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Electrochemical pretreatment of electrochromic WO₃ films gives greatly improved cycling durability

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ABSTRACT

Electrochromic WO₃ thin films have important applications in devices such as smart windows for energy-efficient buildings. Long-term electrochemical cycling durability of these films is essential and challenging. Here we investigate reactively sputter-deposited WO₃ films, backed by indium–tin oxide layers and immersed in electrolytes of LiClO₄ in propylene carbonate, and demonstrate unprecedented electrochemical cycling durability after straight-forward electrochemical pretreatments by the application of a voltage of 6 V vs. Li/Li⁺ for several hours.

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Electrochromic (EC) thin-film devices have numerous applications in contemporary and forthcoming technology [1,2] such as in smart windows for energy efficient buildings with good indoor comfort [3], non-emissive information displays, and surfaces for tunable reflectance or thermal emittance. The optical properties of EC oxide films are changed upon intercalation/deintercalation of small ions such as H^+ or Li^+ and concurrent insertion/extraction of charge balancing electrons. Long-term durability of EC-film-based devices is essential for most applications. Achieving this property is highly challenging and, not surprisingly, durability issues have been the subject of numerous studies [4]. Recent advances towards longevity of EC devices include the use of multi-component mixed oxides [5,6] as well as rejuvenation of degraded oxide thin films through electrochemical extraction of trapped Li ions under galvanostatic or potentiostatic conditions [7–9]. In this Letter we present initial results based on a novel technique and show that it is possible to significantly extend the durability of EC films consisting of tungsten oxide, WO_3 . This is the material in which electrochromism was first discovered [10], and it still remains the most widely investigated EC material; furthermore, thin films based on WO_3 appear to be employed in all of today's full-size EC smart windows [3]. Our new technique for durability enhancement consists of a principally straight-forward high-voltage electrochemical pretreatment of WO_3 films backed by indium–tin oxide layers and immersed in electrolytes of $LiClO_4$ in propylene carbonate (PC).

Thin films of WO_3 were produced by reactive DC magnetron sputtering onto unheated glass substrates with pre-coated transparent and electrically conducting $In_2O_3:Sn$ layers having a resistance/square of 60 Ω . The sputter gas was argon mixed with oxygen (O_2/Ar ratio 0.15), which was introduced via mass flow controlled inlets and maintained at a pressure of 4 Pa during film preparation. The deposition rate was ~ 47 nm per minute, and the film thicknesses were 300 ± 20 nm as determined by surface profilometry. Thickness uniformity was ascertained by rotating the substrate during sputter deposition. Film porosities were $\sim 32\%$ as inferred from Rutherford backscattering measurements combined with film thickness data. X-ray diffractometry showed that all of the investigated WO_3 films were amorphous irrespectively of their treatment. Further details on film manufacture and characterization can be found elsewhere [5].

As-prepared WO_3 films were potentiostatically pretreated by submersion in an electrolyte of 1 M $LiClO_4$ dissolved in PC and application of a potential, with polarity allowing positive-ion expulsion from the sample, for several hours. Fig. 1 reports current density evolution and

simultaneous in situ optical transmittance at a mid-luminous wavelength of 550 nm using a fiber-optic instrument (Ocean Optics) when a sample was subjected to a constant potential of 6.0 V vs. Li/Li^+ during a time span of 24 h. The measurements were performed in an argon-containing glove box with water content less than ~ 0.5 ppm. It is apparent that the current density displays an initial abrupt decrease, which is followed by a conspicuous broad and distinct peak after ~ 4 h and a subsequent slow decline after ~ 6 h. Fig. 1 also shows that the optical transmittance remains high and almost unaltered during the entire electrochemical treatment. Data that are similar to those in Fig. 1, albeit not identical to them, were observed for several other WO_3 films.

