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Environmental Energy Technologies Division

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Presented at the *Electrochemical Society Meeting, Symposium on Electrochromic Materials and Their Application III*, San Antonio, TX, October 6–11, 1996, and to be published in the Proceedings

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ELECTROCHROMIC LITHIUM NICKEL OXIDE THIN FILM BY PULSED LASER DEPOSITION

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ABSTRACT

Thin films of lithium nickel oxide were deposited by pulsed laser deposition (PLD) from targets of pressed $LiNiO_2$ powder with layered structure. The composition, structure and surface air sensitivity of these films were analyzed using a variety of techniques, such as nuclear reaction analysis, Rutherford backscattering spectrometry (RBS), x-ray diffraction, infrared spectroscopy, and atomic force microscopy. Optical properties were measured using a combination of variable angle spectroscopic ellipsometry and spectroradiometry. Crystalline structure, surface morphology and chemical composition of $Li_xNi_{1-x}O$ thin films depend strongly on deposition oxygen pressure, temperature as well as substrate target distance. The films produced at temperatures lower than 600°C spontaneously absorb CO_2 and H_2O at their surface once they are exposed to the air. The films deposited at 600°C proved to be stable in air over a long period. Even when deposited at room temperature the PLD films are denser and more stable than sputtered films. RBS determined that the best electrochromic films had the stoichiometric composition $Li_{0.5}Ni_{0.5}O$ when deposited at 60 mTorr O_2 pressure. Electrochemical tests show that the films exhibit excellent reversibility in the range 1.0 V to 3.4 V versus lithium and long cyclic life stability in a liquid electrolyte half cell. Electrochemical formatting which is used to develop electrochromism in other films and nickel oxide films is not needed for these stoichiometric films. The optical transmission range is almost 70% at 550 nm for 120 nm thick films.

INTRODUCTION

The layered form of lithium nickel oxide $LiNiO_2$ is used as a battery electrode while the cubic form of lithium nickel oxide written as $Li_xNi_{1-x}O$ may have promising electrochromic performance. $Li_xNi_{1-x}O$ can have a wide optical range and more neutral color than tungsten oxide as well as better stability. Furthermore $Li_xNi_{1-x}O$ is anodically coloring so it has the advantage of being complementary to cathodic tungsten oxide.

It has been originally reported by Decker and co-workers (1) that nickel oxide becomes electrochromic after a certain defined electrochemical formatting process. Nickel oxide films grown by a variety of vacuum technologies from NiO powder targets usually have a chemical composition of NiO_z with $z > 1$. The optically active film after electrochemical formatting has a composition of $Li_xNi_{1-x}O$ with x around 0.3-0.5 (not well defined). The actual electrochromic process takes place between clear $Li_{x+y}Ni_{1-x}O$ and colored $Li_{x+y-\delta}Ni_{1-x}O$ with y close to δ. The typical optical transmission range is from 20% - 30% at 550 nm. Electrochromic films that incorporate lithium as-deposited were developed in earlier work at

LBNL (2). Based on this foundation work, we started to look at the thin film with the starting chemical composition of $Li_xNi_{1-x}O$. Eliminating the formatting process is necessary for the development of large-area electrochromic devices. Also it would be interesting to look at the $Li_xNi_{1-x}O$ film with different x in fundamental aspects.

The best results were obtained by pulsed laser deposition (PLD) which has not often been used to deposit electrochromic films. The PLD technique is not well suited for large-area deposition, but it has a number of practical advantages for laboratory development of new materials: speed, small easily fabricated targets, tendency to preserve composition. These factors allow us to generate new materials very quickly. When optimum conditions have been established using PLD, it is then usually possible to duplicate the film by sputtering.

In this paper we describe a method to deposit stoichiometric $Li_{0.5}Ni_{0.5}O$ thin films as well as their physical and chemical properties. We then describe the electrochemical and optical properties of optimized films.

EXPERIMENTAL

Starting from a hexagonal layered-structure $LiNiO_2$ powder targets were isostatically pressed and sintered at 700°C for 48 hours under pure oxygen flow to a final density of $\rho = 4.3$ g/cm^3. After sintering the target was analyzed by XRD. It retains the same layered structure as that of starting powder.

