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Lithiation study of molybdenum oxide thin films: application to an electrochromic system

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The lithiation behaviour of sputtered molybdenum oxide thin films is reported. Results indicate that such films prepared and dry lithiated under certain conditions undergo reversible lithium insertion without exhibiting a significant optical property change in the solar spectral range. Hence, such films have potential for use in electrochromic (EC) systems as counter electrodes for lithium ion storage. An all-solid EC system was fabricated and studied for its optical switching behaviour using an amorphous tungsten oxide film as the base EC layer. Encouraging results were found relative to the application of such MoO_3 films for lithium ion storage.

1. Introduction

The electrochromic (EC) materials in which an optical change can be reversibly triggered have attracted attention in optical switching materials [1, 2]. Among the inorganic materials exhibiting the phenomenon of electrochromism, tungsten oxide and molybdenum oxide films are deemed to be the most versatile materials for these applications. In materials exhibiting cathodic colouration, the EC change is brought about by double injection of positive ions and electrons as follows [3]:

$$\underset{\text{colourless}}{RO_3 + xe^- + xM^+} \rightleftharpoons \underset{\text{coloured}}{M_xRO_3}$$

where R represents tungsten (W) or molybdenum (Mo) and M represents any anion such as H^+, Li^+, Na^+ etc.

To bring about such an EC change the general configuration in a device form is [3]

$$\mathrm{TC1|EC|IC|CE|TC2}$$

where the TC1 and TC2 represent the transparent conductors used for the application of electric field to the system. EC, as mentioned above, is the base electrochromic material where the actual optical change occurs. CE is the counter electrode or the ion storage material exhibiting chemical changes balancing those occurring in the EC layer. IC is the purely ion conducting layer which electrically isolates the CE and EC layers.

An appreciable amount of work has been done on the lithiation behaviour of WO_3 and MoO_3 [1] due to the fact that both these materials exhibit a high order value of mixed ionic and electronic conductivities at room temperature and also present an EC optical modulation, either in the absorption or reflectance mode, depending on the film structure. Work thus far on WO_3 and MoO_3 has been concentrated towards the utilization of these materials for the EC layer. Current work in this field is also concentrated on finding a suitable counter electrode material. The efficient EC coloration behaviour of MoO_3 and WO_3 depends strongly on their stoichiometry, structure and deposition conditions. Several workers obtained films in which reversible lithium insertion without efficient coloration have been obtained [4]. Though such films are less-interesting for EC layer application, they can be very effective as counter electrode materials. The possibility of using MoO_3 and WO_3 films in this capacity of counter electrode for ion storage has not been studied fully thus far. The possibility of utilizing such a 'quasisymmetric' configuration, in which the same material is used both for EC layer and as the CE layer, was recently considered by Domiryont [5].

In this paper the lithiation behaviour of reactively sputtered MoO_3 films has been studied, especially, with the intention of obtaining films in which a reversible lithium insertion can be done without significant optical change. Using the results, complete EC devices have been fabricated and studied for their EC behaviour. Results indicate significant application potential of such lithiated films in the capacity of counter electrodes in EC systems.

2. Experimental details

The molybdenum oxide thin films were prepared by both thermal evaporation and r.f reactive sputtering. Thermal evaporation was carried out in a vacuum chamber at less than 10^{-5} torr pressure, using MoO_3 powder (99.9995%, Johnson Matthey). The source-substrate distance was about 25 cm. Sputter deposition was driven under a pressure of 4×10^{-2} torr using a 4 cm diameter molybdenum target and in

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Ar/O_2 atmosphere at an Ar to O_2 flow rate ratio of 3. Different substrate temperatures ranging from 25 °C to 300 °C were used in these depositions. Film thickness was measured using the quartz crystal method.

