

Designing and Fabrication of Electrochromic Windows Using Tungsten Oxide Films Prepared Through Sol-gel Coating on a Glass

Nayyereh Daroogheh, Elham Karimi, and Seyed Mohammad Bagher Ghorashi*

Department of Physics, Faculty of Physics, University of Kashan, Kashan, Iran

*Corresponding Author's Email: mghorashi@kashanu.ac.ir

Received: Mar. 6, 2018, Revised: May. 29, 2018, Accepted: Sep. 4, 2018, Available Online: Dec. 27, 2019

DOI: 10.29252/ijop.13.2.79

ABSTRACT— In this study, a sol-gel peroxotungstic acid sol was employed to deposit tungsten oxide (WO_3) films by the spin-coating technique. In view of smart window applications, electrochromic windows were then designed and fabricated using a thin tungsten oxide film. For this purpose, Glass/ FTO/ WO_3 / electrolyte/ FTO/Glass could be of use due to its special structure that consists of an electrochromic layer (WO_3) on a transparent conductor (FTO), an electrolyte containing Li^+ cations, and a transparent conductor layer. A voltage was applied on the fabricated sample, which was later assessed for its transmission, switching speed, and coloration efficiency. An increase in the coloration efficiency from $87 \text{ cm}^2/\text{C}^{-1}$ to $99.1 \text{ cm}^2/\text{C}^{-1}$ was found associated with an increase in the deposition speed. Moreover, the increase in the deposition speed led to a decrease in the coloration and bleaching time duration from 11.4 s to 6.2 s and from 12.8 s to 5.2 s respectively. The results obtained on the thin film WO_3 can be useful for electrochromic applications.

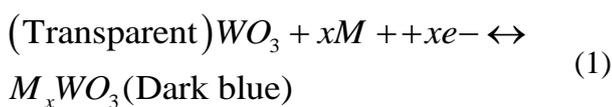
KEYWORDS: Electrochromic material, Sol-gel preparation, Tungsten oxide, Coloration.

I. INTRODUCTION

The growth of the world population and the subsequent growth of demands for energy have brought an awareness of renewable energy resources. However, the uncontrollable and periodic nature of these energy resources has intensified the need for an efficient energy savers system. Electrochemical devices (ECDs), which are formed of EC materials,

electrolytes and electrodes, can save energy and/or convert it [1-3]. Since 1953, when Balzers presented a very clear description of electrochromism in tungsten oxide films or, since 1969, when Deb changed the situation of EC knowledge by his publications, more and more scientists have engaged in the research field of EC materials, and, as a result, more EC materials have been discovered and reported [3,4]. Electrochromic (EC) materials are able to reversibly and persistently change their optical properties at an external voltage. They are considered as one of the most promising candidates for energy-saving smart (ESS) windows [1]. The primary function of glass, particularly in architectural applications, is to transmit light. A smart-window glass would be one whose light transmission properties can be changed in response to an external stimulus such as light, heat, or electrical impulse [3,5]. Well-known examples are photochromic, thermochromic, and electrochromic glasses. Electrochromism is broadly defined as a reversible optical change in a material induced by an external voltage. Many inorganic and organic species show electrochromic properties throughout the electromagnetic spectrum [6-8]. Among them, smart windows have an important application because they can effectively save energy by regulating the solar heat gain and providing indoor comfort through reversible color changes. Many applications have been developed based on these unique properties. The properties have been applied in such things as electrochromic

devices, polymeric batteries, photovoltaic cells, energy storage, optoelectronics, rear-view mirrors for cars and vehicles, and display devices [9-11]. Among metal oxides, tungsten trioxide (WO_3) is a feasible electrochromic material that can be of benefit in practical applications due to its rather highly optical reversible color change induced by an electrochemical process. This process leads to the potential application of the material in smart windows, electrochromic windows, switchable devices, and optical-based gas sensors [12]. Over the past 30 years, a large body of research has been carried out to synthesize tungsten oxide films for electrochromic devices because the films exhibit a fairly good optical modulation and high cyclic stability [13, 14]. The electrochromic phenomenon of tungsten oxide was originally discovered in tungsten oxide WO_3 thin films. The material still remains as the most promising, the most studied, and the most applied electrochromic material for windows and devices. Electrochromism of tungsten oxide is a complex phenomenon, but it is not completely understood yet. As reported in the literature, insertion of ions and electrons in an amorphous WO_3 film can switch it from its bleached state (transparent) to a colored state (dark blue) to form tungsten bronze according to the reaction given in Equation (1).



where M^{+} can be H^{+} , Li^{+} , Na^{+} or K^{+} , $0 < x < 1$, and e^{-} denotes electrons [4,14]. Initially transparent in the visible region, WO_3 is converted to M_xWO_3 (M can be hydrogen or an alkali metal) through a cation intercalation (reduction) process, which leads to strong absorption bands in the visible region and makes it a cathodically coloring material [15, 16].

