

# Molybdenum oxide (MoO<sub>3</sub>) thin film based electrochromic cell characterisation in 0.1M LiClO<sub>4</sub>.PC electrolyte

R. Sivakumar<sup>1</sup>, K. Shanthakumari<sup>2</sup>, A. Thayumanavan<sup>3</sup>, M. Jayachandran<sup>4</sup> and C. Sanjeeviraja\*<sup>1</sup>

Electrochromic thin films of molybdenum oxide (MoO<sub>3</sub>) were prepared on transparent conducting oxide substrates, i.e. fluorine doped tin oxide coated (FTO or SnO<sub>2</sub>:F) glass substrates by electron beam evaporation technique using pure MoO<sub>3</sub> (99.99%) pellets at various substrate temperatures (i.e.  $T_{\text{sub}}$ =room temperature (30°C), 100 and 200°C) under the vacuum of  $1 \times 10^{-5}$  mbar. The room temperature prepared films were further annealed  $T_{\text{anne}}$  at 200 and 300°C for about one hour in the vacuum environment. The electrochemical nature of the films was studied by the cyclic voltammetry technique using a three electrode electrochemical cell in 0.1M LiClO<sub>4</sub>.PC electrolyte. The performance of the films was also tested by making electrochromic cells. The films produced at higher substrate temperature show lesser modulation in the visible spectrum, compared with the films produced at lower temperatures. A maximum colouration efficiency of 66 cm<sup>2</sup> C<sup>-1</sup> was observed in the infrared region for the films prepared at room temperature.

**Keywords:** Smart windows, Molybdenum oxide films, Electrochemical analysis, Electron beam evaporation technique, Colouration efficiency

## Introduction

Electrochromism is well known in semiconducting transition metal oxides. Among the transition metal oxides, molybdenum oxide (MoO<sub>3</sub>) has been found to be a versatile material for electrochromic devices, owing to its excellent electrochromic behaviour.<sup>1</sup> Molybdenum oxide that can undergo reversible lithium intercalation/deintercalation process at ambient temperature is of great technical interest as cathode material for secondary lithium batteries,<sup>2</sup> because it exhibits two dimensional van der Waal bonded layered structure in orthorhombic phase ( $\alpha$ -phase). With ion uptake, the interlayer spacing  $d$  of the MoO<sub>3</sub> host structure changes, usually increasing, but the guest ions are largely accommodated without disrupting the primary Mo–O bonding within the individual MoO<sub>3</sub> type layers.<sup>2</sup> Because the intercalation of MoO<sub>3</sub> is generally accompanied by pronounced changes in colouration and is subject to varying extent of reversibility, this oxide has attracted interest for a number of applications, including

electrochromic devices and optical switching devices.<sup>1</sup> Optical switching devices can be used for windows in a variety of applications where optical and thermal modulation is required. The purpose of this material is to control the flow of light and heat into and out of a window, according to personal comfort or an energy management scheme. The basic property of an optical switching material or smart window is that it shows a large change in optical properties upon a change in light intensity, spectral composition, temperature, electric field or injected charge. Another important feature is that MoO<sub>3</sub> film acts as either a negative or positive photoresist<sup>3</sup> with high contrast capability for focused ion exposure depending on the preparation condition. The intercalation and deintercalation of Li<sup>+</sup> ions in non-aqueous media has been of particular interest, primarily owing to its relation to secondary battery applications.

It is well recognised that the performance of an electrochromic device depends strongly on the technique that is used to prepare the active electrochromic electrode thin film. Apart from the available various preparation techniques of molybdenum oxide, the electron beam evaporation technique is finding ever increasing application in high technology solutions for preparing device quality thin films.<sup>4,5</sup> Establishing optimum parameters or a special technique for thin film preparations may permit films to be prepared with specific microstructures that are relevant to a particular application.<sup>6</sup> Hence the present work has adopted the

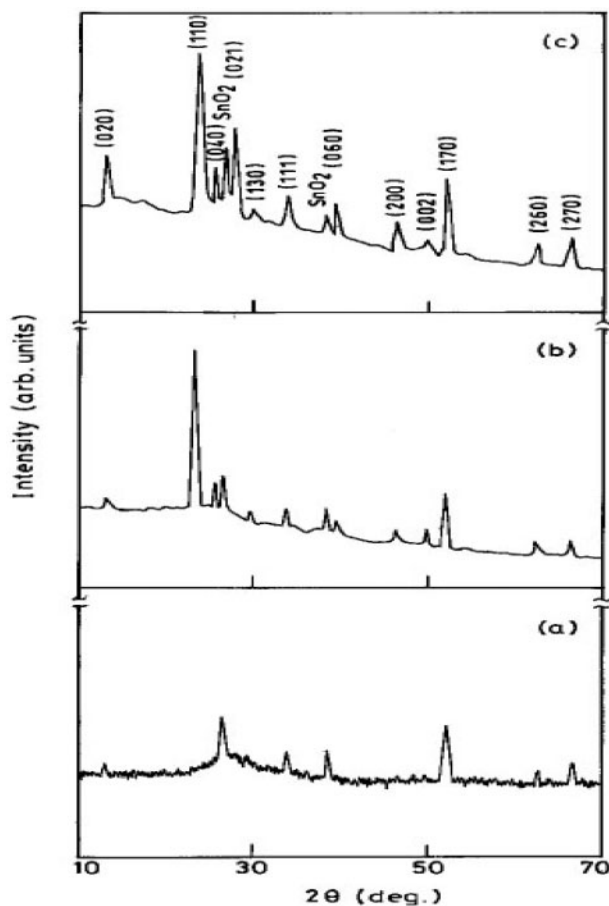
<sup>1</sup>(Formerly Department of Physics, Alagappa University, Karaikudi 630 003, India) Department of Chemical Engineering, National Taiwan University, Taipei 10617, Taiwan

