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## Solution thermolysed tungsten oxide-based electrochromic devices: thickness-dependent step potential analysis

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**Abstract** The characterisation of electrochemical behaviour of electrochromic (EC) devices based on solution thermolysed (ST) tungsten oxide ( $\text{WO}_3$ ) thin films was carried out using the step potential excitation method. The method, based on generating plots of current density ( $J$ ) as a function of passed charge ( $\Delta Q$ ), has been applied for the characterisation of EC- $\text{WO}_3$  thin films in proton-containing aqueous electrolyte. EC devices have been fabricated by employing  $\text{WO}_3$  thin films with variable thickness ( $T$ ) ranging from 0.04 to 0.52  $\mu\text{m}$ . The  $J$  vs time ( $t$ ) responses (chronoamperometry) of these devices were recorded at a fixed applied potential ( $\pm 0.7$  V vs S.C.E.) and values of total passed  $\text{H}^+$  charges ( $\Delta Q$ ) into the  $\text{WO}_3$  host lattice during the coloration process are calculated. The  $J$ - $\Delta Q$  curves corresponding to films of different thickness were plotted as a function of the passed charge volume density,  $\Delta Q/T$ , and an intercalatable film thickness is calculated to be 0.13  $\mu\text{m}$ . The modulation in optical transmittance after coloration and bleaching was studied in the wavelength range between 350 and 850 nm and an optical efficiency ( $\xi_2$ ) is calculated at  $\lambda = 700$  nm. It is found that the  $\xi_2$  wanes with increasing intercalation.

**Keywords** Solution thermolysis · Tungsten oxide · Electrochromism · Thin films · Chronoamperometry

### Introduction

$\text{WO}_3$  has evolved as an excellent host material for intercalating electrochromic devices (ECDs) [1]. Recently the solid-state and solution-based ECDs with  $\text{WO}_3$  were successfully demonstrated [2, 3]. Profound modulation in optical and electrical properties in response to the

applied electric field engenders  $\text{WO}_3$  a unique material for variably absorptive windows, variably reflective mirrors and display applications [4, 5, 6]. When electrons are incorporated in the transparent  $\text{WO}_3$  thin film, charge-balancing cations ( $\text{H}^+$ ,  $\text{Li}^+$ ,  $\text{Na}^+$  or  $\text{K}^+$ ) intercalate into it, which transforms  $\text{WO}_3$  to a material with different properties. It becomes absorbing if it is highly disordered and infrared reflecting if it is sufficiently crystalline [7]. Consequently, a vast amount of work has been and is being done on structural, electrical, optical and electrochemical properties of  $\text{WO}_3$  films deposited by a plethora of physical and chemical techniques [8, 9, 10]. It is observed that the  $\text{WO}_3$  films grown by these techniques invariably contain hydroxyl groups and incorporate water molecules, thereby deviating from its stoichiometry. The extent of stoichiometric deviation depends on the kind of technique used and the preparation conditions. For the aforementioned applications one should have control over the variation of optical behaviour, which correlates strongly with the variation in electrical behaviour. Thus apprehension of electrical behaviour is necessary to elucidate the optical behaviour of the films.

Among all the deposition techniques, ST, analogous to spray pyrolysis can offer a cost-effective way to form uniform and large area EC coatings. A variety of precursor solutions were used to deposit  $\text{WO}_3$  films using the spray pyrolysis technique, namely  $\text{WCl}_6$  in ethanol or  $N,N$ -dimethyl formamide, ammonium metatungstate etc. Effects of substrate temperature and film thickness on thin film properties have been reported [11, 12].

The present paper focuses on the characterisation of ECDs based on solution thermolysed  $\text{WO}_3$  thin films in a proton-containing electrolyte. The film thickness was varied from 0.04 to 0.52  $\mu\text{m}$  and its effect on electrochemical properties is examined using a step potential analysis. The values of total passed charges during intercalation, intercalatable film thickness and optical efficiency for all the samples are estimated. The knowledge of these parameters should facilitate device optimisation and design.

