

# Intercalation studies on electron beam evaporated MoO<sub>3</sub> films for electrochemical devices

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## Abstract

Now-a-days a large number of extensive research has been focused on electrochromic oxide thin films, owing to their potential applications in smart windows, low cost materials in filters, low cost electrochemical devices and also in solar cell windows. Among the varieties of electrochromic transition metal oxides, the molybdenum oxide (MoO<sub>3</sub>) and tungsten oxide (WO<sub>3</sub>), form a group of predominant ionic solids that exhibit electrochromic effect. The electrochromic response of these materials are aesthetically superior to many other electrochromic materials, because WO<sub>3</sub> and MoO<sub>3</sub> absorb light more intensely and uniformly. In the present case, we have discussed about the electrochromic behaviour of electron beam evaporated MoO<sub>3</sub> films. Moreover, the MoO<sub>3</sub> film can also be used as a potential electro-active material for high energy density secondary lithium ion batteries; because it exhibits two-dimensional van der Waals bonded layered structure in orthorhombic phase. The films were prepared by evaporating the palletized MoO<sub>3</sub> powder under the vacuum of the order of  $1 \times 10^{-5}$  mbar. The electrochemical behaviour of the films was studied by intercalating/deintercalating the K<sup>+</sup> ions from KCl electrolyte solutions using three electrode electrochemical cell by the cyclic-voltammetry technique. The studies were carried out for different scanning rates. The films have changed their colour as dark blue in the colouration process and returns to the original colour while the bleaching process. The diffusion coefficient values (*D*) of the intercalated/deintercalated films were calculated by Randle's Servik equation. The optical transparency of the coloured and bleached films was studied by the UV–Vis–NIR spectrophotometer. The change in bonding assignment of the intercalated MoO<sub>3</sub> films was studied by FTIR spectroscopic analysis. A feasible study on the effect of substrate temperatures and annealing

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temperatures on optical density (OD) and colouration efficiency of the films were discussed and explored their performance for the low cost electrochemical devices.

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## 1. Introduction

The transition-metal oxides constitute a very interesting group of semiconducting material because of their technological advantages for application in the field of micro electronics [1] and display systems [2]. Among these materials, molybdenum oxide (MoO<sub>3</sub>)-derived materials have received increasing attention in recent years due to their potential use in charge-density wave conductors [3], optical materials [4] and electrochemical devices [5]. Concerning the MoO<sub>3</sub> used in these applications, there is a fundamental interest to fabricate layered structure of orthorhombic symmetry MoO<sub>3</sub> ( $\alpha$ -phase) with desired chemical stoichiometry and crystallinity. In response to this wide range of application, various preparation techniques have been developed and investigated for the host material MoO<sub>3</sub> [6–8]. In particular, physical properties of MoO<sub>3</sub> such as high volatility have been utilized in thin film growth by vacuum evaporation [9,10]. Furthermore, electron beam evaporation technique [11] has also been investigated in MoO<sub>3</sub> thin film fabrication. Very recently, authors have reported the growth of layered orthorhombic phase electrochromic MoO<sub>3</sub> films by electron beam evaporation technique [12]. The sequential characterization studies like structural, surface morphological, optical, compositional, electrochemical and electrochromic device characterization on electron beam evaporated MoO<sub>3</sub> films have been studied and reported [12–15].

In this work, the effects of substrate temperature ( $T_{\text{sub}}$ ) and annealing temperature ( $T_{\text{anne}}$ ) on electrochromic properties of electron beam-evaporated molybdenum oxide have been reported.

## 2. Experimental

Thin films were deposited by electron beam evaporation technique on fluorine-doped tin oxide-coated glass substrates (FTO or SnO<sub>2</sub>:F) at different substrate temperatures like 30 (room temperature), 100 and 200 °C. The ablated material of MoO<sub>3</sub> pellets were evaporated by means of resultant electron beam produced from tungsten filament of the electron gun. The films were prepared under the vacuum of the order of about  $1 \times 10^{-5}$  mbar. The films deposited at 30 °C were further annealed at 200 and 300 °C.

The electrochromic properties of the films were investigated on a three-electrode electrochemical cell with a platinum wire as the counter electrode and saturated calomel electrode (SCE) as the reference electrode using an EG & G Model 273A scanning potentiostat. The molybdenum oxide film, as the working electrode, was electrochemically cycled in 0.05 and 0.1 M KCl electrolyte solution. Optical measurements were made with a Hitachi-3400 UV–Vis–NIR spectrophotometer. All spectra were taken over the wavelength range 300–2500 nm. In order to identify the bonding assignment of intercalated/deintercalated MoO<sub>3</sub> films cycled in 0.1 M KCl electrolyte solutions, the IR

absorption spectroscopic analysis has been carried out using the Perkin Elmer-make Paragon 500 FTIR spectrometer.