The MoO_3 films were lithiated using a dry method in which the films were exposed to thermally treated $LiNbO_3$ powder under vacuum. Thermal decomposition of $LiNbO_3$ releases lithium atoms which are then intercalated into the bulk of the exposed MoO_3 films. The quantity of lithium thus inserted into the films was initially measured in terms of the frequency change in the quartz crystal oscillator and was noted as the effective mass thickness of lithium inserted. The actual charge injected was obtained by inserting such lithiated MoO_3 films on ITO coated glass substrates in an electrochemical cell containing $LiClO_4$ in propylene carbonate (PC) and extracting the lithium. The charge extracted was obtained by integrating the current of extraction. The electrical resistivity was measured using a Keithley digital multimeter or an electrometer (610CR) depending on the magnitude of resistance. Optical measurements were obtained in the wavelength range from 300 to 2500 nm using a Cary 2400 double beam spectrophotometer. An EG&G potentiostat (273) was used for the electrochemical characterization of the lithium insertion/extraction behaviour.

3. Results and discussion

Figure 1 shows the transmission spectra of MoO_3 films deposited by thermal evaporation at three different substrate temperatures, 100, 200 and 300 °C. The film deposited at 100 °C exhibits a superior transmission (around 80%) through most of the spectral range examined, as compared to films deposited at 200 and 300 °C. The resistivity values for these MoO_3 films deposited at 100, 200 and 300 °C are, respectively, 1.1×10^7, 5×10^5 and $8 \times 10^3\ \Omega\,cm$. This suggests that, with increasing substrate temperature, the film tends towards a polycrystalline state. Similar decrease in transmission and electrical resistivity with increasing substrate temperature is also observed in the case of WO_3 films [6].

Figure 2 shows the transmission spectra of sputter deposited MoO_3 films near room temperature and 100 °C. Unlike the thermally evaporated films, the transmission in sputter deposited films increases with substrate temperature. These films exhibit nearly the same value of resistivity, the value being 6.6×10^5 and $5.4 \times 10^5\ \Omega\,cm$ for sputtered film deposited near room temperature and at 100 °C, respectively. These results indicate strongly that the optical and electrical behaviour of MoO_3 films deposited by sputtering and by thermal evaporation are quite different.

The lithiation of these films was studied by the dry method described earlier. Different mass thicknesses of lithium were inserted in the films and at each step the optical spectra was obtained. Figure 3 shows the optical density variation ΔOD of thermally evaporated MoO_3 films as a function of the effective mass thickness of injected lithium. These optical changes were recorded at a wavelength of 632 nm. A nearly linear increase in the optical density is seen initially, then a saturation in optical change is obtained and, finally, with further lithiation, there is an actual decrease in the optical density in all the three cases. However, the degree of lithiation around which each of these features manifests are different in the three cases. In MoO_3 film deposited at 100 °C, a maximum optical density change occurs at the insertion around 20 nm. The value of ΔOD here corresponds to 0.57. Beyond this, with further

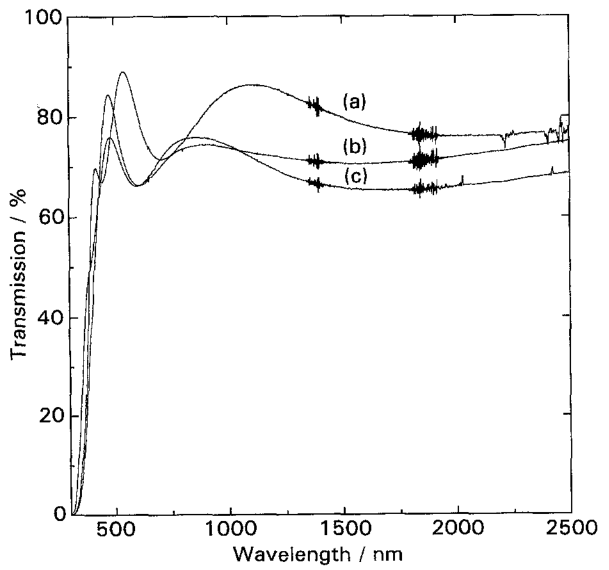

Fig. 1. Transmission spectra of MoO_3 films thermally evaporated on glass substrate at different temperatures: (a) 100 °C, (b) 200 °C and (c) 300 °C.

