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Electrochromism of W–In oxide thin films: Implications for cycling durability

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ABSTRACT

Electrochromic W oxide and W–In oxide thin films were prepared by dual-target reactive DC magnetron sputtering and were cycled voltammetrically in an electrolyte of lithium perchlorate in propylene carbonate. Film degradation was investigated for up to 500 cycles in the voltage ranges 1.5–4.0, 1.7–4.0 and 2.0–4.0 V vs. Li/Li^+, and optical transmittance was recorded concurrently. Indium doping was found to be unambiguously detrimental to electrochromic cycling durability, which resolves an outstanding issue related to recently discovered unprecedented durability of potentiostatically pretreated W oxide films backed by In_2O_3:Sn and gives strong support in favor of beneficial effects of solid-electrolyte interfacial layers.

1. Introduction

Electrochromic (EC) "smart" glazing is an essential component in modern architecture and is able to provide energy efficiency [1] jointly with indoor comfort [2]. Today's EC devices for these applications have a three-layer battery-like construction with tungsten-oxide-based thin films separated from ion-storage films by transparent ion conductors being thin inorganic films or organic polymer layers [3–6]. Optical modulation occurs when charge is shuttled between the tungsten-oxide-based film and the ion-storage film by applying a voltage between transparent electrically conducting thin films, typically based on indium oxide or tin oxide, surrounding the centrally positioned three-layer arrangement.

Long-time durability is an obvious requirement for glazing, and EC devices for such applications must sustain tens of thousands of electro-optical modulation cycles without essential loss of performance. Currently used "smart" glazing meets these demands, but enhanced durability is nevertheless of great importance since it would enable larger optical modulation range and possibly higher modulation rate, and several avenues towards better cycling durability have been explored lately for EC devices [7]. One of these avenues is based on an intriguing recent discovery that EC films of WO_3, backed by transparent conductors of In_2O_3:Sn (known as ITO), can achieve unprecedented EC cycling durability by potentiostatic pretreatment in an electrolyte of lithium perchlorate in propylene carbonate [8]. Subsequent work pointed at two possible sources for the enhanced durability: (i) voltage-induced dissolution of In_2O_3:Sn and ensuing diffusion of predominantly In into the WO_3 film, and (ii) formation of carbonaceous solid-electrolyte interfacial (SEI) layers on the WO_3 film [9,10]. This prior work could not tell which of these mechanisms was dominating or whether they operated in concert.

Here we report results from a study of In-containing WO_3 thin films prepared by co-deposition and demonstrate that the In content tends to *deteriorate* the electrochromism of WO_3, thus giving clear evidence that SEI layers are the prevalent source of the boosted cycling durability of potentiostatically pretreated EC WO_3 films. We are not aware of earlier work on EC W–In oxide films with metal ions being intermixed on an atomic or near-atomic scale, as in the present investigation; however, studies have been reported on nanocomposites of ITO embedded in WO_3 [11–16] wherein ITO contributes to optical modulation rate (due to lowered electrical resistance) and modulation range (due to plasmonic effects [17–20]).

2. Experimental section

Thin films of pure W oxide and W–In oxide were prepared by reactive DC magnetron co-sputtering in a deposition system based on a Balzers UTT 400 unit. Targets were 5-cm-diameter plates of 99.95-%-pure W and of In_2O_3(90 wt%) + SnO_2(10 wt%) with purities of 99.99%. Depositions were made onto glass substrates pre-coated with ITO having a resistance of 60 Ω/square.

The deposition system was first evacuated to ~6×10^{-5} Pa.

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Table 1
Elemental compositions for films of W oxide and W–In oxide. Data are shown on sputter power P and associated deposition rate r.