### 3. Results and discussion

#### 3.1. Electrochromic properties and electrochemical device results

In our previous work [12–15], we showed by XRD measurements, the  $\text{MoO}_3$  films have orthorhombic phase. Also the layered nature of films was identified from the SEM and AFM analysis. The film purity and stoichiometric nature of the films were confirmed from the XPS study. The electrochromic performance of  $\text{MoO}_3$  films and their chemical stability

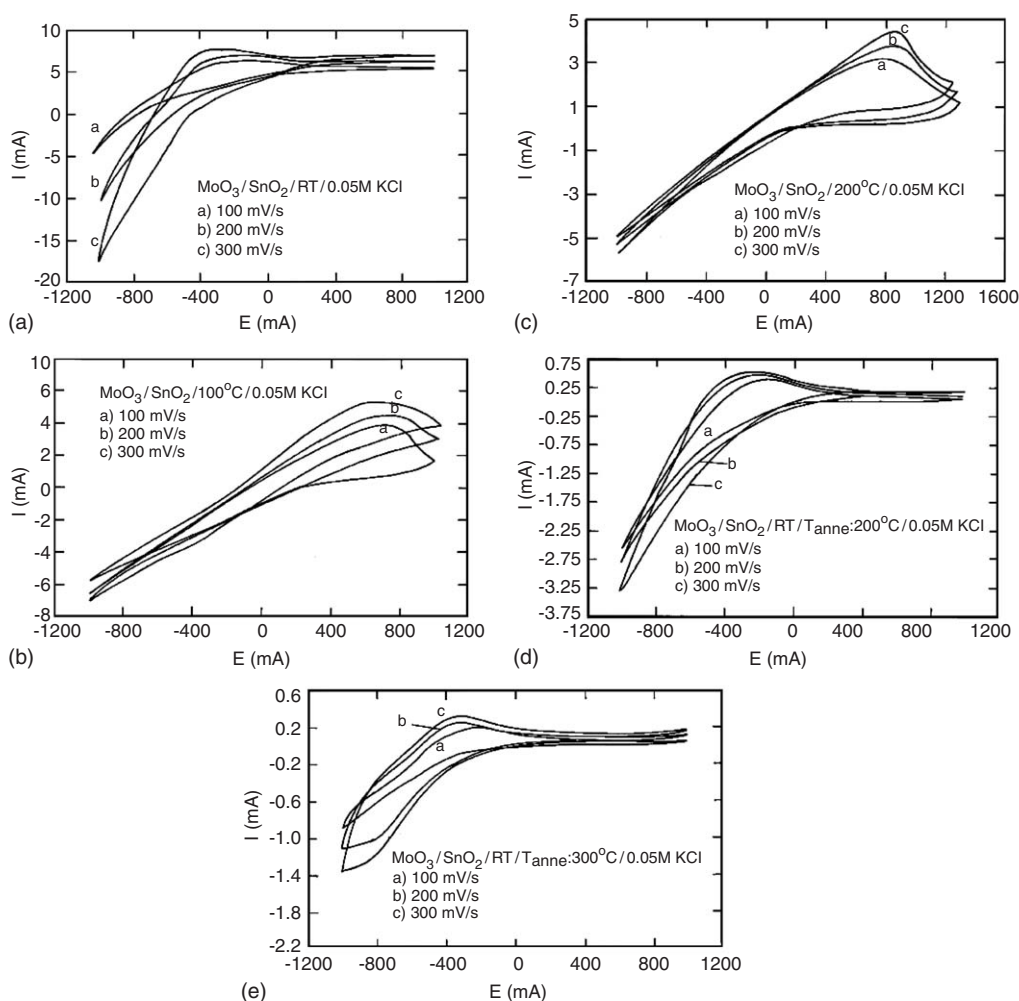


Fig. 1. Cyclic voltammograms of  $\text{MoO}_3$  films prepared at different conditions, cycled in 0.05 M KCl electrolyte solutions: (a)  $T_{\text{sub}} = \text{RT}$ , (b)  $T_{\text{sub}} = 100^\circ\text{C}$ , (c)  $T_{\text{sub}} = 200^\circ\text{C}$ , (d)  $T_{\text{anne}} = 200^\circ\text{C}$  and (e)  $T_{\text{anne}} = 300^\circ\text{C}$ .