A variety of conventional deposition methods have been used to prepare WO_3 films, such as direct current (DC), radio frequency (RF), magnetron sputtering, sol-gel methods, plasma

spraying method, electron beam evaporation, thermal evaporation, and hydrothermal methods [17-19]. There is a strong dependence of electrochromic properties like coloration efficiency, electrochemical kinetics and cyclic durability on layer properties such as layer density and surface morphology. Accordingly, there is a direct relationship between growth techniques and deposition parameters [20,21]. In this study, however, sol-gel processing is most popular because of its cost-effectiveness, ease of deposition, and uniform large-area films for window application. More importantly, it allows tailor making of the microstructure of films by introducing chemical dopants into the reactant sols or by controlling the annealing conditions, which improves the properties of the films [20,16]. Sol-gel technology for deposition of thin films of electrochromic tungsten oxide has gained enough impetus over the past decade owing to its low cost and adaptability to large-area deposition. Describing the merits of sol-gel paves the way for deposition of electrochromic coatings of inorganic transition metal oxides, as the process is easy to scale and, consequently, amenable for coating substrates of even a one-square-meter area. Central to the success of commercially focused electrochromic products, such as smart windows, is the ability to reproducibly deposit electrochromic films that have a good cosmetic quality and a high coloration efficiency [22, 23]. In the present study, WO_3 films are prepared by the sol-gel technique and with respect to the structural, morphological, electrical and optical properties of WO_3 [24, 25].

II. NOVELTY OF THE STUDY

Owing to the wide industrial and commercial applications of electrochromic glasses and the increasing need for energy and appropriate ways of using it, the aim of this study was set to be fabrication of an electrochromic glass through a combination of sol-gel and spin-coating techniques, which is the lowest-cost process. The manufactured cells proved to have a better function in terms of light transmission, response time, and dye

efficiency. To the best of our knowledge, these cells are superior to many other ones developed by costly methods and vacuum-based procedures; therefore, they can be of benefits for industrial, commercial, and household purposes.

III. EXPERIMENTS

A. Preparation of the sol

Dissolution of 3 grams of a tungsten metal powder (Merck) in a mixture of 20 ml of hydrogen peroxide (H₂O₂; Qualigens, glaxo) and 2 ml of deionized water yielded a colorless solution of peroxotungstic acid. The reaction being exothermic was conducted between 0°C and 10°C. Then, a clear solution was obtained by filtration, and 20 ml of glacial acetic acid (Merck) was added to it. The resulting solution was refluxed at 55°C for six hours. The white, dense and viscous solution thus obtained was then dried under vacuum at 55°C to recover a flaky pale yellow peroxotungstic acid product (APTA). The deposition solution was prepared by dissolving 1 g of APTA in 3 cc of absolute alcohol (99.9%, E-Merck). The dissolution rate was catalyzed by slight heating at about 55°C.

B. Preparation of the films

The coatings were deposited by the spin-coating method (from the speed of 1500 rpm to 3500 rpm for 30 seconds). On an FTO (1.5cm×2cm), coated glass substrates (8 Ω/sq) had previously been cleaned and rinsed with distilled water, methanol, and aston and then dried at 90°C. All the films were annealed from room temperature to 100°C, held at this temperature for two hours, and then brought back to room temperature.

C. Characterization techniques

The X-ray diffraction (XRD) patterns of all the films were recorded in the 2θ range from 10 °C to 90°C, and the wavelength of the Cu Kα radiation was found to be 1.54 Å. The average grain/crystallite size was determined using Scherrer's formula as follows:

$$D_{hkl} = \frac{K\lambda}{\Gamma_{hkl} \cos\theta_{hkl}} \frac{360}{2\pi} \quad (2)$$

where λ is the wavelength of the incident beam, Γ_{hkl} is the full width at half maximum (FWHM) of the peak, θ_{hkl} is the Bragg angle, and K is a dimensionless constant [26,27]. AFM studies were used to calculate the particle size and the average roughness of the films. Transmittance variation and color changes were detected through a Uv-vis (Cintra6) spectrometer at a visible wavelength ranging from 350 nm to 1100 nm. Optical modulation and switching studies were carried out in a two-electrode system for ±3V. There exist few reports about inorganic ECDs based on two-electrode films. Therefore, all the electrochemical studies were carried out in an electrolyte of 1.0 M LiClO₄ in propylene carbonate (PC). Fig. 1 provides the configuration of the electrochemical device. In this electrochemical design, the window is an electrochemical cell in which two glass panels are separated by an electrolyte material. The EC device consists of a thin film of EC (WO₃) material and a conductive ion layer (IC) between two layers of transparent conductive oxide (TCO). In the open-circuit voltage, the window is on. This means that both the working electrode and the counter electrode are transparent to the sun, allowing heat and natural light to enter the room [28]. Upon arriving in the voltage range from 1 to 3 volts, the window changes to darkness, limiting the amount of heat and natural light entering the room [29].

