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January 1996

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OPTICAL AND ELECTROCHROMIC PROPERTIES OF SOL-GEL DEPOSITED DOPED TUNGSTEN OXIDE FILMS

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SUMMARY

The goal of this study is to investigate the effects of doping of tungsten oxide on its electrochromic properties. The work is directed toward the development of neutral coloring tungsten oxide materials with properties superior to undoped tungsten oxide. Two basic types of sol-gel formulations were used for experimentation. Type 1 used a WOCl_4 precursor. Type 2 used a proprietary (Donnelly) tungsten complex precursor. The Type 2 precursor was used only for comparison to Type 1. Doping experiments were performed using the Type 1 chemistry. The dopants studied were Co, Cr, Nb, Ti, V and Y. The range of dopant was 1-12 mole %. Improved electrochromic behavior was observed for tungsten oxide films doped with V and Ti.

Analysis of the films included x-ray diffraction, ellipsometry, cyclic voltammetry and spectrophotometry. X-ray diffraction showed that all films heat treated at temperatures below 300°C were amorphous in structure. The refractive indices for undoped films were measured. We found the n , k values of the Type 1 films to be lower than the Type 2 films. The n and k values were $n=1.79$ and $k=2.8 \times 10^{-3}$, and $n=2.08$ and $k = 3.6 \times 10^{-3}$ at 550 nm, for Type 1 and Type 2 films respectively. Both types of tungsten oxide films showed low absorption and high transparency in the visible range. As expected, we found that the film density, and hence the refractive index and extinction coefficient, depended on coating solution chemistry, hydration, and densification procedures. Undoped Type 1 films showed slightly higher lithium diffusion coefficients (D_{Li}), compared to undoped Type 2 films, $D_{\text{Li}}=1.36 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ and $1.31 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$, respectively.

We also noted that the properties of the films could be reproduced for any coating chemistry and densification scheme. The electrochemical and optical behavior were determined by using an *in-situ* cuvette cell with a 1M LiClO_4 / propylene carbonate electrolyte. Cyclic voltammetric measurements showed that doped Type 1 films exhibited electrochemical reversibility beyond 1200 cycles without change in charge capacity. A slight lowering of charge capacity was noted for the undoped films after cycling. The charge capacity for the V doped film was 16.9 mC/cm^2 compared to undoped film, 9.6 mC/cm^2 . Spectrophotometry showed that doped films tended to exhibit a higher absorbance in their colored state compared to undoped films. Considerable improvement in the lithium diffusivity was noted for all the doped films. The greatest change was a factor of 20x for vanadium doping. Doping appeared to increase the cyclic durability of all the tungsten films out

to 1200 cycles. Color changes by doping were noted for several dopants. The doped films with the best overall properties were about 8% vanadium and titanium tungsten oxide. The optimum concentration lies in the range of 7 to 12 mol%. The electrochromic color was a neutral brownish-blue for vanadium and grayish-blue for titanium doped tungsten oxide.

INTRODUCTION

Over the past decade, many metal oxides have been examined for their use in electrochromic switching devices, including large-area building glazing applications (1,2). Tungsten oxide still appears to be the best inorganic electrochromic compound. Its advantages are high coloration efficiency, reasonable stability, and relatively low cost. For building applications, however, the bright blue color of WO_3 films in the reduced state is not as favorable as neutral gray or bronze colors for most building applications. In this study, we concentrate on films made by sol-gel deposition and the use of metal dopants to alter the coloration of WO_3 films. This study extends prior work done at Donnelly Corporation (6). The sol-gel process is preferred because of its lower capital investment (4,5).

From the viewpoint of sol-gel deposition, the most studied coating for electrochromics is tungsten oxide. In this study, doped films are prepared from mixed solutions. Solutions of metal alcoxides are mixed with the tungsten precursor solution. Two types of tungsten oxide precursor solutions are utilized. Type 1 uses a $WOCl_4$ precursor, while Type 2 uses a proprietary (Donnelly) tungsten complex precursor. Doping experiments were performed using the Type 1 precursor. Cobalt, chromium, niobium, titanium, vanadium and yttrium were selected as dopants. The range of dopant concentration was 1-12 mole % for these studies. Films made from the Type 2 precursor are only used for comparison. The Type 2 films have better transmittance contrast than Type 1 films. Doping of the Type 2 films will be performed at Donnelly Corporation using the guidance from the Type 1 film experiments. In sol-gel processes it is known that the starting precursor molar ratio is generally preserved in the final films. The doping ratios given in this work are the molar ratios of the starting mixtures. Further analysis would have to be done for exact compositional determination. The solution chemistry is controlled by the prehydrolysis reaction. Also, heat treatment conditions are customized for each file type to give the best film porosity, density, and crystallinity. The quality of an electrochromic material is measured by its achievable transmittance contrast between colored and bleached states relative to injected charge or coloration efficiency, response time, and chemical stability. These properties depend strongly on density and porosity of the WO_3 films.

EXPERIMENTAL

Preparation of Coatings

The two tungsten oxide coating solutions were prepared from different precursors. The Type 1 precursor solution was prepared by hydrolysis of $WOCl_4$ in reagent grade ethanol under a stream of argon at $40^\circ C$. The resulting precursor solution consists of monodispersed particles. The measured pH was 4.5 and the solution viscosity was 1.4 cP. The Type 2 precursor solution was

prepared by dissolving a special Donnelly tungsten complex in a reagent grade ethanol under ambient conditions. The $M:WO_3$ samples were prepared from precursor Type 1. The metal doping was achieved by adding metal alkoxides, such as titanium isopropoxide, vanadium isopropoxide, chromium ethoxide, niobium ethoxide, cobalt methoxy ethoxide and yttrium ethoxide. The doped mixed sol-gel precursors were stable for several weeks (except for vanadium). The addition of the dopant precursor tended to stabilize the mixture. All solutions were prepared at least 24 hours in advance of deposition and appeared chemically stable. Using these solutions, films were coated onto $SnO_2:F/glass$ (LOF Glass, Tec 20), float glass (soda-lime), and quartz substrates. The coatings were made using a spin-coater (SCS Model P6204). The films were deposited under ambient atmosphere with a spinning rate of 1200 rpm. The films were heat-treated at $100^\circ C$ for 2 hours to complete hydrolysis, condensation, and densification. The undoped coatings were labeled $WO_3(1)$ or Type 1, and $WO_3(2)$ or Type 2. A slight increase of the film thickness with increasing dopant content was observed, due to increased solution viscosity. All films were uniform and continuous.