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## Experimental

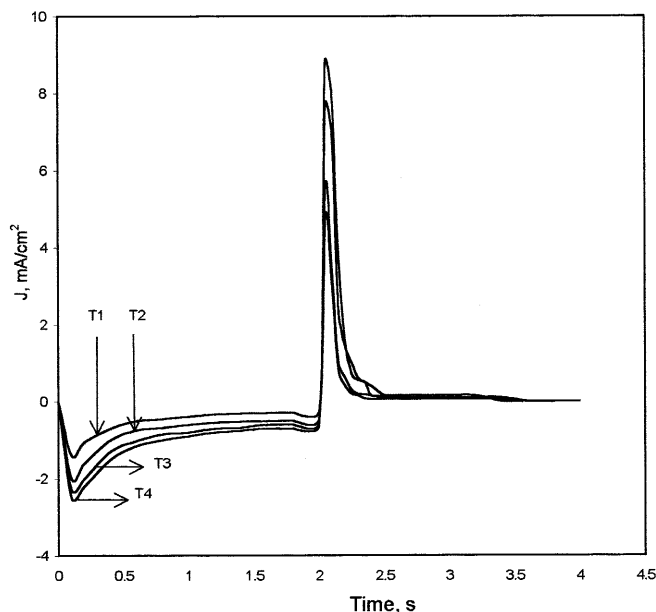
WO<sub>3</sub> thin films were prepared by the solution thermolysis technique. Ammonium tungstate solution of 2.5 mmol/l concentration was used as a precursor solution, to be sprayed. Films were prepared by spraying different quantities of solution onto the fluorine doped tin oxide (F.T.O.) coated glass substrates maintained at 300 °C, which were then used as working electrodes in a three-electrode EC cell. Film thickness was estimated with the help of a Dektak 3030 profilometer. Films of 1 cm<sup>2</sup> area were used as working electrode (WE), graphite was a counter electrode (CE) and 0.05 N H<sub>2</sub>SO<sub>4</sub> was an electrolyte. The voltages were measured with respect to the saturated calomel electrode (SCE).

Chronoamperometry (C-A) was carried out using a scanning potentiostat EG and G model PAR-362 and X-Y(t) recorder and the variation of coloration and bleaching current with respect to time at fixed applied potential ( $\pm 0.7$  V vs SCE) were recorded. Optical absorption spectra of the coloured and bleached films were recorded using a Hitachi-330 spectrophotometer.

## Results and discussion

Thermal decomposition of ammonium tungstate solution onto the FTO coated glass substrates results in a tungsten oxide (WO<sub>3</sub>) thin film, at optimised preparation conditions. Attempts have been previously made to optimise substrate temperature (300 °C) spray rate (2.5 ml/min.) and solution concentration (2.5 mmol/l) with a view to obtain uniform, adherent and pin-hole free thin films [13]. More details on the spraying method are given in the literature [14]. By keeping all these conditions fixed and varying the quantity of a precursor solution we could obtain WO<sub>3</sub> thin films with different thicknesses. The quantity of the precursor solution to be sprayed onto the substrates was varied as 10, 20, 30 and 40 c.c. and the resulting films are denoted as T1-WO<sub>3</sub>, T2-WO<sub>3</sub>, T3-WO<sub>3</sub> and T4-WO<sub>3</sub>, respectively. The deposited samples, examined by the X-ray diffraction technique, were found to be amorphous or microcrystalline hydrated WO<sub>3</sub>.

A simple three-electrode electrochemical cell has been formed by employing T1-WO<sub>3</sub>, T2-WO<sub>3</sub>, T3-WO<sub>3</sub> and T4-WO<sub>3</sub> samples, alternatively as working electrodes. Graphite was used as a counter electrode and 0.05 N H<sub>2</sub>SO<sub>4</sub> was electrolyte. The potentials were measured with respect to saturated calomel electrode (S.C.E.). The electrochemical characterisation of these samples was carried out in aqueous acidic medium by intercalating the films with protons. The chronoamperometric responses of the films were studied. The potential of working electrodes (samples T1-WO<sub>3</sub>, T2-WO<sub>3</sub>, T3-WO<sub>3</sub> and T4-WO<sub>3</sub>) was stepped between  $\pm 0.7$  V (SCE) and the 'J' vs 't' dependence was monitored. Figure 1a-d shows the variation of 'J'-'t' transients for all the samples in 0.05 N H<sub>2</sub>SO<sub>4</sub> electrolyte. After application of  $-0.7$  V (SCE) cathodic current sharply increases, which wanes away with respect to time. This cathodic wave is associated with the coloration process. Whereas, after reversal of the polarity of the applied potential, the anodic current increases



**Fig. 1** Chronoamperometric response of the T1-WO<sub>3</sub>, T2-WO<sub>3</sub>, T3-WO<sub>3</sub> and T4-WO<sub>3</sub> samples. Cathodic current wave is the result of application of  $-0.7$  V (SCE) and anodic current wave is due to application of  $+0.7$  V (SCE) between working electrode and counter electrode for 2 s

sharply, followed by a rapid decay with respect to time. This anodic current wave corresponds to the bleaching process. The coloration and bleaching transients for all the samples differ quite noticeably, with more time being needed for coloration than bleaching. The asymmetric behaviour in current response has been discussed in our previous paper [15].