Fig. 1. Current density (left-hand scale) and optical transmittance at 550 nm (right-hand scale) for a ~ 300 -nm-thick WO_3 film in $\text{LiClO}_4\text{-PC}$. Data show property evolution upon extended potentiostatic treatment at 6.0 V vs. Li/Li^+ . Arrows indicate applicable scale.

Cyclic voltammetry (CV), as well as the earlier mentioned potentiostatic treatments, were carried out with conventional equipment (Solartron 1286 Electrochemical Interface). The electrochemical cell was of standard three-electrode type with the $\text{In}_2\text{O}_3\text{:Sn}$ -backed WO_3 film serving as working electrode and with Li foil used as counter and reference electrodes. Figs. 2a and 2b show CV data recorded in the potential range of 1.5–4.0 V vs. Li/Li^+ at a sweep rate of 20 mV s^{-1} for an as-deposited WO_3 film and after this film had been subjected to the

potentiostatic pretreatment, respectively. The potential range is considerably wider than in most other studies of EC WO_3 films and was chosen in order to allow degradation studies within convenient time spans.

Fig. 2. Cyclic voltammograms (panels a and b) and corresponding optical transmittance at a wavelength of 550 nm (panels c and d) for a ~ 300 -nm-thick WO_3 film in as-deposited state (panels a and c) and after potentiostatic pretreatment in LiClO_4 -PC at 6.0 V vs. Li/Li^+ for 24 h (panels b and d). Arrows indicate voltage sweep direction.

The cyclic voltammograms of the as-deposited film (Fig. 2a) change radically during the course of the harsh CV cycling, and the charge exchange—governed by the area encircled by the CV data—goes from $\sim 53 \text{ mC cm}^{-2}$ for the initial CV cycles to as little as $\sim 6 \text{ mC cm}^{-2}$ after 40 CV cycles. Corresponding data for the potentiostatically pretreated WO_3 film (Fig. 2b) look strikingly different; the charge exchange is $\sim 33 \text{ mC cm}^{-2}$ during the first CV cycles and remains as large as $\sim 26 \text{ mC cm}^{-2}$ after 40 CV cycles. Hence the potentiostatic pretreatment tends to lower the initial charge capacity of the WO_3 film to some extent but, more importantly, the pretreatment radically diminishes the decline of the charge capacity upon extended voltammetric cycling.

Electrochromism is intimately connected with charge exchange, and Figs. 2c and 2d illustrate the evolution of the optical transmittance modulation for the WO₃ films whose CV data were reported in Figs. 2a and 2b, respectively. The as-deposited film (Fig. 2c) displays initial transmittance changes between ~ 0.90 and ~ 0.10 , i.e., a modulation span that is ~ 0.80 at the beginning of the experiment but shrinks to a mere ~ 0.06 after 40 harsh CV cycles. The potentiostatically pretreated film (Fig. 2d) also has an initial modulation span of ~ 0.80 ; remarkably, this modulation range stays as large as ~ 0.77 after the completion of the voltammetric cycling. The slight loss of optical modulation during the CV cycling of the pretreated film corresponds to a minor increase of the dark-state transmittance while the transparent state remains virtually intact.

The conclusion of our work is clear and unambiguous: A potentiostatic high-voltage treatment of WO₃ films, backed by a transparent electrical conductor of In₂O₃:Sn and immersed in a Li-ion-conducting electrolyte, is able to produce a great improvement of the films' electrochromic performance. We foresee that this technique can be used either on its own or in conjunction with other measures for durability promotion, such as those mentioned above. The study reported in this Letter is strictly empirical and clearly needs to be complemented by detailed materials analysis, which we envisage will be carried out in future work. Irrespectively of this analysis, however, our results are potentially of much significance for electrochromic device technology, which is important for glazing in energy efficient "green" buildings [11,12]. We note that buildings are responsible for 30–40% of the global use of primary energy [13]—which currently and for decades to come is dominated by fossil fuel—and larger deployment of electrochromic glazing hence will diminish the injection of carbon dioxide into the earth's atmosphere and thereby mitigate climate change [14].

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