Characterization

Electrochemical measurements were made using a PAR digital coulometer. A three-electrode cell with Li metal counter electrode and Li reference electrode was used. The electrolyte was 1 M $LiClO_4$ / propylene carbonate (PC). Voltammetric cycling was performed at voltages between 2.0 V and 4.0 V relative to lithium with a scan rate between 5 mV/s and 50 mV/s. Current was recorded during 10, 100, 500, 1000 cycles under the conditions described above. The spectrophotometry of the films was performed on a Perkin-Elmer Lambda 19 double-beam spectrophotometer. The spectral region used in this work was 350 to 2100 nm. X-ray diffraction (XRD) spectra were collected for undoped and doped films deposited onto float glass. A Siemens Krystalloflex diffractometer with a Ni-filtered CuK_α source was used for XRD. Thickness, refractive index, and extinction coefficient of the undoped films were determined by ellipsometry. A variable-angle spectroscopic ellipsometer (J.A. Woollam) was used over the extended visible range (300-1000 nm). Ellipsometric measurements were run on the WO_3 films deposited on quartz substrates. The samples were analyzed using three different incident angles of 67° , 62° , and 57° . Film thickness measurements determined ellipsometrically were confirmed by a Dektak II (Veeco Inst. Inc.) surface profiler.

RESULTS AND DISCUSSION

The X-ray diffraction measurements of both Type 1 and Type 2 undoped films and doped films showed that these films were amorphous. The refractive index and extinction coefficient of the sol-gel deposited films are shown in Figs. 1 and 2. From these figures it is concluded that WO_3 films deposited from the Type 1 solution have a lower refractive index and extinction coefficient value than Type 2 films. The n versus λ plots of WO_3 films show both normal dispersion, $\delta n/\delta \lambda < 0$ and anomalous dispersion, $\delta n/\delta \lambda > 0$. Dispersion becomes dominant at $\lambda < 370$ nm for Type 1 film and at $\lambda < 400$ nm for Type 2 film. The main feature observed in Fig 2 is the dramatic increase of k with decreasing wavelengths for the $\lambda < 350$ nm region. This strong absorption and dispersion indicates that the energy gap of WO_3 is located in this region. The extinction coefficient spectra of the undoped films revealed that Type 2 films exhibit higher absorption than Type 1 films over the

entire spectral region. If the refractive index values of the films are taken as indicative of density, the index is expected to increase with decreasing film density. Since lower density films are required to produce a fast switching EC coatings, the coating prepared from solution 1 is favored.

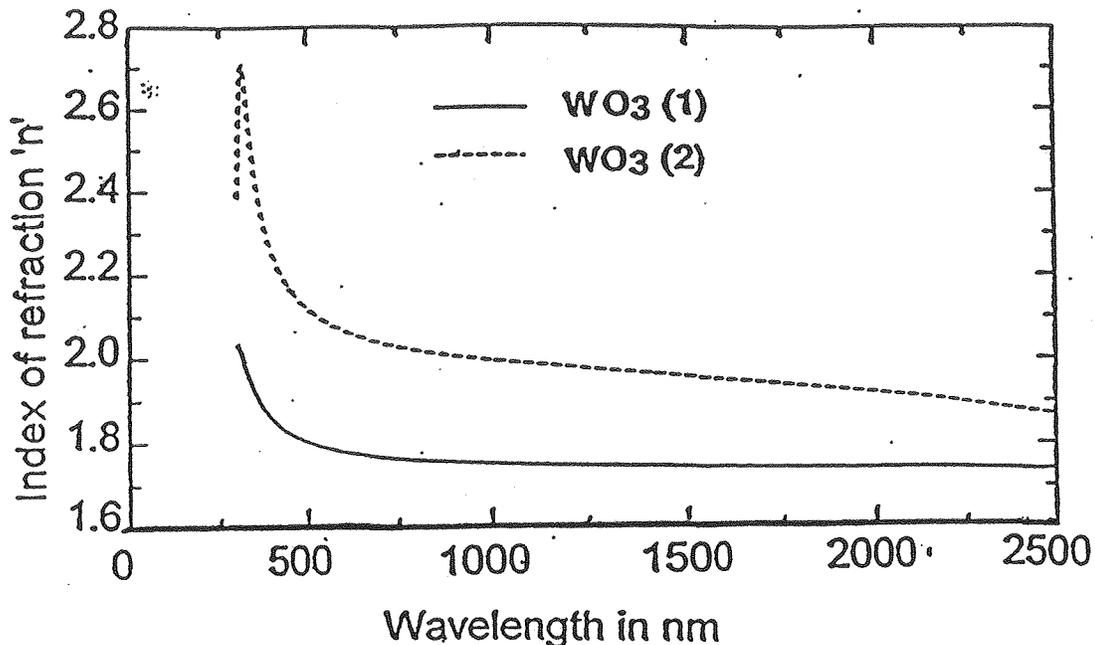


Fig. 1. Refractive index (n) spectra of undoped (250 nm thick) sol-gel WO_3 films deposited on fused silica substrate and heat treated for 2 h at 100°C . Two types of deposition precursors were used to make the films: (1) WOCl_4 solution and (2) Donnelly tungsten complex solution.