Film composition	P_W [W]	P_{In} [W]	r_W [nm/min]	r_{In} [nm/min]
WO_3	200	—	38	—
$W_{0.93}In_{0.07}O_3$	200	50	38	1.5
$W_{0.88}In_{0.12}O_3$	200	75	38	2.5
$W_{0.86}In_{0.14}O_3$	200	100	38	3.0
$W_{0.84}In_{0.16}O_3$	200	125	38	3.6

Oxygen and argon with purities of 99.997% were then introduced into the deposition chamber so that the O_2/Ar ratio was 0.133 and the total pressure was 4 Pa. The power to the pure W target, P_W, was set at 200 W while the power to the In_2O_3 + SnO_2 target, P_{In}, was set at a value of 50–125 W in order to prepare films with different In contents (the minor amount of Sn is considered insignificant and is omitted in the discussion below). The target–substrate distance was 13 cm and the substrate was rotated during deposition to assure uniform film thickness. Deposition rates r were derived from single-target depositions by dividing film thickness—measured ex situ using a Bruker Dektak XT surface profilometer—by sputtering time. Table 1 lists P_W and P_{In} and the associated values of r_W and r_{In}. Film thicknesses were 300 ± 20 nm.

Elemental compositions of the films, denoted $W_{1-x}In_xO_y$, were inferred from r_W and r_{In} with consideration of the fact that the densities of WO_3 and In_2O_3 are almost the same, specifically being 7.16 and 7.18 g/cm^3, respectively, for bulk materials. Reactively deposited thin films are expected to have lower densities, as studied in detail for WO_3 [21,22], and 5.2 g/cm^3 was reported for films prepared under conditions similar to those in the present work [23]. The corresponding density decrease is not known for In_2O_3 but is expected to be similar to that for WO_3. Given these conditions, and accounting for the fact that WO_3 has one metal atom per formula unit whereas In_2O_3 has two, we obtain the compositions stated in the first column of Table 1. We put $y = 3$, which is in accord with results from earlier work on sputter-deposited films of W–Ti oxide [24], W–Ti–Mo oxide [25] and W–Ti–Ni oxide [26]. The elemental compositions of the films may be subject to some systematic errors due to the fact that the density of reactively deposited thin films of In_2O_3 is not known and that the role of Sn is neglected, but the data in Table I are fully adequate for the present essentially qualitative study.

The films were studied by cyclic voltammetry (CV) using a BioLogic Science Instruments SP-200 electrochemical interface together with a standard three-electrode cell. Thin films of W oxide and W–In oxide on ITO-coated glass served as working electrode and Li foil was used as reference and counter electrodes; the electrolyte was 1 M $LiClO_4$ dissolved in propylene carbonate. All potentials are stated versus Li/Li$^+$. CV measurements were carried out at a scan rate of 20 mV/s, and the potential was swept in the ranges 1.5–4.0, 1.7–4.0 and 2.0–4.0 V. Mid-luminous optical transmittance was recorded concurrently in situ at a wavelength of 528 nm. The 100-%-level for optical transmittance corresponded to the value obtained with nothing but electrolyte in the cell. All electrochemical and optical measurements were carried out in argon atmosphere in a glove box with water content below 1 ppm.

Complementary ex situ investigations by X-ray diffraction, using a Siemens D5000 instrument working with Cu K_α radiation, showed nothing but peaks due to ITO, and hence all the present films were amorphous. Furthermore, studies with X-ray photoelectron spectroscopy (XPS), employing a PHI Quantum 2000 Scanning ESCA Microprobe, demonstrated signals due to In 3d, W 4f, O 1s, and C 1s in fully bleached and colored samples corresponding to the endpoints of the voltammetric scans. In 3d and W 4f peaks in samples of the various compositions were in general agreement with literature data for In $(OH)_3$ [27] and WO_3 [9]. Differences in peak positions between colored and bleached samples were within experimental uncertainty and cannot be used to ascertain, for example, specific changes in valence states for In. XPS data for C 1s, expectedly, did not show evidence for C—O bonded species previously [9] associated with the presence of SEIs.

