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To cite this article: Miguel A Arvizu *et al* 2016 *J. Phys.: Conf. Ser.* **764** 012009

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Rejuvenation of degraded electrochromic MoO₃ thin films made by DC magnetron sputtering: Preliminary results

Miguel A Arvizu, Claes G Granqvist and Gunnar A Niklasson

Department of Engineering Sciences, The Ångström Laboratory, Uppsala University,
P. O. Box 534, SE-751 21 Uppsala, Sweden

E-mail: Miguel.Arvizu@angstrom.uu.se

Abstract. Molybdenum oxide thin films were deposited by reactive DC magnetron sputtering and were subjected to voltammetric cycling in an electrolyte comprised of lithium perchlorate in propylene carbonate. The films were heavily degraded during 20 voltammetric cycles in an extended voltage range. The films were subsequently rejuvenated by use of potentiostatic treatments under different voltages during 20 hours. Optical changes were recorded during the electrochemical degradation and ensuing rejuvenation.

1. Introduction

Electrochromic (EC) materials are capable of going through reversible and persistent optical changes when subjected to a potential difference exerting insertion/extraction of ions and electrons [1]. Some transition metal oxides exhibit remarkable EC properties and are excellent candidates for use in technical applications such as “smart windows”, *i.e.*, devices intended to allow a user to control the throughput of visible light and solar energy into buildings, thereby making these devices an excellent option for energy saving purposes [2].

Electrochromism in molybdenum oxide (MoO₃) was first discovered some 40 years ago [3], and this material is among the most studied cathodic EC materials (darkening under insertion and bleaching under extraction of ions and electrons) [1]. Another, even more widely studied, cathodic EC material is tungsten oxide (WO₃) [1]. Durability under electrochemical cycling is an issue for EC oxides, at least when the goal is to develop commercial products with long lifetime. Addition of titanium has proven to be useful to stabilize the EC properties both for MoO₃ [4] and WO₃ [5].

Research in the field of EC materials recently received new impetus when it was shown that degraded WO₃ thin films can recover their original EC properties by means of driving a constant current, on the order of 10⁻⁵ A/cm², through the films for several hours; this procedure is called *galvanostatic* “rejuvenation” [6]. The surmised reason for the degradation of the films—*viz.*, trapped lithium ions—as well as the removal of these ions with galvanostatic treatment were experimentally confirmed by use of Time-of-Flight Elastic Recoil Detection Analysis (ToF-ERDA) applied to as-deposited, degraded and rejuvenated samples [7]. Very recently, *potentiostatic* treatments were performed on WO₃ films, and the possible types and nature of ion traps were elucidated [8]. Furthermore, rejuvenation is feasible via galvanostatic and potentiostatic treatments of titanium oxide (TiO₂), which is another important cathodic EC material [9].

In this present work we prepared MoO₃ thin films by reactive DC sputtering and studied their EC performance using voltammetric cycling in an extended voltage range to ensure degradation within 20 insertion/extraction cycles for ions and electrons. The films were then subjected to potentiostatic



treatments with different voltages in order to rejuvenate them, and finally the films were cycled again in a more restricted “normal” voltage range to check their EC performance. The results were compared with data for films cycled using a “normal” voltage range already from the beginning.

2. Thin film deposition

Prior to thin film deposition, the sputter system was evacuated to 2×10^{-4} mTorr. Argon and oxygen, both of 99.997% purity, were then introduced through mass-flow controlled gas inlets. The O₂/Ar gas flow ratio was set to 0.14 and the working pressure was ~30 mTorr. Substrates for optical and electrochemical measurements were unheated 5×5 cm² glass plates pre-coated with transparent and electrically conducting layers of In₂O₃:Sn (ITO) having a resistance of 40 Ω/square. The target–substrate separation was 13 cm. Pure MoO₃ films were obtained using a 5-cm-diameter Mo target with 99.95% purity. The discharge power was set to 300 W. Film thicknesses were ~300 nm as determined by surface profilometry using a Bruker DektakXT instrument.