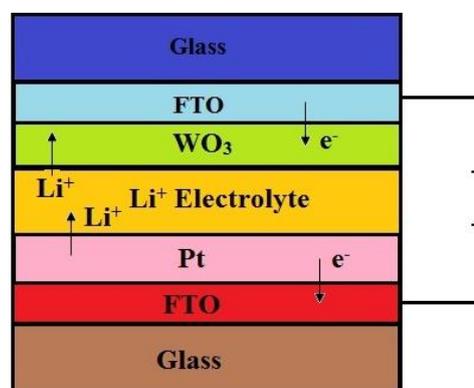


Fig. 1. Schematic display of the electrochromic device.

IV. RESULTS AND DISCUSSION

A. Results and discussion

Figure 2 shows the X-ray diffraction patterns of the annealed WO_3 films as a function of temperature. Figures 2(a) and 2(b) show the XRD pattern of the $\text{WO}_3/\text{FTO}/\text{Glass}$ structure at the temperatures of 100°C and 250°C respectively. There are some peaks observed which stem from the FTO substrate. However, there are no peaks detected associated with the WO_3 layer, indicating an amorphous WO_3 film. In both films, a wide range is observed in the range from 20 to 30 degrees, which is a characteristic of their amorphous structure. Another finding, as reported in the literature as well, is the crystallization of WO_3 films occurring at 500°C [30-32].

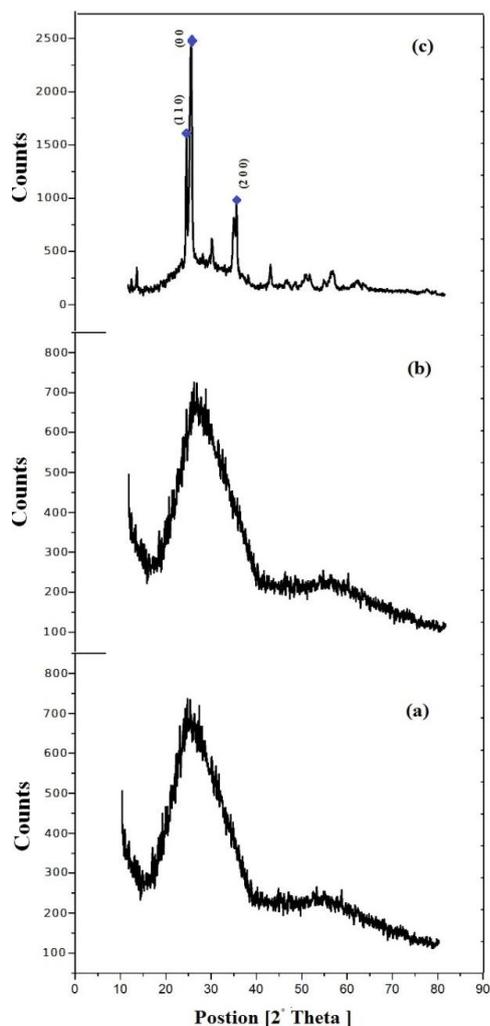


Fig. 2. XRD patterns of an as-deposited WO_3 film and the films annealed at (a) 100°C , (b) 250°C , and (c) 500°C prepared by the spin-coating technique; the substrates have been $\text{SnO}_2:\text{F}$.

At this annealing temperature, a significant narrowing of Bragg's peaks is observed for all the films, which is consistent with the increase of the grain/crystallite size in the WO_3 films. Figure 2c displays the XRD pattern of the spin-coated film annealed at 500°C . The pattern shows three dominant diffraction peaks at $d=3.87\text{\AA}$ ($h\ k\ l=0\ 0\ 1$), $d=3.71\text{\AA}$ ($h\ k\ l=1\ 1\ 0$) and $d=2.63\text{\AA}$ ($h\ k\ l=2\ 0\ 0$). Using these values and Scherrer's formula, the grain size was estimated to be $5\ \text{\AA}$. With regard to similar trends as reported in the literature, amorphous tungsten oxide films generally exhibit better electrochromic performance than their crystalline counterparts [33]. Thus, heat treatment is focused on 100°C , at which amorphous and transparent tungsten oxide films can be obtained [34].

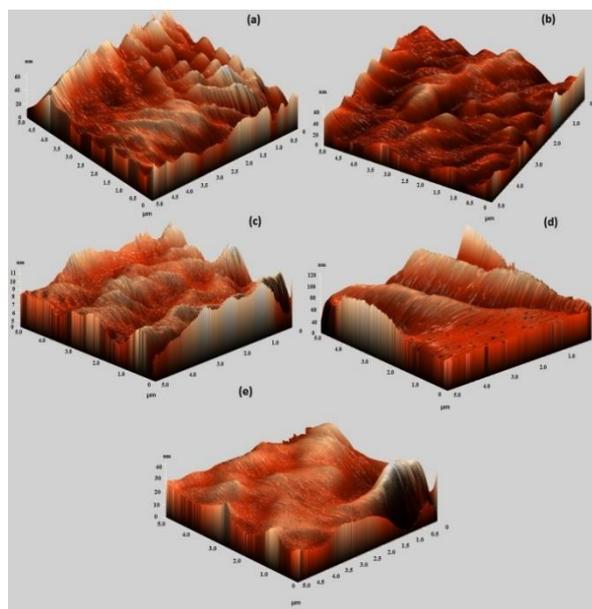


Fig. 3. AFM images of the WO_3 thin films deposited at the speeds of (a) 1500 (b) 2000 (c) 2500 (d) 3000 and (e) 3500 rpm.