<sup>2</sup>Department of Physics, SASTRA University, Thirumalai Samudram 613 402, India

<sup>3</sup>AVVM Sri Pushpam College, Poondy 613 503, India

<sup>4</sup>ECMS Division, Central Electrochemical Research Institute, Karaikudi 630 006, India

\*Corresponding author, email sanjeeviraja@rediffmail.com



a  $T_{\text{sub}} = \text{RT}$ ; b  $T_{\text{sub}} = 100^\circ\text{C}$ ; c  $T_{\text{sub}} = 200^\circ\text{C}$

1 X-ray diffraction pattern of MoO<sub>3</sub> films deposited on SnO<sub>2</sub>:F substrate at different temperatures

electron beam evaporation technique for the preparation of MoO<sub>3</sub> films. The authors have reported the detailed preparation procedures for MoO<sub>3</sub> films by electron beam evaporation technique and also reported the structural, morphological, compositional and optical properties of MoO<sub>3</sub> films in the authors' previous papers.<sup>4,5,7</sup> The present work describes the detailed characterisation of the electrochromic properties of molybdenum oxide thin film based device by inserting/extracting the Li<sup>+</sup> ions. The colouration/decolouration process in 0.1M LiClO<sub>4</sub>.PC electrolyte is investigated. The effect of substrate temperature and post-annealing temperature on the electrochromic properties of the films were studied. The complete description for the cyclic voltammetry analysis and the construction of electrochromic cell concerning the intercalation/deintercalation of H<sup>+</sup> and K<sup>+</sup> ions is elaborately discussed in the authors' earlier reported works.<sup>8,9</sup>

## Experimental

Thin MoO<sub>3</sub> films were prepared by electron beam evaporation of dry MoO<sub>3</sub> pellets under a chamber pressure of  $1 \times 10^{-5}$  mbar on fluorine doped tin oxide coated glass substrates (FTO or SnO<sub>2</sub>:F) ( $R_{\text{sh}} \approx 15 \Omega^{-2}$ ) at different substrate temperatures  $T_{\text{sub}}$  like 30°C (room temperature, RT), 100 and 200°C. Later on, the MoO<sub>3</sub> films deposited at room temperature were subsequently annealed for one hour in vacuum atmosphere  $T_{\text{anne}}$  at 200 and 300°C. The electrochemical analysis was

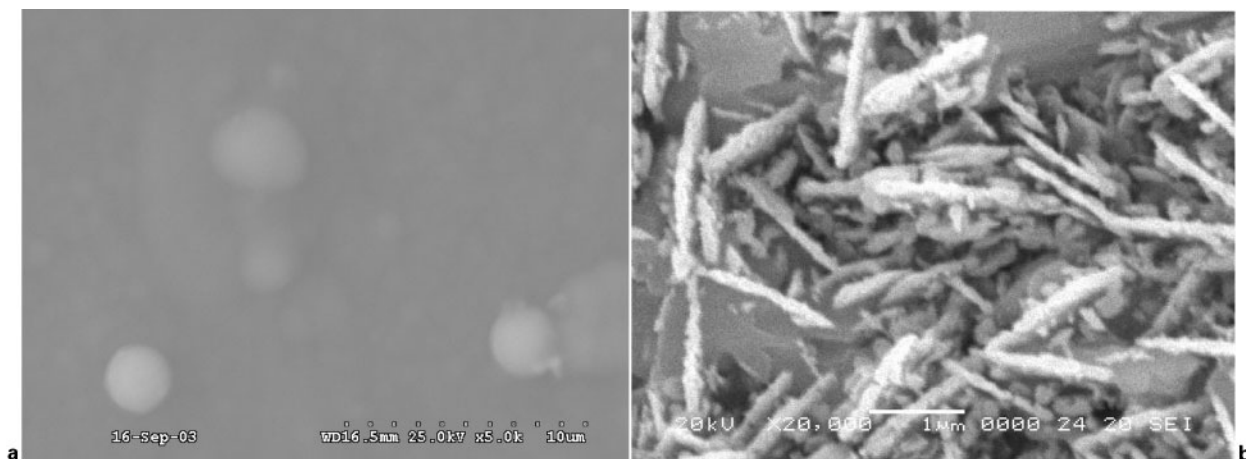
performed using an EG&G Princeton applied research 273A potentiostat. During the electrochemical measurement using cyclic voltammetry technique, the working electrode was the FTO bearing electrochromic oxide films (MoO<sub>3</sub>), while counter electrode was the platinum foil. Saturated calomel electrode (SCE) was used as the reference electrode (RE). Whereas in the electrochromic cell analysis, the FTO plate was used as the counter electrode and the platinum wire was acting as pseudo-RE and was placed at equidistant between the working electrode and counter electrode. In both the analysis, 0.1M LiClO<sub>4</sub> in propylene carbonate (PC) was used as the electrolyte. The optical transmittance of coloured and bleached MoO<sub>3</sub> films was carried out by Hitachi-3400 UV-Vis-NIR spectrophotometer. The infrared (IR) investigations of the films were performed by using a Perkin-Elmer Paragon Fourier transform infrared (FTIR) spectrometer (model: 500) in the range 4000–400 cm<sup>-1</sup>.