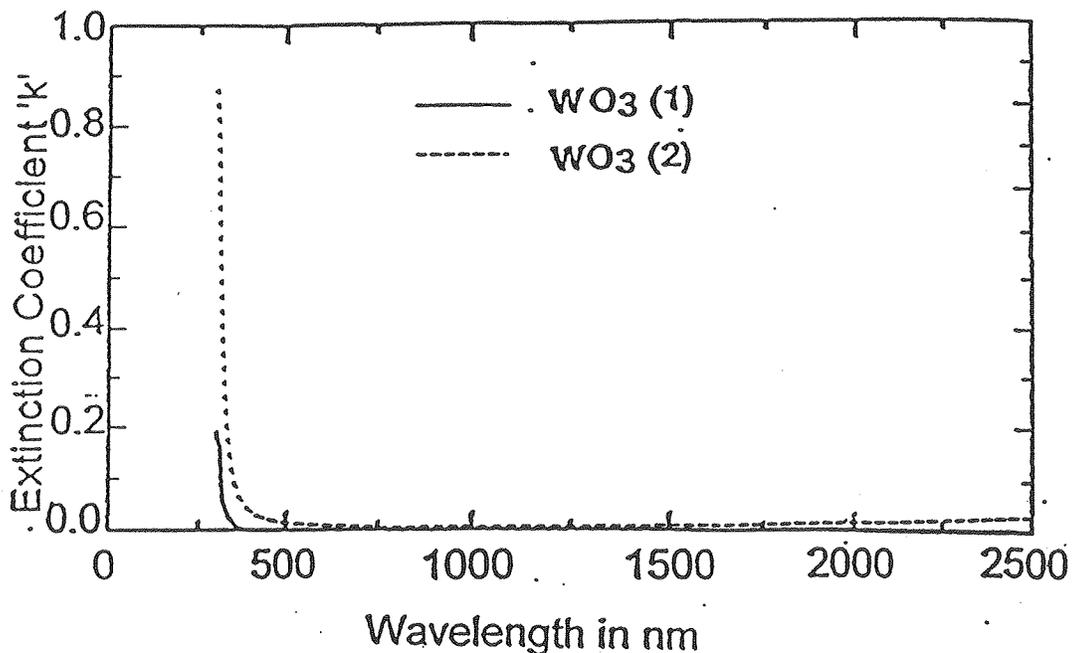


Fig. 2. Extinction coefficient (k) spectra of undoped sol-gel WO_3 films. (Same samples as Fig. 1.)

The cyclic voltammograms (CV) of both types of tungsten oxide films on Tec 20 glass substrates are shown in Figs. 3 and 4. These figures show that both films have similar characteristics. The oxidative electron/ion transfer reactions associated with the peaks at 2.32 V and 2.46 V vs. Li⁺ are associated with the electrochromic transition from dark blue to transparent state for Type 1 and Type 2 films, respectively. The CV was recorded as a function of scan rate (v_s). From the gradient of the peak current with respect to v_s , we can derive the lithium diffusion coefficient D_{Li} (8). This assumes planar diffusion and Li⁺ is only ionic species responsible for transport. From Figs. 3 and 4, the calculated D_{Li} values were found to be $1.36 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ and $1.31 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ for undoped Type 1 and Type 2 films, respectively. Cyclic voltammograms (CV) for sol-gel deposited doped tungsten oxide films are shown in Figs. 5-11. These plots show that intercalation of lithium occurs over a wide range of potential depending on the dopant. Generally the doping of tungsten oxide improved the switching properties of the films, showing faster Li⁺ ion transport through the film. The CV measurements indicate that ions were more easily inserted into the 8% doped films than in undoped films. The CV curves for doped films exhibit a strong dependence on dopant amount. Films with dopant content below 8 mol % show similar features. Bleaching peaks moved to more positive potentials when dopant content increases for high scan rates. The best symmetrical anodic and cathodic peaks were obtained for a composition around 8% for most dopants. Generally, current and charge densities increased with increasing dopant content for these films to about 8%. Films with dopant content above 8% incorporate only about two thirds as much charge as undoped films. Similar analysis of CV data to that undoped films also allowed diffusion coefficients to be obtained for all the doped tungsten oxide films. Table 1 shows that diffusion coefficients for Li⁺ ions are faster through doped films than through undoped films.

Table 1. The lithium diffusion coefficient, D_{Li} calculated using cyclic voltammetry and the Randles-Sevcik equation (8)

Oxide	Type 1 Film $D \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$	Type 2 Film $D \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$
W	1.36	1.31
Cr:W	14.1	-
Co:W	21.4	-
Nb:W	14.2	-
Ti:W	24.2	-
V:W	28.4	-
Y:W		-