The surface topography of the films was studied using atomic force microscopy (AFM) in a tapping mode. Figures 3a-e show the atomic force microscopy (AFM) images of the WO_3 thin films recorded in a $1\text{mm}\times 1\text{mm}$ area as a function of deposition speed. The root mean square (RMS) roughness values of the WO_3 films are presented in Table 1. The RMS roughness calculated in a $1\text{mm}\times 1\text{mm}$ area, as shown in Table 1, is more than 3 nm for all the films deposited at a speed less than 3500 rpm,

but it decreases to 2 nm at the speed of 3500 rpm. It is to be noted that the films are randomly set on the surface [30]. As it is observed, the particle size decreases with an increase in the deposition speed. It may be due to the agglomeration of the grains once the deposition speed increases. Also, as in Fig. 3, at the speed of 3500 rpm, the film surface morphologically seems to be almost the same as a smooth surface; it is an amorphous structure with nanometric grains.

Table 1. RMS roughness values calculated from a 1mm×1 mm area

Deposition speed (rpm)	RMS (nm)
1500	7.01522
2000	8.87050
2500	3.33174
3000	17.9731
3500	2.91146

The surface and the cross-sectional morphology features of the WO_3 films deposited at the deposition speed of 3500 rpm (i.e. best speed) are illustrated in Fig. 4. Those features suggest the crevice-free homogeneous structure of the films. All the films reveal a typical columnar and dense structure. Some cracks exist in their texture, which is due to the strain imposed on the layers during the heat treatment and the removal of water. Our study revealed that these cracks do not affect the electrochromic properties of the films.

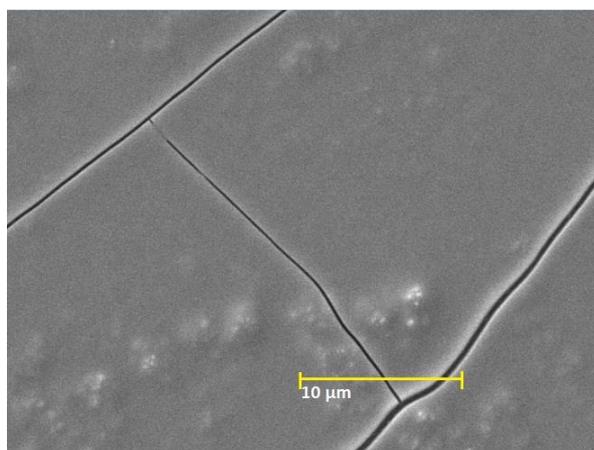


Fig. 4. SEM image of the WO_3 thin film deposited at 3500 rpm (best speed).

B. Electrochromic properties

The transmittance spectra within the wavelength range of $350 \leq \lambda \leq 1100$ nm for the spin-coated films annealed at 100°C , colored, and bleached are illustrated in Fig. 5. By applying various voltages ranging from 0 V to 1.0 V, the WO_3 films were colored from clear to dark blue. It was seen that the transmission would decrease sharply when the film was colored dark blue [35, 36]. In general, the transmittance of these films lies in the range of ≈ 50 –36% in the visible region, but it decreases in a non-monotonic manner as a function of increasing wavelength in the NIR region. The transmittance modulation occurs at the wavelength of 650 nm (designated as ΔT_{650}) for a tungsten oxide film. It can be noted that tungsten oxide films at the of speed 3500 rpm exhibit better electrochromic performance than their counterparts with ($\Delta T_{650}=53/16\%$).

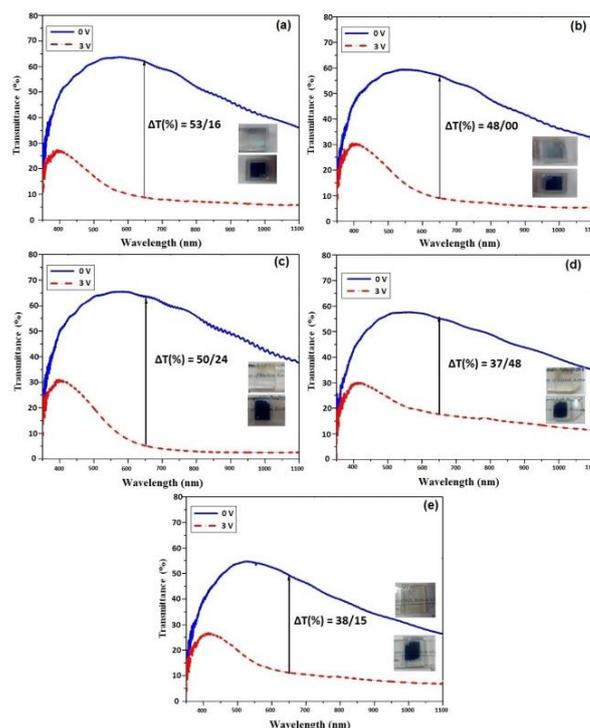


Fig. 5. Transmission spectra of the WO_3 electrochromic cells prepared at various speeds of (a) 3500 rpm, (b) 3000 rpm, (c) 2500 rpm, (d) 2000 rpm and (e) 1500. rpm.