## Results and discussion

### Structural and morphological studies

The authors' earlier work,<sup>4,5,7</sup> has reported the results of systematic characterisation on the change in structural, morphological, compositional and optical properties of electron beam evaporated MoO<sub>3</sub> films with different substrate and annealing temperatures. Generally, the electrochromic performance of MoO<sub>3</sub> films can be mainly depending on its structural and surface morphological properties. Hence, in order to correlate the present work of electrochemical properties of MoO<sub>3</sub> films, some results of authors' earlier work<sup>5</sup> have been presented. Figure 1a–c shows the XRD pattern of MoO<sub>3</sub> films deposited on SnO<sub>2</sub>:F substrate at RT, 100 and 200°C respectively. It has been clearly observed that the crystallinity of films is mainly dependent on the substrate temperature. The XRD pattern of Fig. 1a shows the moderately developed crystallinity of RT deposited films with the peaks along (020), (111), (170), (260) and (270) directions. On the other hand, the films deposited at 100°C (Fig. 1b) have the crystalline peaks along (020), (110), (040), (130), (111), (060), (200), (002), (170), (260) and (270) directions. The predominant peak is observed along the (110) orientation. Whereas in the case of MoO<sub>3</sub> films deposited at 200°C indicates the improved crystallinity with increased intensity of the predominant peak along (110) direction and other peaks along (020), (040), (021), (130), (111), (060), (200), (002), (170), (260), and (270) orientations. The standard XRD data (JCPDS card no. 05-0508) shows that the presence of predominant 100% peak along (021) and 82% peak along (110) corresponds to fully crystallised MoO<sub>3</sub> films.

In the present study, it has been observed that the lesser intensity of crystalline peaks in the XRD pattern for the RT deposited film (Fig. 1a) and no predominant peak (110) and (021) were observed. This shows their less crystalline nature. On comparing the integral peak intensities of these three films with respect to the standard XRD peak intensity, the crystallinity of the films were found as 19, 52 and 85% for RT, 100 and 200°C deposited films respectively, which clearly indicates the lesser crystalline nature of room temperature prepared films. The crystalline SnO<sub>2</sub>:F substrate promotes specific alignment of the arriving atoms and



a  $T_{\text{sub}} = \text{RT}$ ; b  $T_{\text{sub}} = 200^\circ\text{C}$

## 2 Images (SEM) of MoO<sub>3</sub> films deposited on SnO<sub>2</sub>:F substrate at different temperatures

enhances the crystallinity of the films. At higher deposition temperatures, the atomic, molecular or ionic species of MoO<sub>3</sub> impinging on the substrate surface acquire a large thermal energy and hence a large mobility. As a result, a large number of nucleus are formed which coalesce at elevated temperature to form a continuous film with large grains on the substrate. The scanning electron microscopic image also suggested that the lesser crystalline nature of RT deposited (Fig. 2a) MoO<sub>3</sub> films than the higher substrate temperature prepared films (i.e. 200°C; Fig. 2b). The surface morphology of MoO<sub>3</sub> films deposited at RT (Fig. 2a) shows the very smooth surface without any fragmentation features, however, few small spherical grains are observed, which enumerated the less crystalline nature of the films. On the other hand the well crystalline nature of MoO<sub>3</sub> films have been clearly identified from the dense and needlelike crystallite morphology (Fig. 2b) for the films deposited at 200°C. This inference is independently corroborated by the authors' XRD analysis.

