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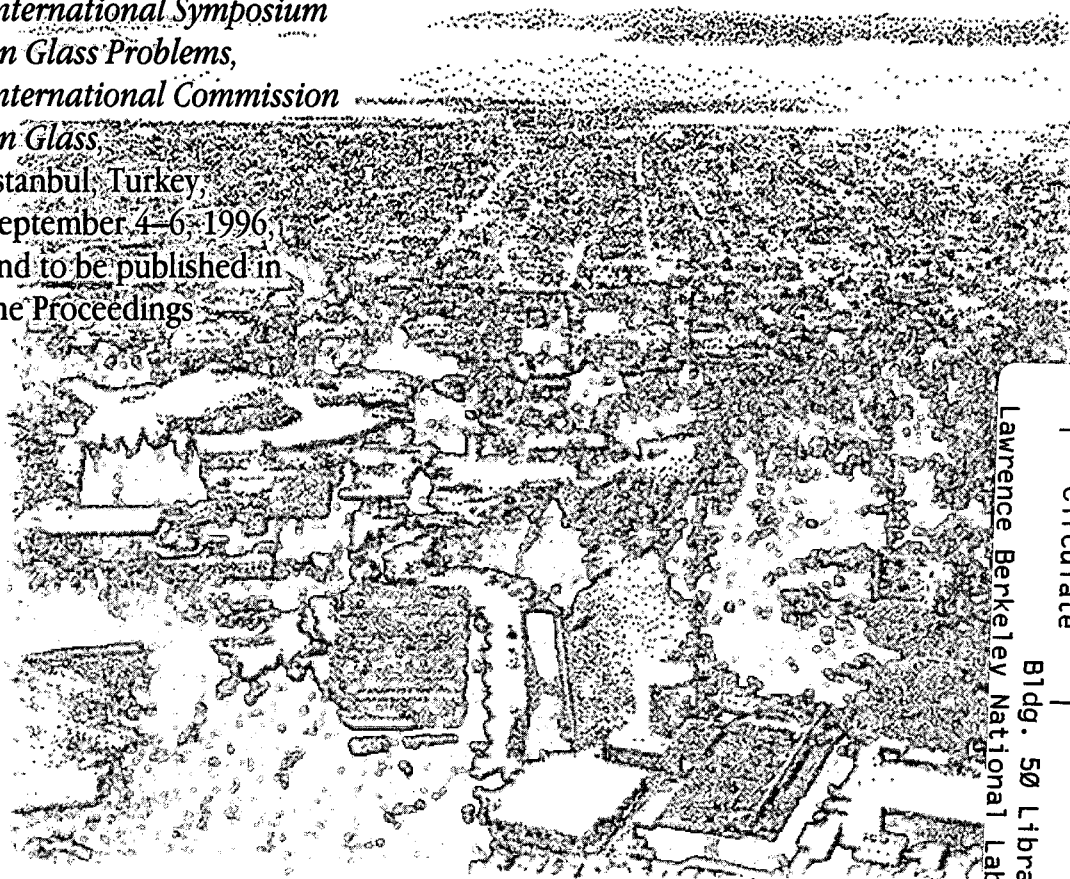
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**Environmental Energy  
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## **Sol-Gel Deposited Electrochromic Films for Electrochromic Smart Window Glass**

