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CHARACTERIZATION OF INDIUM OXIDE FOR THE USE AS A COUNTER-ELECTRODE IN AN ELECTROCHROMIC DEVICE

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ABSTRACT

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Thin films of indium oxide, In_2O_3 (4000 Å), deposited on commercially available In_2O_3 : Sn (ITO)/glass by rf sputtering, have been examined for potential application as a counter-electrode material in an electrochromic device, based on their chemical, structural, and optical properties. Cyclic voltammetry experiments showed that mobile lithium ions can be inserted (chemical reduction) and removed (chemical oxidation) from the host structure of indium oxide. Coulometric titrations showed that the films exhibited a hysteresis behavior for the injection and removal of lithium ions in $\text{Li}_x\text{In}_2\text{O}_3$ ($x=0-0.23$). Structural investigation of the indium oxide films, utilizing electron diffraction techniques, indicated that they were crystalline with a crystallite size of 175 Å, in agreement with x-ray diffraction results. Differences in optical transmission between the lithiated and delithiated thin films were no more than 5% in the visible/near-infrared regions of the spectrum.

INTRODUCTION

Electrochromic materials are currently being investigated for potential application as architectural glazings. An electrochromic window can be thought of as a series of five thin films deposited on glass: a transparent conductor, an electrochromic material (working electrode), an ion conductor, an electrochromic material (counter-electrode), and a transparent conductor (Fig. 1).

Fig.1 Electrochromic window.

By applying a current between the electrodes, the optical transmission and/or reflection of the working electrode can be modulated; such a window could offer dynamic control of visible and near-infrared solar radiation, providing significant savings for heating/cooling loads in buildings.

Although much work has been done on studying the properties of promising working electrode materials (e.g. crystalline WO_3), there has been less work done on counter-electrode (CE) materials. The requirements for a CE material are: (1) to reversibly allow ions to be inserted/removed into/out of

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the host structure and (2) be optically complementary or optically passive with respect to the working electrode. There have been some optical and chemical studies reported for the CE material $\text{In}_2\text{O}_3:\text{Sn}$ (ITO) [1, 2, 3], but there has been no work reported to this date on In_2O_3 . This paper will address the fundamental electrochemical, chemical, structural, and optical properties of In_2O_3 for its application as a counter-electrode in an electrochromic device.

EXPERIMENTAL

Thin films of indium oxide were prepared by radio frequency (rf) sputtering. Deposition conditions included a substrate to target distance of 5.5 cm, a substrate temperature of 200°C , a power setting of 100 W, a duration of 120 minutes, and a gas mixture of 15×10^{-3} torr of O_2 and 7×10^{-3} torr of Ar. A commercial five inch diameter In_2O_3 target (Cerac Corporation) was used to deposit the material on ITO coated glass (Donnelly Glass Corporation, Holland, MI) and Ni substrates. Film thicknesses were then measured using a profilometer, and were approximately $4000 \pm 100 \text{ \AA}$. Densities of the films were measured using a crystal quartz oscillator before and after the deposition; it was 6.17 g/cm^3 .

Characterization included electrochemical, chemical, structural, and optical analysis of the films. Electrochemical experiments, using a potentiostat/galvanostat and a programmer, included cyclic voltammetry (CV), coulometric titrations, and galvanostatic intermittent titration techniques (GITT) [4, 5]. The electrochemical set-up was in an argon-filled glove box (Vacuum Atmospheres Company) so as to avoid oxygen and water contamination. The cell used for all experiments consisted of a three electrode arrangement: a working electrode ($\text{In}_2\text{O}_3/\text{ITO}/\text{glass}$), a reference electrode, Li metal and a counter-electrode, Li metal. The electrolyte used was 1M $\text{LiClO}_4/\text{propylene carbonate}$. For the CV experiments, the potential range was 1.000-4.000 V vs. Li/Li^+ . The coulometric titration was done galvanostatically, with an applied current of $10 \mu\text{A}$, followed by voltage equilibration. The GITT experiments were similar, but with very small steps.