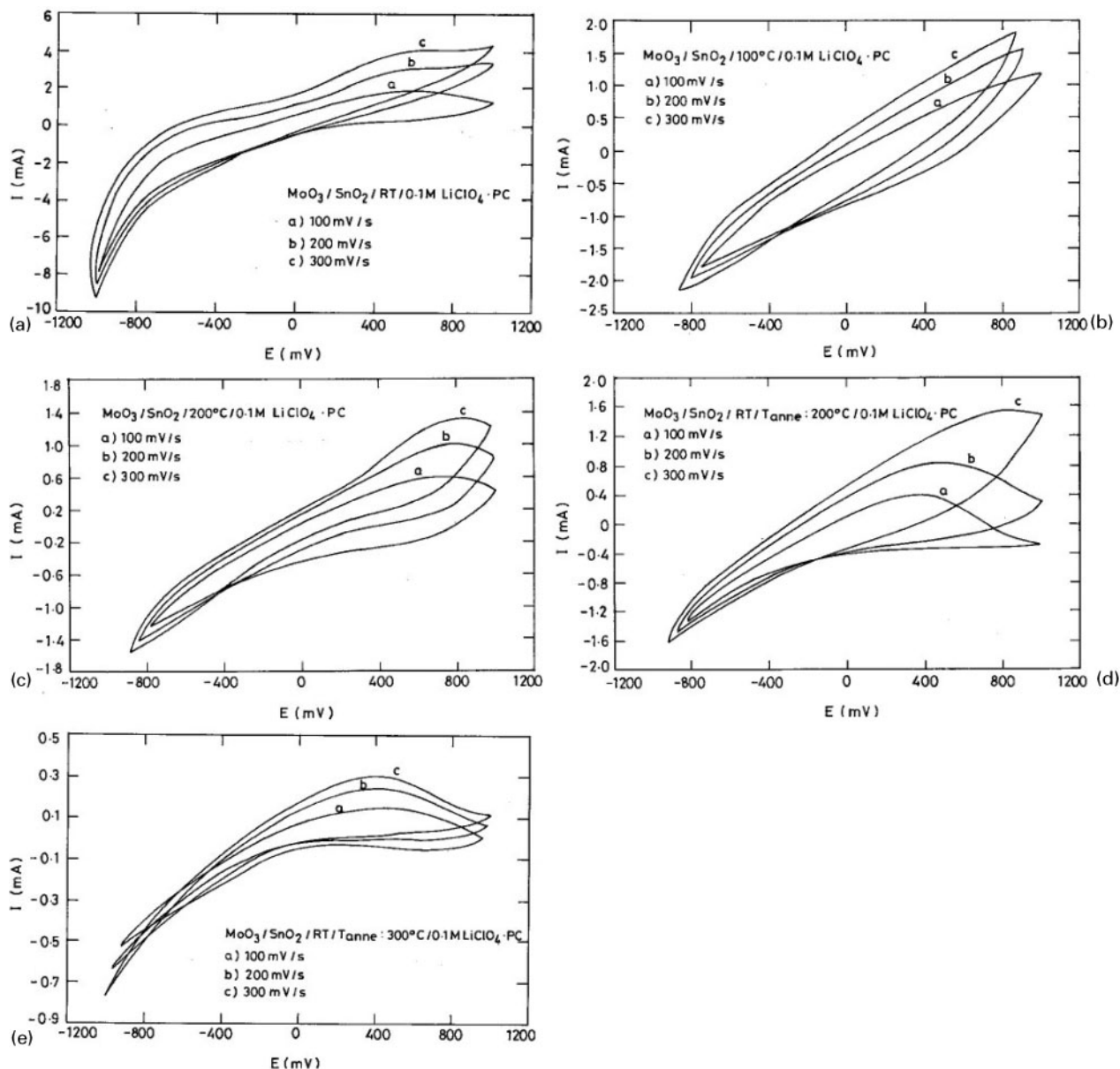
### Cyclic voltammetry studies

This investigation has concentrated on the electrochemical analysis of MoO<sub>3</sub> films in 0.1M LiClO<sub>4</sub>.PC electrolyte using the three electrode cyclic voltammetry technique and also by constructing the electrochromic cell. The authors' very recent work,<sup>8,9</sup> has discussed in detail about the electrochemical analysis and the construction details of the electrochromic cell. The process of Li<sup>+</sup> ion intercalation and deintercalation in MoO<sub>3</sub> films was noted during the cycling of the applied potential ranging from -1.0 to +1.0 V<sub>SCE</sub> at different sweep rates such as 100, 200 and 300 mV s<sup>-1</sup>. To observe the reversibility, cathodic scanning was started from +1.0 to -1.0 V<sub>SCE</sub> during which scan colouration was observed and then the bleaching process was observed on reversing the potential from -1.0 to +1.0 V<sub>SCE</sub>. The colouration process of the films occurred in the negative potential region and the bleaching mechanism was associated with the positive potential scan. The current resulting from these scan rates were measured during the colouration and bleaching process and are denoted as cathodic spike current  $i_{\text{pc}}$  and anodic peak current  $i_{\text{pa}}$  respectively. This is attributed mainly to the reversible electrochemical

process involving colouration/bleaching of MoO<sub>3</sub> film and governed by the mixed electronic and ionic insertion/extraction of electrons (e<sup>-</sup>) and Li<sup>+</sup> ions leading to the formation of 'molybdenum bronze' according to the reaction<sup>10</sup>



The recorded cyclic voltammograms in 0.1M LiClO<sub>4</sub>.PC electrolyte for MoO<sub>3</sub> films deposited at different substrate temperatures, i.e. 30, 100, 200°C, annealed films at 200 and 300°C are shown in Fig. 3a-e respectively. While the cathodic peaks are ill resolved, the anodic peaks are observed to be prominent to some extent and found centered in the potential range between +400 to +800 mV. The observed efficient colouration  $\rightleftharpoons$  bleaching mechanism of MoO<sub>3</sub> films confirms that the effective electrochromic nature of the films associated with the electrochemical intercalation and deintercalation of Li<sup>+</sup> ions and electrons into MoO<sub>3</sub> lattice. The diffusion coefficient of Li<sup>+</sup> ions  $D_{\text{Li}^+}$  was calculated by the Randles-Sevcik equation<sup>1</sup> and they are listed in Table 1 along with different electrochemical parameters. The values of  $D_{\text{Li}^+}$  are found to change between  $4.05 \times 10^{-12}$  and  $8.65 \times 10^{-9}$  cm<sup>2</sup> s<sup>-1</sup> with respect to substrate temperature and annealing temperature. It is observed from the cyclic voltammetry analysis that the magnitudes of both  $i_{\text{pc}}$  and  $i_{\text{pa}}$  are high in the films prepared at room temperature than the higher substrate temperature prepared films and also the annealed films. This could be explained that the lower substrate temperature favours the irregular arrangement of atoms and also minimise the extent of crystallinity of the films. Hence the intercalated ions are favoured to move fast into and out of the films which produces higher magnitudes in anodic and cathodic currents in these amorphous like films. Such a film morphology imparts a porous structure to the room temperature and unannealed MoO<sub>3</sub> films. This porous matrix contains a large number of Bronsted acid sites, i.e. a molecular entity capable of donating a proton to a base or the corresponding chemical species, which allow enhanced Li<sup>+</sup> exchange reactions.<sup>11</sup> These reactions seem to predominate and overwhelm the redox changes leading to the formation of coloured Mo<sup>5+</sup> sites. At the same time, when the disordered films turn to crystalline ones, the structure not only becomes ordered but also changes