in electrochemical cell was evaluated by the cyclic-voltammetry technique and electrochromic device cell characterization, cycled in  $\text{H}_2\text{SO}_4$  electrolyte solutions. In the present work, we focused on how the electrochromic performance of  $\text{MoO}_3$ -based cell towards KCl electrolyte solution is modified by the substrate and annealing temperatures. Moreover, compared with  $\text{WO}_3$  films there are some limited reports available for the electrochemical analysis of  $\text{MoO}_3$  films. Some of them are related to electrochromic behaviour of  $\text{MoO}_3$  films by the insertion/extraction of  $\text{Li}^+$  and  $\text{H}^+$  ions [5,16]. At the same time, to the best of our knowledge no reports are available for the intercalation of  $\text{K}^+$  ions from KCl electrolyte solution for electron beam-evaporated  $\text{MoO}_3$  films.

The electrochromic properties of  $\text{MoO}_3$  thin film electrode was evaluated by inserting  $\text{K}^+$  ions in an electrochemical cell containing 0.05 and 0.1 M KCl electrolyte solutions. The process of ion intercalation and deintercalation was noted during cycling of different sweep rates such as 100, 200 and 300 mV/s. In these processes the applied potential lies in the range between  $-1.2$  to  $+1.2 V_{\text{SCE}}$ . During negative potential of the scan (i.e., cathodic scan), we observed a dark blue colouration of the films whereas the films became colourless in the positive potential (i.e., anodic scan). This is attributed mainly to the electrochemical process involved with the reaction represented by the formation of ‘molybdenum bronze’. All the samples were stable throughout the scan rates and also up to  $1 \times 10^3$  cycles of colouration/bleaching. Hence, the observation of film colouration  $\leftrightarrow$  bleaching behaviour further confirmed their perfect electrochemical performance. The diffusion coefficient ( $D$ ) of ions during intercalation and deintercalation can be evaluated by employing the Randles–Servcik equation [15].

Figs. 1(a)–(e) show the cyclic voltammograms (CV) recorded in 0.05 M KCl solution for  $\text{MoO}_3$  films prepared at  $T_{\text{sub}} = 30^\circ\text{C}$ ,  $T_{\text{sub}} = 100^\circ\text{C}$ ,  $T_{\text{sub}} = 200^\circ\text{C}$ ,  $T_{\text{anne}} = 200^\circ\text{C}$  and  $T_{\text{anne}} = 300^\circ\text{C}$ , respectively. The extracted electrochemical parameters (anodic peak

Table 1

Extracted electrochemical parameters of  $\text{MoO}_3$  films in 0.05 M KCl electrolyte solution

Sample	Scan rate, $v$ (mV/s)	Cathodic spike current, $i_{\text{pc}}$ (mA)	Anodic peak current, $i_{\text{pa}}$ (mA)	Diffusion coefficient, $D$ ( $\text{cm}^2/\text{s}$ )	
				For $i_{\text{pc}}$	For $i_{\text{pa}}$
$\text{MoO}_3/\text{RT}$	100	5.00	6.20	$1.35 \times 10^{-8}$	$2.07 \times 10^{-8}$
	200	10.60	6.80	$3.03 \times 10^{-8}$	$1.25 \times 10^{-8}$
	300	17.50	7.90	$5.51 \times 10^{-8}$	$1.12 \times 10^{-8}$
$\text{MoO}_3/100^\circ\text{C}$	100	5.70	4.00	$1.75 \times 10^{-8}$	$8.65 \times 10^{-9}$
	200	6.40	4.40	$1.10 \times 10^{-8}$	$5.23 \times 10^{-9}$
	300	7.10	5.40	$9.08 \times 10^{-9}$	$5.25 \times 10^{-9}$
$\text{MoO}_3/200^\circ\text{C}$	100	5.00	3.10	$1.35 \times 10^{-8}$	$5.19 \times 10^{-9}$
	200	5.30	3.70	$7.59 \times 10^{-9}$	$3.70 \times 10^{-9}$
	300	5.70	4.30	$5.85 \times 10^{-9}$	$3.33 \times 10^{-9}$
$\text{MoO}_3/\text{RT}/$ $T_{\text{anne}}: 200^\circ\text{C}$	100	2.50	0.40	$3.37 \times 10^{-9}$	$8.65 \times 10^{-11}$
	200	2.80	0.47	$2.11 \times 10^{-9}$	$5.97 \times 10^{-11}$
	300	3.30	0.56	$1.96 \times 10^{-9}$	$5.65 \times 10^{-11}$
$\text{MoO}_3/\text{RT}/$ $T_{\text{anne}}: 300^\circ\text{C}$	100	0.9	0.20	$4.37 \times 10^{-10}$	$2.16 \times 10^{-11}$
	200	1.1	0.25	$3.27 \times 10^{-10}$	$1.68 \times 10^{-11}$
	300	1.3	0.32	$3.04 \times 10^{-10}$	$1.84 \times 10^{-11}$