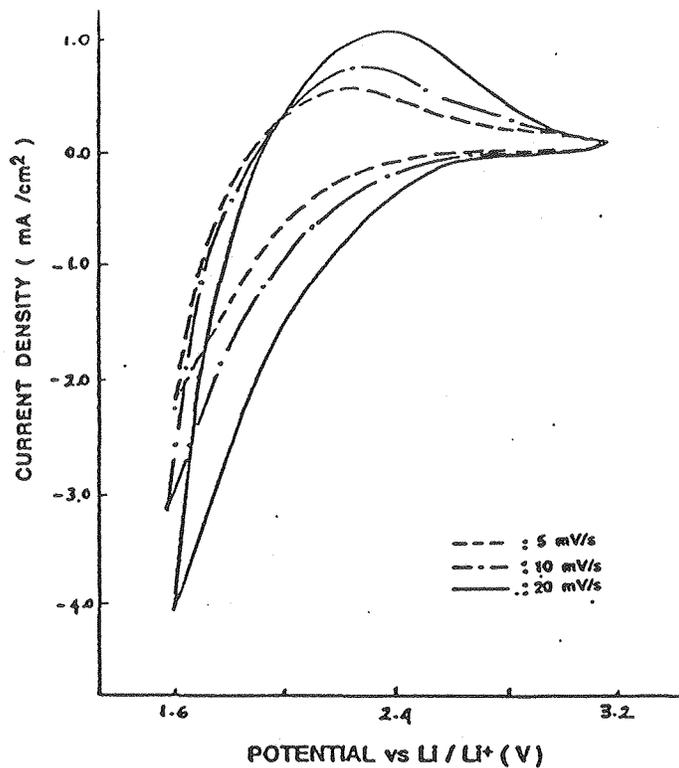


Fig. 3. Cyclic voltammety of Lithium intercalation in films for undoped WO_3 (Type 1) films deposited on Tec 20 glass. Different potential scan rates are shown. The electrolyte was 1 M LiClO_4/PC . The counter and reference electrodes were lithium.

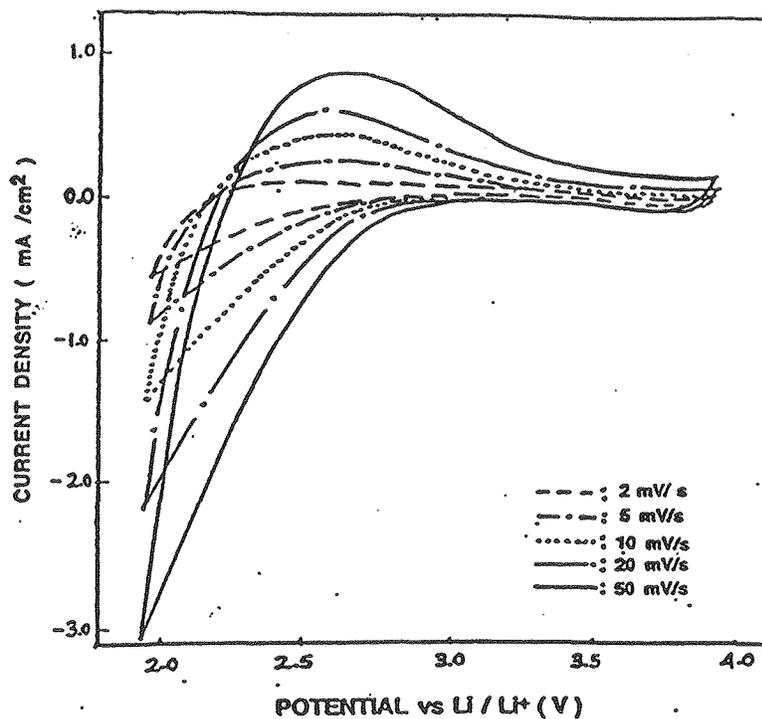


Fig. 4. Cyclic voltammety of lithium intercalation in undoped WO_3 (2) films deposited on Tec 20 glass. Different potential scan rates are shown. The electrolyte was 1 M LiClO_4/PC . The reference and counter electrodes were lithium.

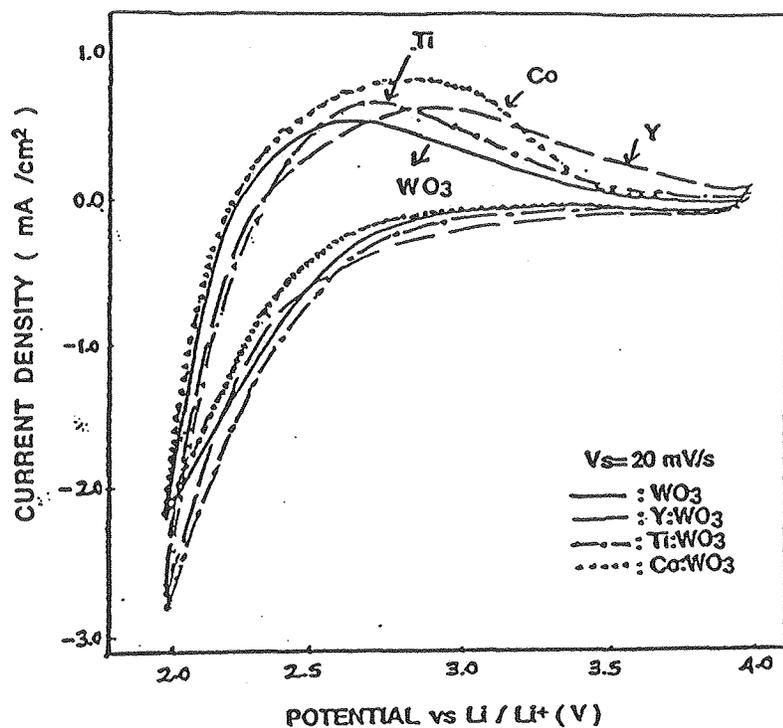


Fig. 5. Cyclic voltammetry of undoped and 8% doped WO₃ (Type 1) films on Tec 20 glass. The scan rate was 20 mV/s. The electrolyte was 1 M LiClO₄/PC. The reference and counter electrodes were lithium.

