Journal of Marine Science and Technology

Volume 20 | Issue 4 Article 3

EXPERIMENTAL STUDY OF THE ELECTROCHROMIC PROPERTIES OF WO3 THIN FILMS DERIVED BY ELECTROCHEMICAL METHOD

Chin-Guo Kuo
Department of Industrial Education, National Taiwan Normal University, 162, He-ping East Road, Section 1, Taipei 10610, Taiwan, R.O.C.

Chih-Yin Chou
Department of Industrial Education, National Taiwan Normal University, 162, He-ping East Road, Section 1, Taipei 10610, Taiwan, R.O.C.

Ya-Chieh Tung
Department of Industrial Education, National Taiwan Normal University, 162, He-ping East Road, Section 1, Taipei 10610, Taiwan, R.O.C.

Jung-Hsuan Chen
Industrial Technology Research Institute, 195, Sec. 4, Chung Hsing Rd., Chutung, Hsinchu 31040, Taiwan, R.O.C., jhc@itri.org.tw

Recommended Citation

Kuo, Chin-Guo; Chou, Chih-Yin; Tung, Ya-Chieh; and Chen, Jung-Hsuan (2012) "EXPERIMENTAL STUDY OF THE ELECTROCHROMIC PROPERTIES OF WO3 THIN FILMS DERIVED BY ELECTROCHEMICAL METHOD," *Journal of Marine Science and Technology*: Vol. 20: Iss. 4, Article 3.
DOI: 10.6119/JMST-011-0221-2
Available at: https://jmstt.ntou.edu.tw/journal/vol20/iss4/3

EXPERIMENTAL STUDY OF THE ELECTROCHROMIC PROPERTIES OF WO3 THIN FILMS DERIVED BY ELECTROCHEMICAL METHOD

Acknowledgements

This work was supported by National Taiwan Normal University under contract No. 98031017.

Journal of Marine Science and Technology, Vol. 20, No. 4, pp. 365-368 (2012)
DOI: 10.6119/JMST-011-0221-2

EXPERIMENTAL STUDY OF THE ELECTROCHROMIC PROPERTIES OF WO_3 THIN FILMS DERIVED BY ELECTROCHEMICAL METHOD

Chin-Guo Kuo[1], Chih-Yin Chou[1], Ya-Chieh Tung[1], and Jung-Hsuan Chen[2]

Key words: transmittance, electrolyte filled volume, electrochromic.

ABSTRACT

This study aimed at the effect of electrolyte filled volume on transmittance and coloration efficiency of the electrochromic device. The device mainly consisted of ITO, WO_3 template and electrolyte (PC + $LiClO_4$). The experimental results showed the transmittance of visible light reduced with increasing the electrolyte filled volume. In addition, when the electrolyte filled volume was 100 mm^3, the coloration efficiency could reach the maximum CE, 15.2 cm^2/C.

I. INTRODUCTION

With the progress of nanotechnology, it becomes possible to fabricate various nanostructures by lots of methods. Recently, a large attention has been paid to self-organized porous structures due to the unique electrical, thermal, magnetic and optical properties [1, 3]. Hence, the assembly methods deeply affected the nanostructure characteristics and applications. Electrochromic (EC) technology based on nanoporous thin films (NTF), several methods have been developed to fabricate NTF, such as thermal evaporation, chemical vapor deposition, sol-gel coating and electrochemical anodization (ECA). ECA has become one of the most popular processing ways used for formation of porous structures, such as Al_2O_3 [5, 9], WO_3 [8, 12] and TiO_2 [10, 14]. These nanostructured materials have found applications in many areas such as EC devices [13], photovoltaic devices, gas sensors [4], coatings for batteries [7] and flat panel displays [6].