a  $T_{\text{sub}}=\text{RT}$ ; b  $T_{\text{sub}}=100^\circ\text{C}$ ; c  $T_{\text{sub}}=200^\circ\text{C}$ ; d  $T_{\text{anne}}=200^\circ\text{C}$ ; e  $T_{\text{anne}}=300^\circ\text{C}$

### 3 Cyclic voltammograms of MoO<sub>3</sub> films prepared at different conditions, cycled in 0.1M LiClO<sub>4</sub>.PC electrolyte

**Table 1** Electrochemical parameters of MoO<sub>3</sub> films associated with intercalation and deintercalation of Li<sup>+</sup> ions cycled in 0.1M LiClO<sub>4</sub>.PC electrolyte

Sample	Scan rate $v$ , $\text{mV s}^{-1}$	Cathodic spike current $i_{\text{pc}}$ , mA	Anodic peak current $i_{\text{pa}}$ , mA	Diffusion coefficient $D$ , $\text{cm}^2 \text{s}^{-1}$	
				For $i_{\text{pc}}$	For $i_{\text{pa}}$
MoO <sub>3</sub> /RT	100	8.00	1.80	$8.65 \times 10^{-9}$	$4.37 \times 10^{-10}$
	200	8.60	3.50	$4.99 \times 10^{-9}$	$8.27 \times 10^{-10}$
	300	9.30	4.50	$3.89 \times 10^{-9}$	$9.12 \times 10^{-10}$
MoO <sub>3</sub> /100°C	100	1.70	1.20	$3.90 \times 10^{-10}$	$1.94 \times 10^{-10}$
	200	2.00	1.50	$2.70 \times 10^{-10}$	$1.52 \times 10^{-10}$
	300	2.10	1.80	$1.98 \times 10^{-10}$	$1.45 \times 10^{-10}$
MoO <sub>3</sub> /200°C	100	1.20	0.60	$1.94 \times 10^{-10}$	$4.86 \times 10^{-11}$
	200	1.40	1.00	$1.32 \times 10^{-10}$	$6.75 \times 10^{-11}$
	300	1.50	1.30	$1.01 \times 10^{-10}$	$7.61 \times 10^{-11}$
MoO <sub>3</sub> /RT/ $T_{\text{anne}}$ : 200°C	100	1.30	0.40	$2.28 \times 10^{-10}$	$2.16 \times 10^{-11}$
	200	1.50	0.80	$1.52 \times 10^{-10}$	$4.32 \times 10^{-11}$
	300	1.60	1.50	$1.15 \times 10^{-10}$	$1.01 \times 10^{-10}$
MoO <sub>3</sub> /RT/ $T_{\text{anne}}$ : 300°C	100	0.52	0.15	$3.65 \times 10^{-11}$	$3.04 \times 10^{-12}$
	200	0.62	0.24	$2.59 \times 10^{-11}$	$3.89 \times 10^{-12}$
	300	0.77	0.30	$2.67 \times 10^{-11}$	$4.05 \times 10^{-12}$

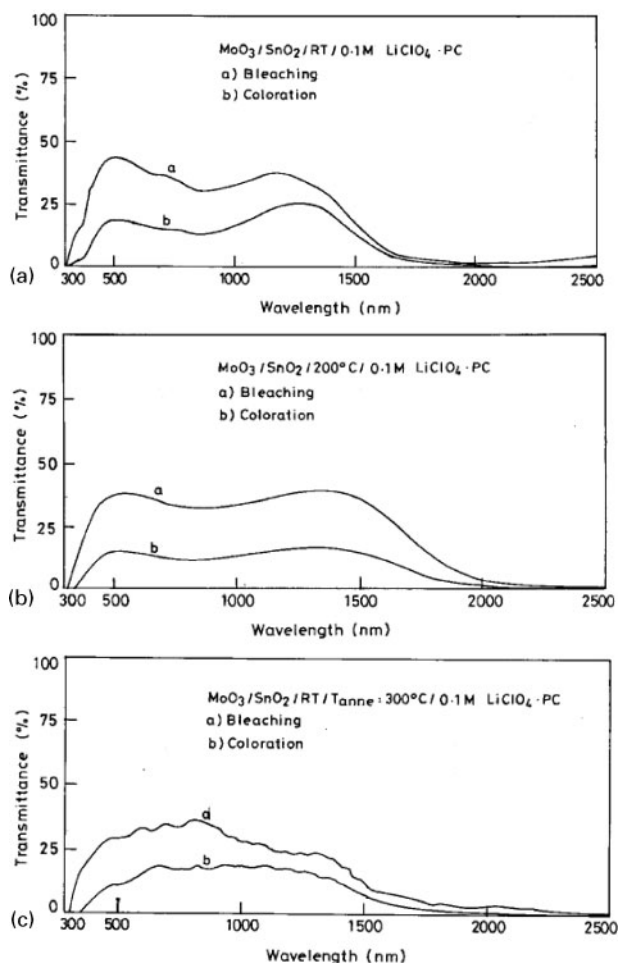
its electronic structure, which restricts the rate of insertion and extraction of ions in the films due to a reduction in the number of Bronsted acid sites. In the crystalline films, the extent of colouration/decolouration would be slightly reduced because:

- (i) it is difficult for the counter ions to enter the crystallites
- (ii) difference in morphology: the film becomes more dense and harder due to which the movement of the counter ions are slowed down.