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August 1996

## SOL-GEL DEPOSITED ELECTROCHROMIC FILMS FOR ELECTROCHROMIC SMART WINDOW GLASS

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### Abstract

Electrochromic windows offer the ability to dynamically change the transmittance of a glazing. With the appropriate sensor and controls, this smart window can be used for energy regulation and glare control for a variety of glazing applications. The most promising are building and automotive applications. This work covers the use of sol-gel deposition processes to make active films for these windows. The sol-gel process offers a low-capital investment for the deposition of these active films. Sol-gel serves as an alternative to more expensive vacuum deposition processes. The sol-gel process utilizes solution coating followed by a hydrolysis and condensation. In this investigation we report on tungsten oxide and nickel oxide films made by the sol-gel process for electrochromic windows. The properties of the sol-gel films compare favorably to those of films made by other techniques. A typical laminated electrochromic window consists of two glass sheets coated with transparent conductors, which are coated with the active films. The two sheets are laminated together with an ionically conductive polymer. The range of visible transmission modulation of the tungsten oxide was 60% and for the nickel oxide was 20%. We used the device configuration of glass/ SnO<sub>2</sub>:F/ WO<sub>3</sub>/polymer/Li<sub>2</sub>NiO<sub>x</sub>H<sub>y</sub>/SnO<sub>2</sub>:F glass to test the films. The nickel oxide layer had a low level of lithiation and possibly contained a small amount of water. Lithiated oxymethylene-linked poly(ethylene oxide) was used as the laminating polymer. Commercially available SnO<sub>2</sub>:F / glass (LOF-Tec glass) was used as the transparent conducting glass. We found reasonable device switching characteristics which could be used for devices.

### 1. INTRODUCTION

Electrochromism (EC) can be broadly defined as a persistent and reversible color change as a function of injected/extracted charge and their coloration can be controlled via the number of coulombs passed during electrochromic reaction. Electrochromic materials are attractive candidates for smart window applications (1). Electrochromic devices consist of thin films that provide optical modulation, ion conduction and transparent electrical conduction.

Electrochromic smart windows can be constructed in several different ways (2). One design these windows consist of oxide layers that are deposited on two conductive glass

substrates. These coated glass substrates are then laminated together with the appropriate ion conductor(3). The electrochromic layer and ion storage layers conducts both ions and electrons. When a small current is applied across the multilayer film, ions will be inserted into or extracted from the electrochromic oxide layer. As a result, the film changes its optical properties due to absorption and electron density changes, giving the switching effect. Such a window can change in transmittance continuously over a wide range (such as 80-15 %) in a time period of seconds to less than one minute depending on window size. The window will retain its optical properties once the power is turned off, and is fully reversible after many cycles.

Smart windows can be used in buildings to control day lighting to create efficient work conditions. Controlled modulation of solar radiation through smart windows has a large potential in buildings for energy savings(4). Properly designed and managed smart windows have the technical potential to save 50-70 % of the lighting energy used in exterior offices (2). Recently a number of tandem smart window systems have been investigated, and most have used  $WO_3$  as the working electrochromic layer (5-9). Typically these windows consist of vacuum deposited layers. It is desirable for costs to be below \$ 150/m<sup>2</sup> for large area applications. Sol-gel processing requires less capital to deposit coatings over large areas than conventional vacuum methods, and hence offers a possible solution for lowering the deposition cost of these windows. Sol-gel processing also offers advantages in controlling the microstructure or depositing films containing multiple cations. These parameters can influence kinetics, durability, coloring efficiency and charge storage in the windows (10-11).

In this study, we present the characteristics of a sol-gel deposited smart window, using a  $Li^+$  conducting polymer layer. A  $WO_3$  / polymer electrolyte /  $Li_2NiO_xH_y$  electrochromic window is fabricated. Potentiostatic cycling coupled with transmittance measurement was performed at room temperature on the complete window in order to evaluate the performance of the window.

## 2. EXPERIMENTAL

Electrochromic  $WO_3$  and  $NiO_xH_y$  layers were deposited by sol-gel spin coating technique onto transparent conductive F :  $SnO_2$  coated glass substrates (LOF-Tec type).  $WO_3$  is used as the working electrode and electrochemically lithiated  $NiO_xH_y$  is used as the counter electrode.  $WO_3$  coatings have been deposited from colloidal solutions of tungsten oxachloride in isopropyl alcohol.  $NiO_xH_y$  coatings have been deposited from solutions of nickel methoxyethoxide in methoxyethanol (12). These films were amorphous to X-ray diffraction. Their thickness, measured by a profilometer with an accuracy of  $\pm 10$  nm was 120 nm for  $NiO_xH_y$  and 250 nm for  $WO_3$ . The films were electrochemically characterized after heat treatment at 300°C. Lithiation of  $NiO_xH_y$  film was carried out by electrochemical insertion of lithium into the film from solution.