WO_3 is one of the most widely used EC materials owing to its relatively easy synthesis, strong electrical and optical properties. The general EC phenomena of WO_3 is due to the formation of tungsten bronze ($MxWO_3$) according to the following equation:

$$\underset{\text{(transparent)}}{WO_3} + xM^+ + xe^- \rightarrow \underset{\text{(blue)}}{M_xWO_3} \quad (1)$$

where for each atom injected an electron enters the conduction band of the host oxide and a deep blue coloration develops. At the same time, the electronic conductivity of the oxide rapidly increases [2]. Thus it remains until now the most promising, most studied and most applied EC material in EC windows and devices. Due to the previous studies have never investigated the filled volume effect of electrolyte on coloured and bleached rate. Therefore, the present study tried to compare the EC performance with the various filled volume of electrolyte solution.

II. EXPERIMENTAL

Thin tungsten films were prepared by sputtering of pure tungsten (purity 99.5%, 6 mm thickness) in DC sputtering system. A cathode tungsten target was placed at 60 mm over the stage. The substrates on which tungsten was sputtered were ITO glass (20 mm × 40 mm × 2 mm, 8 Ω/sq). The ITO glass were cleaned by sonicating in acetone, isopropanol, deionized water, and finally dried with N_2 stream. Prior to electrochemical treatments, the pure tungsten was annealed for 2 hours with 400°C. And then it were electro-polished (a constant voltage of 60 V) using a solution of H_2SO_4 and methanol at 20°C.

Recent years manufactured the WO_3 thin film by the anodic oxidation process the research, mostly pure take some sole chemistry solution and parameter as object of study [11, 15, 16], therefore aimed at each kind parameter that cause the tungsten form nanoporous film using the electrochemistry anodic process to be worth testing and the discussion. Anodization was performed using an anode (tungsten sample, 20 mm^2) and cathode (platinum, 20 mm^2) system, where a DC

Paper submitted 03/05/10; revised 01/09/11; accepted 02/21/11. Author for correspondence: Jung-Hsuan Chen (e-mail: jhc@itri.org.tw).
[1] *Department of Industrial Education, National Taiwan Normal University, 162, He-ping East Road, Section 1, Taipei 10610, Taiwan, R.O.C.*
[2] *Industrial Technology Research Institute, 195, Sec. 4, Chung Hsing Rd., Chutung, Hsinchu 31040, Taiwan, R.O.C.*

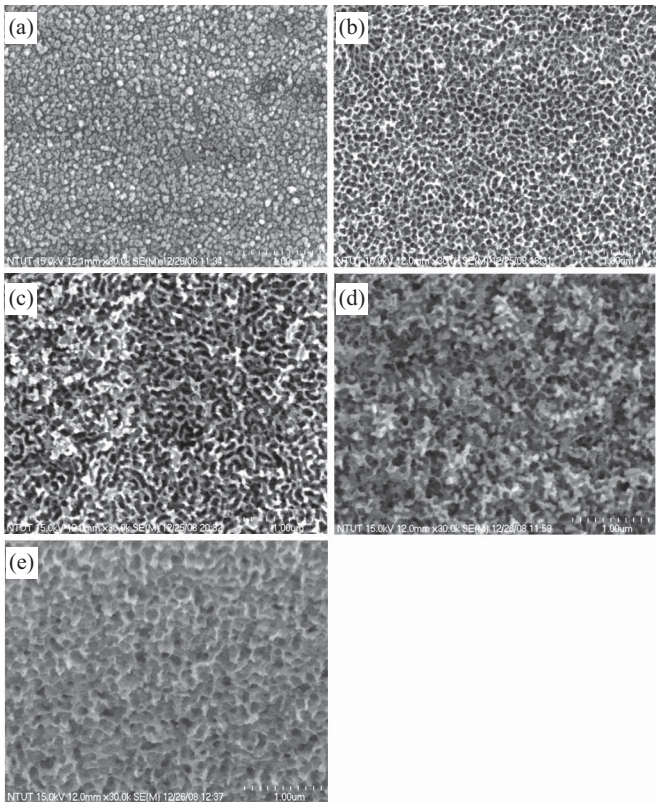

Fig. 1. SEM images of AWO formed at: (a) 20 V, (b) 40 V, (c) 60 V, (d) 80 V and (e) 100 V, in 0.4 wt% NaF.

