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Cycling Durability of Electrochromic W–Ti Oxide Thin Films: Optical Transmittance Data Signal Dual Degradation Modes

Idris Sorar^{a,b,*}, Claes G. Granqvist^a, and Gunnar A. Niklasson^a

^aDepartment of Engineering Sciences, The Ångström Laboratory, Uppsala University, P.O.
Box 534, SE-75121 Uppsala, Sweden

^bDepartment of Physics, Hatay Mustafa Kemal University, TR-31060 Antakya/Hatay, Turkey

Abstract

Electrochemical degradation of electrochromic W oxide and W–Ti oxide thin films, prepared by reactive DC magnetron sputtering, were studied by voltammetric cycling in potential intervals from 1.5–4.0 to 2.0–4.0 V *vs.* Li/Li⁺ in an electrolyte of lithium perchlorate in propylene carbonate. Cycling-dependent evolution of the upper and lower limits for the optical modulation range was critically dependent on potential interval. This phenomenon was analyzed through an extension of a previously formulated model for power-law dynamics; it was discovered that the upper and lower limits for the optical modulation range varied in distinctly different ways, and that only data acquired in the interval 2.0–4.0 V *vs.* Li/Li⁺ could be reconciled with dispersive chemical kinetics. We thus find that our data on optical transmittance degradation lends strong support to the existence of dual degradation modes for electrochromism upon extended electrochemical cycling. This result is of large importance for the development of highly durable electrochromic devices such as smart windows for energy-efficient buildings.

Keywords: Electrochromism; Thin films; Tungsten oxide, Titanium oxide; Sputter deposition; Degradation; Transmittance

*Corresponding author: idrissorar@gmail.com

Introduction

Electrochromic (EC) thin films are able to vary their optical absorption by insertion/extraction of small ions—usually being H^+ or Li^+ —together with charge-balancing electrons.^{1,2} The most widely investigated EC devices, and the largest ones in terms of area, concern “smart” glazing that is able to yield energy efficiency as well as indoor comfort in buildings.^{3,4} Such glazing typically embraces a five-layer structure with a central ion-conducting layer joining a primary EC thin film and another thin film that serves as a repository for mobile ions and also may exhibit EC properties that are complementary to those of the primary EC film; this three-layer construction is positioned between transparent electrically conducting thin films serving as electrodes. The primary EC thin film in today’s “smart” glazing is based on W oxide,^{3,4} which is the material wherein electrochromism was first discovered.⁵ It can be noted that EC technology is an example of the current wide-ranging endeavors to develop oxide optoelectronics and optoionics.^{6–9}

Long-term durability, and its assessment, are obviously desired for practical glazing and have garnered considerable attention in recent years.¹⁰ One aspect concerns additions to the primary EC oxide film, and it is well known that Ti is able to extend the service lifetime of amorphous W-oxide-based EC thin films.^{11–14} This has been ascribed to the ability of Ti to retard the crystallization of W oxide films.^{15,16} Regarding durability under extended charge insertion/extraction and ensuing optical modulation, it was discovered recently that good estimates could be obtained from a power-law expression that describes the decline in exchanged charge density Q as a function of cycle number x according to^{17,18}

$$Q(x) = A_{Q_2} + \frac{A_{Q_1} - A_{Q_2}}{1 + \left(\frac{x-1}{x_Q}\right)^{p_Q}}, \quad (1)$$

where A_{Q_1} is initial charge density, A_{Q_2} is eventual residual charge density after many cycles, x_Q is the cycle number for which the drop in Q has reached half of its final value, and p_Q is a power-law exponent.

Although useful for practical applications, Eq. 1 captures only the general degradation of the electrochromic modulation span but is unable to separately assess the cycling-dependent changes of the bright-state and dark-state transmittance. Here we go beyond the earlier analysis¹⁴ encapsulated in Eq. 1 and formulate analogous equations for evolution of optical

performance. By doing so, we are able to identify dual degradation modes, as elaborated below.

Experimental

Thin films of W oxide and W–Ti oxide were prepared by reactive DC magnetron sputtering from 5-cm-diameter targets of W, W(95 wt.%) + Ti(5 wt.%), and W(90 wt.%) + Ti(10 wt.%) onto glass plates coated with transparent $\text{In}_2\text{O}_3\text{:Sn}$ having a sheet resistance of 60 Ω . Deposition was performed at a constant power of 200 W and a total argon + oxygen pressure of 30 mTorr; the O_2/Ar ratio was 0.133. The substrates were unheated and were rotated in order to assure a uniform thickness, which was found by surface profilometry to be 300 ± 20 nm.

