



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

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Key words: transmittance, electrolyte filled volume, electrochromic.

ABSTRACT

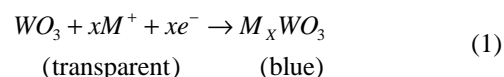
This study aimed at the effect of electrolyte filled volume on transmittance and coloration efficiency of the electrochromic device. The device mainly consisted of ITO, WO₃ template and electrolyte (PC + LiClO₄). The experimental results showed the transmittance of visible light reduced with increasing the electrolyte filled volume. In addition, when the electrolyte filled volume was 100 mm³, the coloration efficiency could reach the maximum CE, 15.2 cm²/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 Al₂O₃ [5, 9], WO₃ [8, 12] and TiO₂ [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].

WO₃ 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 WO₃ is due to the formation of tungsten bronze (M_xWO₃) according to the following equation:



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 N₂ 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 H₂SO₄ and methanol at 20°C.

Recent years manufactured the WO₃ 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 mm²) and cathode (platinum, 20 mm²) system, where a DC

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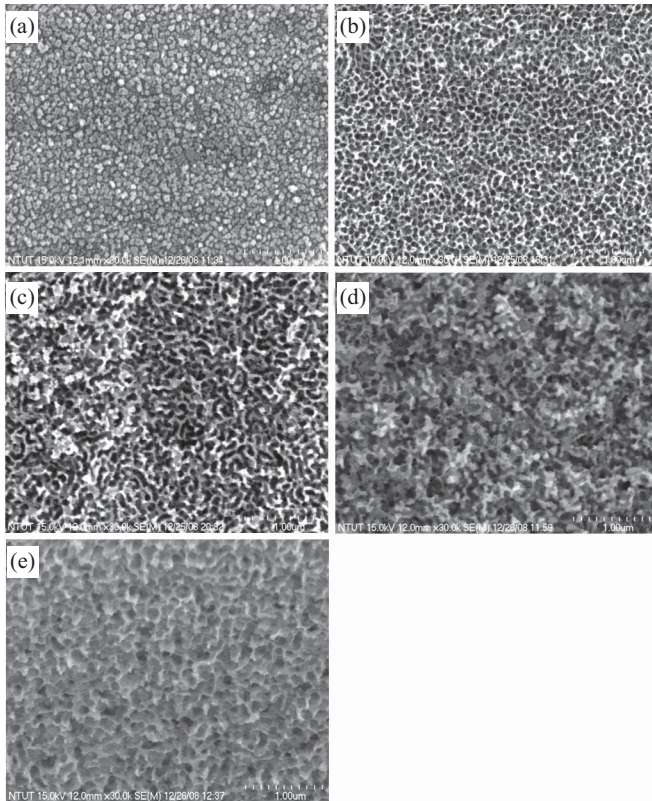


Fig. 1. SEM images of AWO formed at: (a) 20 V, (b) 40 V, (c) 60 V, (d) 80 V and (e) 100 V, in 0.4 wt% NaF.

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 LiClO₄ 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 WO₃ 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:

$$\Delta OD = \log \frac{T_{bleached}}{T_{coloured}} \quad (2)$$

Coloration efficiency (CE) is the power efficiency of the

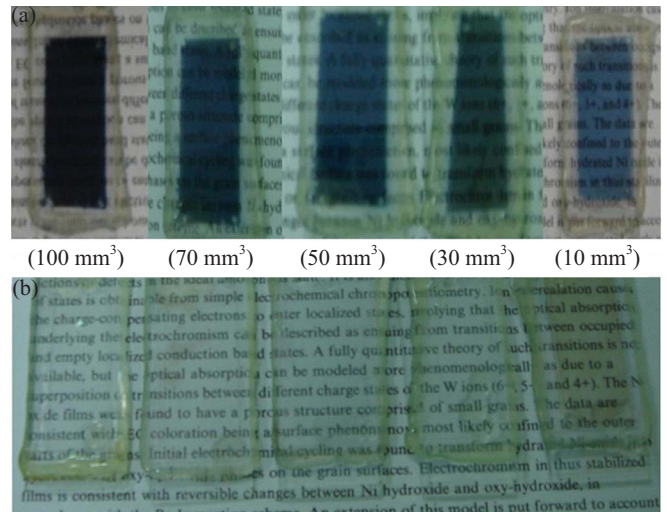


Fig. 2. Images of EC device with various electrolyte filled volume (10 mm³ to 100 mm³): (a) coloured state and (b) bleached state.

