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HIGHLY REVERSIBLE ELECTROCHEMICAL INSERTION OF LITHIUM, ACCOMPANIED WITH A MARKED COLOR CHANGE, OCCURING IN MICROCRYSTALLINE LITHIUM NICKEL OXIDE FILMS

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Thin films of lithium-nickel oxide, whose texture consists of microcrystallites with an average grain size of 50 Å, permit highly reversible electrochemical insertion of lithium ions in Li^+ conducting electrolytes. Therefore, the corresponding materials would be of great interest for energy storage applications. In addition, the lithium insertion/extraction reactions in the nickel-based layers are accompanied with a marked color change, making these films of interest for the development of electrochromic displays for the control of light transmission in windows ("smart windows").

1. INTRODUCTION

Thin film-electrochromic (EC) materials (ECM) and displays (ECD) present a basis for light modulators and other electro-optic devices. The ECD can be presumed as a system $E_1/M_1/I/M_2/E_2$, containing an ECM (M_1), an ion conducting material (I), and the so-called counter-electrode (M_2) between two electronic conductors (E_1 and E_2) serving as ohmic contacts. If M_1 is an ECM which colors during the cathodic process when electrons and small cations (H^+, Li^+, Na^+, and others) are being injected, then M_2 must be reversible to ions involved in the EC reaction. However, the most promising ECD are those containing two ECM, i.e. coloring cathodically (M_1) and coloring anodically (M_2): that leads indeed to an increase of the optical efficiency of the ECD. The most important problem in the development of such ECD is the compatibility of M_1 and M_2 with the solid electrolyte (I). In this prospect, M_1 and M_2 should be selected among transition metal oxides, such as:
(i) WO_3, MoO_3, V_2O_5, TiO_2; they color cathodically and, therefore, constitute in thin film the M_1 electrodes of the ECD (1–3).
(ii) IrO_xH_y, NiO_xH_y; they behave, in thin films, as M_2 electrodes as they color

anodically, i.e. upon removal of cations (4–6). Therefore they behave optically in a complementary fashion to M_1.

Concerning class (ii) oxides, reversible charge insertion processes have been mainly observed in aqueous electrolytes (4–6). However, long term electochemical stability, at elevated temperatures, of ECD is likely to occur when Li^+ rather than H^+ is used as the mobile species (7–10). We have recently reported on a new strategy,* and related experiments, that have enabled us of bringing to light a new family of ECM_2 electrodes operating with Li^+ ions (designated below as ECM_2 (Li^+)) (11, 12).

This paper presents the results of some of our investigations, within the framework of this strategy, on a new ECM_2 (Li^+) of composition:

$$Li^+_{2-x}Ni^{II}_{1-x}Ni^{III}_xO_2$$

For sake of clarity we will mainly focus on the EC properties of the films (results concerning the determinations of film structure and texture, chemical and physical analysis, transport properties, etc., will be reported elsewhere (13)). In this prospect, their similar optical properties with "X-ray amorphous" WO_3 films (13) will also be evaluated. Finally, the EC properties of complete polymeric-solid-state ECD, using WO3 as ECM_1, and nickel or chromium-based ECM_2 will be investigated.

2. EXPERIMENTAL

Float-glass substrates of 50 × 50 mm size, coated with a thin layer of transparent, electronic-conductive material (E_1 E_2 ITO) have been used.

The nickel-based ECM_2 electrodes are prepared by RF sputtering at room temperature of home made targets of 100 mm diameter (table I). It is followed by an electrochemical treatment performed in a dry box; the procedure makes use of a two-electrode cell configuration, namely, the Ni-based films and a lithium counter-reference electrode. Both electrodes are immersed in a $1MLiClO_4$ propylene carbonate electrolyte. The film is then polarized at 1.5V for 20 mn in order to get the final X-ray amorphous material Li_2NiO_2.

As for the WO_3 electrodes (1100 Å thick), they were prepared by DC sputtering of a metallic W target (10).

The EC properties of each separate ECM were studied in a dry box using the above mentioned electrochemical cell.

A polyurethane-based polymer containing $LiClO_4$ (10) was used as the electrolyte in a complete ECD. The basic structure of the corresponding laminated-lithium-

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* It takes into consideration polycrystalline lithiated semiconducting films: the reversible-electrochemical insertion process of lithium would be all the more efficient as the crystallite size is reduced. It would be highly efficient for X-ray amorphous lithiated films whose texture consists of microcrystallites of less than 50 Å size.

TABLE I
Experimental conditions for the reactive RF sputtering of lithium and nickel-based films.