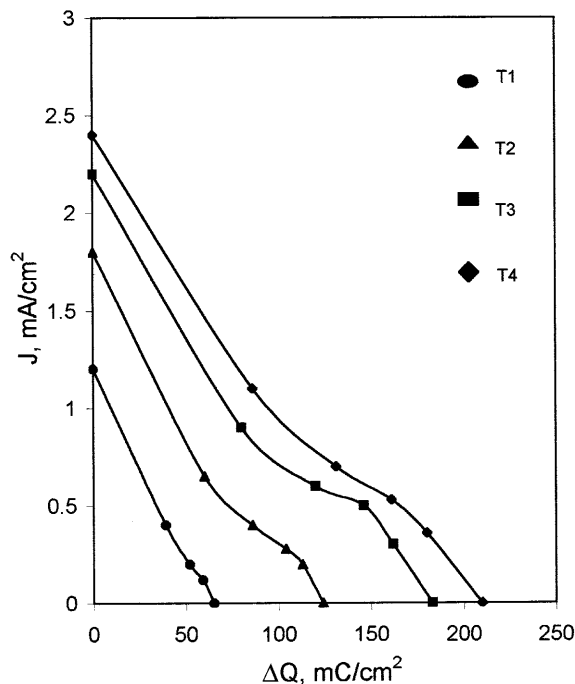
It is manifested that an application of a potential,  $V_a$ , results in transport of H<sup>+</sup> species from the reservoir (electrolyte) to the host (WO<sub>3</sub>) or vice-versa, leading to modulation in optical properties. The transport continues until built-in potential,  $V_{bi}$ , sufficient to counteract ' $V_a$ ' is generated between WE and CE. Since the magnitudes of cathodic and anodic currents vary with respect to the film thickness, as evidenced in Fig. 1, it can be concluded that the amount of passed charge (H<sup>+</sup>) depends on film thickness.

Amount of passed charge during time 't' is calculated as

$$\Delta Q = \int J(t)dt \quad (1)$$

The amount of charge intercalated will be used as a variable, indicating the state of the intercalation electrode. The variation of J with  $\Delta Q$  is obtained from the elimination of 't' from  $\Delta Q$ -(t) and J-(t). The transformation from J-(t) to J- $\Delta Q$  space for all the samples is shown in Fig. 2. The 'y' intercepts give the values of initial current,  $J_o$ , from which an initial device resistance,  $R_o$ , is calculated as

$$R_o = \eta_o/J_o \quad (2)$$



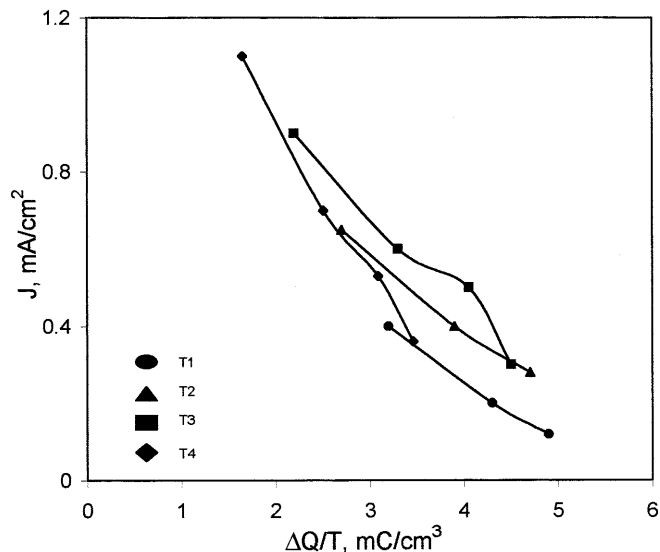
**Fig. 2** Variation of current density ( $J$ ) vs charges  $\Delta Q$  for all the samples

where  $\eta_o = V_a - V_o$ , is the driving force. The 'x' intercepts give estimates of total passed charge  $\Delta Q_f$  into the  $WO_3$  film. Further, the estimation of  $\Delta Q_f$  facilitates in determining the intercalation capacity,  $I_{cap}$ , by normalising  $\Delta Q_f$  with  $V_a$ . These parameters were estimated for all the samples and are given in Table 1. It is clearly observed that the device resistance, total passed charges and  $I_{cap}$  increase with increase in film thickness.

If intercalation occurs uniformly throughout the film thickness,  $T$ , of a given film and if the device resistance is independent of the film thickness, then  $J$ - $\Delta Q$  curves corresponding to films of different thickness should collapse to a single curve, when plotted as a function of the passed charge volume density,  $\Delta Q/T$  [16]. However, in the present case, the device resistance varies with 'T'. This evinces that in a macroscopic sense, intercalation does not occur uniformly throughout the  $WO_3$  film. Therefore 'T' has been treated as an empirical parameter and varied to bring about the 'best collapse'. It is found that  $T = 0.17 \mu m$  brings about the best possible collapse as shown by the variation of  $J$ - $\Delta Q/T$  plot in Fig. 3. This thickness indicates an effective film thickness or intercalatable film thickness.