current ( $i_{pa}$ ), cathodic spike current ( $i_{pc}$ ) and diffusion coefficient ( $D$ )) from these CV diagrams are given in Table 1. The electrochemical curves and their evaluated parameters for  $\text{MoO}_3$  films cycled in 0.1 M KCl solution are shown in Figs. 2(a)–(e) and Table 2, respectively. In this case, the evaluated  $D$  values of  $\text{MoO}_3$  films vary between  $8.65 \times 10^{-11}$  and  $5.51 \times 10^{-8} \text{ cm}^2/\text{s}$  and  $6.50 \times 10^{-12}$  and  $1.72 \times 10^{-8} \text{ cm}^2/\text{s}$  for 0.05 and 0.1 M electrolyte solutions, respectively. Crystalline  $\alpha\text{-MoO}_3$  bulk samples have diffusion constants that are strongly orientation dependent, which is expected from the layered crystal structure. Thus, the diffusion coefficient of  $\text{H}^+$  ion lie between  $10^{-8}$  and  $10^{-6} \text{ cm}^2/\text{s}$  along the  $\text{MoO}_6$ -based chains and was  $\sim 10^{-15} \text{ cm}^2/\text{s}$  perpendicular to them [16–18]. In addition, the magnitude of anodic peak and cathodic spike current decreases with increasing substrate and annealing temperature than the room temperature-prepared films.