Guerfi *et al.*<sup>12</sup> observed a reduction in the electrochromic performance for their electrodeposited MoO<sub>3</sub> films when increasing the annealing temperature beyond 260 up to 450°C and cycled in 1M LiClO<sub>4</sub>.PC electrolyte. Julien *et al.*<sup>13,14</sup> studied the Li<sup>+</sup> ion intercalation into MoO<sub>3</sub> films made by flash evaporation and their results showed the  $D_{Li^+}$  values between 10<sup>-12</sup> and 5 × 10<sup>-12</sup> cm<sup>2</sup> s<sup>-1</sup>. The  $D_{Li^+}$  values for bulk α-MoO<sub>3</sub> electrode is reported to be in the range 10<sup>-11</sup>–10<sup>-10</sup> cm<sup>2</sup> s<sup>-1</sup>.<sup>15</sup> A comparative analysis of these values reveals that the  $D_{Li^+}$  values observed for the electron beam evaporated MoO<sub>3</sub> films, in the present work, are in good agreement with the values for the MoO<sub>3</sub> electrodes in thin film or bulk form prepared by different techniques. In addition, the observed cyclic voltammograms in the present work are consistent with the earlier reports,<sup>12–14</sup> where the reversibility of MoO<sub>3</sub> films is confirmed. Hence, the observed performance of the MoO<sub>3</sub> films during the electrochemical analysis emphasised that these films may act as one of the best working electrodes in efficient electrochromic devices.

### Electrochromic cell analysis

The MoO<sub>3</sub> films deposited on FTO substrates at conditioned  $T_{sub}=RT$ ,  $T_{sub}=200^\circ C$  and  $T_{anne}=300^\circ C$ , have been used as the working electrodes in electrochromic cell (0.1M LiClO<sub>4</sub>.PC electrolyte). In this process the applied potential lies in the range between -1.0 and +1.0 V with respect to Pt (pseudo-RE). When a negative external potential (-1.0 V) was applied to the cell, a blue colour bronze was observed by the insertion of electrons and Li<sup>+</sup> ions simultaneously into the MoO<sub>3</sub> film matrix. The reverse happens for the bleaching process (for positive potential, +1.0 V). The optical transmittance of the coloured and bleached films was studied in the wavelength range 300–2500 nm. Samples were removed from the electrolyte for spectral transmittance measurements, but the spectra were complete within minutes of the colouration being completed, so self-bleaching<sup>16</sup> of the films was not expected to be a problem in this work. Figure 4a–c shows the optical transmittance spectra of coloured and bleached films deposited at  $T_{sub}=RT$ ,  $T_{sub}=200^\circ C$  and  $T_{anne}=300^\circ C$  respectively. The insertion of Li<sup>+</sup> ions changes the transmissivity from near UV up to the near infrared range and the reversible colour of the film from transparent to blue. In addition, the observed optical transmittance spectra possess higher optical modulation in the visible region and lower optical modulation in the infrared region. From these marked variations between the transmission spectra of coloured and bleached states, it is observed that all the films show good electrochromic colouration. The transmittance in the visible range has been found to be significantly different for the films in bleached and coloured states though the shape has no apparent change. Further, the coloured MoO<sub>3</sub> films are



a  $T_{sub}=RT$ ; b  $T_{sub}=200^\circ C$ ; c  $T_{anne}=300^\circ C$

4 Optical transmittance spectra of MoO<sub>3</sub> films in ECD cells, coloured and bleached in 0.1M LiClO<sub>4</sub>.PC electrolyte

showing lower near infrared characteristics. This would benefit to utilise these films in smart window applications. However, the films produced at 200°C exhibit a lower transmission in the visible region compared to the film deposited at  $T_{sub}=RT$ . The annealed films ( $T_{anne}=300^\circ C$ ) also show a lower range in their visible region. Light scattering due to large crystal grains is thought to be the reason for such low transmittance and its electrochromic properties may be influenced by the reaction between FTO and MoO<sub>3</sub> films.

It can be explained that the higher substrate temperature and post-annealing temperature is one of the key parameters which control the microstructure of the films as shown in Fig. 2. In addition, the increasing substrate and annealing temperatures can improve the crystallinity of MoO<sub>3</sub> film (Fig. 1), however, its Li<sup>+</sup> ion capacity is affected, probably owing to the microstructure change of the film. Further, it was observed that the increase in surface roughness of the films with increasing substrate and annealing temperatures using the atomic force microscopic studies,<sup>7</sup> which indicates the dense microstructure of MoO<sub>3</sub> films leading to the enhanced crystallisation. This dense microstructure obstructs the movement of Li<sup>+</sup> ions into and out of the films. Therefore, the charge injected into the crystalline film is much less than into the amorphous or less crystalline film, and both the Li<sup>+</sup> intercalation/deintercalation reaction and Mo<sup>6+</sup> ⇌ Mo<sup>5+</sup> redox reaction lead to

film colouration/decolouration process. Hence, the crystalline films produce lesser performance during the electrochromic analysis.