Target	$LiNiO_2$
Initial pressure	10^{-5} mbar
Atmosphere	Ar(80%)-O_2(20%)
Pressure	10^{-2} mbar
Sputtering time	80 mn
Film thickness	1100 Å

based ECD is:

$$\text{Float glass ITO} \quad Li_x\,Wo_3 \quad \underset{Li+}{\text{SPE}} \quad Li_{2-x}\,NiO_2 \quad \text{ITO Float glass} \qquad [1]$$

With SPE symbolizing the Solid Polymer Electrolyte.

The cycling and optical tests were obtained with standard electrochemical and optical equipment (12).

3. ELECTROCHEMICAL-CHROMIC PROPERTIES OF SEPARATE EC LAYERS: study of "Li/$LiClO_4$-pc/$Li^+_{2-x}Ni^{II}_{1-x}Ni^{III}_xO^{2-}_2$/ITO/glass," "Li/$LiClO_4$-pc/$Li^+_xW^{5+}_xW^{6+}_{1-x}O_3^{-2}$/ITO/glass," cells

The electrochemi-chromic testing must be processed within an appropriate voltage range to avoid electrolyte oxidation on the one hand and (eventual) ITO reduction on the other hand.

In this prospect, the electrochemical stability of the $LiClO_3$-PC, of the $LiClO_4$-based polurethane electrolyte, and of ITO was first established by cyclic voltammetry using a bare ITO-coated glass. The resulting voltammograms reveal an electrochemical-stability range confined between 1.5 V and 3.8 V vs Li (fig. 1).

Corresponding coloring and bleaching cycles of the ECM, performed within the electrochemical stability range fixed above and using the above mentioned cell configuration are reported in fig. 2 (a-b).

For all films the Li^+ electrochemical (des)insertion was readily reversible. The charge transferred was as high as $2.5 \times 10^3 C/cm^3$ even after 10^4 cycles. The knowledge of the range of film specific weigh of 3-4 g/cm^3 (13) would give, for all samples, a modulation of the lithium content of about 0.4–0.5.

We will present evidence elsewhere, from textural characterizations (TEM, SEM, RBS analysis) and by using pulse-based electrical techniques, that the kinetics of the electrochemical process is mainly controlled by diffusion of Li^- ions through the films on the crystallite surface (14).

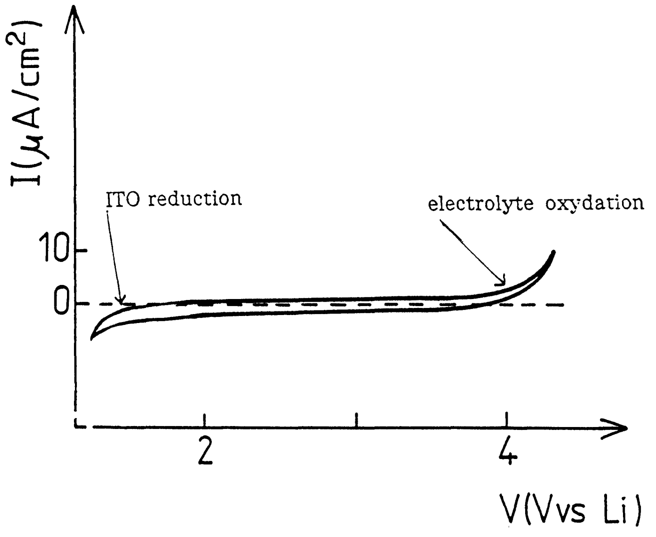

FIGURE 1 Electrochemical stability range of the system: $LiClO_4$ – PC (or $LiClO_4$-based polyurethane) electrolyte/ITO (30 Ω/M) coated float-glass.

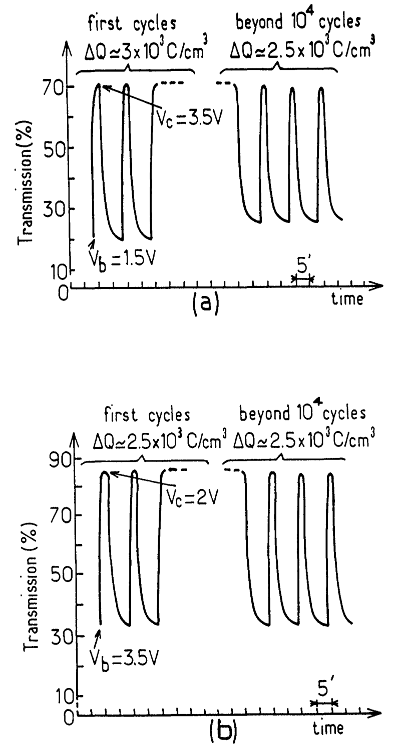

FIGURE 2 Transmission (λ = 550 nm) vs time, for repeated coloring and bleaching cycles, of the ECM (Li^-).
(a) $Li^+_{2-x}\ Ni^{II}_{1-x}\ Ni^{III}_x\ O^{2-}_2$
(b) $Li^+_x\ W^{6+}_{1-x}\ W^{5+}_x\ O^{2-}_3$