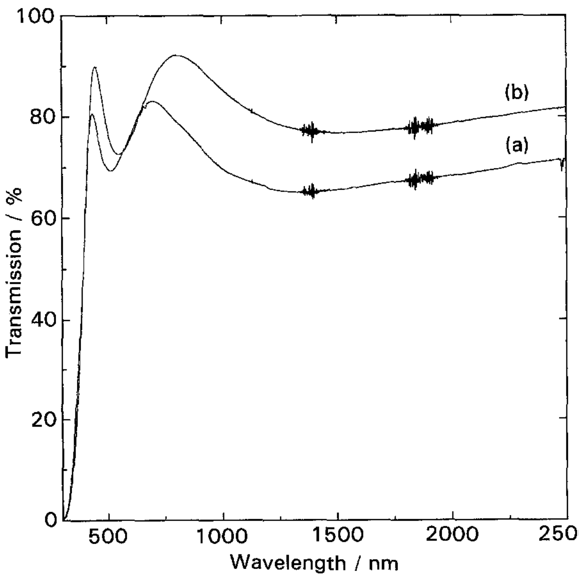

Fig. 2. Transmission spectra of sputter deposited MoO_3 films at different substrate temperatures: (a) near room temperature and (b) 100 °C.

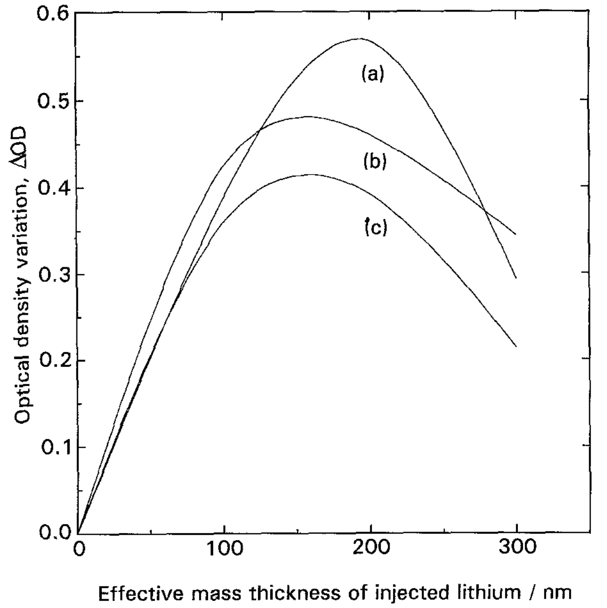

Fig. 3. Dependence of the optical density change (ΔOD) on the amount of lithium mass inserted in thermally evaporated MoO_3 films deposited at 100 °C (a), 200 °C (b) and 300 °C (c).

lithiation, a steep reversal of ΔOD occurs. However, in the case of MoO_3 films deposited at 200 and 300 °C the ΔOD saturation occurs at around 15 nm of lithium mass thickness and then a gradual decrease in ΔOD follows with increasing lithium. The saturation values of ΔOD in the case of films deposited at 200 and 300 °C are, respectively, 0.48 and 0.4; this is significantly less than that seen in film deposited at 100 °C. Hence, these features indicate that if MoO_3 films were to be used as electrochromic layers, the film deposited at 100 °C is more suitable than those deposited at 200 and 300 °C. However, compared to MoO_3 [7] and WO_3 [8] films studied by others for EC layer application, the saturation ΔOD obtained here, even with film deposited at 100 °C, is not very efficient.