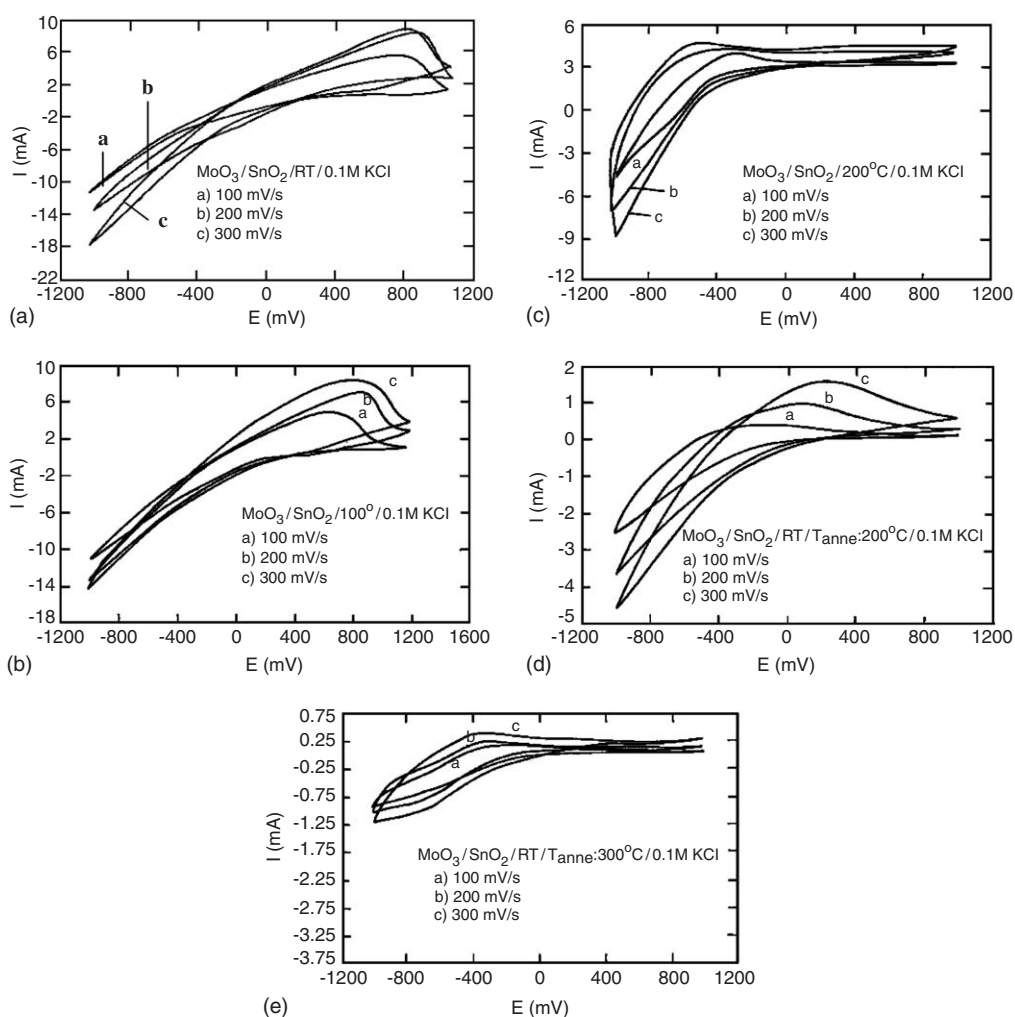


Fig. 2. Cyclic voltammograms of  $\text{MoO}_3$  films cycled in 0.1 M KCl electrolyte solutions: (a)  $T_{\text{sub}} = \text{RT}$ , (b)  $T_{\text{sub}} = 100^\circ\text{C}$ , (c)  $T_{\text{sub}} = 200^\circ\text{C}$ , (d)  $T_{\text{anne}} = 200^\circ\text{C}$  and (e)  $T_{\text{anne}} = 300^\circ\text{C}$ .

Table 2

Extracted electrochemical parameters of MoO<sub>3</sub> films in 0.1 M KCl electrolyte solution

Sample	Scan rate, $v$ (mV/s)	Cathodic spike current, $i_{pc}$ (mA)	Anodic peak current, $i_{pa}$ (mA)	Diffusion coefficient, $D$ (cm <sup>2</sup> /s)	
				For $i_{pc}$	For $i_{pa}$
MoO <sub>3</sub> /RT	100	11.30	5.30	$1.72 \times 10^{-8}$	$3.79 \times 10^{-8}$
	200	14.00	8.10	$1.32 \times 10^{-8}$	$4.43 \times 10^{-8}$
	300	18.00	8.60	$1.45 \times 10^{-8}$	$3.33 \times 10^{-8}$
MoO <sub>3</sub> /100 °C	100	11.00	4.80	$1.63 \times 10^{-8}$	$3.11 \times 10^{-9}$
	200	13.30	7.10	$1.19 \times 10^{-8}$	$3.40 \times 10^{-9}$
	300	14.50	8.50	$9.47 \times 10^{-9}$	$3.25 \times 10^{-9}$
MoO <sub>3</sub> /200 °C	100	5.20	3.90	$3.65 \times 10^{-8}$	$2.05 \times 10^{-9}$
	200	7.30	4.30	$3.60 \times 10^{-9}$	$1.24 \times 10^{-9}$
	300	9.00	4.70	$3.64 \times 10^{-9}$	$9.95 \times 10^{-10}$
MoO <sub>3</sub> /RT/ $T_{anne}$ : 200 °C	100	2.50	0.35	$8.44 \times 10^{-10}$	$1.65 \times 10^{-11}$
	200	3.60	1.00	$8.75 \times 10^{-10}$	$6.75 \times 10^{-11}$
	300	4.50	1.50	$9.12 \times 10^{-10}$	$1.01 \times 10^{-10}$
MoO <sub>3</sub> /RT/ $T_{anne}$ : 300 °C	100	0.93	0.13	$1.16 \times 10^{-10}$	$2.28 \times 10^{-12}$
	200	1.06	0.25	$7.59 \times 10^{-11}$	$4.22 \times 10^{-11}$
	300	1.25	0.38	$7.03 \times 10^{-10}$	$6.50 \times 10^{-12}$

This shows that the films produced at lower substrate and annealing temperatures could be intercalated to a greater extent than higher temperature-produced films. As observed in our earlier work [12,13], the lower temperature-produced films is amorphous and highly disordered. Reichman and Bard [19] said that the disorder enhances the electrochromic effect. The MoO<sub>3</sub> films deposited at  $T_{sub} = 200$  °C and  $T_{anne} = 300$  °C are highly crystalline and preferably oriented along (021) planes, and therefore leads to the minimum values of anodic peak current and cathodic spike current as indicated in Tables 1 and 2.

The detailed description of electrochemical cell characterization for MoO<sub>3</sub> films was reported earlier [15]. The change in optical transmittance of the coloured and bleached films was studied by using Hitachi-3400 UV–Vis–NIR spectrophotometer. 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 [20] of the films was not expected to be a problem in this work. The optical transmittance spectra of MoO<sub>3</sub> films prepared at  $T_{sub} = 30$ , 200 °C and  $T_{anne} = 300$  °C, cycled in 0.1 M KCl electrolyte solution are shown in Figs. 3(a)–(c), respectively. The observed optical transmittance of coloured and bleached states enumerated the films are having good electrochromic colouration. From these optical transmittance spectra of coloured and bleached states, the optical density (OD) and colouration efficiency (CE) of the films were calculated at two different wavelengths like 633 and 1033 nm and they are summarized in Table 3. Molybdenum oxide is known to have optical absorption maximum closer to the human eye sensitivity maximum. Hence, we would like to study spectral transmittance of MoO<sub>3</sub> films in the visible region ( $\lambda \sim 633$  nm). The transmittance in the visible range has been found to be significantly different for the films in bleached and coloured states though