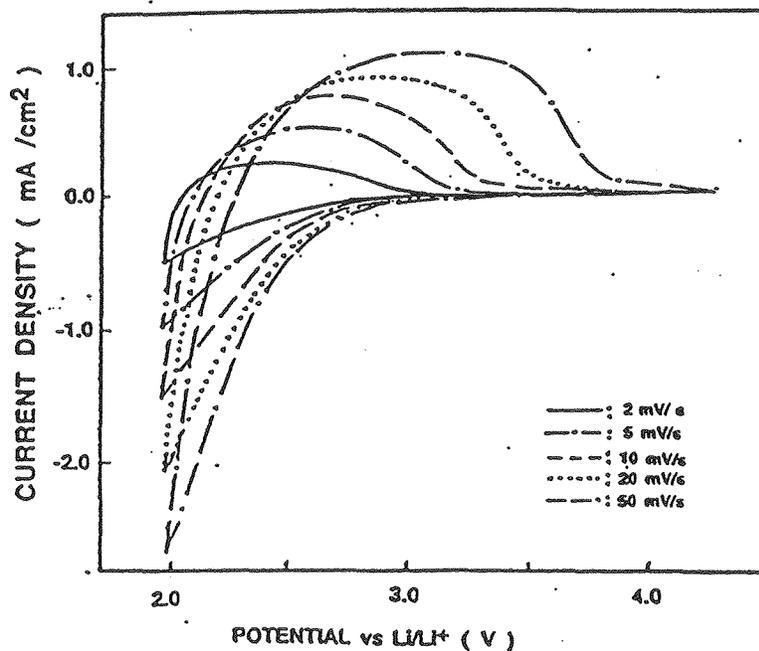


Fig. 6. Cyclic voltammetry of 7% cobalt doped WO₃ (Type 1) film on Tec 20 glass. The electrode was cycled in 1 M LiClO₄/PC. The reference and counter electrodes were lithium.

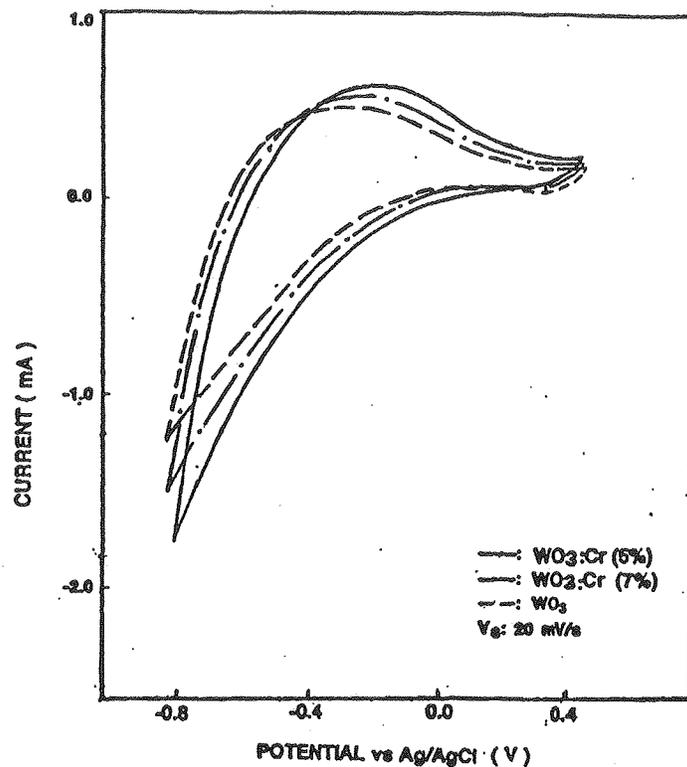


Fig. 7. Cyclic voltammograms of chromium doped WO₃ (Type 1) film on a Tec 20 glass substrate. The electrode was cycled in 1 M LiClO₄/PC. The reference and counter electrodes were lithium.

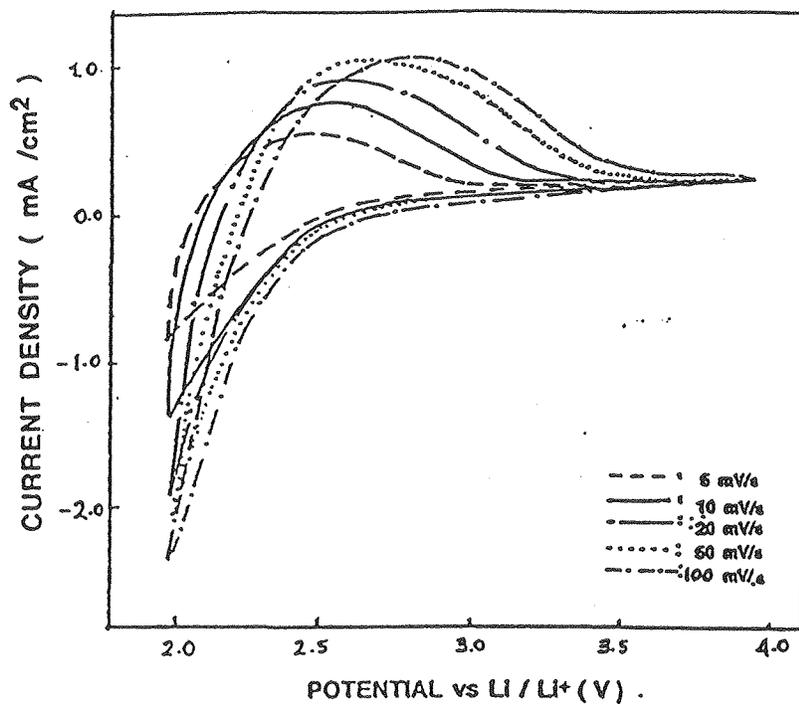


Fig. 8. Cyclic voltammetry of 8% niobium doped WO₃ (Type 1) film on a Tec 20 glass substrate. The electrode was cycled in 1 M LiClO₄/PC. The reference and counter electrodes were lithium.

