Effect of bias voltage on the electrochromic properties of WO₃ films

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Abstract. Electrochromism is the phenomena of reversible colour change in electrochromic (EC) materials due to a small applied voltage. Tungsten oxide (WO₃) is one of the most studied cathodic electrochromic materials for its applications in smart windows, displays and rear-view mirrors. In this work, WO₃ films were fabricated on indium tin oxide (ITO) coated glass via the sol-gel spin-coating method. The influence of bias voltage on the EC properties of the fabricated WO₃ films was studied. The optical properties were characterised by using ultraviolet-visible (UV-Vis) spectrophotometer and the EC properties were characterised by the chronoamperometry (CA) method. The fabricated WO₃ films exhibited an optical transmittance of 80 % in the visible range. CA measurements revealed an increase in colouring and bleaching time and intercalated charge density as bias voltage was increased. Moreover, the colouring and bleaching transmittance of the WO₃ films were found to decrease as bias voltage was increased. Within our measurement range, bias voltage of 1.0 V was found to be the optimum bias voltage where it corresponds to 34 % optical modulation and higher colouration efficiency of 22.6 cm²/C.

1. Introduction

Electrochromism has gained widespread interest among researchers since the discovery by Deb in the 1970s [1]. It is a phenomena where a small applied voltage is capable of inducing reversible colour change in electrochromic (EC) materials [2]. The colour change in EC materials is due to the intercalation and deintercalation of ions which is controlled by the voltage applied between the transparent conducting oxide (TCO) layers [3].

Among the EC materials, tungsten oxide (WO₃) is one of the most studied materials owing to its distinctive properties such as fast response time and high colouration efficiency [4]. Furthermore, it has been used in applications such as smart windows [5], displays [6] and rear-view mirrors [7].

In this work, EC WO₃ films were fabricated on indium tin oxide (ITO) coated glasses via the sol-gel spin-coating method. The bias voltage was varied between ±0.5 V to ±2.0 V in order to study its effect on optical and EC properties of the WO₃ films. In addition, this study provides an insight on the optimum bias voltage in order to achieve a high optical modulation and colouration efficiency. The
switching characteristics, intercalated charge density, colouring and bleaching transmittance are elucidated in this paper.

2. Methodology
Tungsten hexachloride powder, absolute ethanol, glacial acetic acid and hydrogen peroxide were used as WO$_3$ precursor, solvent, chelating agent and strong oxidising agent, respectively. 1g of tungsten hexachloride powder was dissolved in 20 ml of absolute ethanol and 2 ml of glacial acetic acid was added to the mix. Then, the mixture was stirred at room temperature. Next, 2 ml of hydrogen peroxide was added to the mixture and was further stirred to yield a homogenous transparent solution. Subsequently, the WO$_3$ solution was spin-coated on ITO coated glasses. Finally, the as-deposited WO$_3$ films were annealed in ambient.

The optical properties of the fabricated WO$_3$ films were measured by the ultraviolet-visible (UV-Vis) spectrophotometer in the wavelength range of 280 nm to 1000 nm. Chronoamperometry (CA) measurements were performed by adopting a three-electrode configuration where WO$_3$ films were used as working electrode, Pt sheet was used as counter electrode and Ag/AgCl was used as reference electrode.

3. Results and Discussions
Figure 1 shows the schematic of the three-electrode system adopted for the CA measurements. It is made up of WO$_3$ films as working electrode, Ag/AgCl as reference electrode and Pt sheet as counter electrode. All electrodes were immersed in 1 M PEG:LiI electrolyte where it facilitates the movement of ions and electrons in and out of the WO$_3$ films [8]. The three-electrode system was connected to a potentiostat and a computer.

![Figure 1. Schematic of the three-electrode system](image)

The influence of colouring voltages on the switching characteristics of the WO$_3$ films was investigated by using the CA technique. The colouring time ($t_c$), bleaching time ($t_b$) and intercalated charge density ($Q_i$) at different bias voltage were measured while simultaneously recording the optical transmittances in the coloured and bleached states. Voltages ranging from ± 0.5 V to ± 2.0 V were applied at the working electrode for 60 s and their respective $t_c$ and $t_b$ were tabulated in Table 1. It is worth mentioning that the choice of voltage range was selected based on literature [9–11].
Table 1. Colouring and bleaching time of the WO$_3$ films

| Bias Voltage (V,V) | Colouring Time (t$_c$, s) | Bleaching Time (t$_b$, s) |
|-------------------|---------------------------|--------------------------|
| 0.5               | 23.95                     | 10.93                    |
| 1.0               | 36.74                     | 12.90                    |
| 1.5               | 44.73                     | 14.97                    |
| 2.0               | 43.62                     | 16.20                    |

From Table 1, it can be seen that the colouring and bleaching of the WO$_3$ films are faster at lower bias voltages. Similar results on the response time of WO$_3$ films was reported by Jiao et al. where it is explained by the shallow level colouration for small bias voltage due to the involvement of fewer Li$^+$ ions in the colouring process of the WO$_3$ films [11]. It is observed that the bleaching time is shorter than the colouring time regardless of the applied bias voltage. In the coloured state, the WO$_3$ films are highly conductive compared to when in bleached state which is insulative. This is an indication where the conductive to insulative transition is much faster than the insulative to conductive transition [10].