Elemental compositions of the films were recorded by Time-of-Flight Elastic Recoil Detection Analysis, which gave unambiguous depth profiles for W, Ti, and O as well as trace signals for H and C and, at the expected depth, also for In + Sn. Detailed analyses demonstrated that films deposited from the three types of targets could be designated WO_3 , $\text{W}_{0.87}\text{Ti}_{0.13}\text{O}_3$, and $\text{W}_{0.80}\text{Ti}_{0.20}\text{O}_3$.¹⁴ Structural characterization by X-ray diffraction showed that these films were amorphous.

Cyclic voltammetry (CV) was carried out with a BioLogic Science Instruments SP-200 electrochemical interface and a three-electrode electrochemical cell including a film of W oxide or W–Ti oxide as working electrode and Li foil as counter and reference electrodes. The electrolyte was 1 M LiClO_4 dissolved in propylene carbonate. Potentials are given with reference to Li/Li^+ . CV measurements were performed in the potential ranges 1.5–4.0, 1.6–4.0, 1.7–4.0, and 2.0–4.0 V at a scan rate of 20 mV s^{-1} . Optical transmittance T was determined concurrently *in situ* at the wavelength 528 nm. The 100-%-level for transmittance was obtained by measuring with nothing but electrolyte in the cell. All opto-electrochemical measurements were performed under Ar atmosphere in a glove box with less than 1 ppm water content.

Further details on experimental techniques and procedures can be found elsewhere.¹⁴

Results and Discussion

Figure 1 shows maximum and minimum values of the optical transmittance for up to 500 CV cycles in the shown potential ranges for films of the stated compositions and demonstrates

vividly that film composition and potential interval are important for the evolution of the bleached-state transmittance T_b as well as of the colored-state transmittance T_c . Considering first the potential range 2.0–4.0 V, it is found that $T_b(x)$ remains at ~96% irrespective of cycle number and that $T_c(x)$ rises from a level that is lower for WO_3 than for $\text{W}_{0.87}\text{Ti}_{0.13}\text{O}_3$ and $\text{W}_{0.80}\text{Ti}_{0.20}\text{O}_3$; the cycling-dependent increase of T_c is fastest for WO_3 and reaches 40% at $x \approx 500$ whereas this transmittance is found at $x \approx 300$ for $\text{W}_{0.87}\text{Ti}_{0.13}\text{O}_3$ and $\text{W}_{0.80}\text{Ti}_{0.20}\text{O}_3$. When harsher CV cycling was exercised by extending the potential interval to 1.7–4.0, it is noted that $T_b(x)$ is no longer constant but displays a monotonic drop, which after 500 CV cycles is ~20% for WO_3 , ~10% for $\text{W}_{0.87}\text{Ti}_{0.13}\text{O}_3$, and ~3% for $\text{W}_{0.80}\text{Ti}_{0.20}\text{O}_3$; the corresponding evolution of $T_c(x)$ is analogous and becomes less pronounced as the Ti content was increased. Looking, finally, at data for the potential intervals 1.6–4.0 and 1.5–4.0 V, the drop of $T_b(x)$ and the rise of $T_c(x)$ become strikingly accelerated, especially for the widest potential interval, and the strongest variations of the transmittance data take place already at the initial CV cycling; it is noteworthy that the changes are slower in the WO_3 film than in the Ti-containing films for the widest potential intervals. We hypothesize that the ability of Ti to retard the crystallization is no longer an advantage for the durability in these potential intervals.

In order to develop further understanding of the evolution of $T_b(x)$ and $T_c(x)$, we now reformulate Eq. 1 into power-law expressions for bleached-state and colored-state transmittance. To this end we first note that one can write

$$T \approx (1 - R) \exp(-\alpha d), \quad (2)$$

where R is reflectance, α is absorption coefficient and d is film thickness. The reflectance of our films is as low as 0.1 – 0.2 and almost independent of coloration level. Hence it is a good approximation to neglect the reflectance losses. We implicitly assume that α is proportional to Q and that the absorption process is due to transitions between only one set of isoenergetic localized states, which in the case of tungsten oxide is taken to be primarily electronic $\text{W}^{6+} \leftrightarrow \text{W}^{5+}$ transitions.¹⁹ In the case of mixed W–Ti oxides, the situation is probably more complex, but we will neglect the complications due to the Ti additions in the present paper. In addition, our assumption that α is proportional to inserted charge is not strictly correct except when Q is small, *i.e.*, as long as “site saturation” is not prevalent.^{19,20} In the site saturation regime, α is predicted to attain a maximum when the Li/W ratio, denoted y , is 0.5 and to decrease for larger magnitudes of y .²⁰ Specifically, this parameter can be estimated from $y = QM/(eAdpN_A)$, where M is molar mass of a formula unit of the oxide, e is elementary charge,