Lithium analysis was performed by atomic absorption to determine the quantity of lithium in In_2O_3 for both the reduced (lithiated) and oxidized (delithiated) states. Analyses were made of indium oxide films on both ITO and nickel coated glass substrates.

Lithiated, delithiated, and as-deposited films were examined by transmission electron microscopy. In_2O_3 samples were again prepared by rf sputtering where the substrates used were SiO_2/Ni grids; thicknesses were approximately $300 \text{ \AA}$. The lithiation was done galvanostatically in the glove box, up to $x=0.23$ in $\text{Li}_x\text{In}_2\text{O}_3$. The d spacings were calculated and compared to standard tabulated powder values.

Optical transmission/absorption was measured for In_2O_3 in the lithiated, delithiated, and as-deposited states in the UV/VIS region.

RESULTS AND DISCUSSION

The electrochemical cyclic voltammetry experiments demonstrated that indium oxide thin films undergo a charge transfer or reduction/oxidation reaction, taken to be the insertion/removal of lithium. Fig. 2 showed a typical CV obtained for $\text{In}_2\text{O}_3/\text{ITO}/\text{glass}$ with repeated cycling (1,912 cycles), where the total injected (reduced) and removed (oxidized) charge was $24 \pm 4 \text{ mC/cm}^2$.

Fig. 2 Cyclic voltammogram of $\text{In}_2\text{O}_3/\text{ITO}/\text{glass}$ at 10 mV/sec.

Faster scan rates resulted in a noticeable decrease in the amount of insertion/removal over time. For example, at 20 mV/sec., the initial cathodic insertion corresponded to 20 mC/cm^2 but after 655 cycles it had dropped to 8 mC/cm^2 . Furthermore, utilizing atomic absorption spectroscopy, lithium was found in long term cycled (10 mV/sec.) $\text{Li}_x\text{In}_2\text{O}_3/\text{ITO}/\text{glass}$ (1,738 cycles) and $\text{Li}_x\text{In}_2\text{O}_3/\text{Ni}/\text{glass}$ (2,253 cycles). These samples had been removed from their separate electrochemical lithium baths after completing their final anodic sweep; the retained lithium corresponded to $\text{Li}_{0.21}\text{In}_2\text{O}_3$ and $\text{Li}_{0.41}\text{In}_2\text{O}_3$ in the two samples. Residual lithium was also found even after only twelve cycles at 10 mV/sec. in $\text{Li}_x\text{In}_2\text{O}_3/\text{ITO}/\text{glass}$ corresponding to a x value of 0.015.

Variable sweep rate experiments showed kinetic limitations on the charge transfer process. The sweep rates were 5, 10, 20, 50, 100 mV/sec. For the anodic sweeps, the potential at which the removal began was independent of the sweep rate, approximately 1.60 V vs. Li/Li^+ . However, for the cathodic cycles, there was a slight shift in potential as insertion proceeded; the potential decreased as the sweep rates became larger. Plots of the peak current density for both the anodic and cathodic cycles vs. $\sqrt{\text{sweep rate}}$ showed a linear dependence, indicating a diffusion-controlled mechanism for the oxidation and reduction process (Fig. 3).

The diffusion constant of lithium in $\text{In}_2\text{O}_3/\text{ITO}/\text{glass}$ was measured using the GITT method, developed by Wepner and Huggins [4, 5]. In_2O_3 was initially galvanostatically reduced to $\text{Li}_{0.23}\text{In}_2\text{O}_3$. This electrode was then reduced again with an applied current of 10 $\mu\text{A}/\text{cm}^2$ for a period of 10 sec.; the open circuit voltage (OCV) was then immediately measured and allowed to reach a steady state value. The typical diffusion constant for both insertion and removal was $1.0 (\pm 0.2) \times 10^{-11} \text{ cm}^2/\text{sec}$.

Fig. 3 Cyclic voltammogram sweep rate experiment of In₂O₃/ITO/glass and its peak current density (mA/cm²) vs. $\sqrt{\text{sweep rate}}$.