voltage was applied while electrolyte temperature kept constant at 25°C. The electrolytes were prepared NaF solutions and deionized water. In order to obtain a uniform porous anodic tungsten oxide template, the anodized samples were annealed by a standard laboratory furnace at 3 hours. The surface appearance and thickness of galvanized membrane were analyzed by the thermal field emission scanning electron microscope (FE-SEM, JEOL-JSM-6500F) and the atom force microscopy (AFM, Digital Instrument-Dimension 3100). The element components were analyzed by the energy dispersive spectrometer (EDS). After that, the mixed liquid electrolytes containing propylene carbonate (PC) + 0.1 M $LiClO_4$ solutions were injected and followed by sealing the device.

The coloured state and bleached state transmittance spectra of EC devices were measured by a Hitachi U3310 spectrophotometer biasing the WO_3 film at 3.5 and -2.5V, with respect to the electrolyte. In addition, the change in optical density (ΔOD) was calculated using the measured transmittance of the device in the coloured ($T_{coloring}$) and bleached ($T_{bleached}$) state by applying the equation:

$$\Delta OD = \log \frac{T_{bleached}}{T_{coloured}} \tag{2}$$

Coloration efficiency (CE) is the power efficiency of the

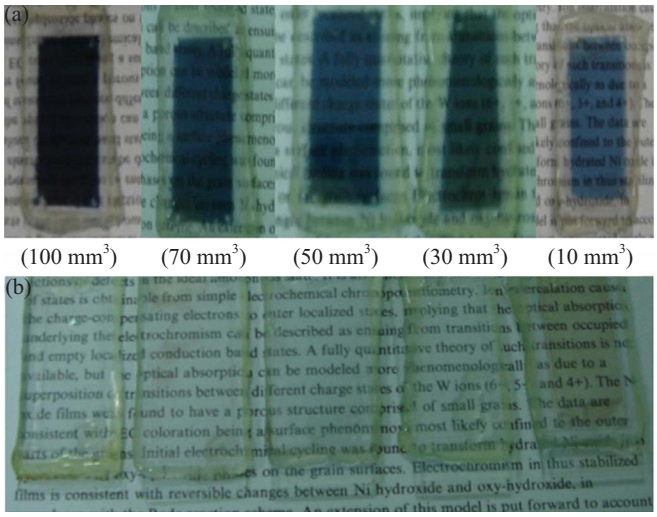

Fig. 2. Images of EC device with various electrolyte filled volume (10 mm^3 to 100 mm^3): (a) coloured state and (b) bleached state.

EC devices and can be calculated via ΔOD using the following equation:

$$\text{Coloration Efficiency} = \frac{\Delta OD}{Q} \tag{3}$$

where Q is the amount of charge density injected.

III. EXPERIMENTAL RESULTS

In this work, a nanoporous WO_3 structure anodized in NaF 0.4% wt/DI-water solution from the sputtered tungsten thin films on the transparent and conductive ITO glass substrates. Fig. 1 showed the SEM images of AWO formed with different voltages. As seen in Fig. 1(a), the 20V sample has the first anodized WO_3 nanotubular layer. In the case of 40 V, a regular nanoporous structure is observed as shown in Fig. 1(b). With increasing the applied voltages, the more non-uniform porous appeared in Fig. 1(c) to Fig. 1(e). This indicates that an increase of the applied voltage results in enhanced etching of the oxide layer. In particular, in 100 V, oxide layers are almost etched by NaF and exhibit a mesh-like porous structures rather than a single pore.

Fig. 2 showed the colored state and bleached state of the EC device. The colored depth of colored EC device increases with increase electrolyte (PC + $LiClO_4$) filled volume (EFV), as shown in Fig. 2(a). At bleached state, 100 mm^3 EFV was completely bleached compared with other EFV, as shown in Fig. 2(b). Fig. 3 and Fig. 4 illustrated the EFV effect of spectral transmittance in the colored and bleached states. The experimental results indicated the transmittance are in the following descending order: 100 mm^3 > 70 mm^3 > 50 mm^3 > 30 mm^3 > 10 mm^3. It indicated that transmittance of visible light reduced with increasing the EFV. Fig. 5 showed the relationship between CE and EFV. When the EFV was