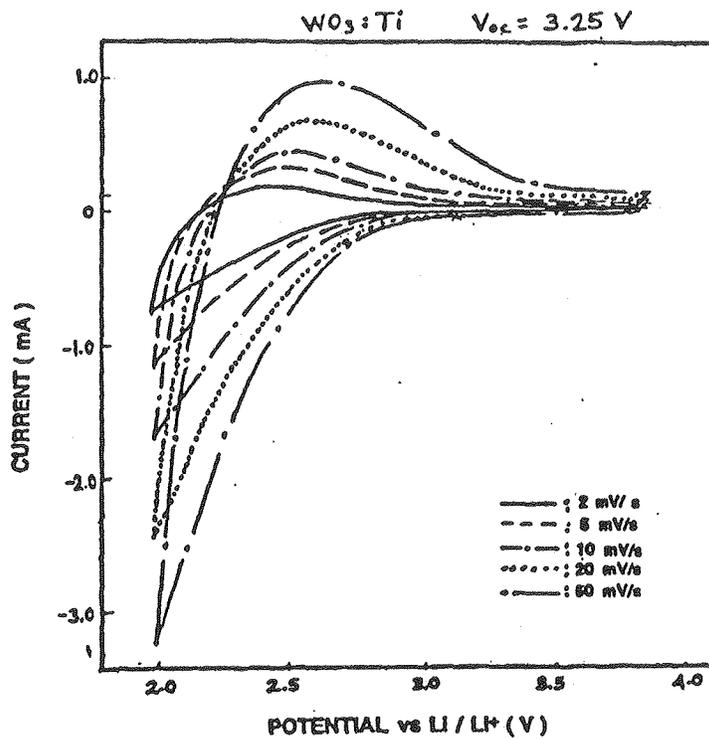


Fig. 9. Cyclic voltammetry of 9% titanium doped WO_3 (1) film on a Tec 20 glass substrate. The electrode was cycled in 1 M LiClO_4/PC . The reference and counter electrodes were lithium.

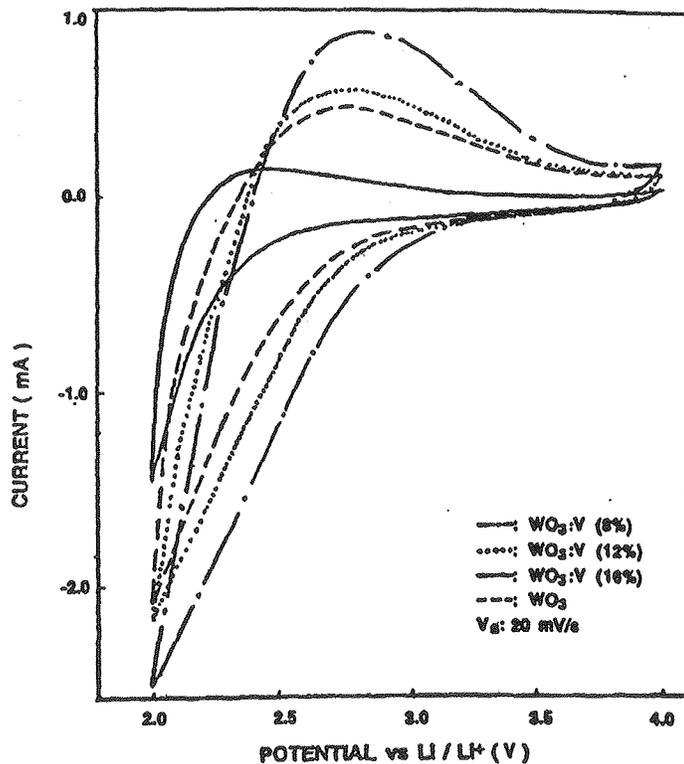


Fig. 10. Cyclic voltammetry of 8% vanadium doped WO_3 (Type 1) film on a Tec 20 glass. The electrode was cycled in 1 M LiClO_4/PC . The reference and counter electrodes were lithium.

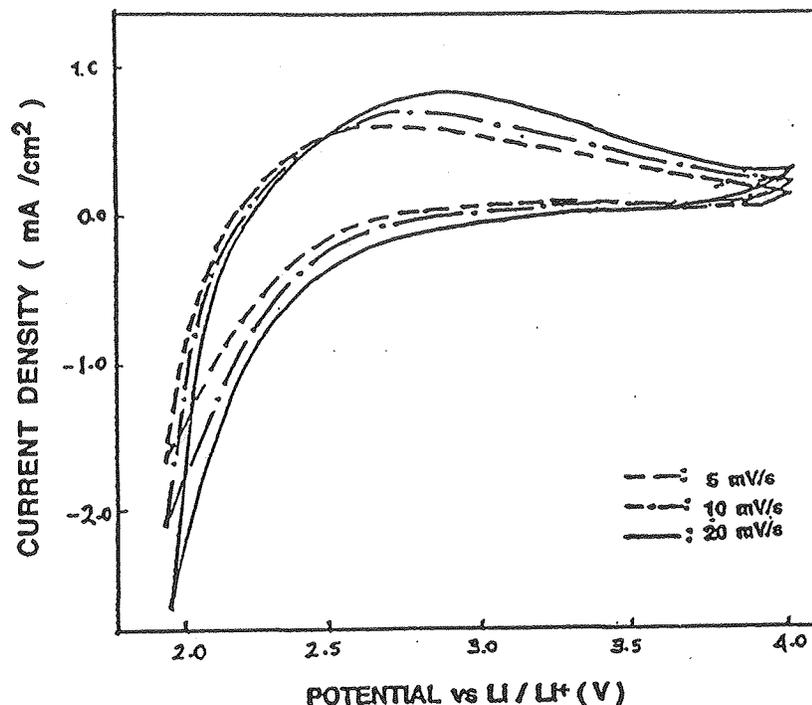


Fig. 11. Cyclic voltammetry of 12% yttrium doped WO_3 (Type 1) film on Tec 20 glass substrates cycled in 1 M LiClO_4/PC . The reference and counter electrodes were lithium.

The transmittance spectra of the doped tungsten oxide films in the bleached and colored states were measured with the spectrophotometer in the wavelength range between 300 and 1100 nm. For spectral measurements, the samples were taken out of the electrolyte solution in their dark state, rinsed with tetrahydrofuran and ethanol and wiped dry. In Figs. 12-15, transmittance spectra are shown after 100 cycles of switching. Extended cycling to 1000 cycles resulted no significant change for doped films and a slight decrease in switching range for the undoped films. After 7 weeks of storage in air in the colored state, both doped and undoped tungsten oxide films bleached almost completely. Undoped films self-bleach faster than doped films when they are exposed to air.

