INVESTIGATION ON ELECTROCHEMICAL PROPERTIES OF ELECTROCHROMIC TUNGSTEN TRIOXIDE THIN FILMS

Mono Zaw [1], Kyaw Kyaw [2], Nyein Wint Lwin[3], Than Zaw Oo[4]

Abstract

Electrochemical properties of electrochromic (EC) tungsten trioxide (WO_3) thin films on the fluorine doped tin oxide (FTO) coated glass substrates have been studied. Different molar concentrations of WO_3 precursor solution were sprayed on FTO glass substrates to synthesize amorphous and crystalline phase tungsten trioxide thin films by conducting different annealing temperature. From the different WO_3 precursor concentrations, 0.05 M enabled to increase current densities of WO_3 film. The present study indicated that the optimum processing condition of annealing temperature 400 ^oC and WO_3 precursor concentration 0.05 M would produce the WO_3 film with higher electrochemical current densities which is attributed to a higher crystallinity and lower band gap energy. In examining the electrochromic performance of WO_3 film, its color is blue upon coloring and colorless upon bleaching and the coloration efficiency is 1.89 cm^2C^{-1} in KI and 2.01 cm^2C^{-1} in KCl electrolytes. The color change would be associated with the intercalation (deintercalation) of K^+ ions. The diffusion of ions in the insertion/ extraction process thus play a role. The diffusion coefficient of WO_3 film is observed to be quite high and is in the range of $1.1 – 1.4\times 10^{-12}$ cm^2s^{-1} in both KI and KCl electrolytes. The higher electrochemical activity renders it as promising material for smart windows and energy saving applications.

Keywords: Tungsten trioxide film, Electrochromic behaviors, Smart Window

Introduction

Tungsten trioxide (WO_3) is the most studied among the electrochromic materials and exhibits an n-type semiconducting behavior with a band gap energy of 2.5-3.3 eV. [Jayachandran M. *et al*.,]. Specifically, it is a cathodic electrochromic material used as a working electrode in electrochromic devices. It is a transition metal oxide with excellent chemical and thermal stability. It has promising electrochromic properties such as high coloration efficiency and fast switching response. It is used as a functional layer in the applications of gas sensors, solar cells and electrochromic devices such as smart windows can meet the market demand of energy-saving devices. There are various choices for preparing WO_3 films with the development of thin film technology. These include sputtering, chemical vapor deposition, spray pyrolysis, evaporation, sol-gel and laser ablation deposition. Among these, spray pyrolysis method is the most cost-effective for producing large-area films, and enables a better control over the film growth and hence more homogenous and more transparent films are yielded [M.F. Daniel *et al*., (1987].

Materials and Methods

Preparation of Tungsten trioxide (WO_3) thin films

Tungsten trioxide (WO_3) film was prepared using spray pyrolysis method to be used as electrochromic layer in the electrochromic device. Electorochromic devices (ECDs) are normally composed of five layeres as shown in Figure 1. Tungsten trioxide (WO_3) powder (0.03 M, 0.05 M and 0.07 M) was dissolved in 50 ml of ammonia at 80 ^oC under continuous stirring for 30 min to form tungsten trioxide (WO_3) precursor solution. The obtained WO_3 solution was diluted with 10 ml of deionized water and then cooled down to room temperature and filtered. After that, the

[1] Department of Physics, University of Mandalay, Mandalay, Myanmar
[2] Department of Physics, University of Mandalay, Mandalay, Myanmar
[3] Department of Physics, University of Mandalay, Mandalay, Myanmar
[4] Department of Higher Education, Ministry of Education, Myanmar

final WO_3 solution was sprayed on the FTO substrate (substrate temperature is 300 ^oC) by using spray pyrolysis method to obtain WO_3 films. The resulting WO_3 films with the varying concentration of (0.03 M, 0.05 M and 0.07 M) were annealed at 400 ^oC for 1 h.