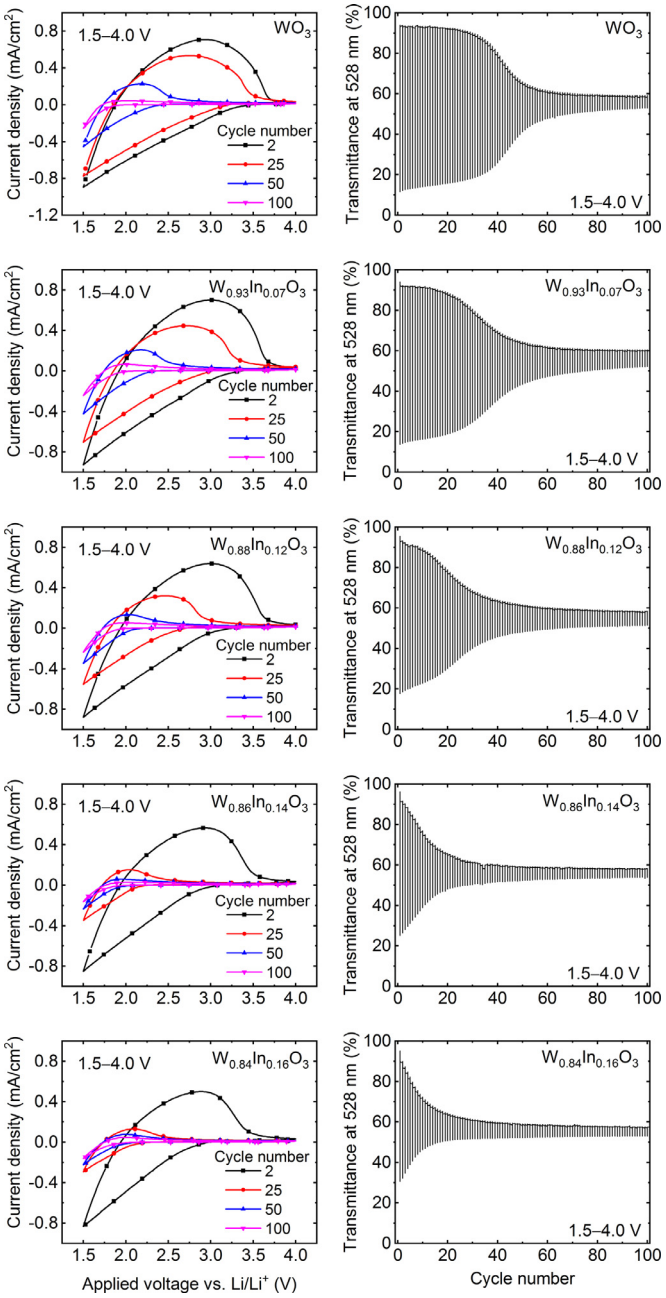

Fig. 1. Cyclic voltammograms (left-hand panels) and corresponding optical modulation at a wavelength of 528 nm (right-hand panels) for thin films of W oxide and W–In oxide with the shown compositions. Data were recorded during up to 100 voltammetric cycles in the potential range 1.5–4.0 V vs. Li/Li$^+$ at a scan rate of 20 mV/s.

3. Results and discussion

Figs. 1–3 display the main results of our investigations on cyclic voltammetry and associated optical modulation pertaining to the potential intervals 1.5–4.0, 1.7–4.0 and 2.0–4.0 V, respectively. Looking first at CV data for 1.5–4.0 V (Fig. 1, left-hand panels), it is evident that the voltammograms change rapidly during the first 100 cycles and that the encircled areas—signifying charge capacity—shrink, which implies that the amount of inserted and extracted charge goes down drastically.