A is sample area, $\rho \approx 5.5 \text{ g cm}^{-3}$ is film density,²¹ and N_A is Avogadro's constant. The maximum charge exchange in our samples occurs for a WO_3 film subjected to treatment in the potential range 1.5–4.0 V.¹⁴ The analysis delineated above indicates that site saturation would be important primarily in the initial CV cycles for the widest potential ranges, *i.e.*, when the charge exchange is very high, and be most significant in the case of the WO_3 films. We thus write

$$\ln[T_b(x)] = A_{b_2} + \frac{A_{b_1} - A_{b_2}}{1 + \left(\frac{x-1}{x_b}\right)^{p_b}} \quad (3)$$

and

$$-\ln[T_c(x)] = A_{c_2} + \frac{A_{c_1} - A_{c_2}}{1 + \left(\frac{x-1}{x_c}\right)^{p_c}} \quad (4)$$

to account for the facts that T_b drops and T_c rises during degradation. Here A_{b_1} , A_{b_2} , A_{c_1} , A_{c_2} , x_b , x_c , p_b , and p_c are defined in analogy with corresponding symbols in Eq. 1. We regard Eqs. 3 and 4 as empirical relations, which will be validated below by comparison with experimental data.

Figures 2 and 3 illustrate $\ln(T_b)$ and $-\ln(T_c)$, respectively, as a function of x for the 500 CV cycles of our experiment (*cf.* Figure 1) and using the fitting parameters reported in Table SI1 in Supporting Information. In general, experimental results and data from Eqs. 3 and 4 are in good, or at least acceptable, accord although deviations can be noted particularly during the ten first CV cycles of harsh electrochemical treatment. Interestingly, these deviations occur in the fitting of data for the colored state and are largest in the case of W oxide and for the largest potential ranges. These are the situations wherein site saturation is predicted to be most significant. The exchanged charge increases considerably with the width of the potential interval,¹⁴ and the addition of Ti could delay the onset of site saturation since Ti oxide also colors in the considered potential intervals. Interestingly, the deviations are absent in the potential range 2.0–4.0 V and are not significant for the sample with the highest Ti content. We hypothesize that the deviations may be connected with variations in coloration efficiency at low cycle numbers that were observed previously,¹⁴ or that they may indicate a more complex degradation process than assumed in Eq. 4.

In-depth insights into the degradation of the electrochromism can be gleaned by discussing the power-law exponents pertinent to bleached-state and colored-state optical

properties, *i.e.*, p_b and p_c (*cf.* Table SI1). These parameters are reported in Table 1 for the various samples and potential ranges; also included are data on p_Q as derived from charge density evolution in our earlier work.¹⁴

A number of observations can be made from Table 1: Firstly, it is seen that $p_c \approx p_Q$, which indicates that critical exponents for degradation of electrochromic films indeed can be derived conveniently from optical transmittance evolution and do not have to rely on more complicated charge-density measurements. This result also indicates that the deviations between experimental data and our degradation model do not significantly influence the evaluation of T_c data. Secondly, power-laws such as those stated here allow a discussion of underlying physico-chemical processes with consideration of dispersive chemical kinetics.^{22–24} Exponents less than or equal to unity are expected for diffusion-limited chemical kinetics,^{22,23} which appears to apply to colored-state transmittance evolution for the case of narrow potential ranges. Larger critical exponents may be consistent with enhanced diffusion processes,²⁴ but the possible origin of those processes remains uncertain. Thirdly, the fact that p_b and p_c are distinctly different is a significant new result and indicates that degradation of electrochromism upon electrochemical cycling of W-oxide-based films proceeds by different modes for coloration and for bleaching.