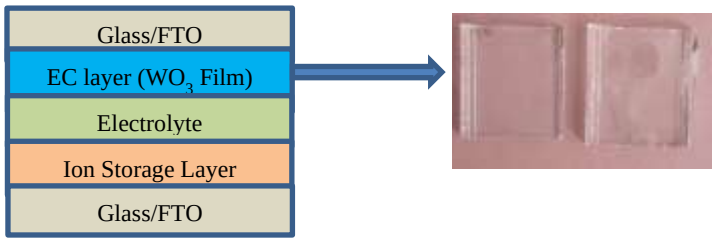


Figure 1 Basic design of electrochromic device

Characterization of WO_3 Films

The structural properties of WO_3 films were investigated X-ray diffractometer (RIGAKU Multiflex (Japan)). The optical properties of WO_3 films were performed using UV-vis spectrophotometry (Genesys 10S). The electrochemical properties of WO_3 films were characterized by cyclic voltammetry. (Electrochemical Workstation- CorrTest CS350). Taking the optimum WO_3 films (annealing temperature 400 °C, 0.05 M) the coloration efficiency of WO_3 films with different electrolyte (KI & KCl) were measured. Cyclic voltammetry was used to obtain the electrochemical properties of the WO_3 films under oxidation state. During coloration the WO_3 film becomes blue color and turns into colorless during the bleaching. The transmission of the samples at colored state and bleached state was measured by UV-vis spectrophotometry.

Results and Discussion

Crystalline Structure of WO_3 Films

XRD profiles of WO_3 films annealed at different temperatures are depicted in Figure 2. From the XRD measurement, WO_3 films annealed at 300 °C shows amorphous nature. At the elevated temperatures 400 °C and 500 °C, WO_3 films reveal the orthorhombic structure. The main diffraction peak positions of WO_3 films for 400 °C and 500 °C are observed at 2θ angle of 22°, 23°, 24° and 34° with the corresponding plane of (020), (002), (200) and (220). The main diffraction peak intensity of WO_3 films annealed at 400 °C shows the stronger peak intensity. It may be due to the formation of better crystallinity. At the annealing temperature 500 °C, the main diffraction peak positions WO_3 films are still the same but the width of the diffraction peak position and intensity are slightly broad and declined.

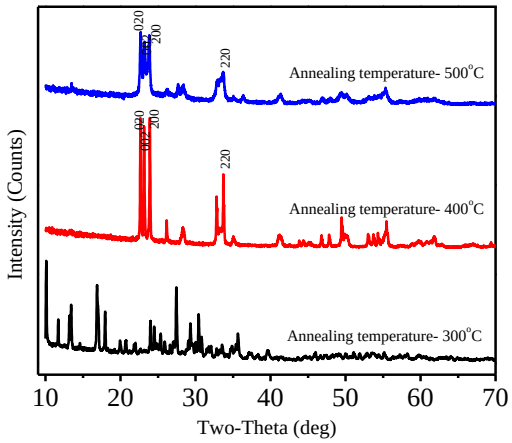


Figure 2 XRD profiles of WO_3 films with varying annealing temperatures

Optical Transmission and Band Gap Energy of WO_3 Films

Figure 3 (a) shows the optical transmission spectra of WO_3 films for all WO_3 precursor concentrations. As can be seen in Figure 3 (a), the values of the optical transmission of WO_3 films decreased from 80% to 65% upon increasing WO_3 precursor concentrations. It may be due to the higher content of WO_3 precursor and thicker film formation. Figure 3 (b) shows the plot of $(\alpha h\nu)^{1/2}$ versus $h\nu$ graph. The optical band gap energy of WO_3 films was determined from Tauc's plot equation, $(\alpha h\nu)^n = A\,(h\nu - E_g)$, where α is absorption coefficient, $h\nu$ is incident light energy, and E_g is the band gap of the material. The exponent 'n' indicates the transition type of the material. The value of n is 1/2 for indirect transition and 2 for direct transition. The value of the optical band gap energy of WO_3 films was obtained by extrapolating the linear portion of the curve to photon energy axis. The optical band gap energy of WO_3 films decreased from 3.3 eV to 2.8 eV when the WO_3 precursor increased from 0.03 M to 0.07 M. The decreasing trend of optical transmission and band gap energy was observed upon increasing WO_3 precursor concentrations. The band gap energy depends on the materials preparation conditions.