Coulometric titration curves were obtained on films after pre-conditioning them; this involved cycling them first at a scan rate of 10 mV/sec. between a potential range of 1.000-4.000 volts vs. Li/Li⁺ in order to obtain a reproducible CV as in Fig. 2. After charge injection/removal, OCVs were measured until a steady state was attained; this corresponded to a change of 1 mV after seven minutes. For all experiments, 20 mC/cm² was the maximum amount of charge injected/removed. Fig. 4 showed a typical coulometric titration curve for Li_xIn₂O₃/ITO/glass, where lithium was inserted in 2 mC/cm² intervals, followed by removal of lithium in 1 mC/cm²

increments. The OCVs reported were lower than Golden and Steeles' values for ITO [3]. However, if the films were not pre-conditioned, then these values were comparable to those of ITO.

Fig. 4 Coulometric titration of $\text{Li}_x\text{In}_2\text{O}_3/\text{ITO}/\text{Glass}$ ($x=0-0.23$).

The hysteresis behavior shown was reproducible, but required that the pre-conditioning procedure was performed again on the film.

Electron diffraction investigations of lithiated, delithiated, and as-deposited $\text{Li}_x\text{In}_2\text{O}_3/\text{SiO}_2/\text{Ni}$ ($x=0-0.23$) showed that all samples were crystalline. In particular, the d spacings determined for each sample were similar, corresponding to the standard tabulated powder values [6]. The lattice spacings determined for lithiated and delithiated films suggested no structure modifications (Table 1). The same held true for as-deposited indium oxide.

Experimental [Lithiated]				Experimental [Delithiated]			
Avg. $a=10.25 \pm 0.112 \text{ \AA}$				Avg. $a=10.22 \pm 0.113 \text{ \AA}$			
Rings	d(Å)	a(Å)	$h^2+k^2+l^2$	Rings	d(Å)	a(Å)	$h^2+k^2+l^2$
1	4.291	10.51	6	1	4.278	10.48	6
2	2.952	10.23	12	2	2.970	10.29	12
3	2.609	10.44	16	3	2.595	10.38	16
4	2.396	10.17	18	4	2.372	10.06	18
5	2.168	10.26	22	5	2.175	10.20	22
6	1.991	10.15	26	6	1.984	10.17	26
7	1.786	10.10	32	7	1.797	10.17	32
8	1.654	10.20	36	8	1.658	10.22	36
9	1.531	10.16	44	9	1.536	10.21	44
10	1.464	10.14	48	10	1.467	10.16	48
11	1.168	10.18	76	11	1.171	10.21	76
12	1.035	10.14	96	12	1.034	10.13	96

Table 1 Electron diffraction d spacings of $\text{Li}_x\text{In}_2\text{O}_3/\text{SiO}_2/\text{Ni}$ ($x=0-0.23$).

Optical transmission was measured in the ultra-violet/visible region for two sister samples of $\text{Li}_x\text{In}_2\text{O}_3/\text{ITO}/\text{glass}$ ($x=0.23$ and $x=0.079$). The difference in transmission between $\text{Li}_{0.23}\text{In}_2\text{O}_3$ and $\text{Li}_{0.079}\text{In}_2\text{O}_3$ was no more than 5% in

the ultra-violet/visible regions of the spectrum (Fig. 5). The transmission curve for as-deposited In_2O_3 was similar.

Fig. 5 Optical transmission of $\text{Li}_{0.23}\text{In}_2\text{O}_3$ (colored) and $\text{Li}_{0.079}\text{In}_2\text{O}_3$ (bleached) for the ultra-violet and visible region of the solar spectrum.

CONCLUSION

The optical behavior of indium oxide films upon electrochemical oxidation/reduction is appropriate for application as an optically passive counter-electrode in an electrochromic window. The electrochemical behavior is more equivocal. The films show ready insertion/removal of lithium ions, and are capable of long-term cycling at slow sweep rates. They also show irreversibility by retaining lithium and by the hysteresis in the coulometric titration. This behavior may be connected with cycling in the essentially infinite lithium ion reservoir of the liquid electrolyte, and thus be irrelevant to all solid state devices with limited lithium available.

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