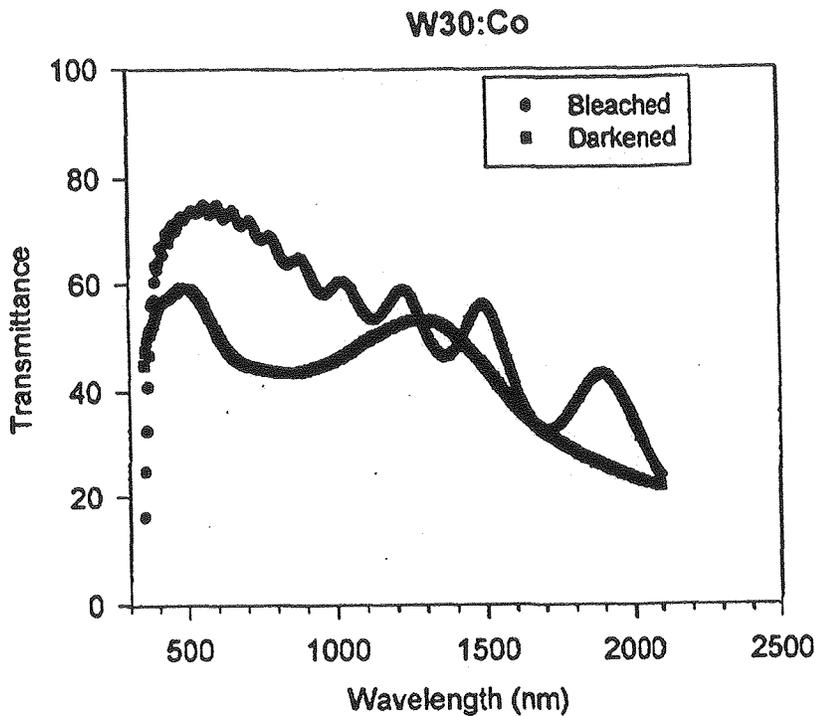


Fig. 12. Spectral transmittance of a 7% Cobalt doped WO_3 (Type 1) film on a Tec 20 glass substrate. The electrode was cycled in 1 M LiClO_4/PC . The film colored at $2\text{V}/(\text{Li}/\text{Li}^+)$ and bleached $4\text{V}/(\text{Li}/\text{Li}^+)$.

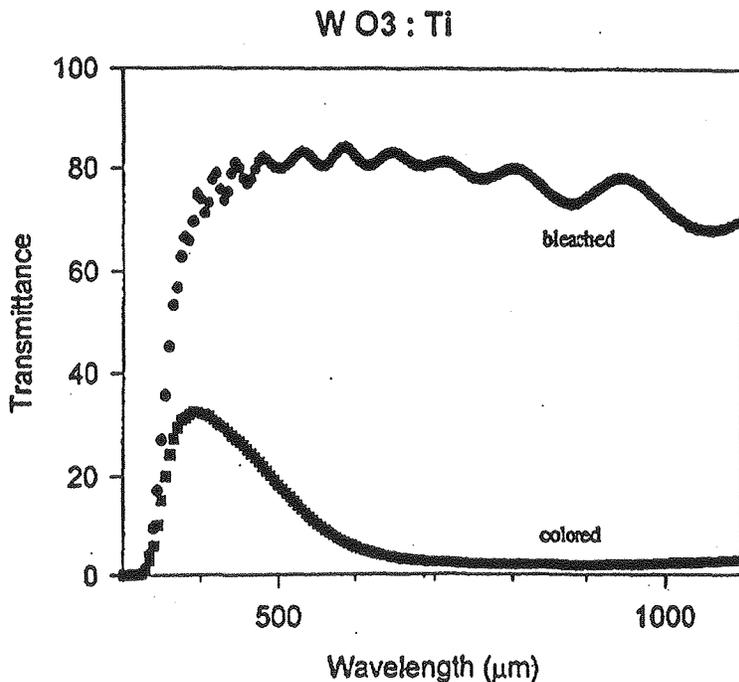


Fig. 13. Spectral transmittance spectra of 9% titanium doped WO_3 (Type 1) film on a Tec 20 glass substrate. The electrode was cycled in 1 M LiClO_4/PC . The film colored at $2\text{V}/(\text{Li}/\text{Li}^+)$ and bleached $4\text{V}/(\text{Li}/\text{Li}^+)$.

Optical Spectra of Y:WO₃ Film

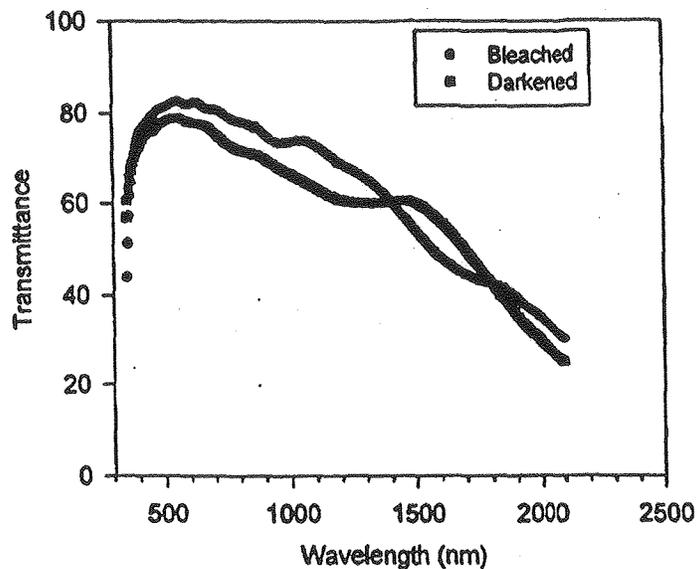


Fig. 14. Transmittance spectra of 12% yttrium doped WO₃ (Type 1) film on a Tec 20 glass substrate. The electrode was cycled in 1 M LiClO₄/PC. The film colored at 2V/(Li/Li⁺) and bleached at 4 V/(Li/Li⁺).