The reversal of optical density change occurring beyond a certain degree of lithiation in MoO_3 films is a peculiar behaviour also observed in WO_3 films [7]. Films of MoO_3 coloured to this degree were found to be irreversible with respect to lithium extraction. Other changes following this ΔOD reversal are: (a) the increase in film resistivity, (b) gradual paling of the deep blue colouration and the film becoming brownish. All these characteristics are similar to the high density lithium insertion in WO_3 [9] which has been found to be due to the formation of a tungstate phase. Our FTIR studies reported elsewhere [10] have also shown the presence of a similar molybdate phase after a certain degree of lithiation. For electrochromic consideration this irreversible phase is not very interesting. However, such a study would indicate the maximum charge density of lithium that can be injected into the film without driving the film into irrreversible phase.

Figure 4 shows the ΔOD changes as a function of lithium thickness in films deposited by sputtering.

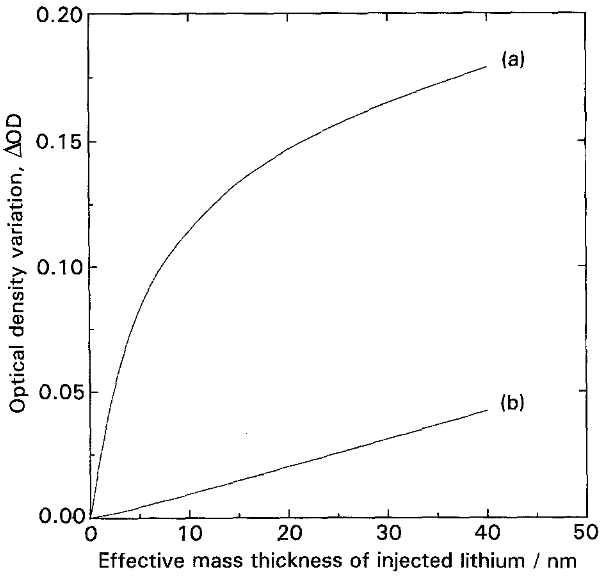

Fig. 4. Optical density change (ΔOD) as a function of lithium mass thickness in sputter deposited MoO_3: (a) near room temperature and (b) 100 °C.

The behaviour in these films is quite different than that observed in thermally evaporated films. First, in the film deposited near room temperature the initial linear increase in ΔOD is similar to those seen in Fig. 3 but the degree of optical change is extremely small. With further increase in lithium mass thickness there is a gradual, but slow, increase in the ΔOD value. Even at 40 nm of lithium mass thickness insertion this film yields a ΔOD value of only about 0.18. For the film deposited at 100 °C the optical density change is almost negligible yielding a ΔOD value of less than 0.05, even at a lithiation of 40 nm. Such films with very passive coloration change upon lithium insertion are also obtained in the case of tungsten oxide [4]. However, the study of such films has been totally neglected in order to obtain films with efficient coloration for use on EC layers in electrochromic systems. Our earlier FTIR study of lithium intercalation in MoO_3 films [10] shows very different lithiation behaviour than for the thermally evaporated case. Upon lithium insertion in sputtered films there is preferential formation of lithium molybdate, unlike in thermally evaporated films, where the tendency is to form coloured lithium bronze. The latter molybdate phase is formed only upon heavy lithium injection. In this work it is also found that even at a small degree of lithiation of the sputtered MoO_3 films there is coexistence of the molybdate and bronze phases. Hence, the passive coloration of these sputtered films, especially that deposited at 100 °C, is due to the preferential formation of the molybdate phase, which is a fairly transparent state.

The interest here is to use such passively colouring films for efficient lithium ion storage. With this in view the rest of the work is concentrated mostly on films deposited by sputtering, particularly those yielding reversible low efficiency colouration in the solar spectral range. To evaluate the overall solar spectral behaviour of these films, integrated transmission

Table 1. Integrated transmission values of MoO_3 films before and after lithiation

Lithium/nm	*Sputter MoO_3 25 °C*		*Sputter MoO_3 100 °C*		*Thermal MoO_3 300 °C*	
	T_{vis}/%	T_{solar}/%	T_{vis}/%	T_{solar}/%	T_{vis}/%	T_{solar}/%
0	78	73	80	81	73	70
10	67	63	78	80	40	35
20	65	64	75	78	33	18
30	64	65	74	75	20	17
40	63	66	72	74	18	16
50	64	67	70	73	17	15
60	66	68	71	71	16	15

values have been calculated in the visible and solar regions in different types of MoO_3 films, both before and after lithiation. These results are given in Table 1 for MoO_3 films sputtered near room temperature and at 100 °C. The behaviour of a thermally evaporated film deposited at 300 °C is also shown in this table for comparison.