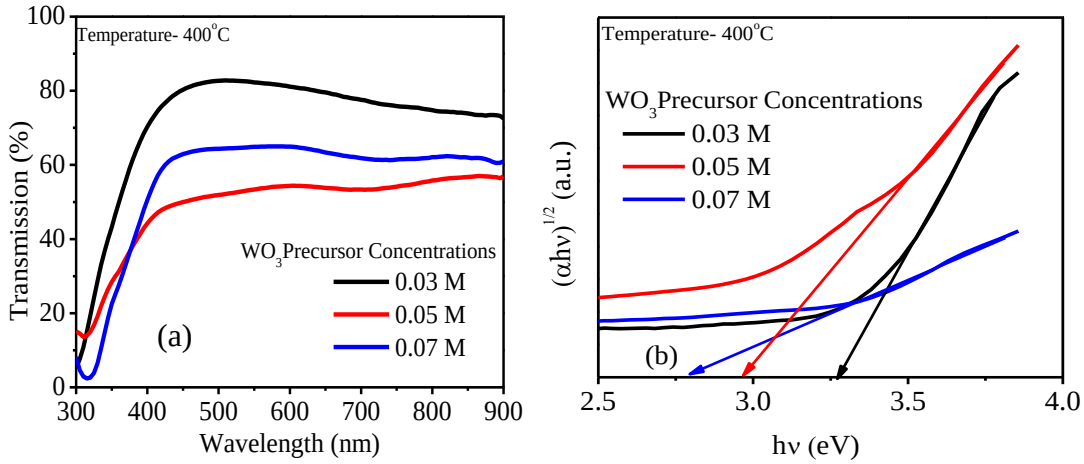


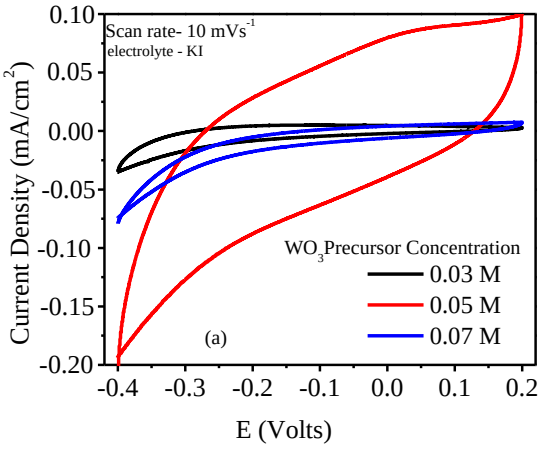
Figure 3 (a) Optical transmission spectra and (b) Plot of $(\alpha h\nu)^{1/2}$ versus $h\nu$ of WO_3 films prepared from different WO_3 precursor concentrations

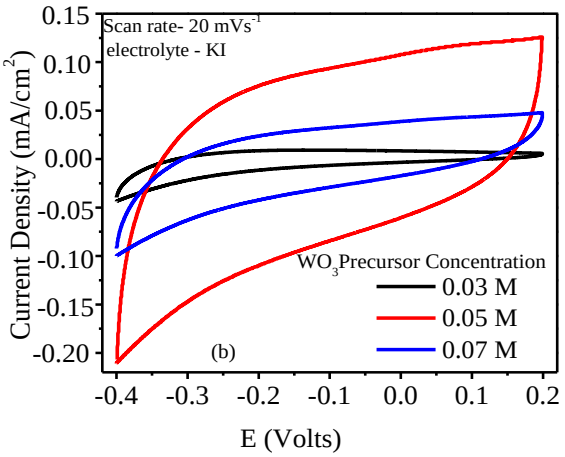
Electrochemical Properties of WO_3 Films