The deposited films displayed X-ray diffraction patterns characteristic of amorphous materials. The films were stored in a dark and dry place for five months before their EC properties were studied.

3. Results and discussion

3.1. Electrochromic performance under a “normal” voltage range

Cyclic voltammetry (CV) measurements were performed using a Solartron 1286 Electrochemical Interface and a three-electrode electrochemical cell. The electrolyte was 1 M LiClO₄ in propylene carbonate, and lithium foils served as reference and counter electrodes. All measurements were performed inside a glove box with inert Ar atmosphere. The voltage sweep rate was 10 mV/s.

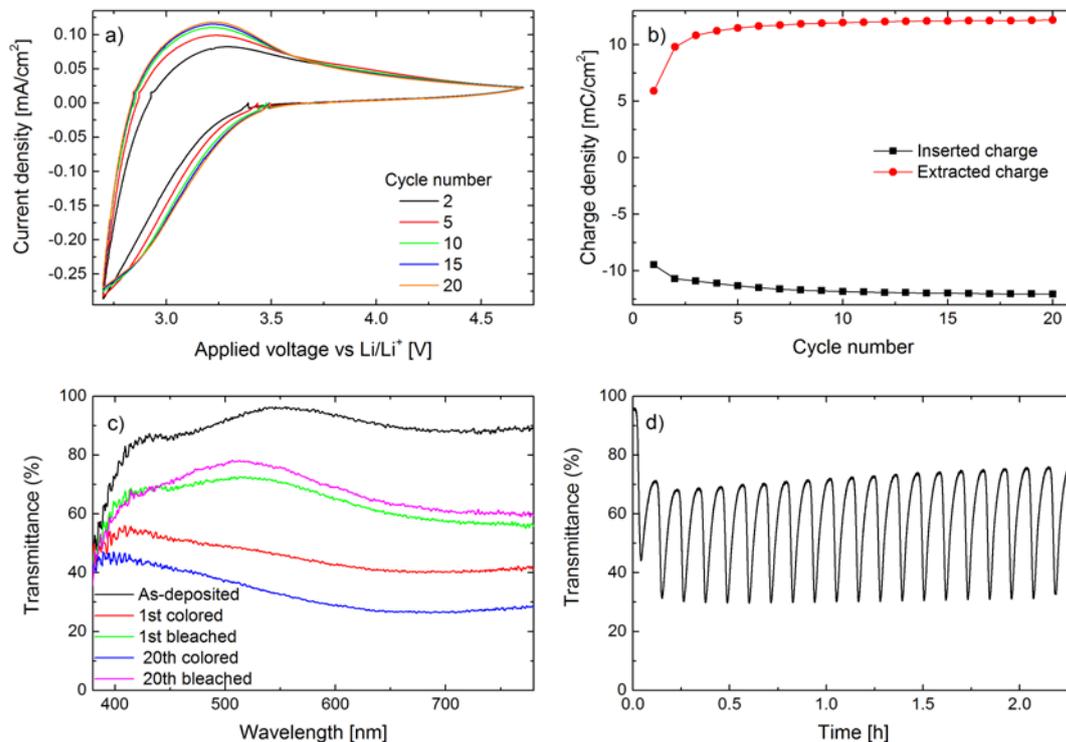


Figure 1. Electrochromic performance of as-deposited MoO₃ films in the voltage range 2.7–4.7 V vs. Li/Li⁺. (a) Selected cyclic voltammograms. (b) Evolution of the inserted and extracted charge; symbols denoting data were joined by straight lines. (c) Spectral transmittance for the indicated coloured and bleached states. (d) Evolution of the transmittance at the wavelength 550 nm.