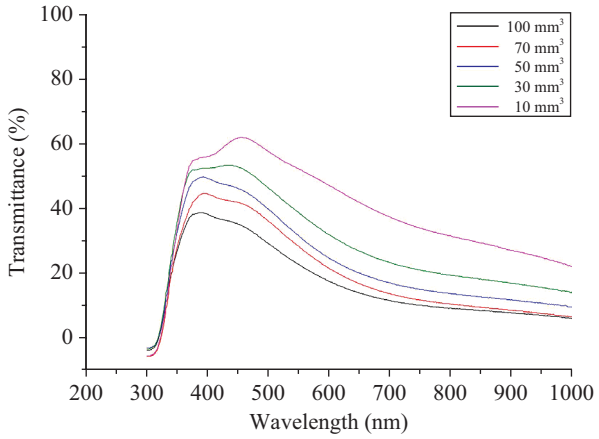

Fig. 3. Transmittance spectra with various electrolyte filled volume in coloured state.

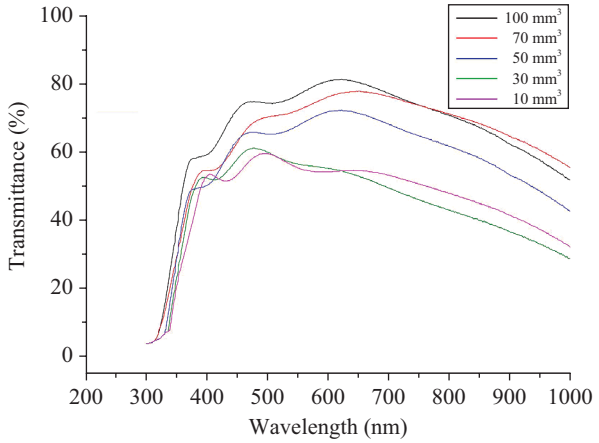

Fig. 4. Transmittance spectra with various electrolyte filled volume in bleached state.

100 mm^3, the CE could reach the maximum CE, 15.2 cm^2/C. A color change was from colorless to blue of the EC device due to the intercalated protons was from the electrolyte to balance the charge passed at the working electrode. Thus, the reason for experimental was the more electrolyte filled volume could provide a sufficient protons to complete the electrochromic phenomena and CE.

IV. SUMMARY

The object of this study was to fabricate a nanoporous WO_3 structure and investigate the influence of EFV on coloration efficiency of electrochromic devices. The electrolyte consisted of PC + 0.1 M $LiClO_4$. The experimental results are as follows:

1. A uniform porous structure was fabricated by a suitable applied voltage.
2. The transmittance and coloration efficiency of EC device dependent on the EFV.

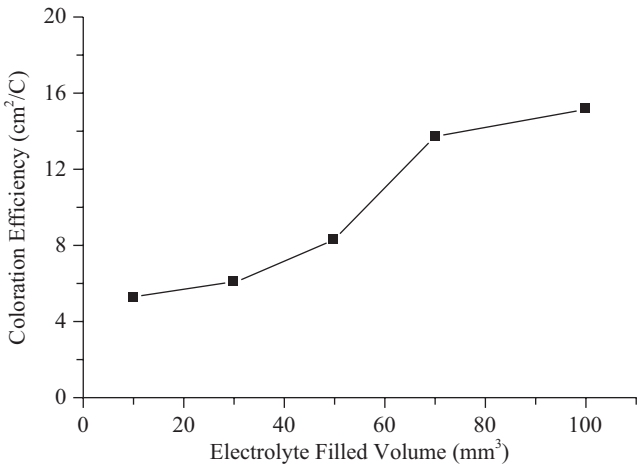

Fig. 5. Coloration efficiency *vs.* various electrolyte filled volume.

In this investigation, the design of EC device considered not only the EC films, but also the EFV. Further studies will focus on the device reliability by cyclic voltammetry.

ACKNOWLEDGMENTS

This work was supported by National Taiwan Normal University under contract No. 98031017.