From these optical transmittance spectra, the optical density  $OD$  of MoO<sub>3</sub> films at a particular wavelength  $\lambda$  was calculated by using the expression<sup>17</sup>

$$OD = \log\left(\frac{T_{b\lambda}}{T_{c\lambda}}\right) \quad (2)$$

where  $T_{b\lambda}$  is the transmittance in the bleached state (deintercalation) and  $T_{c\lambda}$  is the transmittance in the coloured state (intercalation). The colouration efficiency (CE) is defined as below

$$CE = \frac{OD_{\lambda}}{Q_{in}} (\text{cm}^2 \text{C}^{-1}) \quad (3)$$

where  $Q_{in}$  ( $\text{mC cm}^{-2}$ ) is the charge injected during the colouration cycle. The  $Q_{in}$  was calculated by integrating the current density of the colouration cycle between the starting and ending time of each period according to the following equation

$$Q = \int_{t_1}^{t_2} j(t) dt \quad (4)$$

The optical density values are found to vary between 0.20 and 0.44 and the colouration efficiency value fluctuates between 15 and 66  $\text{cm}^2 \text{C}^{-1}$  and are summarised in Table 2. The maximum colouration efficiency of 66  $\text{cm}^2 \text{C}^{-1}$  was observed for the room temperature prepared films. In order to have a better insight on the results of electrochromic performance of the films with crystallinity, now the percentage of crystallinity has been compared with the colouration efficiency. This reveals the maximum colouration efficiency of 66  $\text{cm}^2 \text{C}^{-1}$  for the RT deposited films whose crystallinity is 19%. It can be mentioned here that, the comparison of the optical transmittance modulation values and diffusion coefficient  $D$  values are not sufficient to evaluate the performance of electrochromic cells, because it does not take into account the variations of the injected charge per area necessary to achieve the reported colouration efficiency (CE) values. It is important to emphasise that the CE value characterises the whole cell's performance, and not only that of the electrolyte. Furthermore, it is a technologically important parameter that is not always straightforward to interpret because it is typically strongly influenced by the working electrode (MoO<sub>3</sub> thin film) preparation method, the ensuing microstructure, the amount and way of charge insertion.<sup>18</sup> Hence it could be concluded that the electrochromic response of MoO<sub>3</sub> films is strongly affected by the crystallinity, grain size, porosity and possible contents of oxygen in the films, influenced by substrate temperatures and annealing conditions

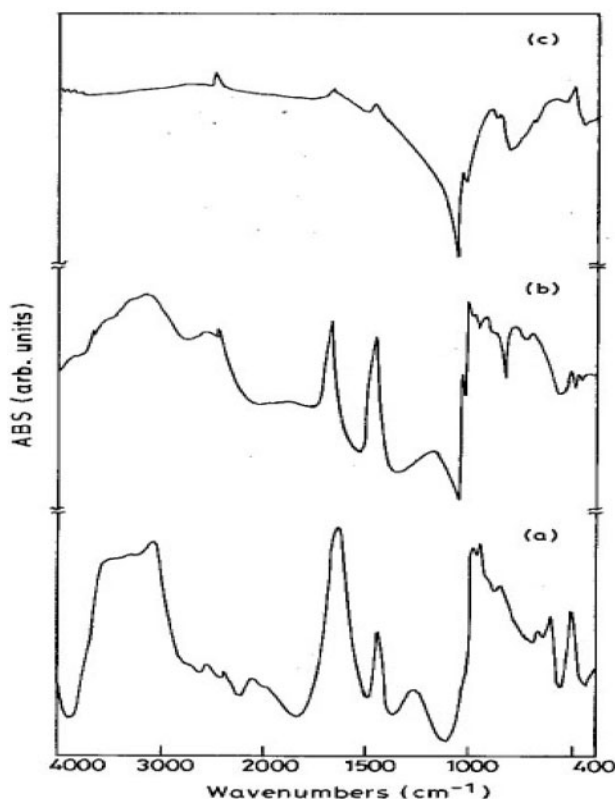
adopted during film preparation, and the availability of Li<sup>+</sup> ion for migration to the electrochromic film. The authors have reported earlier<sup>4,5,7</sup> the results on the investigations of the above require specific experiments, which are consistent with the performance of the present electrochromic cell. In addition, the possible role of the content of oxygen ion in MoO<sub>3</sub> films and their colouration mechanism can be discussed as follows: it can be mentioned here that, the formation of oxygen ion vacancies  $V_{\text{O}}^{\cdot\cdot}$  in MoO<sub>3</sub> films with increasing substrate and annealing temperatures was corroborated independently by XPS studies.<sup>8</sup> These vacancies are capable of capturing one or two electrons and form  $V_{\text{O}}^{\cdot}$  and  $V_{\text{O}}$  centres respectively.<sup>19</sup> Since the most apparent trapping positions for electrons are these ion vacancies, it is certain that the colour centres in MoO<sub>3</sub> are formed as a result of free electrons being trapped in them. The observed colouration of MoO<sub>3</sub> can be attributed to the filling up of  $V_{\text{O}}^{\cdot\cdot}$  by electrons associated with the acceptor levels and also to the ionisation of the  $V_{\text{O}}$  centres, whose level is close to the conduction band, which increases the number of the  $V_{\text{O}}^{\cdot}$  centres. The ionisation of  $V_{\text{O}}^{\cdot}$  centres is intensely favoured in higher substrate temperature and/or annealed films, a fact that is confirmed from the significant reduction in transmittance values for higher substrate temperature ( $T_{\text{sub}}=200^{\circ}\text{C}$ ; Fig. 4b) and annealed ( $T_{\text{anne}}=300^{\circ}\text{C}$ ; Fig. 4c) MoO<sub>3</sub> films. Kitao and Yamada<sup>20</sup> evaluated the colouration efficiency of MoO<sub>3</sub> films at different wavelength ranges and their magnitudes are in the range 40–80  $\text{cm}^2 \text{C}^{-1}$ . It can be mentioned here that Belanger and Laperriere<sup>21</sup> reported that the CE of MoO<sub>3</sub> films are 45 and 30  $\text{cm}^2 \text{C}^{-1}$ . In addition, it has been reported<sup>22</sup> that the colouration efficiency of MoO<sub>3</sub> films decreases with increasing the substrate temperature and/or annealing temperature, which is more consistent with the authors' results.