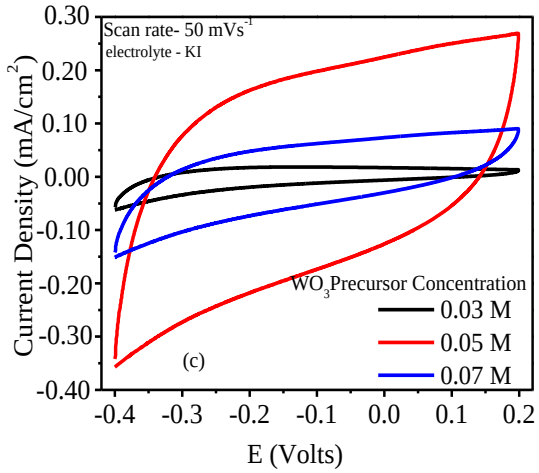
The electrochromic behavior of WO_3 films was tested by cyclic voltammetry (CV) for different WO_3 precursor concentrations. Figure 4 (a-f) shows the CV graph of WO_3 films prepared from various WO_3 precursor concentrations in KI and KCl electrolyte for each scan rate. The cyclic voltammograms of WO_3 films were recorded in the potential range from – 0.4 V to + 0.2 V for each scan rate. From the CV measurement, the values of the anodic peak current densities of WO_3 films are extracted. The obtained values of the anodic peak current density of WO_3 films are listed in Table 1. The highest anodic peak current density of WO_3 films was observed at 0.05 M for each scan rate. The highest anodic peak current density of WO_3 films was observed at WO_3 precursor concentration of 0.05 M. The values of the anodic peak current density of WO_3 films with different WO_3 precursor concentrations are varied upon changing electrolyte. It would be related to the surface roughness of the WO_3 films. Since, the ion insertion/extraction reaction depends on the number of reaction sites on the surface.

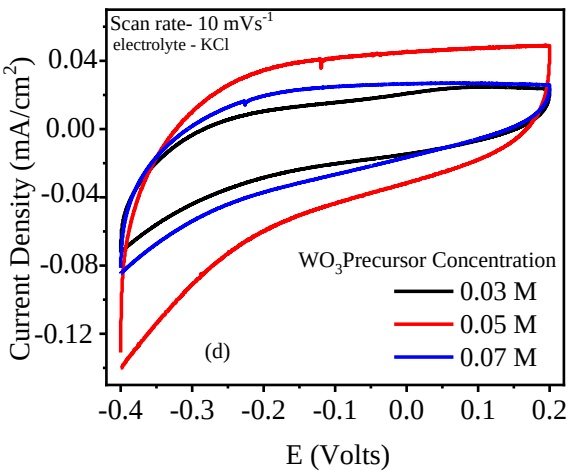
Table 1 The value of anodic peak current densities of WO_3 films with varying WO_3 precursor concentrations in KI & KCl electrolyte

Scan Rate (mV/s)	WO_3 precursor concentrations	Potential (V)	Anodic Peak Current Density (mA/cm^2) KI electrolyte	Anodic Peak Current Density (mA/cm^2) KCl electrolyte
10	0.03 M	0.08	0.01	0.02
	0.05M	0.08	0.09	0.05
	0.07 M	0.08	0.01	0.03
20	0.03 M	0.08	0.01	0.03
	0.05M	0.08	0.12	0.10
	0.07 M	0.08	0.03	0.05
50	0.03 M	0.08	0.01	0.07
	0.05M	0.08	0.24	0.21
	0.07 M	0.08	0.09	0.12









