahen, and J. Manassen, *Nature*, **260**, 312 (1976).
- K. L. Hardee and A. J. Bard, *This Journal*, **124**, 215 (1977).
- C. E. Derrington, W. S. Godek, C. A. Castro, and A. Wold, *Inorg. Chem.*, **17**, 977 (1978).
- W. Gissler and R. Memming, *This Journal*, **124**, 1711 (1977).
- W. A. Gerrard, *J. Electroanal. Chem.*, **86**, 421 (1978).
- R. N. Noufi, P. A. Kohl, S. N. Frank, and A. J. Bard, *This Journal*, **125**, 246 (1978).
- A. Fujishima, K. Honda, and S. Kikuchi, *J. Chem. Soc. Jpn.*, **72**, 108 (1969).
- C. C. Dutoit, F. Cardon, F. V. Kerchove, and W. P. Gomes, *J. Appl. Electrochem.*, **8**, 247 (1978).
- B. Reichman and A. J. Bard, Abstract B-9 presented at The 20th Conference on Electronic Materials, University of California, Santa Barbara, California, June 1978.
- X-ray Powder Diffraction File, Search Manual, ASTM file No. 24-747, 20-1323, L. G. Berry, Editor, Philadelphia, Pa. (1975).
- A. Di Paola, F. Di Quarto, and C. Sunseri, *This Journal*, **125**, 1344 (1978).
- S. Gottesfeld, M. Yaniv, D. Laser, and S. Srinivasan, *J. Phys. Paris*, **38**, C5-154 (1977).
- P. G. Dickens and M. S. Whittingham, *Q. Rev., Chem. Soc.*, **22**, 30 (1968).
- A. B. Ellis, S. W. Kaiser, and M. S. Wrighton, *J. Am. Chem. Soc.*, **98**, 1635 (1976).
- B. Reichman, D. Laser, and A. J. Bard, *This Journal*, In press.