The coloration efficiency (also referred to as electrochromic efficiency) is a practical tool to measure the power requirements of an electrochromic material. In essence, it determines the amount of optical density

change (ΔOD) induced as a function of the injected/ejected electron charge Q_d , i.e., the amount of charge necessary to produce the optical change. The coloration efficiency (CE) at a given wavelength is the variation of the optical density (ΔOD) for the charge (q) applied per unit of the electrode area (A). It is given by the following equation:

$$\eta = \frac{\Delta OD}{Q_d} = \log \frac{[T_b / T_c]}{Q_d} \quad (3)$$

where η ($\text{cm}^2/\text{C}^{-1}$) is the coloration efficiency at a given λ , and T_b and T_c are the bleached and colored transmittance values respectively [37]. In fact, Q_d the same area is under the color chart of the film, which is measured by an oscilloscope. On the other hand, the response time (T_a and T_b) is calculated using the same oscilloscope and calculations in Excel software. Five films with different speeds are chosen to further investigate the effect on their electrochromic performance. Table 2 lists the coloration efficiencies and the transmission modulations of five spin-coated films along with the calculated errors.

Table 2. Styles of different parts of the manuscript

Deposition speed of the film (rpm)	Transmission modulation $\Delta T_{650}(\%)$	Optical density (ΔOD)	Charge intercalated $Q_d(\text{C})$	coloration efficiency $\eta(\text{cm}^2/\text{C}^{-1})$
1500±30	38.1±0.1%	0.6±0.02	3.5±0.1	179.2±0.2
2000±40	37.4±0.1%	0.4±0.02	5.1±0.1	99.1±0.2
2500±50	50.2±0.1%	0.7±0.02	4.1±0.1	194.1±0.1
3000±60	48.0±0.1%	0.8±0.02	2.7±0.1	294.2±0.2
3500±70	53.16±0.1%	0.8±0.02	2.9±0.1	295.3±0.2

The coloration efficiency for the ECD device made at the speed of 1500 rpm is found to be $197.2 \text{ cm}^2/\text{C}^{-1}$, and it increases to $295.3 \text{ cm}^2/\text{C}^{-1}$ for the ECD device made at the speed of 3500 rpm. These values are compatible with and even much more than those for tungsten oxide films reported in the literature [38, 39]. Generally, an increase in the deposition speed leads to a decrease in the layer thickness, and, as a result, a significant decrease occurs in the coloration efficiency. The best efficiency value

is found to be $295.3 \text{ cm}^2/\text{C}^{-1}$ for the film deposited at the speed of 3500 rpm.

Table 3. Response time of spin-coated WO_3 films along with the calculated error

Deposition speed of the film (rpm)	Coloration time $t_c(\text{s})$	Bleaching Time $t_b(\text{s})$
1500±30	11.1±0.1	12.8±0.1
2000±40	11.4±0.2	12.6±0.2
2500±50	13.1±0.1	11.1±0.1
3000±60	6.5±0.2	5.5±0.2
3500±70	6.9±0.1	5.2±0.1

EC response time is another important parameter in evaluation of electrochemical cells. Switching speed is often reported as the time required for the coloring/bleaching process of an EC material. It is important especially for applications such as dynamic displays and switchable mirrors. Table 3 provides a summary of coloration-bleaching response times along with the calculated error for five ECD devices. These response times are noticeably shorter than those for the electrochromic films reported in the literature. It has been well proved that films deposited at higher speeds have faster responses due to their larger uniform surface areas. So, this kind of structure is very good for diffusion of ions into materials, which decreases the response time.

One of the benefits of using an electrochromic material in a display, as opposed to a light-emitting material, is its optical memory (also called open-circuit memory). A memory effect refers to a situation where the optical properties remain the same for extended periods of time without a charge insertion from the drive circuit [40]. The term “memory effect” is used to describe the ability of an ECD to retain the set state of its color after the voltage is removed from the device. We kept the ECD in a colored state without an external voltage and then recorded the change of its transmittance.

The curve in Fig. 6 shows the relationship between relative transmittance and time. It is understood from the curve that, as the time

passes, the relative transmittance is increased at the wavelength of 650 nm for all the cells. The longest memory, which is found to be about ten days, belongs to a film deposited at the speed of 3500 rpm. This result indicates that the ECD device developed in this study has a good memory function.