Finally, we discuss some implications of the inequality between p_b and p_c . In Eq. 3, the power-law expression models the decrease of T_b during cycling, which we interpret as being due to charge trapping yielding gradually decreasing transmittance of the bleached state. However, Eq. 4 for the colored-state transmittance is not so straightforward to interpret. Taken at face value, it would be proportional to the total charge giving rise to T_c . However, the trapped charge gives only a small contribution to $-\ln(T_c)$ as can be seen from an analysis of $\ln(T_b/T_c)$ shown in Supplementary Information (Figure SI1 and Table SI2). The resulting exponent values from this latter analysis, denoted p_d , are much closer to p_c than to p_b . It can be argued that the decay of p_d is due to the decreasing charge reversibly shuttled in and out of the electrochromic material. The decrease might be due to charge trapping in combination with the formation of Li compounds with low absorption at potentials below 2.0 V.²⁵ Within this picture, it is not surprising that the power-law exponents p_c and p_b are different, since the charge that can be reversibly extracted and inserted probably occupies a different set of localized states than the trapped charge.

Conclusion

We investigated the degradation of electrochromic properties for W oxide and W–Ti oxide thin films prepared by reactive DC magnetron sputtering, which is the most common deposition technique for variable-transmittance “smart” glazing.³ Degradation was accelerated by using cyclic voltammetry, in an electrolyte of lithium perchlorate in propylene carbonate, within potential intervals as wide as 1.5–4.0 V. The bleached-state transmittance was lowered (except for cycling at 2.0–4.0 V) and the colored-state transmittance was increased upon voltammetric cycling. These phenomena were analyzed by using power laws—reconcilable with dispersive chemical kinetics—and it was concluded that different degradation modes pertain to electrochromic bleaching and coloring. This is a new result of considerable interest for the development of durable electrochromic devices such as smart windows for energy-efficient windows with good indoor comfort. The details of the degradation cannot be inferred from our present experiments and analyses, however, and deserve further work.

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Table 1. Power-law exponents in Eqs. 1,3 and 4 for samples with the shown compositions. Data were extracted from voltammetric cycling in the stated potential ranges at a scan rate of 20 mV s⁻¹.

Sample	Potential range (V)	p_b	p_c	p_Q
WO ₃	1.5 – 4.0	3.96	2.95	2.40
	1.6 – 4.0	8.40	3.24	3.26
	1.7 – 4.0	7.19	2.20	2.29
	2.0 – 4.0	---	1.01	0.78
W _{0.87} Ti _{0.13} O ₃	1.5 – 4.0	3.94	2.86	2.73
	1.6 – 4.0	4.90	2.24	2.33
	1.7 – 4.0	3.31	1.26	1.63
	2.0 – 4.0	---	1.03	0.76
W _{0.80} Ti _{0.20} O ₃	1.5 – 4.0	2.85	2.13	2.08
	1.6 – 4.0	3.37	1.66	1.74
	1.7 – 4.0	---	1.00	1.22
	2.0 – 4.0	---	1.35	0.91

Figure 1. Transmittance in bleached and colored states at a wavelength of 528 nm for ~300-nm-thick films of WO₃ (panel A), W_{0.87}Ti_{0.13}O₃ (panel B), and W_{0.80}Ti_{0.20}O₃ (panel C). Data were recorded during cyclic voltammetry in the indicated voltage ranges at a scan rate of 20 mV s⁻¹.

Figure 2. $\ln(T_b)$ vs. cycle number for ~ 300 -nm-thick films of WO_3 (panels Aa–Ac), $\text{W}_{0.87}\text{Ti}_{0.13}\text{O}_3$ (panels Ba–Bc), and $\text{W}_{0.80}\text{Ti}_{0.20}\text{O}_3$ (panels Ca–Cb). Data were obtained from bleached-state optical transmittance at a wavelength of 528 nm recorded during cyclic voltammetry in the indicated voltage ranges at a scan rate of 20 mV s^{-1} . Symbols represent experimental data and curves were drawn from Eq. 3 using parameters in Table SI1. Note that the degradation for some of the narrower potential ranges was too slow to allow any analysis by use of Eq. 3.

Figure 3. $-\ln(T_c)$ vs. cycle number for ~ 300 -nm-thick films of WO_3 (panels Aa–Ad), $\text{W}_{0.87}\text{Ti}_{0.13}\text{O}_3$ (panels Ba–Bd), and $\text{W}_{0.80}\text{Ti}_{0.20}\text{O}_3$ (panels Ca–Cd). Data were obtained from colored-state optical transmittance at a wavelength of 528 nm recorded during cyclic voltammetry in the indicated voltage ranges at a scan rate of 20 mV s^{-1} . Symbols represent experimental data and curves were drawn from Eq. 4 using parameters in Table SII.