All films are deposited under the same conditions except for varying oxygen partial pressure. Oxygen partial pressure during deposition significantly affects chemical composition, surface morphology and electrochemical-optical performance of the films. The KrF excimer laser was operated at 10 pulses/sec, and 600 mJ per pulse per 2 mm^2 for 8 minutes. The substrate was not heated and did not exceed 50°C during deposition. Target-substrate distance was 7 cm. The diameter of the target is 0.5 inch, which typically results in 1-2 cm^2 films. The base pressure in the chamber was 0 to 200 mTorr.

Optical measurements were made with a variable-angle spectroscopic ellipsometer (VASE) from 250 nm to 1000 nm using an instrument from the J.A.Woollam Co. In order to cover the whole solar spectrum, transmittance and reflectance measurements from 250 nm to 2500 nm were added; these measurements were taken at near-normal incidence on a Perkin-Elmer Lambda 19 spectrophotometer.

Rutherford Backscattering Spectrometry (RBS) and Nuclear Reaction Analysis (NRA) was used to determine the film composition Ellipsometry was used not only as part of the optical analysis but also to measure film thickness. Other types of structural analysis were performed with x-ray diffraction (XRD), infrared spectroscopy and atomic force microscopy (AFM).

Electrochemical measurements were performed with an Arbin multi-channel battery cycling instrument. This instrument was configured with an auxiliary input/output for each channel to allow for the recording of optical transmittance data in conjunction with electrochemical data. Measurements on films were made inside a He-filled glove box at less than 1 ppm of O_2. The films were tested in a three electrode liquid cell system in which the counter electrode is a lithium foil and the reference electrode is a lithium wire. The electrolyte is PC:EC/$LiPF_6$(1M) with PC/EC ratio of 1. The electrolyte was used as received from EM Industry, Inc. and has a water content less than 1 ppm.

RESULTS AND DISCUSSION

Most of our films were deposited at room temperature. All such films were found to be amorphous by x-ray diffraction (XRD). We still can get some local structural information from XRD on films deposited at higher temperatures and then comparing to supplementary FTIR data at both high and low temperatures. XRD of PLD films deposited at 400°C or 600°C shows a cubic structure corresponding to $Li_xNi_{1-x}O$. FTIR spectra of PLD films deposited at room temperature have the same Ni-O (or Li-O) absorption bands as those of the PLD film deposited at elevated temperatures of 400°C or 600°C. The low-temperature films, especially with composition different from $Li_{0.5}Ni_{0.5}O$, however, are sensitive to the atmosphere, showing absorption bands of H_2O and CO_2 not present in the high-temperature films. Both high temperature and low temperature films deposited under 60 mTorr oxygen partial pressure for XRD and FTIR analysis had approximately the same chemical composition, namely $Li_{0.5}Ni_{0.5}O$. Nevertheless the films deposited at 600°C proved to be more stable in air over a long period than those deposited at low temperature.

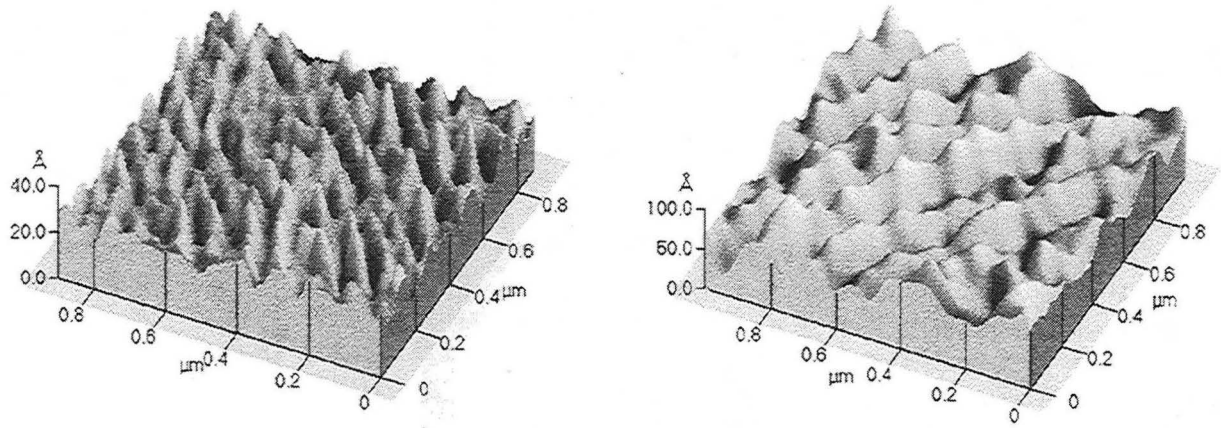


Figure 1. Surface of $Li_xNi_{1-x}O$ at a) 60 mTorr oxygen pressure with rms roughness 4 Å and b) 200 mTorr oxygen pressure with rms roughness 14 Å.