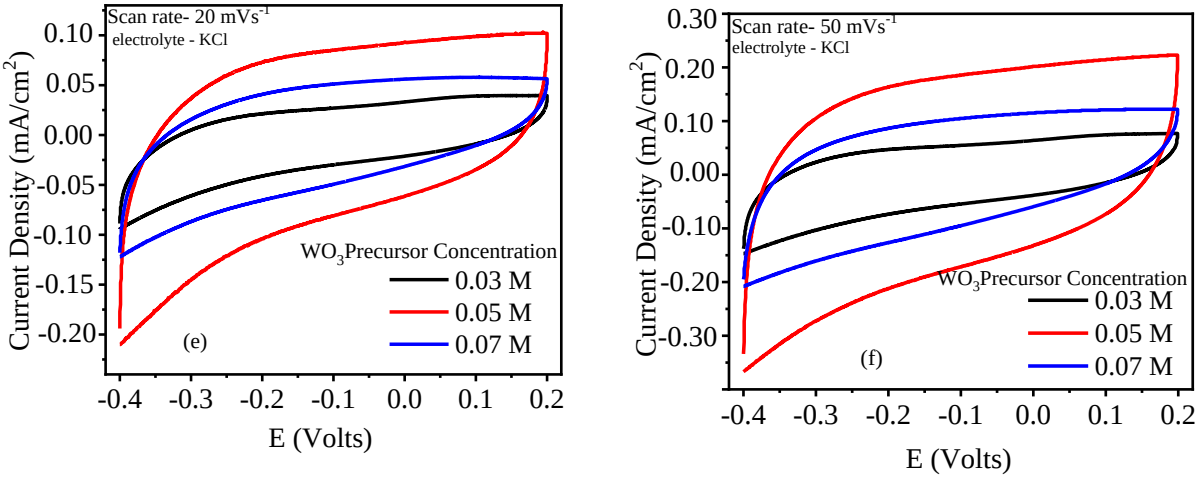


Figure 4 (a–f) Cyclic voltammogram of WO_3 films varying WO_3 precursor concentrations (0.03 M, 0.05 M and 0.07 M) in KI & KCl electrolytes

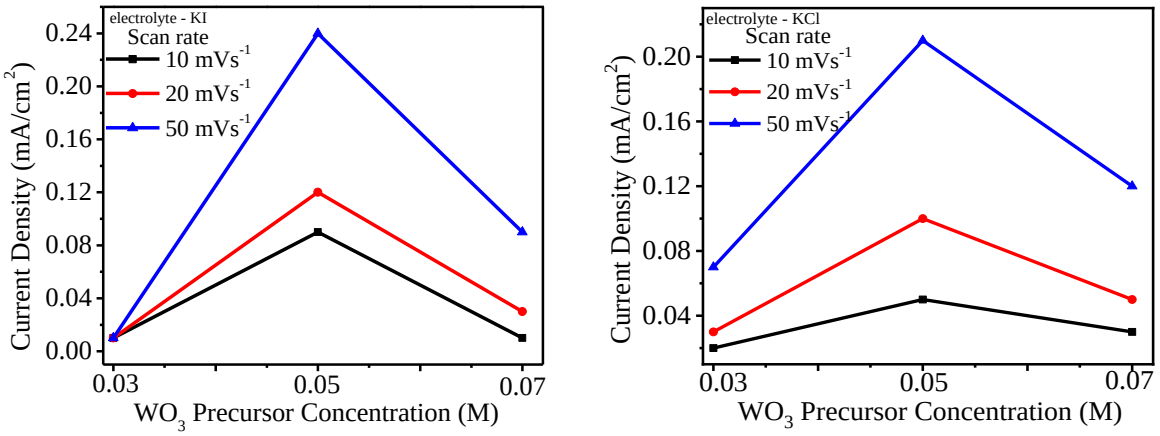


Figure 5 Plot of current density (mA/cm^2) vs WO_3 precursor concentration (M) in KI and KCl electrolyte