Figure 1 shows data for a MoO₃ film cycled in the voltage range 2.7–4.7 V vs. Li/Li⁺. The first cycles exhibit anomalous data, which is a common feature for many EC oxides, but the following CV cycles tended to remain stable, as shown in panel (a). Figure 1(b) indicates that also the calculated inserted and extracted charge densities were different in absolute value for the first cycles, which indicates that some charge is trapped, but then the charge densities stabilized at similar absolute values. Figure 1(c) reports *in situ* optical transmission, measured with a fiber-optics-based Ocean Optics instrument using an uncoated substrate as a reference, and shows high transparency of the as-deposited films as well as evidence of optical interference. The first bleached state does not reach the initial transparency of the film, which looks slightly bluish in this condition. Nonetheless, the bleached state improves somewhat towards the end of the 20 CV cycles and also the colored state becomes more pronounced at the end of the cycling than for the first cycle. These results are verified by examining the evolution of the monochromatic mid-luminous transmittance at the wavelength of 550 nm, as displayed in figure 1(d). The latter figure also confirms the relative optical stability during the cycling.

3.2. Electrochromic performance under an extended voltage range

Drastic changes appeared when the MoO₃ thin films were cycled within the wider voltage range of 2.2–4.7 V vs. Li/Li⁺, with all of the other parameters kept the same, as can be seen in figure 2(a). The voltammograms shrank monotonically during the CV cycling, thus indicating that less and less charge was inserted and extracted, as quantified in figure 2(b).

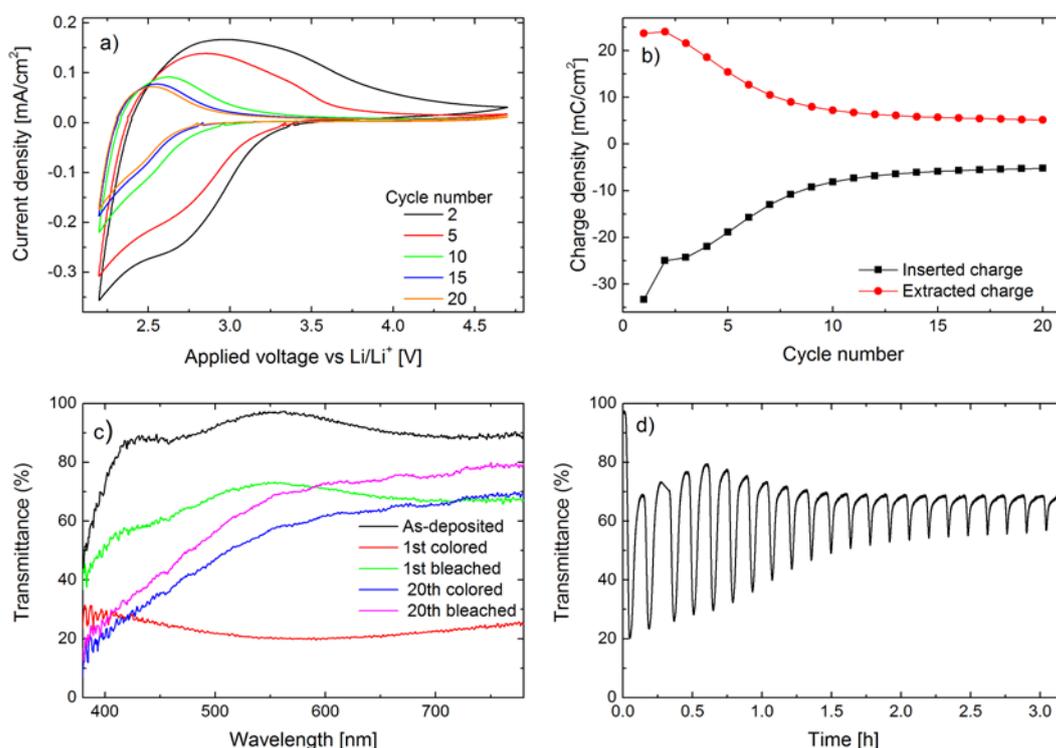


Figure 2. Electrochromic performance of as-deposited MoO₃ films in the voltage range 2.2–4.7 V vs. Li/Li⁺. (a) Selected cyclic voltammograms. (b) Evolution of the inserted and extracted charge; symbols denoting data were joined by straight lines. (c) Spectral transmittance for the indicated coloured and bleached states. (d) Evolution of the transmittance at the wavelength 550 nm.