As shown from this table, different lithiation degrees of MoO_3 for all the three films exhibit a fairly good visible and solar transmissions. However, the real difference is seen in the lithiation behaviour. In the case of the thermally evaporated film, with increasing lithium, there is a sharp decrease in solar and visible transmission. This result demonstrates the electrochromic behaviour of MoO_3 films. For a lithiation of 60 nm mass thickness the transmission saturates at a value below 20%. Hence, a fairly significant optical modulation can be expected from such thermally evaporated films. These films, as observed before, are good candidates for EC layer application.

Now, the visible and solar spectral changes are less drastic in the case of sputtered films. In the film deposited near room temperature the visible transmission changes from 78% to 66% and solar transmission from 73% to 68%. The same passive degree of change from 80% to 70% and 81% to 71% in the visible and solar spectral regions, respectively, are seen in the case of the film sputter deposited at 100 °C. Hence, both the sputter deposited films exhibit a very passive optical change even under a lithiation of 60 nm mass thickness and can be employed as very effective counter electrodes (CE) for lithium ion storage. Since, the film deposited at 100 °C exhibits superior transmission, especially in the solar spectral region, further work was carried out with this film.

The lithiation work thus far was obtained with the dry method described earlier using the effective mass thickness as the injected charge parameter. In order to use the MoO_3 film as a counter electrode for lithium ion storage, it is essential to know the relation between the mass thickness and the injected charge density. To this end, the sample of interest, that is, MoO_3 film sputter-deposited on an ITO coated glass substrate at 100 °C and lithiated with 30 nm effective mass thickness of lithium, was then inserted in an electrochemical cell containing $LiClO_4$ in PC. Lithium was extracted from this film. From the extraction current the lithium charge injected was estimated to be around 7 mC cm^{-2}. Compared to other works on WO_3 [6] a lithium mass thickness of 30 nm corresponded to an extracted charge of 20 mC cm^{-2}. The small quantity of charge extracted from the MoO_3 film is consistent with the irreversible formation of the molybdate phase as found in earlier FTIR studies [10]. Hence, out of the 20 mC cm^{-2} of charge injected only about 7 mC cm^{-2} was available in reversible form. To examine the cyclability of this quantity of lithium in and out of the MoO_3 film, cyclic voltammetry of this film was carried out in the electrochemical cell. The first few cycles were not very reproducible. However, after a dozen such cycles the system stabilized and very reproducible voltammograms, as shown in Fig. 5, were obtained. The figure corresponds to a voltammogram recorded after 20 cycles of lithium insertion/extraction. During each of these reproducible cycles a charge density of about 8 mC cm^{-2} was cycled in and out of the MoO_3 film. These cyclic voltammograms were obtained by applying a triangular potential varying between −1 and +1 V with respect to the standard calomel electrode (SCE) at a sweep rate of 33 mV s^{-1}. Hence, a molybdenum oxide film sputter