### Studies of FTIR

In order to identify the bonding assignments of coloured/bleached MoO<sub>3</sub> films cycled in 0.1M LiClO<sub>4</sub>.PC electrolyte, the IR absorption spectroscopic analysis has been carried out using the Perkin-Elmer Paragon 500 FTIR spectrometer. Figure 5 shows the IR absorption spectra of intercalated/deintercalated MoO<sub>3</sub> films prepared at conditions  $T_{\text{sub}}=\text{RT}$ ,  $T_{\text{sub}}=200^{\circ}\text{C}$  and  $T_{\text{anne}}=300^{\circ}\text{C}$ . The observed peaks around 551–447  $\text{cm}^{-1}$  are related to the typical stretching modes of Mo–O of orthorhombic structure ( $\alpha\text{-MoO}_3$ ), which is consistent with the result of Julien *et al.*<sup>23</sup> In addition, the group of peaks between 650 and 550  $\text{cm}^{-1}$  could be observed as same as that of MoO<sub>3</sub> powder.<sup>24</sup> The peak corresponding to Mo–O bond vibrations in orthorhombic modification of MoO<sub>3</sub> was observed at  $\sim 833 \text{ cm}^{-1}$ .<sup>25</sup> The observed peak at about 942–964  $\text{cm}^{-1}$  is assigned to the Mo and single Mo coordinated oxygen stretching.<sup>26</sup> Also it is clearly seen

**Table 2** Evaluated ECD cell parameters of MoO<sub>3</sub> films in 0.1M LiClO<sub>4</sub>.PC electrolyte

Sample	Optical density (OD)		Colouration efficiency (CE) $\text{cm}^2 \text{C}^{-1}$	
	$\lambda \approx 633 \text{ nm}$	$\lambda \approx 1033 \text{ nm}$	at $\lambda \approx 633 \text{ nm}$	$\lambda \approx 1033 \text{ nm}$
MoO <sub>3</sub> /RT	0.28	0.37	50	66
MoO <sub>3</sub> /200°C	0.41	0.44	41	44
MoO <sub>3</sub> /RT/ $T_{\text{anne}}$ : 300°C	0.20	0.30	15	22



a  $T_{\text{sub}}=\text{RT}$ ; b  $T_{\text{sub}}=200^{\circ}\text{C}$ ; c  $T_{\text{anne}}=300^{\circ}\text{C}$

5 Fourier transform infrared spectra of cycled MoO<sub>3</sub> films in 0.1M LiClO<sub>4</sub>.PC electrolyte

that this peak is shifted towards higher wave number region ( $\sim 995\text{ cm}^{-1}$ ) for higher substrate temperature and annealing temperature, which suggests the stronger types of Mo–O and Mo–O–Mo bonding being developed.<sup>19</sup> The colouration peak was observed at  $\sim 3700\text{ cm}^{-1}$ . The observed Mo–O and Mo–O–Mo bond peaks revealed the stability of the films in the electrochemical analysis.

## Conclusions

This paper has presented a systematic investigation on the electrochromic properties of MoO<sub>3</sub> films by cyclic voltammetric studies and electrochromic cell analysis. The effect of substrate temperature at which the films were prepared and the influence of the post-annealing treatment on the electrochromic properties were studied. The maximum colouration efficiency of  $66\text{ cm}^2\text{ C}^{-1}$  was observed in the IR region for the films prepared at room temperature whose crystallinity is 19%. Further, the colouration efficiency is found decreasing with the

increasing substrate temperature. As observed from these results, the MoO<sub>3</sub> films deposited at room temperature are found to exhibit better electrochromic performance and colouration efficiency than those films deposited and annealed at higher temperatures. Hence, it can be concluded that the electrochromic performance of the electron beam evaporated MoO<sub>3</sub> films are strongly dependent on their crystallinity which also depend on the preparative conditions like the substrate temperature and the post-annealing temperatures.

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