Higher particle energies associated with lower O_2 pressures might be expected to damage and roughen the surface or perhaps the opposite trend could occur and the higher energies would increase surface mobility to produce smoother films. We observe that $Li_xNi_{1-x}O$ films deposited by PLD are generally quite smooth with lower O_2 pressures resulting in the smoothest films (see Figure 1) . The same trend is also observed in a number of other lithium metal oxides (3). As discussed below, the exceptionally smooth film of Figure 1a deposited at 60 mTorr is far better in its electrochromic properties than the rougher film deposited at 200 mTorr. This result runs counter to the frequent supposition that rougher, more open films will intercalate charge more readily. A possible explanation for the rough surface of the film deposited at 200 mTorr oxygen partial pressure is that the film is reactive to H_2O and CO_2. while the stoichiometric film $Li_{0.5}Ni_{0.5}O$ film is more stable in air.

The deposition rate or film thickness increases linearly over the entire range of deposition O_2 pressure (Figure 2). This effect is somewhat surprising because increasing chamber pressure in this regime often slows the deposition rate strongly due to increasing collision cross sections, especially in case of sputtering. The ejected particles in the plume, consisting predominately of atomic species, may be limited from reacting on the surface by the availability of oxygen. The Li/Ni and Li/O ratios also increase with O_2

pressure as shown in Figure 2 and Figure 3. The stoichiometric composition $Li_{0.5}Ni_{0.5}O$ can be only achieved at a very narrow oxygen pressure range around 60 mTorr. As we shall see below this composition corresponds to the best electrochromic properties. At pressures higher than 60 mTorr, the formation of an unidentified second phase is observed by XRD. At pressures lower than 60 mTorr the films usually are lithium deficient and consist of a single cubic phase.

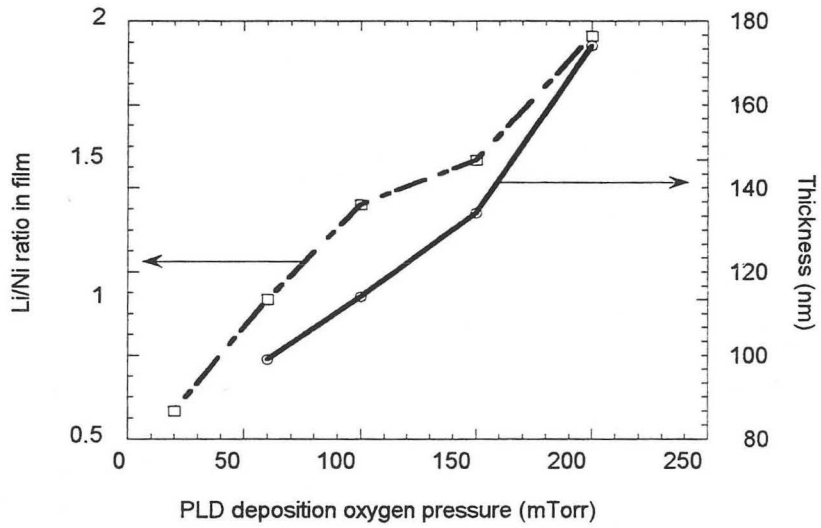


Figure 2. Film thickness and Li/Ni ratio as function of O_2 PLD deposition pressure