Figure 2 shows the variation of the colouring and bleaching transmittance at voltages ranging from 0.5 V to 2.0 V recorded between the 280 nm and 1000 nm wavelength. It can be seen in Figure 2 that the higher the bias voltage, the lower the optical transmittance in both the coloured and bleached states. In general, the colouring and bleaching of the WO$_3$ films are due to the intercalation and deintercalation of ions which is according to the following equation [12]:

\[
\text{WO}_3 \text{(bleach)} + x\text{Li}^+ + xe^- \leftrightarrow \text{Li}_x\text{WO}_3 \text{(dark blue)}
\]

where Li$^+$ are the cations in the electrolyte and $x$ represents the concentration. Therefore, the above reaction can be made reversible by controlling the polarity of the applied voltage. By increasing the bias voltage, more colouration was shown by the WO$_3$ films and thus it is logical that the optical transmittance was much lower, as depicted in Figure 2. When the WO$_3$ films were in the coloured state, the highest optical transmittance occurred around 450 nm due to Li$_x$WO$_3$ which is dark blue. At higher bias voltages, more Li$^+$ ions could overcome the confinement of relatively high energy barrier and therefore larger amount of them are being accommodated in the WO$_3$ films [13]. As a result, the
WO$_3$ films appear to be darker and show lower optical transmittance in a given amount of colouration time compared to WO$_3$ films biased at a lower voltage. It is worth mentioning that the observed reduction in bleaching transmittance at higher voltages is due to the increase in x value from equation 1 [14]. This can be attributed to the trapped Li$^+$ ions in deep traps which could not be extracted during bleaching process [15]. Consequently, this leads to large optical absorption and degrades the bleaching transmittance.

When 0.5 V was applied, the WO$_3$ films were able to retain most of its optical transmittance of 75 % in the bleached state while having 63 % optical transmittance in the coloured state. At 1.0 V, the WO$_3$ films exhibited 68 % and 34 % in the bleached and coloured states, respectively. At high colouring voltages (1.5 V and 2.0 V), the optical transmittance in the bleached state was 37 % in the visible range which is a vast difference from its original optical transmittance of 80 %. Besides that, the WO$_3$ films at 1.5 V and 2.0 V had optical transmittances of 12 % and 17 %, respectively in the coloured state. The optical modulation was found to be 12 %, 34 %, 25 % and 23 % with increasing voltage. The observed behavior of the WO$_3$ films suggests saturation of the colouration transmittance starting from 1.5 V onwards and a colouration voltage greater than 2.0 V will not further reduce the coloured transmittance of the WO$_3$ films.

Figure 3 shows the plot of intercalated charge ($Q_i$) against bias voltage. $Q_i$ was found to increase proportionally from 3.61 mC/cm$^2$ to 37.6 mC/cm$^2$ with increasing bias voltage. It is logical to think that as the higher bias voltage increases, the greater the electric field between the electrodes. Therefore, more electrons and Li$^+$ ions are being transported across in a fixed period of time. The increasing $Q_i$ with increasing bias voltage subsequently gives rise to decreasing coloured transmittance in the WO$_3$ films which correspond to the increase in x value in Li$_x$WO$_3$.

![Figure 3. Intercalated charge density vs bias voltage](image)

The results obtained here can be further used to calculate one important parameter for EC films, which is the colouration efficiency, CE. It is defined as $CE = \Delta OD/Q_i$, where $\Delta OD$ is the change in optical density. The CE of the WO$_3$ films at different bias voltage is presented in Figure 4. CE was found to be 21.0 cm$^2$/C, 22.6 cm$^2$/C, 19.3 cm$^2$/C and 9.88 cm$^2$/C for 0.5 V, 1.0 V, 1.5 V and 2.0 V, respectively. The low CE at bias voltage of 2.0 V is mainly due to the small optical modulation of the WO$_3$ films. It can be concluded that 1.0 V is the optimum bias voltage to achieve a considerably high bleaching transmittance and low colouring transmittance while having a greater intercalated film area per unit charge.
4. Conclusion
In conclusion, WO₃ films were fabricated on ITO coated glasses by the sol-gel spin-coating method. The influence of bias voltage on EC properties was investigated. CA results showed increase in colouring and bleaching time with increasing colouration voltage due to the shallow level colouration at small colouring voltage. The decrease in colouring transmittance was caused by the accommodation of larger amount of Li⁺ ions in the WO₃ films. The decrease in bleaching transmittance was caused by Li⁺ ion trapping in deep traps. The optical modulation was as high as 34 % at 1.0 V colouration voltage. Besides that, CA results revealed increase in intercalated charge density with increasing bias voltage which gives rise to lower optical transmittance in the coloured state. In this study, 1.0 V was found to be the optimum colouration voltage as WO₃ films had a CE of 22.6 cm²/C.

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