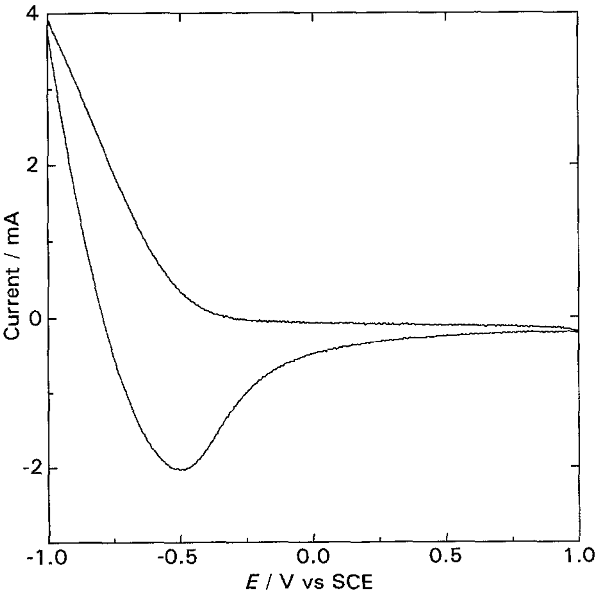

Fig. 5. Cyclic voltammogram of MoO_3 film sputter deposited at 100 °C.

deposited at 100 °C and charged with 30 nm effective mass thickness of lithium (corresponding to about 20 mC cm^{-2} charge density), out of which only 7 mC cm^{-2} of lithium was cyclable, was considered as counter electrode for lithium ion storage. Hence, such a lithiated system capable for storing 7 mC cm^{-2} reversible lithium was considered the central point in the further work of designing an electrochromic system.

To examine the functioning of such lithiated MoO_3 film as counter electrode for lithium storage in an actual electrochromic system, an all-solid EC system of the type:

$$glass|ITO|Li_2MoO_4{-}Li_xMoO_3|LiBO_2|WO_3|Au$$

was fabricated. The lithium borate ($LiBO_2$), tungsten oxide (WO_3) and gold films were used in the capacity of ionic conductor, electrochromic material and outer transparent electrode, respectively.

It is well known that tungsten oxide is an excellent candidate as an electrochromic layer exhibiting a very efficient degree of optical modulation upon double insertion of ions and electrons [1]. From earlier study of the electrochromic behaviour of tungsten oxide films it is known that the films deposited at 200 °C by thermal evaporation are amorphous and exhibit high efficiency absorption modulation upon lithium injection. Hence, such a film was chosen as the EC layer in our all-solid system. Similarly, earlier work has demonstrated that thermally evaporated lithium borate [11] films exhibit an exceedingly good optical transmission (around 90%) in the solar wavelength and a fairly high degree of lithium ion conductivity (around 8.13×10^{-8} S cm^{-1}) when deposited at 200 °C. Hence, this film was employed as the lithium ion conductor in the all-solid system.

For the fabrication of the complete system, ITO coated glass substrates were partially etched and cleaned. Then a thin film of molybdenum oxide was sputter deposited onto this substrate field at 100 °C. This film was subsequently dry lithiated with 30 nm effective mass thickness. Then the other films of $LiBO_2$, WO_3 and gold (12 nm) were sequentially deposited. Silver paint contacts where then applied to the bottom ITO electrode and the outer gold electrode for robust physical contacts before the system was tested for electrochromic performance.

Figure 6 shows the transmission spectra of the all-solid system in the extremely coloured and bleached states obtained by the application of −3 and +3 V potential with respect to the ITO electrode. A good degree of optical modulation is apparent in the visible and near i.r. wavelengths. The high absorption due to the gold film and the strong interference effects mask the actual degree of modulation. For an estimation of the order of modulation, integrated transmission values in the solar and visible regions in the coloured and bleached states of the system were calculated. The values were found to be T_{solar}(bleached) = 25%, T_{solar}(coloured) = 8%, T_{vis}(bleached) = 38% and T_{vis}(coloured) = 15%. To observe the cyclic ability of such a system between coloration and bleaching, a square wave potential varying between ±3 V was applied. The optical changes were recorded at a fixed wavelength of 632 nm as a function of time. Figure 7 shows the coloration/bleaching cycles of the all-solid system. The transmission of the system at this wavelength varies between about 42% in the clear state to around 14% in the coloured state, corresponding to an optical density change, ΔOD, value of 0.48. This value and the earlier indicated integrated values of the coloured and bleached states of the system compare roughly with the earlier observed ΔOD values in the WO_3 films for the insertion/extraction of 7–8 mC cm^{-2} [6]. These