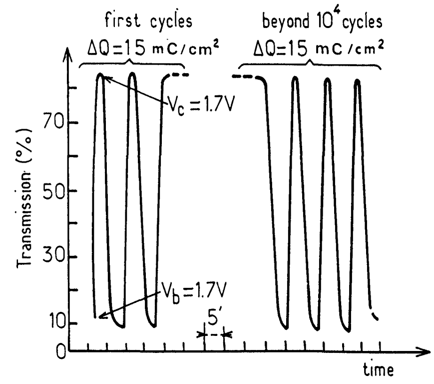

FIGURE 3 Transmissions (λ = 550 nm) vs time, for repeated colouring and bleaching cycles, of the ECD: Li_x WO_3/SPE (Li^+)/Li_{2-x} NiO_2.

4. ELECTROCHROMIC EVALUATION OF THE ECD

Figure 3 presents evidence of the expected repetitive-cycling behavior, associated with a net electrochromic effect, of the polymeric solid state ECD. The electro-chemi-chromic effect involves the passage of lithium from one electrode to the other, depicted by the reaction:

$$\underset{\text{clear (Ni}^{\text{II}})}{Li_2^+Ni^{II}O_2^{2-}} + \underset{\text{clear(W}^{6-})}{W^{6+}O_3^{2-}} \xrightleftharpoons{\text{xLi+ exch.}} \underset{\text{brown (Ni}^{\text{III}})}{Li_{2-x}^+Ni_{1-x}^{II}Ni_x^{III}O_2^{2-}} + \underset{\text{blue (W}^{5-})}{Li_x^-W_{1-x}^{6-}W_x^{5+}O_3^{2-}} \quad [2]$$

5. CONCLUSION

We have shown that the texture of the new ECM_2 (Li^+) presented here provides fast-reversible electrochemical insertion of lithium.

Two reasons accounting for this process, and which are presently explored (14), can be postulated. Indeed the film texture, which consists of microcrystallites with an average grain size of 50Å (13), would provide: (i) a random network of channels sufficiently large to permit easy access of Li^+ ionic species into the bulk of the film; (ii) vacant sites (dangling bonds), at the surface of the crystallites, which themselves supply the ionic species with temporary bonding sites. We have recently described such a phenomena for "similarly amorphous" strontium-titanium oxide films (15, 16).

Finally we are inclined to conclude that by configurations similar to [1], new and efficient "smart windows" may be developed.

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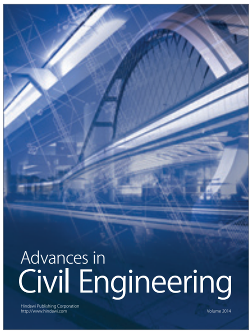
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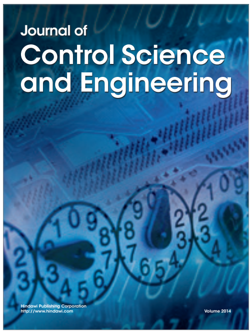
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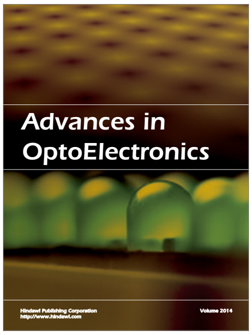
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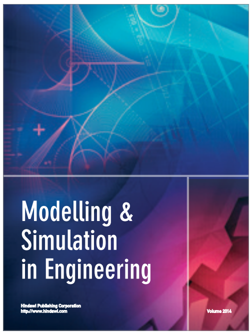
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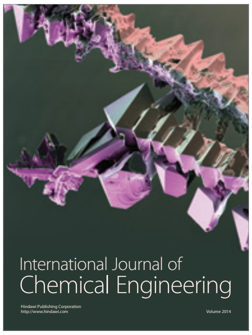
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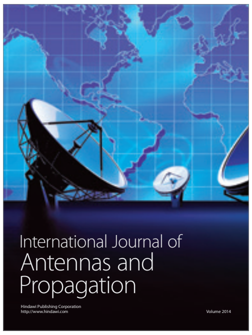
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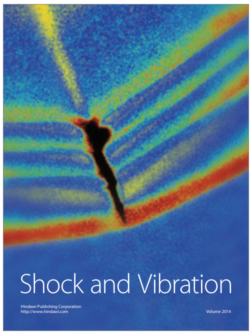
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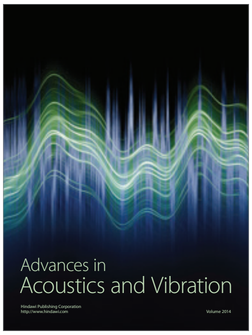
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