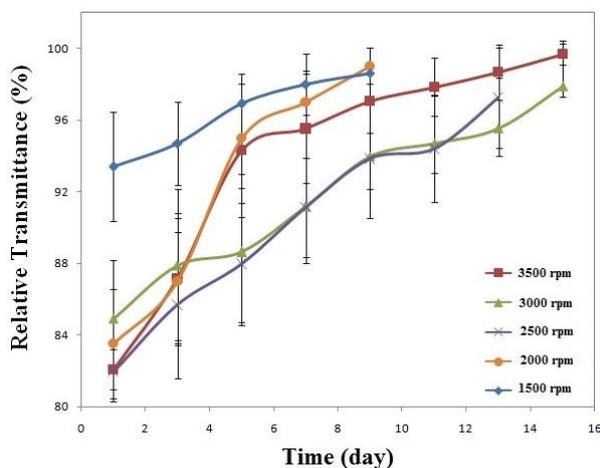


Fig. 6. The diagram of the open-circuit memory of the electrochromic cells at $\lambda=650$ nm with error bars.

V. CONCLUSION

In this paper, the role of tungsten oxide (WO_3) is discussed in fabricating electrochromic films and modulating electrochromic properties. Tungsten oxide films were prepared by sol-gel and spin-coating methods using PTA as the precursor sol. X-ray analysis revealed the amorphous nature of the films for all the investigated speeds. The results indicated the structure of WO_3 films annealed at 100°C result in better electrochromic properties. Thus, heat treatment is focused on 100°C , at which amorphous tungsten oxide films can be obtained. Also, a comparison was made of the electrochromic properties of the tungsten oxide films obtained by spin-coating at various speeds and annealed at 100°C . Not only the transmittance modulation but also the coloration efficiency and the response time were improved by an increase in the deposition speed of the tungsten oxide films. Extensive characterization of these films showed that their better electrochromic performance was correlated with their thickness and deposition speed. Indeed, a

decrease in the thickness of an electrochromic layer and an increase in the deposition speed can improve its performance. Among the tungsten oxide films investigated in the present study, the film doped at the speed of 3500 rpm exhibited the best electrochromic performance with a transmittance modulation of 53.1%, high coloration efficiency of $295.3\text{ cm}^2/\text{C}^{-1}$, fast-switching times ($T_c = 6.9\text{ s}$ and $T_b = 5.2\text{ s}$), and a good memory effect for about ten days. Through electrochromic measurements, it was indicated that WO_3 films deposited at the speed of 3500 rpm are highly promising for application in energy-saving smart windows.

REFERENCES

- [1] H. Naja and A. Bahari, "Optical structural and electrochromic behavior studies on nanocomposite thin film of aniline toluidine and WO_3 ," *Opt. Mater.* Vol. 58, pp. 210–218, 2016.
- [2] G.H. Shim and S.H. Foulger, "Coupling of crystalline colloidal arrays with intrinsically conductive polymers: Reflection-type electrochromic devices," *Photonics Nanostruct* Fundam. Appl. Vol. 10, pp. 440-446, 2012.
- [3] C.G. Granqvist, "Electrochromic for smart windows: Oxide-based thin films and devices," *Thin Solid Films*, Vol. 564, pp. 1-38, 2014.
- [4] M. Kamalisarvestani, F.S. Javadi, S. Mekhilef, and R.Saidur, "Performance, materials and coating technologies of thermochromic thin films on smart windows," *Renewable Sustainable Energy Rev.* Vol. 26, pp. 353-364, 2013.
- [5] L. Mohan, C. Anandan, and N. Rajendran, "Electrochemical behaviour and bioactivity of self-organized TiO_2 nanotube arrays on Ti-6Al-4V in Hanks solution for biomedical applications," *Electrochim. Acta*, Vol. 155, pp. 411–420, 2015.
- [6] K.C. Cheng, F.R. Chen, and J.J. Kai, "Electrochemical behaviour and bioactivity of self-organized TiO_2 nanotube arrays on Ti-6Al-4V in Hanks solution for biomedical applications," *Sol. Energy Mater. Sol. Cells*, Vol. 90, pp.1156–1165, 2006.