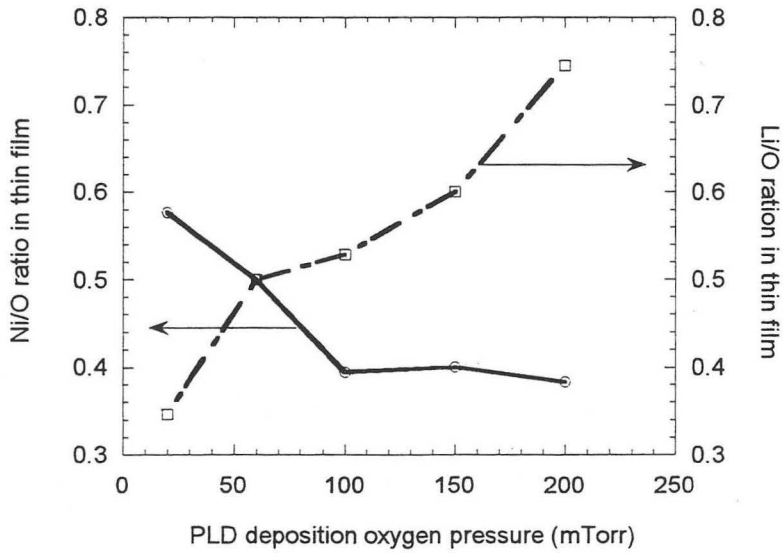


Figure 3. Li/O and Ni/O ratios as function of O_2 PLD deposition pressure

Cyclic voltammograms and long term cycling were obtained from fresh PLD $Li_{0.5}Ni_{0.5}O$ films. The films were cycled in 1M $LiPF_6$ in 1:1 ethylene carbonate/propylene carbonate over the range 1.0 to 4.5 V vs. Li/Li^+ using lithium foil counter and reference electrodes. The stoichiometric $Li_{0.5}Ni_{0.5}O$ PLD film

(Figure 4) was very stable over eight cycles and achieved its full optical range on the first cycle. The maximum transmission change for film of 120 nm is 70% under a voltage sweep rate of 1mV/s and remains stable during long-term cycling. While scanning at a much higher rate of 10 mV/s, this film still shows more than 30% visible transmission modulation. The long term CV cycling behavior was tested over 1000 cycles. Last cycles are shown in Figure 5. The testing was stopped before any degradation of electrochromic performance could be detected. The smaller visible transmission modulation is due to the faster voltage sweep rate that does not allow to intercalate the same amount of charge into and from the film. Otherwise the optical coloration and bleach efficiency is the same considering the coloration and bleach charge quantity.

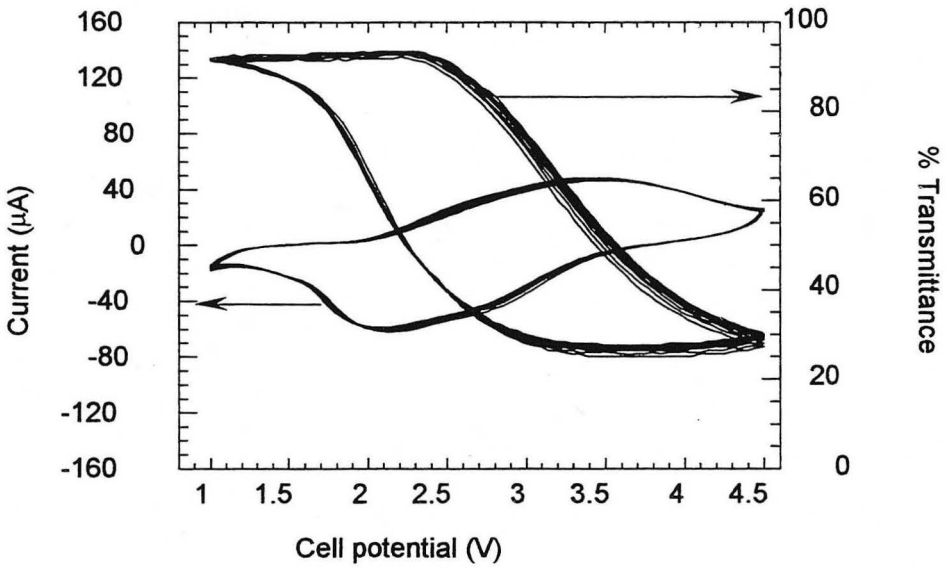


Figure 4. Cyclic voltammograms and transmittance of PLD $Li_{0.5}Ni_{0.5}O$ at 1mV/s