As expected, the film was darker in the initial colored state than when the film was cycled at 2.7–4.7 V *vs.* Li/Li⁺, as evident from a comparison of data in figures 1(c) and 2(c). Furthermore, the first bleached state was less transparent than the as-deposited film. At the end of the 20 CV cycles, the film acquired a yellowish tint and the EC performance was poor; the transmittance of the bleached and colored states was close. The transmittance modulation at 550 nm was also greatly diminished as the number of CV cycles increased, as apparent in figure 2(d). All of these results are very similar to those observed for EC WO₃ films when cycled in extended voltage ranges [5–7].

3.3. Rejuvenation by potentiostatic treatment

The degraded MoO₃ films were subjected to potentiostatic treatment at a constant voltage for 20 h. The selection of voltages—specifically 5.25, 5.50 and 5.75 V *vs.* Li/Li⁺—were guided by recent work on EC WO₃ films [8] and regarding that the “normal” voltage range is 2.0–4.0 V *vs.* Li/Li⁺ for the latter films whereas a range of 2.7–4.7 V *vs.* Li/Li⁺ is more adequate for MoO₃ films. We also have to consider that higher voltages, exceeding 6.2 V *vs.* Li/Li⁺, lead to the risk of altering the electrolyte; in fact, the electrolyte turned slightly yellowish at too large voltages.

Figure 3(a) shows the evolution of the current density during potentiostatic treatments. Despite some noise from the experimental set-up, we could ascertain that a clear difference in the data took place between 5.75 V *vs.* Li/Li⁺ and the two lower voltages. Unlike data for WO₃ films, strong maxima were not displayed but only some weak peak-like features after ~11 h for the lower voltages and after ~7 h for 5.75 V *vs.* Li/Li⁺. It is worth noting that the feature appeared earlier for the higher voltage, which concurs with results for WO₃ [8].

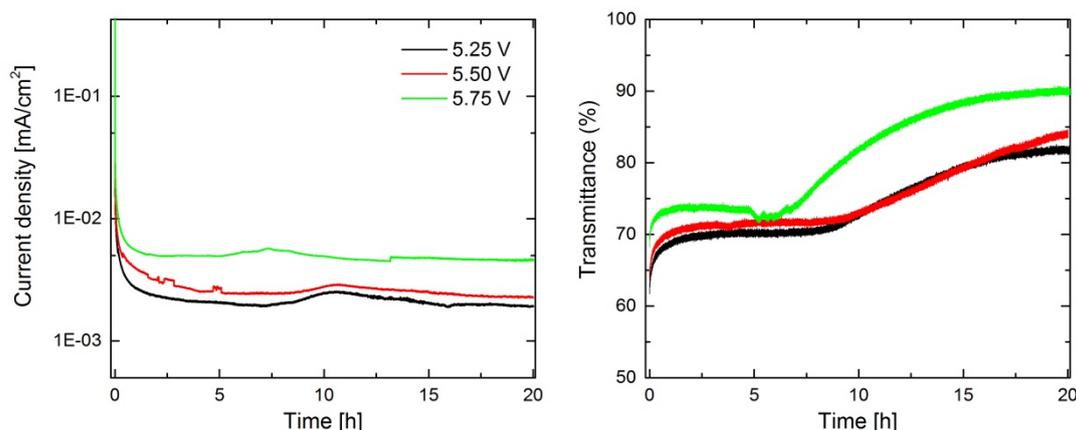


Figure 3. Rejuvenation of degraded MoO₃ films under potentiostatic treatments. (a) Current density and (b) optical transmittance at a wavelength of 550 nm as a function of time at the indicated voltage *vs.* Li/Li⁺.