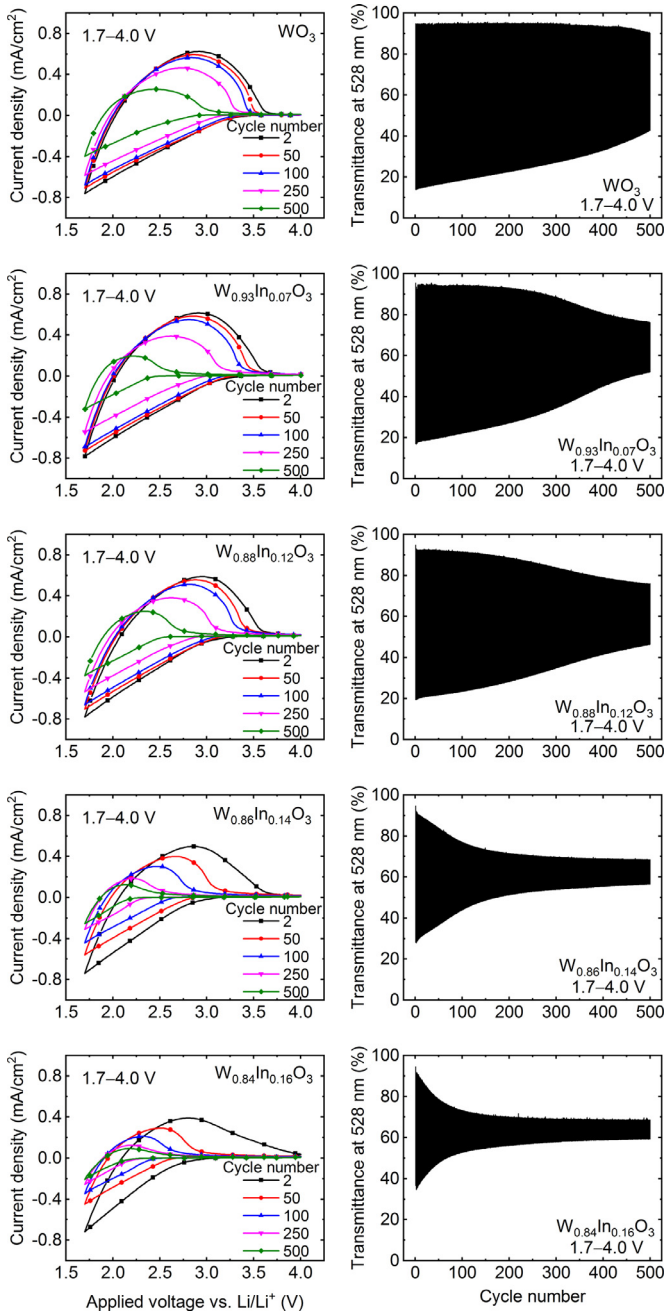

Fig. 2. Cyclic voltammograms (left-hand panels) and corresponding optical modulation at a wavelength of 528 nm (right-hand panels) for thin films of W oxide and W–In oxide with the shown compositions. Data were recorded during up to 500 voltammetric cycles in the potential range 1.7–4.0 V vs. Li/Li^+ at a scan rate of 20 mV/s.