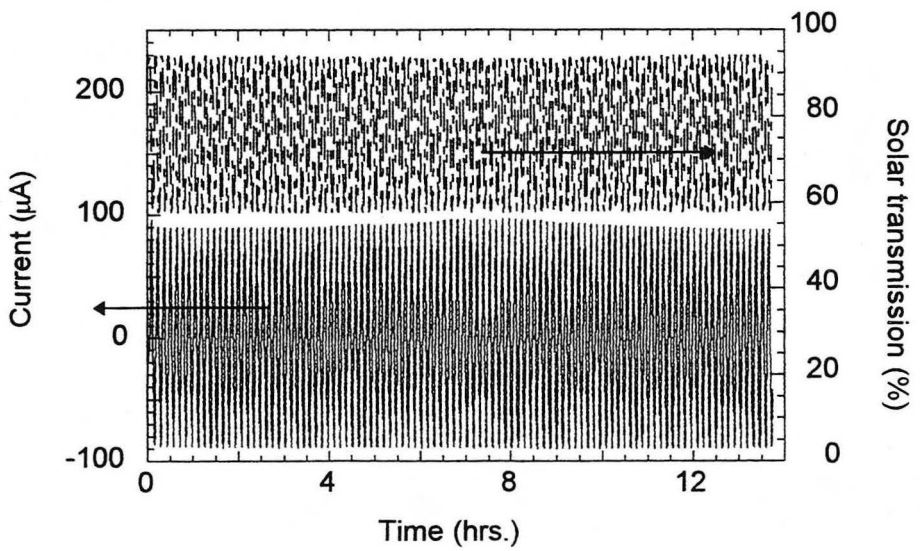


Figure 5. Cyclic voltammograms and transmittance of PLD $Li_{0.5}Ni_{0.5}O$ at 10mV/s

Spectral transmittance data shows that the as-deposited $Li_{0.5}Ni_{0.5}O$ film exhibits a neutral grayish color (Figure 6),which is an advantage for building applications. Since the absorption in the dark state is especially significant in the UV and lower visible part of the spectrum, combination of a WO_3 electrode with an active $Li_{0.5}Ni_{0.5}O$ counter electrode eliminates the strong blue color typically found in WO_3-based devices.

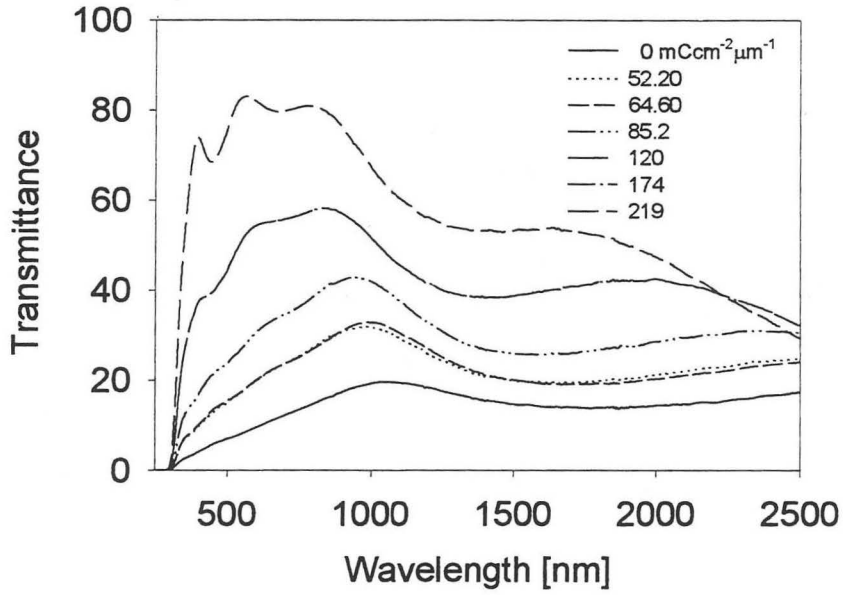
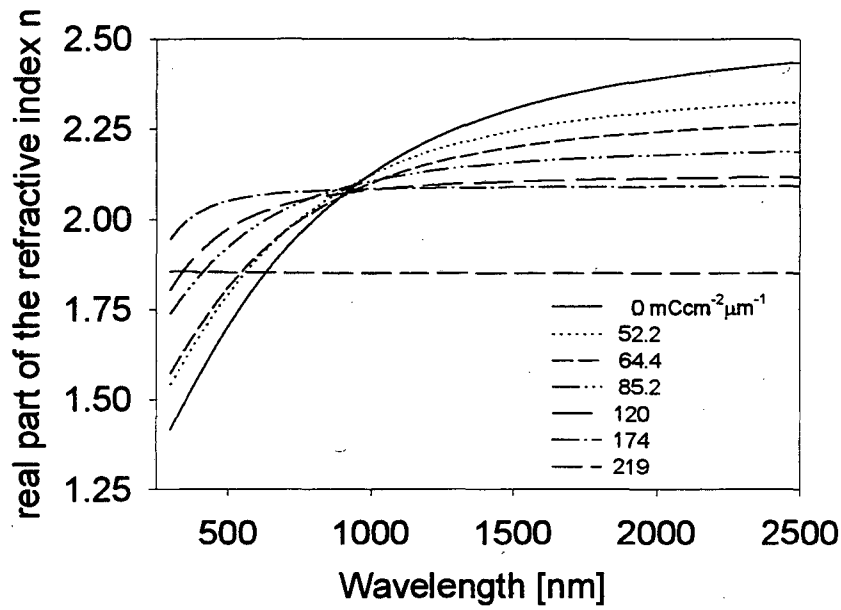