Figure 3(b) displays how the transmittance at 550 nm changes upon various applied voltages. As for the current density, there was little difference when the potentiostatic treatments were performed with 5.25 and 5.50 V *vs.* Li/Li⁺: after a first abrupt increase of the transmittance, both curves remained at a constant value for ~8 h and then increased steadily. Intriguingly, the main peak-like features in the current density also took place after ~8 h. For 5.25 V *vs.* Li/Li⁺, the transmittance seemed to stabilize at the end of the curve, while for 5.50 V *vs.* Li/Li⁺ it appeared that the transmittance could increase even more if the treatment were continued. For 5.75 V *vs.* Li/Li⁺, the steady increase of the transmittance occurred somewhat earlier, specifically after ~7 h. The transmittance started to drop somewhat about two hours prior to its main rise which is in principle agreement with observations for WO₃ [8]; the reason for this phenomenon is unknown. The transmittance value in this case seemed to stabilize after 18 h.

3.4. Electrochromic performance after potentiostatic rejuvenation

Once the rejuvenation process was finished, we waited for two hours to let the film relax and attain an open circuit potential similar to that for the as-deposited samples [7]. The films were then cycled again in the range 2.7–4.7 V vs. Li/Li⁺. All films behaved similarly, and we only display data for the sample rejuvenated after potentiostatic treatment at 5.75 V vs. Li/Li⁺. Figure 4(a) shows that the shape and stability within 20 CV cycles resemble what we obtained for the as-deposited samples. Furthermore, the evolution of the inserted and extracted charge density, shown in figure 4(b), was similar to the data in the corresponding figure 1(b); even the quantitative charge densities tended to stabilize at similar values in the two cases. The transmittance spectrum for the rejuvenated film, shown in figure 4(c), was not entirely the same as for the as-deposited sample, which may be due to the fact that some minor amount of lithium remains in low-energy traps in the MoO₃ structure, as previously discussed for WO₃ [6–8], and moreover one cannot discard the possibility that the insertion of lithium modifies the structure of the oxide film to some extent. As noticed before [8], the transmittance of the first bleached state was not as high for the rejuvenated film. Figure 4(d) shows that the improvement in both the last bleached and coloured states, as compared to results for the first state, is even more marked than in the case of the as-deposited sample. Furthermore, figure 4(d) confirms the recovery of the EC properties of the rejuvenated MoO₃ film, and the evolution of the transmittance at 550 nm looks rather stable during the CV cycles. Nonetheless, comparing figures 1(d) and 4(d) reveals that the transmittance modulation is slightly diminished for the rejuvenated film at the end of the 20 CV cycles.