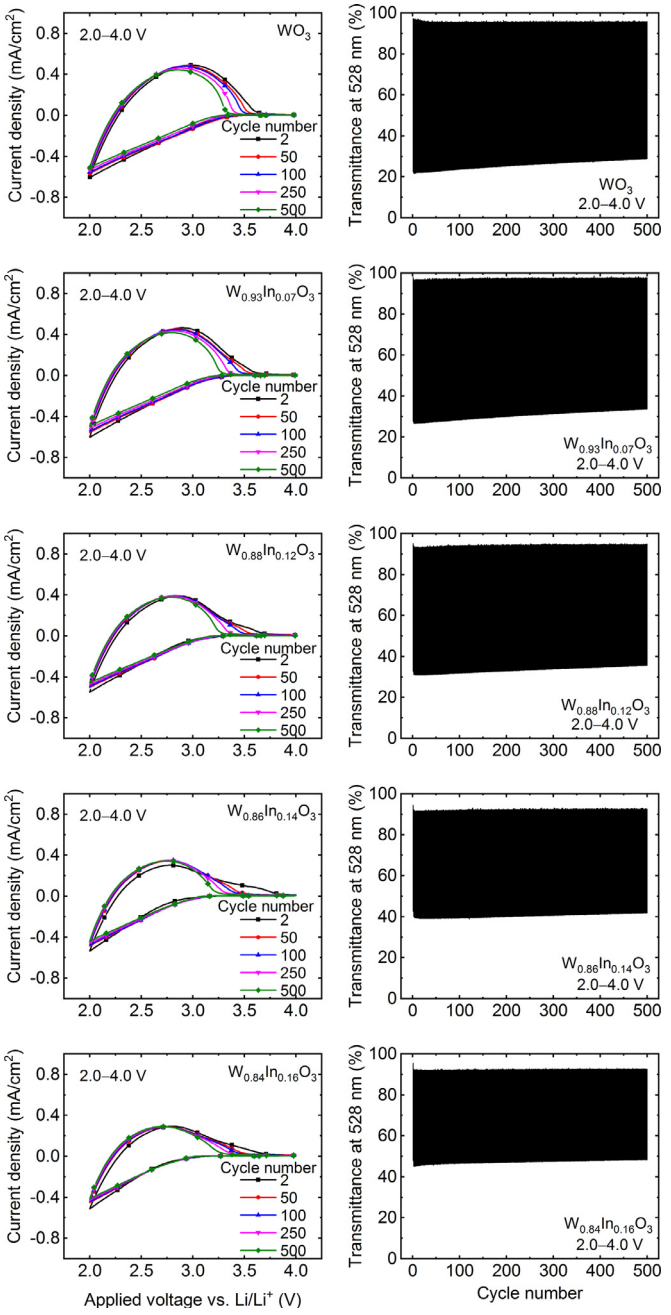

Fig. 3. Cyclic voltammograms (left-hand panels) and corresponding optical modulation at a wavelength of 528 nm (right-hand panels) for thin films of W oxide and W–In oxide with the shown compositions. Data were recorded during up to 500 voltammetric cycles in the potential range 2.0–4.0 V vs. Li/Li^+ at a scan rate of 20 mV/s.

Interestingly, the deterioration of the charge capacity becomes progressively more severe as the In doping is increased. The corresponding optical modulation (Fig. 1, right-hand panels) change in correspondence with the diminishing charge capacity, and it is noteworthy that the bright-state transmittance drops and that the dark state transmittance becomes larger during cycling.

Considering the potential interval 1.7–4.0 V, the cycling-dependent change of the voltammograms (Fig. 2, left-hand panels) and the associated alteration in the optical modulation (Fig. 2, right-hand panels) are similar to those recorded at 1.5–4.0 V but progress at a significantly slower pace during the shown 500 CV cycles. For example, the decline in optical modulation for the film of $W_{0.93}In_{0.07}O_3$ is most rapid after ~300 CV cycles for 1.7–4.0 V, whereas the fastest decline occurs after only ~35 cycles for 1.5–4.0 V. Bright-state transmittance as well as dark-state transmittance are affected by the CV cycling at 1.7–4.0 V, but this change is minimal for the WO_3 film and is clearly noticeable only after ~400 cycles.

Finally turning to data for 2.0–4.0 V, the cycle-dependent changes of the voltammograms (Fig. 3, left-hand panels) and optical modulation (Fig. 3, right-hand panels) are more modest than for CV cycling at 1.7–4.0 V (Fig. 2) and, particularly, 1.5–4.0 V (Fig. 1). The bright-state transmittance is essentially unaffected by the CV cycling while the dark-state transmittance is increased by only a few percent. The major effect of the In doping is that the dark-state transmittance is increased in

proportion with the doping level from 21–24% for WO_3 to 42–44% for $W_{0.84}In_{0.16}O_3$.

The main result from the wealth of data presented in Figs. 1–3 is straight-forward: the electrochromism of W oxide films is progressively deteriorated as the In content is increased irrespectively of potential scan range, and there is no sign of any enhanced performance at a small amount of In.

4. Conclusion

The present studies on EC thin films of W oxide and W–In oxide—prepared by dual-target reactive DC magnetron sputtering and voltammetrically cycled in an electrolyte of lithium perchlorate in propylene carbonate—show that film degradation becomes increasingly strong as the voltage sweep range is increased and, more interestingly, as the In content is enhanced. This latter result is important since recent work has shown that potentiostatically pretreated W oxide films backed by ITO could exhibit unprecedented cycling durability [8], which was associated with either electrochemically induced interdiffusion with In, the formation of carbonaceous SEI layers on the WO_3 film, or with a combination of these two effects [9,10]. Our present work showed strong degradation in the absence of an identifiable SEI and hence demonstrates convincingly that SEI layers are the predominant cause of the durability enhancement observed in previous work [8,9]. Such layers are well known in battery technology, though incompletely understood [28], which serves as an illustration of the well-known fact that EC devices and batteries share properties as well as idiosyncrasies.

CRediT authorship contribution statement

Idris Sorar: Investigation, Formal analysis, Writing - original draft. **İlknur Bayrak Pehlivan:** Investigation. **Claes G. Granqvist:** Conceptualization, Writing - review & editing, Supervision. **Gunnar A. Niklasson:** Resources, Writing - review & editing, Supervision.

Declaration of Competing Interest

None.

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