- [7] D.J. Rogers, V.E. Sandana, S. Gautier, T. Moudakir, and M. Razeghi, "Core-shell GaN-ZnO moth-eye nanostructure arrays grown on a-SiO₂/Si (111) as a basis for improved InGaN-based photovoltaics and LEDs," *Photonics Nanostruct. Fundam. Appl.* Vol. 15, pp. 53-58, 2006.
- [8] V.V. Kondalkar, R.R. Kharade, S.S. Mali, R.M. Mane, P.B. Patil, P.S. Patil, S. Choudhury, and P.N. Bhosale, "Nanobrick-like WO₃ thin films: Hydrothermal synthesis and electrochromic application," *Superlattices Microstruct.* Vol. 73, pp. 290-295, 2014.
- [9] S.S. Kalagi, S.S. Mali, D.S. Dalavi, A.I. Inamdar, H. Im, and P.S. Patil, "Transmission attenuation and chromic contrast characterization of R.F. sputtered WO₃ thin films for electrochromic device applications," *Electrochim. Acta*, Vol. 85, pp. 501-508, 2012.
- [10] S.A. Agnihotry, M. Kar, and T.K. Saxena, "Towards electrochromic stability in sol-gel-derived tungsten oxide films: cyclic voltammetric and spectrophotometric investigations," *Sol. Cells*, Vol. 90, pp. 15-24, 2006.
- [11] M.M. Nahass, M.M. Saadeldin, H.A. Ali, and M. Zaghllol, "Electrochromic properties of amorphous and crystalline WO₃ thin films prepared by thermal evaporation technique," *Mater. Sci. Semicond. Process.* Vol. 29, pp. 201-205, 2015.
- [12] A. Mohtar, W. Kassem, M. Tabbal, and M. Roumie, "Formation of WO₃ by remote plasma assisted oxidation of tungsten thin films," *Surf. Coatings Technol.* Vol. 307, pp. 583-589, 2016.
- [13] P. Madhukar, D.S. Jyothi, N. Jayababu, and M.V. Reddy, "Influence of annealing temperature on structural and dielectric properties of e-beam evaporated WO₃ thin films," *Mater. Today Proc.* Vol. 3, pp.4199-4204, 2016.
- [14] S. Adhikari and D. Sarkar, "Electrochimica Acta High Efficient Electrochromic WO₃ Nanofibers," *Electrochim. Acta*, Vol. 138, pp. 115-123, 2014.
- [15] V.R. Buch, A. Kumar, and S.K. Rawal, "Review on electrochromic property for WO₃ thin films using different deposition techniques," *Mater. Today Proc.* Vol. 3, pp. 1429-1437, 2016.
- [16] S. Hassab and J. Padilla, "Electrochemistry Communications Using WO₃ as a transparent, optically passive counter electrode in an unbalanced electrochromic configuration," *Electrochem. Commun.* Vol. 72, pp. 87-90, 2016.
- [17] K. Paipitak, C. Kahattha, W.T. Echitdheera, and S. Porntheeraphat, "Influence of Ti and Zn Dopants on Structural Properties and Electrochromic Performance of Sol-Gel Derived WO₃ Thin Films," *Energy Procedia*, Vol. 9, pp. 446-451, 2011.
- [18] H.P. Quiroz, C.P. Barrera, R.R. González, and A. Dussan, "Evidence of iridescence in TiO₂ nanostructures: An approximation in plane wave expansion method," *Photonics Nanostruct. Fundam. Appl.* Vol. 22, pp. 46-50, 2016.
- [19] Z. Bi, S. Zhang, X. Li, and X. Gao, "A novel nanocomposite of WO₃ modified Al-doped ZnO nanowires with enhanced electrochromic performance," *Mater. Lett.* Vol.160, pp. 186-189, 2015.
- [20] R.R. Kharade, S.S. Mali, S.P. Patil, K.R. Patil, M.G. Gang, P.S. Patil, J.H. Kim, and P.N. Bhosale, "Enhanced electrochromic coloration in Ag nanoparticle decorated WO₃ thin films," *Electrochim. Acta*, Vol. 102, pp. 358-368, 2013.
- [21] L.M. Bertus, C. Faure, A. Danine, C. Labrugere, G. Campet, A. Rougier, and A. Duta, "Synthesis and characterization of WO₃ thin films by surfactant assisted spray pyrolysis for electrochromic applications," *Mater. Chem. Phys.* Vol. 140, pp. 49-59, 2013.
- [22] S. Poongodi, P. Suresh, D. Mangalaraj, N. Ponpandian, P. Meena, Y. Masuda, and C. Lee, "Electrodeposition of WO₃ nanostructured thin films for electrochromic and H₂S gas sensor applications," *J. Alloys Compd.* Vol.719, pp. 71-81, 2017.
- [23] M.F. Kuhaili, S.M. Durrani, E.E. Khawaja, and J. Shirokoff, "Effects of preparation conditions on the optical properties of thin films of tellurium oxide," *J. Phys. D*, Vol. 35, pp. 910-915, 2002.
- [24] A. Sezgin, R. Budako, S. Türküz, and H. Parlar, "Electrochromic properties of