Coloration efficiency and Diffusion coefficient of WO_3 Films

The electrochromic behaviors specially coloration efficiency of WO_3 films in KI and KCl electrolyte were studied. Cyclic voltammetry was used to obtain the electrochemical properties of the WO_3 films under oxidation state. The value of peak current density gave a rough estimation of electrochromical activity of the working electrode. The main parameter that will be determined from the cyclic voltammetry was the current peak I_p, which depends strongly on the diffusion coefficient. Anodic peak refers here to the current peak caused by insertion of K^+ ions into the WO_3 films, while the cathodic peak refers to exertion of K^+ ions. The WO_3 films have electrochromic properties, which is associated with the electrochemical intercalation and de-intercalation of K^+ ions and electrons into the WO_3 film. The experiments were recorded for different scan rates like 10 mVs^{-1}, 20 mVs^{-1} and 50 mVs^{-1} in the KI and KCl electrolyte. During coloration the WO_3 film becomes blue color and turns into colorless during the bleaching. The diffusion coefficients of K^+ ions during intercalation and de-intercalation can be calculated by employing the Randles-Servick equation [P.R.Patil *et al.,* (2004) "Preparation and Characterization of Spray Deposited n-type WO_3 thin Films for Electrochromic Devices" Materials Research Bulletin, United States, vol.39, pp.1479-1489].

$$i_p = 2.72\times 10^5\, n^{3/2}\, D^{1/2} C v^{1/2} \qquad (1)$$

where D is the diffusion coefficient of K^+ions; v, scan rate; C, concentration of electrolyte solution; n, number of electrons and it is assumed to be 1 and i_p is the peak current density. Figure 4 (a-f)

show the CV curves recorded for WO_3 films (0.05 M , 400^{o}C) with different scan rate in potassium iodide (KI) and potassium chloride (KCl) electrolytes. Table 2 shows the various electrochemical parameters: the scan rate and diffusion coefficient extracted from Figure 6 (a-c). In the present work, the calculated diffusion coefficient is (1.08 - 1.35) × 10^{-12} cm^2s^{-1} in KI electrolyte and (1.09 - 1.38) × 10^{-12} cm^2s^{-1} in KCl electrolyte. Diffusion coefficient values for the K^+ ion process using different concentrations of KI, KCl electrolyte were of the order of (1.35 - 3.10) × 10^{-12} cm^2s^{-1} for spray pyrolyzed. From the electrochemical analysis it is observed that the films have changed their colors in accordance with the applied potential. Also the films have the capability to withstand in the electrolyte throughout the entire scan rates; it confirms the better reversibility of the films in the electrochromic process. The electrolyte content and the porosity play a great role in the diffusion coefficient by increasing the diffusion coefficient value with the K^+ ions. From this, WO_3 films prepared in the present work would be suitable for development of low cost electrochromic cells.

Figure 7 shows the UV-Vis spectra of the WO_3 films at colored and bleached state upon being subjected to -0.4 and 0.2 V in KI and KCl solution for 240 s. As shown in Figure 7, both films show a high transmittance which is as high as 80% at positive voltage. When applied to a negative voltage, a significant absorbance in the wavelength ranging from 550 nm to near IR region caused by the K^+ intercalation is observed. Both films turned from blue at colored state to colorless at bleached states as the voltage switched from negative to positive. The coloration efficiency, η, was calculated at constant $\lambda = 550$ nm by applying a constant current on it (I = 1 mA) in the 0.1 M KI and KCl electrolyte solutions for 240 seconds. The charge, Q, inserted in the sample of (area A= 2 cm^2) is:

$$Q = I \times t \tag{2}$$

$$= 0.001 \times 240 = 0.24 \text{ C},$$

$$Q/A = 0.24/4 = 0.06 \text{ Ccm}^{-2}. \tag{3}$$

By using the equation (3), η can be calculated as follows:

$$\eta = \frac{\Delta OD}{\Delta Q} = \frac{\log(\frac{Tb}{Tc})}{(\frac{Q}{A})}, \tag{4}$$

where ΔOD is the optical density difference, T_b and T_c are transmittance at bleached state and colored state respectively as shown in Figure 6. The calculated coloration efficiency is 1.89 cm^2C^{-1} in KI and 2.01 cm^2C^{-1} in KCl electrolyte. The color change is believed to be associated with the intercalation (deintercalation) of the K^+ ions into (or out from) the WO_3 films. The the diffusion coefficient of WO_3 films in KI and KCl electrolyte solutions are not significantly varied. Consequently, the coloration efficiencies (color change) are not significantly varied in KI and KCl electrolytes.