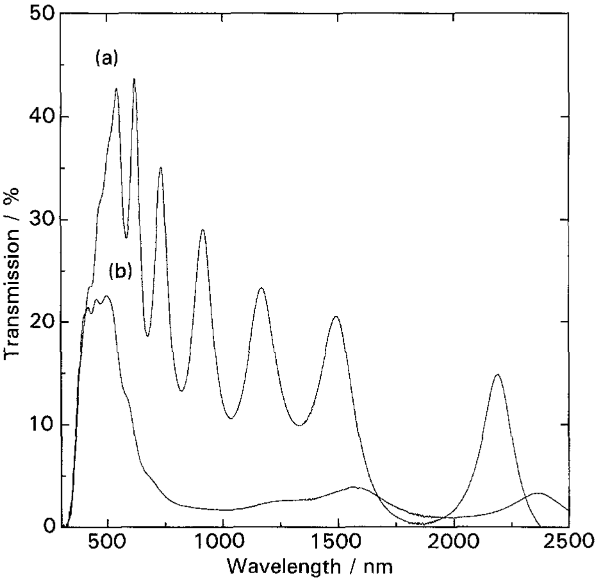

Fig. 6. Transmission spectra of the all-solid electrochromic system in (a) bleached and (b) coloured states with the application ±3 V with respect to ITO electrode.

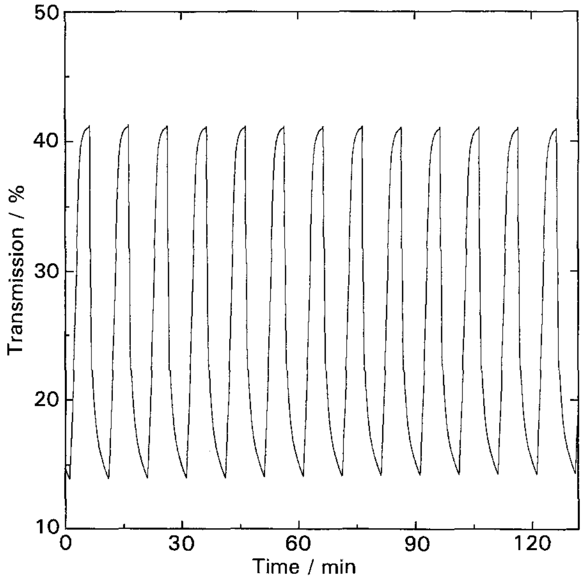

Fig. 7. Coloration and bleaching cycles of the all-solid EC system as a function of time recorded at a fixed wavelength of 632 nm.

coloration/bleaching cycles are found to be very reversible. Each cycle takes about 10 min. Although this is a very slow response from the practical point of view, potential application of sputtered MoO_3 films as counter electrodes for lithium ion storage is amply demonstrated through this work.

4. Conclusion

Thin molybdenum oxide films have been studied for application as base electrochromic layers in electrochromic systems. In this work it has been shown for the first time that sputter deposited MoO_3 films show a passive coloration and, hence, can be employed as efficient counter electrodes for lithium ion storage. Dry lithiation behaviour of thermally evaporated and sputter deposited films are compared. Based on the passive optical behaviour of the sputter deposited MoO_3 films under lithium insertion/extraction, a five-layer monolithic all-solid EC system has been fabricated using a sputter MoO_3 film as counter electrode and a WO_3 film as the base electrochromic layer. Hundreds of coloration/bleaching cycles have been performed on this system without any change in the system. These highly reversible cycles and the optical modulation in the visible and near i.r. regions obtained indicate the potential use of such MoO_3 films as counter electrodes in EC systems. Further work to improve the overall transmission of the system by replacing the outer gold electrode by more transparent ITO is currently under way.

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