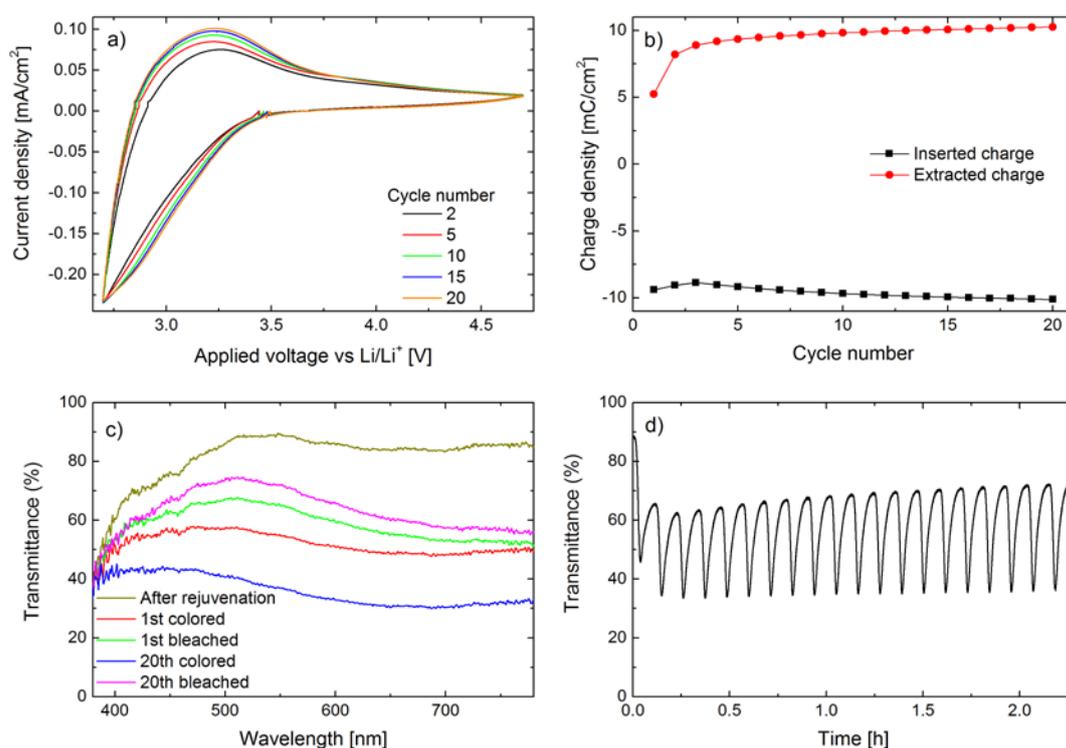


Figure 4. Electrochromic performance of a MoO₃ film after potentiostatic rejuvenation at 5.75 V vs. Li/Li⁺ and in the voltage range 2.7–4.7 V vs. Li/Li⁺. (a) Selected cyclic voltammograms. (b) Evolution of the inserted and extracted charge; symbols denoting data were joined by straight lines. (c) Spectral transmittance for the indicated coloured and bleached states. (d) Evolution of the transmittance at the wavelength 550 nm.

4. Conclusions

We demonstrated that electrochromic MoO₃ films can be potentiostatically rejuvenated after severe degradation upon voltammetric cycling in an extended voltage range. Moreover we were able to establish similarities, as well as some differences, with previous work wherein electrochromic WO₃ films were rejuvenated via similar treatments. We emphasize that the present work is preliminary, and more experiments and analysis are needed to fully elucidate the nature of the rejuvenation of the electrochromic performance.

Acknowledgements

This paper was presented at the INERA Conference on “Vapor Phase Technologies for Metal Oxide and Carbon Nanostructures”, July 5–9, 2016, in Velingrad, Bulgaria. The conference is part of the INERA REPGOT project of the Institute of Solid State Physics, Bulgarian Academy of Sciences. MAA thanks the Mexican Council for Science and Technology (CONACyT) for financial assistance to carry out postdoctoral research at Uppsala University. Our work was supported by the European Research Council under the European Community’s Seventh Framework Program (FP7/2007–2013)/ERC Grant Agreement No. 267234 (“GRINDOOR”).

References

- [1] Granqvist C G 1995 *Handbook of Inorganic Electrochromic Materials* (Amsterdam: Elsevier)
- [2] Granqvist C G 2014 *Thin Solid Films* **564** 1–38
- [3] Deb S K 1975 *Proc. 4th Int. Congr. Reprography and Information* (Hannover, Germany) 115–19
- [4] Kullman L, Azens A, Granqvist C G 2000 *Sol. Energy Mater. Sol. Cells* **61** 189–96
- [5] Arvizu M A, Triana C A, Stefanov B I, Granqvist C G and Niklasson G A 2014 *Sol. Energy Mater. Sol. Cells* **125** 184–89
- [6] Wen R-T, Granqvist C G, Niklasson G A 2015 *Nat. Mater.* **14** 996–1001
- [7] Arvizu M A, Wen R-T, Primetzhofer D, Klemberg-Sapieha J E, Martinu L, Niklasson G A, Granqvist C G 2015 *ACS Appl. Mater. Interfaces* **7** 26387–90
- [8] Wen R-T, Arvizu M A, Morales-Luna M, Granqvist C G, Niklasson G A 2016 *Chem. Mater.* DOI: 10.1021/acs.chemmater.6b01503
- [9] Wen R-T, Niklasson G A, Granqvist C G 2016 *ACS Appl. Mater. Interfaces* **8** 5777–82