REFERENCES

1. Aliev, A. E. and Shin, H. W., "A digital acoustic transceiver for underwater communication without PLL and DLL," *Solid State Ionics*, Vol. 154-155, pp. 425-431 (2002).
2. Avellaneda, C. O., "Thermodynamic study of WO_3 and WO_3 Li^+ thin films," *Materials Science and Engineering: B (Advanced Functional Solid-State Materials)*, Vol. 138, pp. 123-127 (2007).
3. Badilescu, S. and Ashrit, P. V., "Study of sol-gel prepared nanostructured WO_3 thin films and composites for electrochromic applications," *Solid State Ionics*, Vol. 158, Nos. 1-2, pp. 187-197 (2003).
4. Chung, Y. K., Kim, M. H., Um, W. S., Lee, H. S., Song, J. K., and Choi, S. C., "Gas sensing properties of WO_3 thick film for NO_2 gas dependent on process condition," *Sensors and Actuators B: Chemical*, Vol. 60, Nos. 1-2, pp. 49-56 (1999).
5. Crouse, D., Lo, Y. H., Miller, A. E., and Crouse, M., "Self-ordered pore structure of anodized aluminum on silicon and pattern transfer," *Applied Physics Letters*, Vol. 76, pp. 49-51 (2000).
6. Deb, S. K., "Opportunities and challenges in science and technology of WO_3 for electrochromic and related applications," *Solar Energy Materials and Solar Cells*, Vol. 92, No. 2, pp. 245-258 (2008).
7. Guo, Y. G., Hu, J. S., and Wan, L. J., "Nanostructured materials for electrochemical energy conversion and storage devices," *Advanced Materials*, Vol. 20, No. 15, pp. 2878-2887 (2008).
8. Kourosh, K. Z., Sadek, A. Z., Zheng, H., Bansal, V., Bhargava, S. K., and Wlodarski, W., "Nanostructured WO_3 films using high temperature anodization," *Sensors and Actuators B: Chemical*, Vol. 142, pp. 230-235 (2009).
9. Kuo, C. G. and Chen, C. C., "Technique for self-assembly of tin nanoparticles on anodic aluminum oxide (AAO) templates," *Materials Transactions*, Vol. 50, No. 5, pp. 1102-1104 (2009).
10. Li, Y., Yu, X., and Yang, Q., "Fabrication of TiO_2 nanotube thin films and their gas sensing properties," *Journal of Sensors*, Vol. 2009, Article ID 402174, pp. 1-19 (2009).

11. Mogoda, A. S., Hefny, M. M., and El-Mahdy, G. A., "Anodic oxide films on tungsten: formation and dissolution in acetic acid solutions," *Corrosion*, Vol. 46, No. 3, pp. 210-214 (1990).
12. Mukherjee, N., Paulose, M., Varghese, O. K., Mor, G. K., and Grimes, C. A., "Fabrication of nanoporous tungsten oxide by galvanostatic anodization," *Journal of Materials Research*, Vol. 18, pp. 2296-2299 (2003).
13. Ozkan, E., Lee, S. H., Liu, P., Tracy, C. E., Tepehan, F. Z., and Pitts, J. R., "Electrochromic and optical properties of mesoporous tungsten oxide films," *Solid State Ionics*, Vol. 149, pp. 139-146 (2002).
14. Tong, M., Dai, G., Wu, Y., He, X., and Gao, D., "WO_3 thin film prepared by PECVD technique and its gas sensing properties to NO_2," *Journal of Materials Science*, Vol. 36, No. 10, pp. 2535-2538 (2001).
15. Vassil, K. and Martin, B., "Anodic oxidation of tungsten in sulphuric acid solution—influence of hydrofluoric acid addition original research article," *Materials Chemistry and Physics*, Vol. 112, No. 2, pp. 702-710 (2008).
16. Vassil, K. and Martin, B., "Mechanism of anodic oxidation of tungsten in neutral sulphate-fluoride solutions," *Journal of Solid State Electrochemistry*, Vol. 13, No. 2, pp. 309-320 (2009).