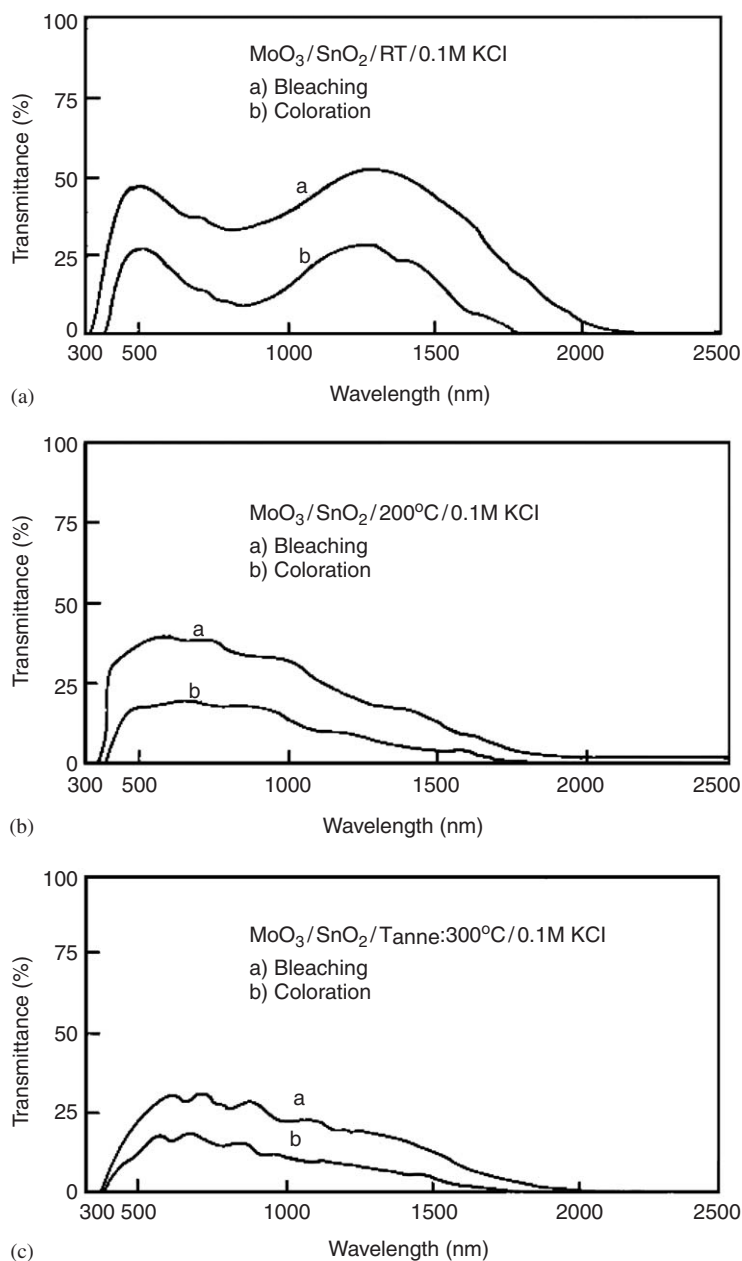


Fig. 3. Optical transmittance spectra of  $\text{MoO}_3$  films in ECD cells, cycled in 0.1 M KCl electrolyte solutions: (a)  $T_{\text{sub}} = \text{RT}$ , (b)  $T_{\text{sub}} = 200^\circ\text{C}$  and (c)  $T_{\text{anne}} = 300^\circ\text{C}$ .

the shape has no apparent change. This effect could make them useful in electrochromic display devices and smart windows applications. Also in order to identify the performance of the films in the infrared range, we have measured the transmittance at a wavelength of

Table 3

Evaluated ECD cell parameters of MoO<sub>3</sub> films in 0.1 M KCl electrolyte solution

Sample	Optical density (OD) at		Colouration efficiency (CE) (cm <sup>2</sup> /C) at	
	$\lambda \sim 633$ nm	$\lambda \sim 1033$ nm	$\lambda \sim 633$ nm	$\lambda \sim 1033$ nm
MoO <sub>3</sub> /RT	0.32	0.37	30	35
MoO <sub>3</sub> /200 °C	0.31	0.40	14	18
MoO <sub>3</sub> /RT/ <i>T</i> <sub>anne</sub> : 300 °C	0.26	0.32	16	20