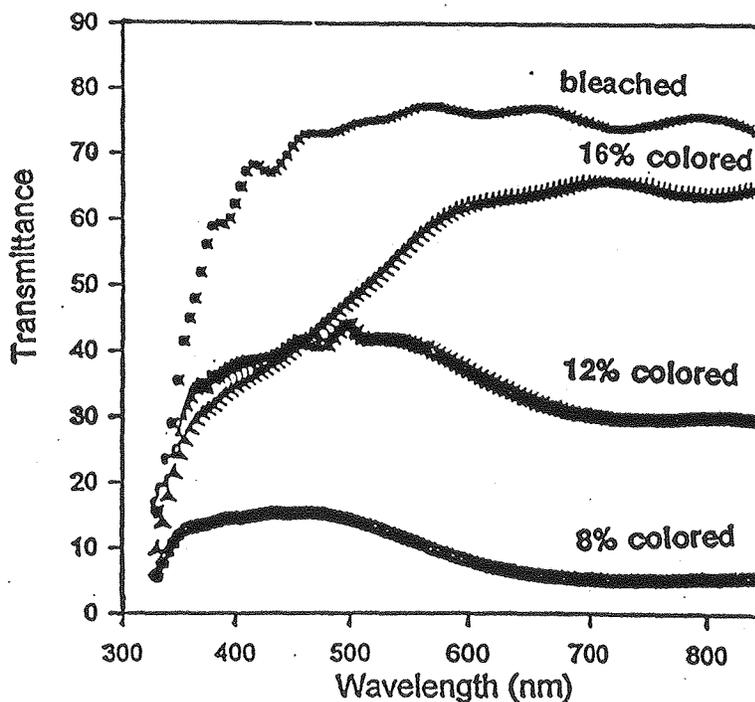


Fig. 15. Transmittance spectra of vanadium doped WO₃ (Type 1) film on a Tec 20 glass substrate. The electrodes were cycled in 1 M LiClO₄/PC. The films colored at 2V/(Li/Li⁺) and bleached at 4 V/(Li/Li⁺). The response for different amounts of dopant (8, 12, 16 %) are shown. The film thickness is constant.

Under the same conditions the V and Ti doped films colored more deeply than the undoped films during cycling. The doped films exhibit slightly higher durability compared to the undoped films over 1200 cycles of testing. In certain cases doping altered the color of the film. Table 2 lists the colors of doped tungsten oxides.

Table 2. Electrochromic coloration of doped and undoped tungsten oxide films (Type 1)

Oxide Film	Color (oxidized form)	Color (reduced form)
W	Transparent	Dark Blue
W:Cr	Transparent	Dark Blue
W:Co	Pale yellow	Brownish Blue
W:Nb	Transparent	Dark Blue
W:Ti	Transparent	Grayish Blue
W:V	Pale brown	Brownish Blue
W:Y	Transparent	Light Blue

Table 3 shows the integrated modulation in transmission in colored (c) and bleached state for the sol-gel deposited films. Primary mechanism of optical modulation over the studied spectral region for both the undoped and doped films is by absorption. The extent of visible and solar modulation in these films, as show in Table 3, is large enough to meet the most automotive and building requirements (9-10).

Table 3. Integrated transmission characteristics of the WO₃ coatings

Oxide Film	Charge (mC/cm ²)	T _{vis} (bleached)	T _{vis} (colored)	T _{sol} (bleached)	T _{sol} (colored)
W	26	0.84	0.11	0.76	0.18
W:Cr	26	0.82	0.12	0.73	0.17
W:Co	26	0.80	0.09	0.71	0.16
W:Nb	26	0.81	0.10	0.73	0.18
W:Ti	26	0.83	0.09	0.72	0.14
W:V	26	0.79	0.04	0.70	0.09
W:Y	26	0.84	0.51	0.75	0.56

CONCLUSIONS and RECOMMENDATIONS

The electrochromic properties of doped films were compared to those of undoped tungsten oxide films. Our investigation showed that M:WO₃ films can be prepared by the sol-gel process from mixed alkoxide solutions. Except for V, the addition of the dopant to sol-gel solution leads to an increased solution stability. The vanadium doped solution was stable for one day. Doped films tend to exhibit a higher absorbance in their colored state compared to undoped films. Considerable improvement, up to 20x of the lithium diffusivity, was noted for all the doped films. Vanadium doping had the greatest effect. Doping appeared to increase the cyclic durability of all the tungsten

films out to 1200 cycles. Color changes by doping were noted for several dopants. The doped films with the best overall properties were about 8% vanadium and titanium tungsten oxide. The optimum concentration lies in the range of 7 to 12 mol%. The electrochromic color was a neutral brownish-blue for vanadium and grayish-blue for titanium doped tungsten oxide.

Recommendations for further work include more tightly optimizing the film properties by changing the film preparation and heat treatment conditions for 8% doped films. Chemical analysis of the deposited films will give a more accurate determination of doping concentration. A doping chemistry should be developed for the Type 2 films following the results of this study.

ACKNOWLEDGMENTS

This research was supported by the Assistant Secretary of Energy Efficiency and Renewable Energy, Office of Building Technologies, Building Systems and Materials Division of the U.S. Department of Energy under Contract No DE-AC03-76SF00098.

The authors wish to thank Drs. Anoop Agrawal and John Cronin, Donnelly Corporation, Tucson, Arizona, for providing us with their WO₃ precursor.

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