**Table 1** Estimated values of device resistance ( $R_o$ ), amount of charges passed during intercalation process ( $\Delta Q_f$ ) and intercalation capacity ( $I_{cap}$ ) for the samples with variable thickness

Sample	$R_o, \Omega$	$\Delta Q_f, mC/cm^2$	$I_{cap}, mC/V cm^2$
T1	290	66	94
T2	318	120	177
T3	388	183	261
T4	583	205	292

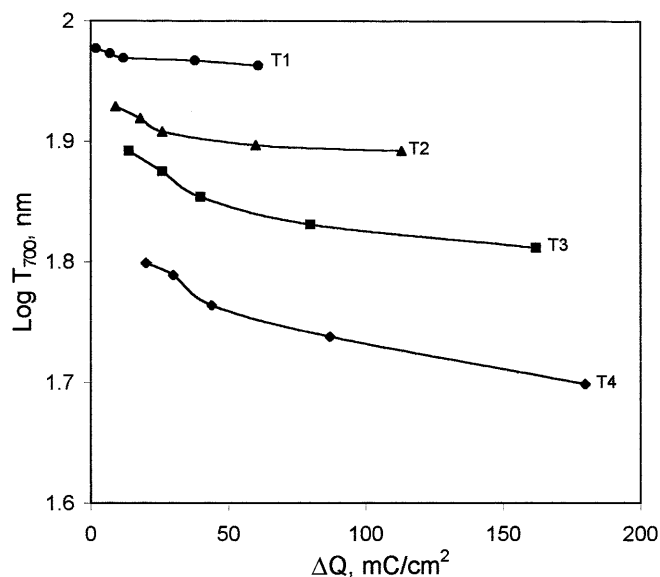


**Fig. 3** Variation of current density ( $J$ ) vs charge volume density,  $\Delta Q/T$  for all the samples

The optical efficiency ( $\xi$ ), the ratio of the change in optical density to the amount of charges passed to bring about the change, has been determined. Figure 4 shows the variation of  $\log T_\lambda$  ( $\lambda = 700 \text{ nm}$ ) vs  $\Delta Q$ , which is non-linear for all the  $WO_3$  samples. This suggests that the optical efficiency is not constant but varies continuously with intercalation. The optical efficiency has been calculated as

$$\xi_\lambda = |\partial \log T_\lambda| \div |\partial \Delta Q| \quad (3)$$

Figure 5 shows the variation of  $\xi_\lambda$  vs  $\Delta Q$ . It is notable that the optical efficiency wanes continuously with increasing intercalation. Similar behaviour of  $\xi_\lambda$  with



**Fig. 4** Variation of  $\log T_\lambda$  ( $\lambda = 700 \text{ nm}$ ) vs  $\Delta Q$  for all the samples

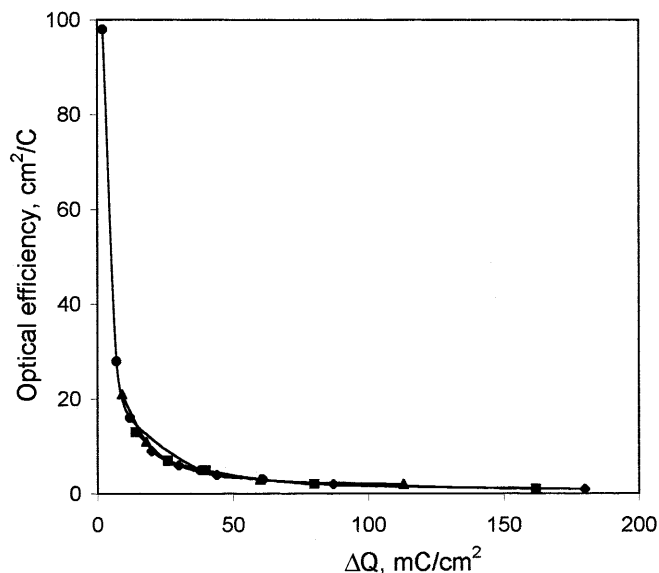


Fig. 5 Variation of optical efficiency vs  $\Delta Q$  for all the samples

intercalation was observed for dip-coated tungsten oxide thin films [17].

### Conclusions

A step potential excitation method was used to characterise ECDs based on ST-WO<sub>3</sub> thin films and determine the parameters useful for the device optimisation and design. At a fixed potential, the amount of

H<sup>+</sup> charges intercalated into the WO<sub>3</sub> depends on film thickness. The magnitudes of device resistance, peak current density and intercalation capacity rely on film thickness. It is concluded that the intercalation of H<sup>+</sup> does not occur uniformly throughout the film. The intercalatable film thickness is estimated to be about 0.17  $\mu\text{m}$ . The optical efficiency wanes continuously with increasing intercalation.

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