1033 nm. The higher optical modulation was observed in the visible range of the spectra; whereas the lower optical modulation was observed in the infrared range, which enumerated the suitability of these films in electrochromic device and smart window applications. Fig. 4 shows the graphical representation of evaluated optical density and colouration efficiency of MoO<sub>3</sub> films cycled in 0.1 M KCl electrolyte solution. The maximum colouration efficiency of 35 cm<sup>2</sup>/C was obtained for films prepared at room temperature. The colouration efficiency reported for molybdenum oxide obtained from oxalatomolybdate complexes is 45 and 30 cm<sup>2</sup>/C, reported by Belanger and Laperriere [21]. Laperriere et al. [22] observed that the coloration efficiency of MoO<sub>3</sub> films decreases with increasing annealing temperature. Thus, it reveals that the observations of present work on electrochemical analysis of MoO<sub>3</sub> films are supported with the reported literature. It enumerated the MoO<sub>3</sub> films prepared in the present work, could be an aesthetic material in electrochemical device applications.

### 3.2. FTIR analysis

The intercalated/deintercalated MoO<sub>3</sub> films in 0.1 M KCl electrolyte solutions have been subjected to IR spectroscopic investigation to identify their bonding assignments. The FTIR spectra of intercalated/deintercalated MoO<sub>3</sub> films prepared at conditioned *T*<sub>sub</sub> = 30 °C, *T*<sub>sub</sub> = 200 °C and *T*<sub>anne</sub> = 300 °C, cycled in 0.1 M KCl electrolyte solution are shown in Figs. 5(a)–(c). A group peaks between 650–550 cm<sup>−1</sup> could be observed as same for the MoO<sub>3</sub> powder [23]. However, the peaks around 551–447 cm<sup>−1</sup> are typical stretching modes of Mo–O of  $\alpha$ -MoO<sub>3</sub> structure [7,24]. The absorption peak at around 833 cm<sup>−1</sup> is related to Mo–O bond vibrations in the orthorhombic modification of MoO<sub>3</sub> [25]. The observation of peak at about 942–964 cm<sup>−1</sup>, is shifted to 995 cm<sup>−1</sup> with increasing substrate and annealing temperatures is assigned to the Mo and single-Mo-coordinated oxygen (i.e., terminal oxygen) stretching [24]. This peak shift suggests stronger types of Mo–O (terminal oxygen) and Mo–O–Mo (common oxygens and bridge oxygens) bonding being developed, which in turn confirms the XRD result that high-temperature condition favours the layered  $\alpha$ -MoO<sub>3</sub> phase [23]. A pronounced H–O–H deformation band was observed at 1631 cm<sup>−1</sup>. This is due to the structural water coordinated as H<sub>2</sub>O molecules from the aqueous KCl electrolyte solutions [26]. A broad band around 3500 cm<sup>−1</sup> corresponds to the O–H stretching vibration. The coloration peak was observed at about 3700 cm<sup>−1</sup>. The observed Mo–O–Mo peak attributes the stability of the films after the intercalation-deintercalation in the electrolytes, which proposes the suitability of MoO<sub>3</sub> films in electrochromic device applications.