Figure 6. Variation in spectral transmittance with injected charge of a $Li_xNi_{1-x}O$ /ITO/glass half cell

To accurately predict the apparent color of a complete device knowledge of the complex refractive index is necessary. Therefore we determined the optical indices of $Li_yLi_{0.5}Ni_{0.5}O$ over the entire solar spectrum in a range of electrochromic states (Figure 7). The real part of the refractive index increases with wavelength which usually can be found in metallic compounds. In the clear state, however, it exhibits a dielectric dispersion. The extinction coefficient does not show a pronounced absorption band as it can be found in WO_3 (4). Optical design of a complete electrochromic device based on a WO_3 electrode and $Li_yLi_{0.5}Ni_{0.5}O$ counter electrode was shown in detail elsewhere (5).



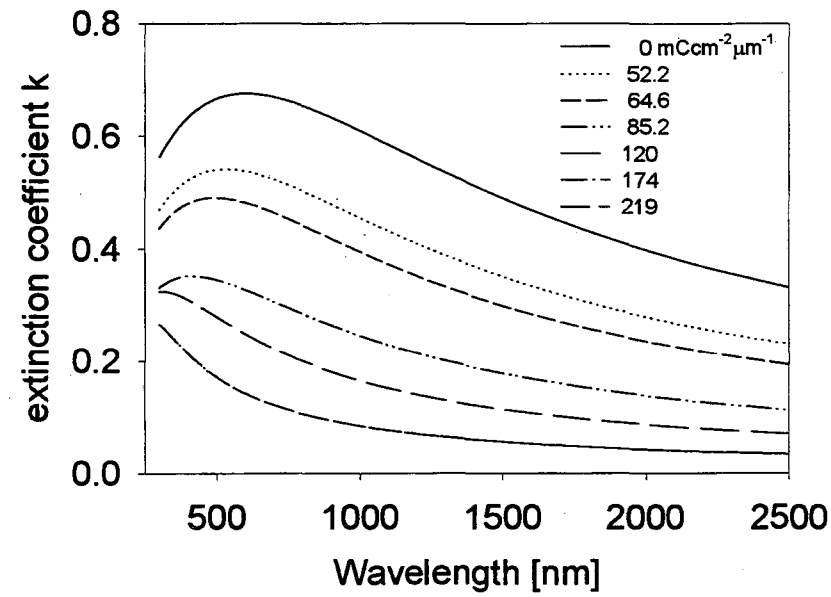


Figure 7. Optical indices of $Li_xNi_{1-x}O$ deposited by PLD at 60 mTorr oxygen partial pressure in various lithiation states: a) real and b) imaginary parts

CONCLUSIONS

PLD is a highly useful technique to produce thin film $Li_{0.5}Ni_{0.5}O$ with optimal electrochromic properties. Modification of sputtering conditions or target stoichiometry should enable us to produce similar films by conventional large-area deposition. Films having the stoichiometric composition switch over a wide optical range, in the class of primary coloring electrodes like WO_3, without the need for initial electrochemical formatting. The films seem also to have good long-term stability.

ACKNOWLEDGMENT

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