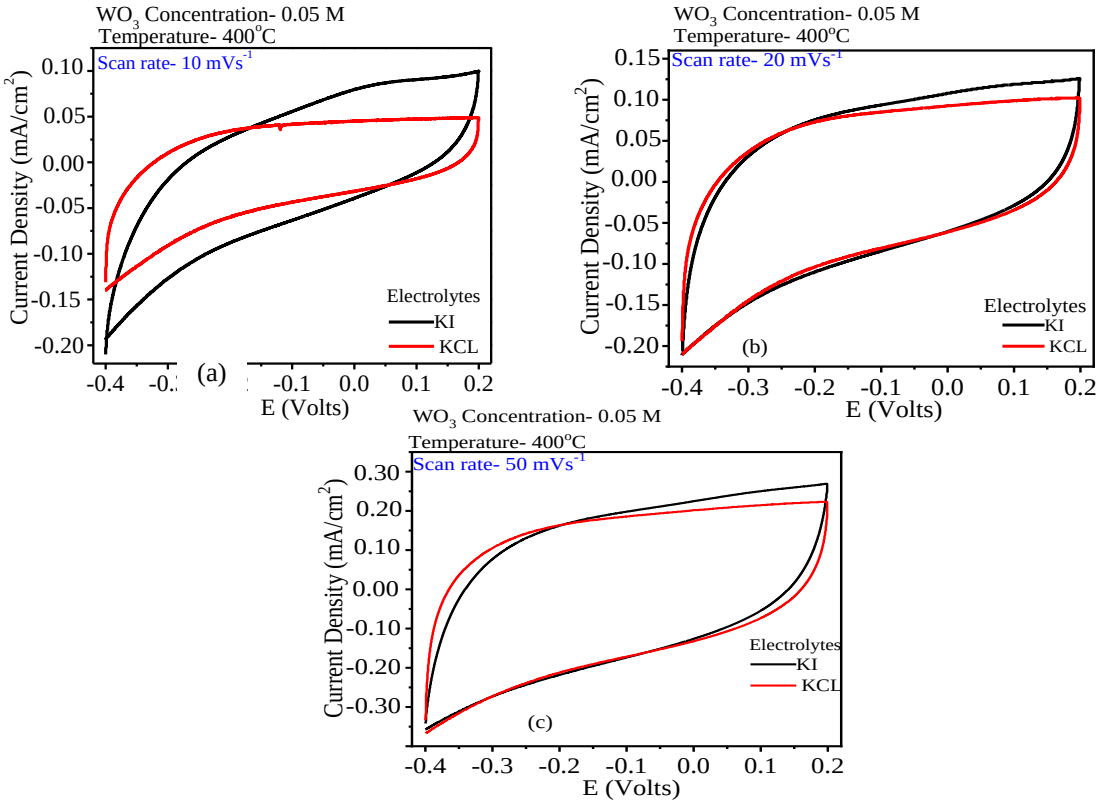


Figure 6 (a–c) Cyclic voltammograms of WO_3 films (400°C and 0.05M) in KI and KCl electrolyte

Table 2 Diffusion coefficients of potassium ions (K^+) calculated using Randles-Sevcik equation for WO_3 films in KI and KCl solution

Scan Rate (mV/s)	Diffusion Coefficient (anodic peak) ($\times 10^{-12} cm^2 s^{-1}$)	
	Electrolyte (KI)	Electrolyte (KCl)
10	1.35	1.38
20	1.14	1.14
50	1.08	1.09