- tungsten trioxide (WO_3) layers grown on ITO / glass substrates by magnetron sputtering," *J. Vac. Sci. Technol. A*, Vol.120, pp. 28–31, 2015.
- [25] K. Paipitak, W. Tachitdheera, and S. Porntheeraphat, "Characterization of Sol-gel Derived Ti-doped Tungsten Oxide Electrochromic Thin Films," *Energy Procedia*, Vol. 34, pp. 689–696, 2013.
- [26] V. Madhavi, P. Kondaiah, O.M. Hussain, and S. Uthanna, "Structural, optical and electrochromic properties of RF magnetron sputtered WO_3 thin films," *Phys. B Condens. Matter*, Vol. 454, pp. 141–147, 2014.
- [27] D.R. Acosta, C. Magaña, F. Hernández, and J. Ortega, "Electrical, optical and electrochromic properties of Ti:WO_3 thin films deposited by the pulsed chemical spray technique," *Thin Solid Films*, Vol. 594, pp. 207–214, 2015.
- [28] K. Sauvet, L. Sauques, A. Rougier, "IR electrochromic WO_3 thin films: From optimization to devices," *Sol. Energy Mater. Sol. Cells*, Vol. 93, pp. 2045–2049, 2009.
- [29] J. De, R.M. Neto, R.M. Torresi, S.I. Cordoba, and D. Torresi, "Electrochromic behavior of WO_3 nanoplate thin films in acid aqueous solution and a protic ionic liquid," *J. Electroanal. Chem.* Vol. 765, pp. 111–117, 2016.
- [30] R. Sydam, M. Deepa, S.M. Shivaprasad, and A.K. Srivastava, "A WO_3 -poly (butyl viologen) layer-by-layer film/ruthenium purple film based electrochromic device switching by volt application," *Sol. Energy Mater. Sol. Cells*, Vol. 132, pp. 148–161, 2015.
- [31] N. Mendoza, F. Paraguay, L. Hechavarría, M.E. Nicho, and H. Hu, "Nanostructured polyethylene glycol-titanium oxide composites as solvent-free viscous electrolytes for electrochromic devices," *Sol. Energy Mater. Sol. Cells*, Vol. 95, pp. 2478–2484, 2011.
- [32] C. Sella, M. Maaza, O. Nemraoui, J. Lafait, N. Renard, and Y. Sampeur, "Preparation, characterization and properties of sputtered electrochromic and thermochromic devices," *Surf. Coatings Technol.* Vol. 98, pp. 1477–1482, 1998.
- [33] E. Ienei, A.C. Milea, and A. Duta, "Influence of spray pyrolysis deposition parameters on the optical properties of porous alumina films," *Energy Procedia*, Vol. 48, pp. 97–104, 2014.
- [34] Y.S. Krasnov, S.V. Volkov, and G.Y. Kolbasov, "Optical and kinetic properties of cathodically deposited amorphous tungsten oxide films," *J. Non. Cryst. Solids*, Vol. 352, pp. 3995–4002, (2006).
- [35] A. Karuppasamy and A. Subrahmanyam, "Studies on electrochromic smart windows based on titanium doped WO_3 thin films," *Thin Solid Films*, Vol. 516, pp.175–178, 2007.
- [36] B. Baloukas, J.M. Lamarre, and L. Martinu, "Electrochromic interference filters fabricated from dense and porous tungsten oxide films," *Sol. Energy Mater. Sol. Cells*, Vol. 95, pp. 807–815, 2011.
- [37] H. Sadiki, J.F. Pierson, C. Rousselot, N. Martin, and G. Terwagne, "Properties and electrochromic performances of reactively sputtered tungsten oxide films with water as reactive gas," *Surf. Coatings Technol.* Vol. 200, pp. 232–235, 2005.
- [38] N. Naseri, R. Azimirad, O. Akhavan, and A.Z. Moshfegh, "Improved electrochromical properties of sol-gel WO_3 thin films by deposited gold nanocrystals," *Thin Solid Films*, Vol. 518, pp. 2250–2257, 2010.
- [39] J.M. León, D.R. Acosta, U. Pal, and L. Castañeda, "Improving electrochromic behavior of spray pyrolysed WO_3 thin solid films by Mo doping," *Electrochim. Acta*, Vol. 56, pp. 2599–2605, 2011.
- [40] K.J. Patel, C.J. Panchal, M.S. Desai, and P.K. Mehta, "An investigation of the insertion of the cations H^+ , Na^+ , K^+ on the electrochromic properties of the thermally evaporated WO_3 thin films grown at different substrate temperatures," *Mater. Chem. Phys.* Vol. 124, pp. 884–890, 2010.



Seyed Mohamad Bagher Ghorashi was born in Shahreza, Iran, in 1978. He received the B.E. degree in Physics from the Yazd University, in 2000, and the M.Sc. degree from Isfahan University, in 2004, and PhD degree from the Yazd University in 2011.

In 2011, he joined the Department of Physics, University of Kashan, as an Assistant Professor. His current research interests include Organic and Polymer Solar Cells, Perovskite Solar Cells, Thin Films, SIGS Solar Cells, Electrochromic Glasses and OLED.



Nayereh Daroogheh was born in Kashan, Iran. She received her B.Sc. in applied physics from the University of Kashan, in 2012. She received her M.Sc. in Optics and Laser from the University of Kashan, in 2015.



Elham Karimi was born in Isfahan, Iran. She received her B.Sc. from Kharazmi University, Iran in 2011. She received her Master's degree from Isfahan University, Iran in 2013. Currently, she is a PhD candidate in Optics and Laser in the University of Kashan, Iran. Her research interest focuses on investigation on perovskite solar cells and organic solar cells.