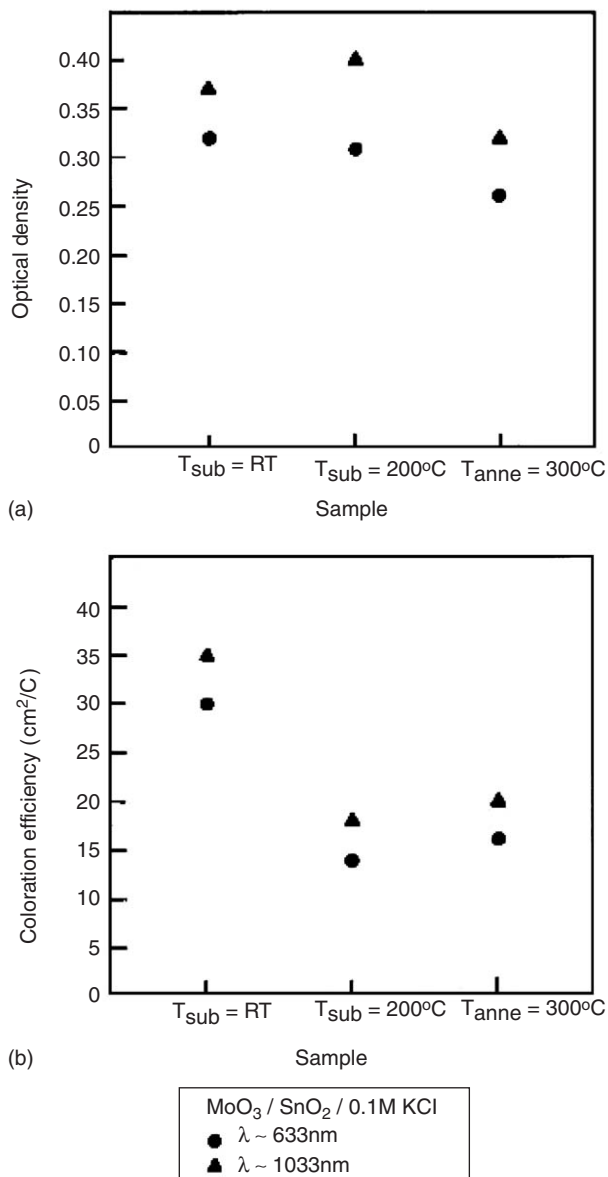


Fig. 4. Variation of the electrochromic device parameters of  $\text{MoO}_3$  films with respect to substrate and annealing temperatures in 0.1 M KCl electrolyte solutions: (a) optical density (OD), (b) colouration efficiency (CE).

#### 4. Conclusions

This paper has described the intercalation studies on  $\text{MoO}_3$  thin films prepared by electron beam evaporation technique. The effect of substrate temperature and annealing temperature on the electrochromic properties was studied by electrochemical and optical techniques. As observed from the results, the as-deposited films at room temperature

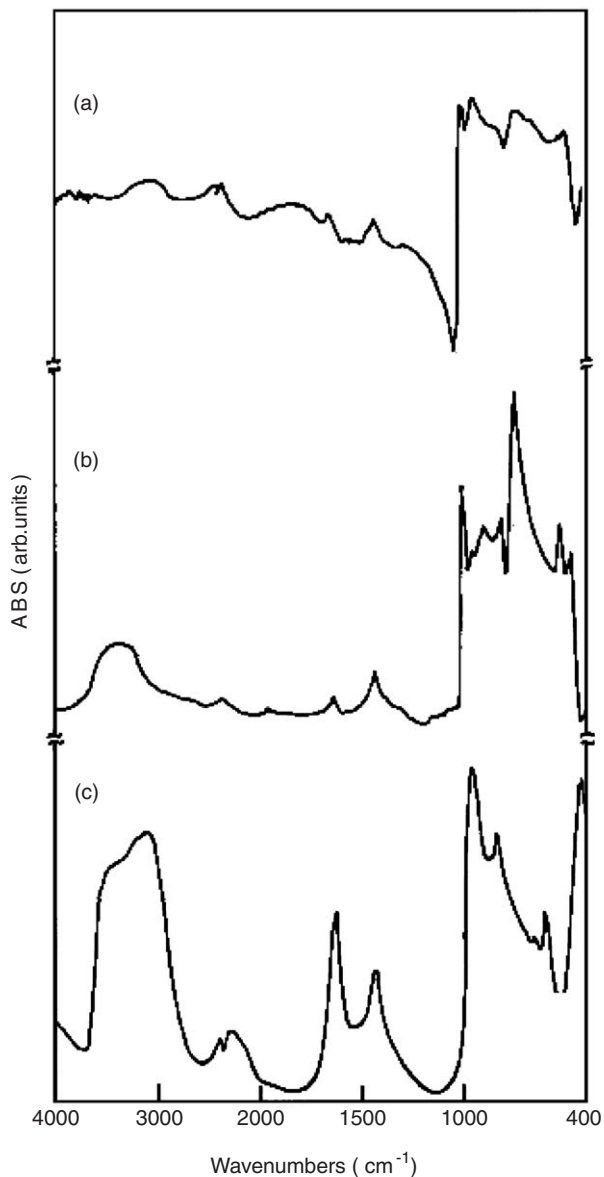


Fig. 5. FTIR spectra of intercalated  $\text{MoO}_3$  films in 0.1 M KCl electrolyte solutions: (a)  $T_{\text{sub}} = \text{RT}$ , (b)  $T_{\text{sub}} = 200^\circ\text{C}$  and (c)  $T_{\text{anne}} = 300^\circ\text{C}$ .

exhibit the good electrochemical performance and colouration efficiency than the higher temperature deposited and annealed films. The cyclic-voltammetry analysis and electrochromic device cell characterization resulted the electron beam evaporated  $\text{MoO}_3$  films are highly stable in the liquid electrolyte solutions. This was also confirmed from the observation of Mo–O–Mo peak in FTIR analysis.

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