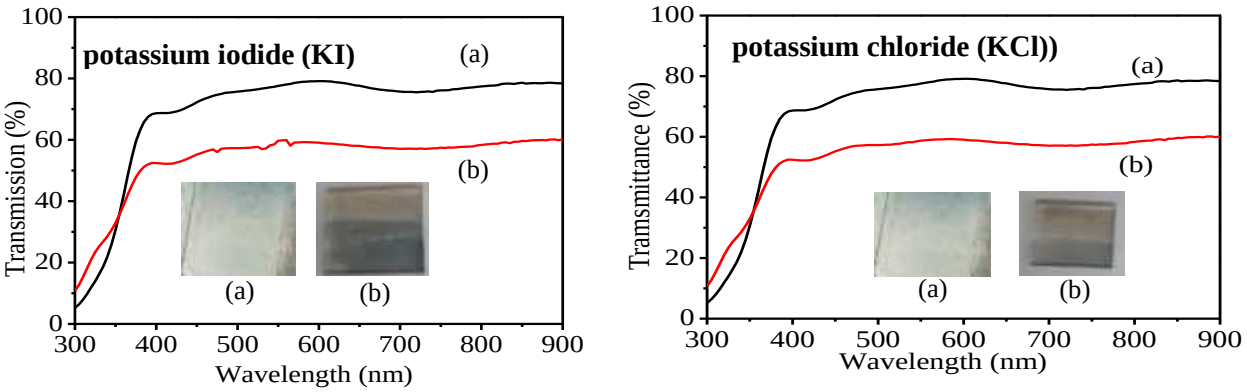


Figure 7 Transmittance spectra of WO_3 films with potassium iodide (KI) and potassium chloride (KCl) at (a) bleached state and (b) colored state

Summary and Conclusion

Tungsten trioxide (WO_3) films were fabricated by spray pyrolysis method varying WO_3 precursor concentrations. The XRD measurement indicated that WO_3 film annealed at 300 °C shows the amorphous phase. When the annealing temperatures increased to 400 °C and 500 °C, WO_3 films reveal the orthorhombic structure. The main diffraction peak positions of WO_3 films annealed at 400 °C and 500 °C remain unchanged but the peak intensities declined. The stronger peak intensity of WO_3 films was observed at annealing temperature 400 °C. The optical transmission and band gap energy of WO_3 films decreased upon increasing WO_3 precursor concentrations. It may be due to the higher content of WO_3 precursor and thicker film formation. In the case of chamge in WO_3 precursor, the highest anodic peak current density was observed in WO_3 films (0.05 M) at each scan rate. Annealing temperature (400°C) and WO_3 precursor concentration (0.05 M) were selected for determining the performance of electrochromic device. The calculated diffusion coefficient is 1.08 - 1.35× 10^{-12} cm^2s^{-1} in KI electrolyte and 1.09 - 1.38× 10^{-12} cm^2s^{-1} in KCl electrolyte. From the electrochemical analysis it is observed that the films have changed their colors in accordance with the applied potential. Also the films have the capability to withstand in the electrolyte throughout the entire scan rates; indicating the better reversibility of the films in the electrochromic process. The higher diffusion coefficient indicates a larger contact area and greater porosity resulting in faster ion insertion/extraction. The coloration efficiency, η calculated at constant $\lambda = 550$ nm is found to be 1.89 cm^2C^{-1} in KI and 2.01cm^2C^{-1} in KCl electrolyte.

Acknowledgement

The authors special thanks to ISP (International Science Program), Sweden, for their support in measurement of cyclic voltammetry (Electrochemical Workstation- CorrTest CS350) and also grateful thank to all the Materials Science Laboratory members (University of Mandalay) for their helpful discussion.

References

Jayachandran M. *et al*., (2005) "Materials Properties, Preparation Techniques and Electrochromic Devices" Transactions of the SAEST, India, vol. 40, pp.42-60.

M.F. Daniel *et al*., (1987) "Infrared and Raman Study of Tungsten Trioxides and Tungsten Trioxide Tydrates" Journal of Solid State Chemistry, United States, vol. 67, pp.235-247.

P.R.Patil *et al.,* (2004) "Preparation and Characterization of Spray Deposited n-type WO_3 thin Films for Electrochromic Devices" Materials Research Bulletin, United States, vol.39, pp.1479-1489.