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

$$\text{Coloration Efficiency} = \frac{\Delta OD}{Q} \quad (3)$$

where Q is the amount of charge density injected.

III. EXPERIMENTAL RESULTS

In this work, a nanoporous WO₃ 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 WO₃ 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 + LiClO₄) filled volume (EFV), as shown in Fig. 2(a). At bleached state, 100 mm³ 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 mm³ > 70 mm³ > 50 mm³ > 30 mm³ > 10 mm³. 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

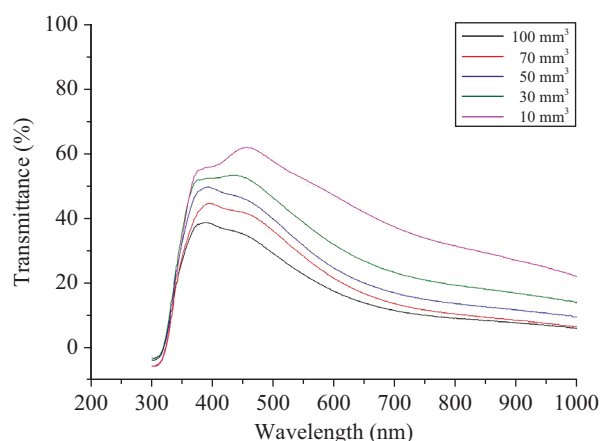


Fig. 3. Transmittance spectra with various electrolyte filled volume in coloured state.

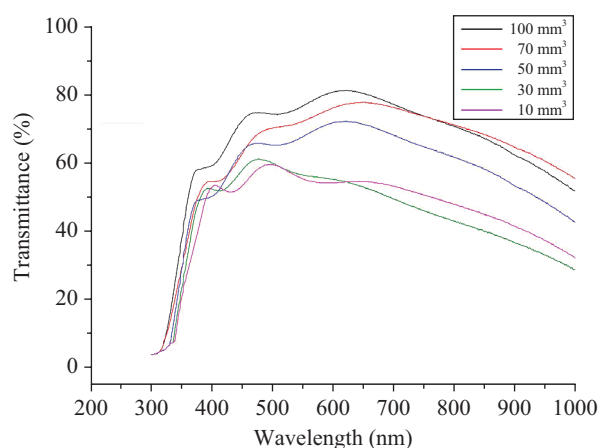


Fig. 4. Transmittance spectra with various electrolyte filled volume in bleached state.

100 mm³, the CE could reach the maximum CE, 15.2 cm²/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 WO₃ structure and investigate the influence of EFV on coloration efficiency of electrochromic devices. The electrolyte consisted of PC + 0.1 M LiClO₄. 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.

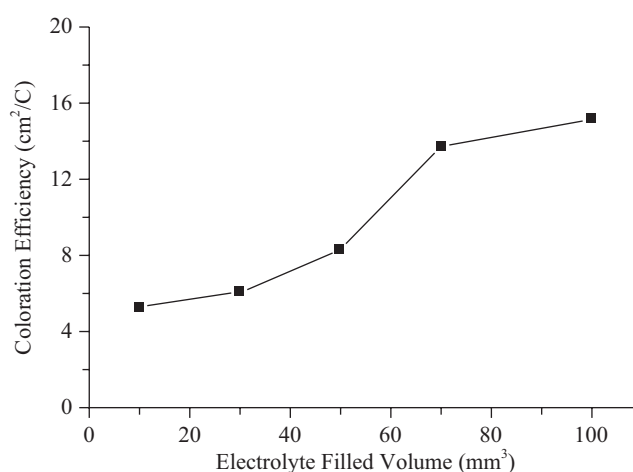


Fig. 5. Coloration efficiency vs. various electrolyte filled volume.

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.

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