The polymer electrolyte was amorphous oxymethylenelinked poly (oxyethylene), [ $\alpha$ -PEO], synthesized by the method given in ref. 13. The ion conducting polymer prepared by dissolving 2 g of  $\alpha$ -PEO and 0.48 g of  $LiClO_4$  in acetonitrile, with a O:Li atomic ratio of 10:1, giving rise to the highest conductivity of  $10^{-4}$   $Scm^{-1}$ . This viscous polymer was dried in vacuum oven and residual solvent was allowed to evaporate slowly at a 40°C.

The electrochromic system was made by joining the pre-lithiated  $\text{LiNiO}_x\text{H}_y$  /  $\alpha$ -PEO /  $\text{F}:\text{SnO}_2$  coated glass with the  $\text{WO}_3$  /  $\text{F}:\text{SnO}_2$  coated glass. The polymeric solid electrolyte was laminated between the two electrodes. The windows were hot-pressed at  $80^\circ\text{C}$  in the dry box and sealed with a low vapor pressure adhesive (Varian Torr-seal). The optical performance of the windows was measured with a Perkin and Elmer Lambda 2 UV / VIS spectrophotometer.

### 3. RESULTS AND DISCUSSION

We have successfully fabricated prototype small area (2 cm x 3 cm) five layer smart window devices. Figure 1 shows the schematic of the laminated smart window. This is a five-layer device that has been deposited on a transparent conducting substrate.  $\text{WO}_3$  is used as cathodically coloring electrode and lithiated  $\text{NiO}_x\text{H}_y$  is used as anodically coloring electrode.

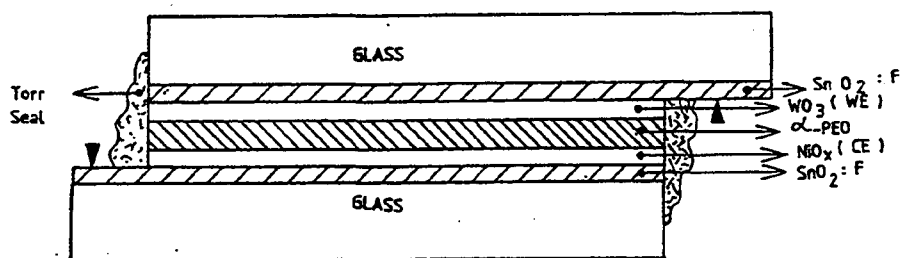
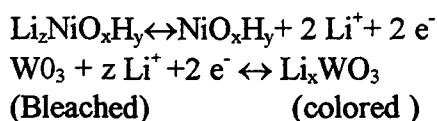


Fig. 1. Schematic diagram of a sol-gel deposited, laminated smart window.

The following reaction takes place as a lithium is transported from the  $\text{NiO}_x\text{H}_y$  layer to  $\text{WO}_3$  via ion conductor.



$\text{WO}_3$  goes through a large optical modulation from transparent to a deep blue tungsten bronze color when lithianated (14).  $\text{NiO}_x\text{H}_y$  changes from colorless state to a brown colored state with lithium extraction. This device exhibits good spectrally selective transmissivity in the visible range. Such a device has been switched between  $\pm 1.4$  V for more than 1200 cycles.

The cyclic voltammetry of the  $\text{WO}_3$  /  $\alpha$ -PEO- $\text{LiClO}_4$  /  $\text{Li}_z\text{NiO}_x\text{H}_y$  window is shown in Figure 2. The window shows a reproducible electrochromic behavior for many cycles. During the cathodic scan the window becomes dark while during the anodic scan the window becomes transparent. Both coloration and bleaching took place in within 15 seconds as judged from visual observation.

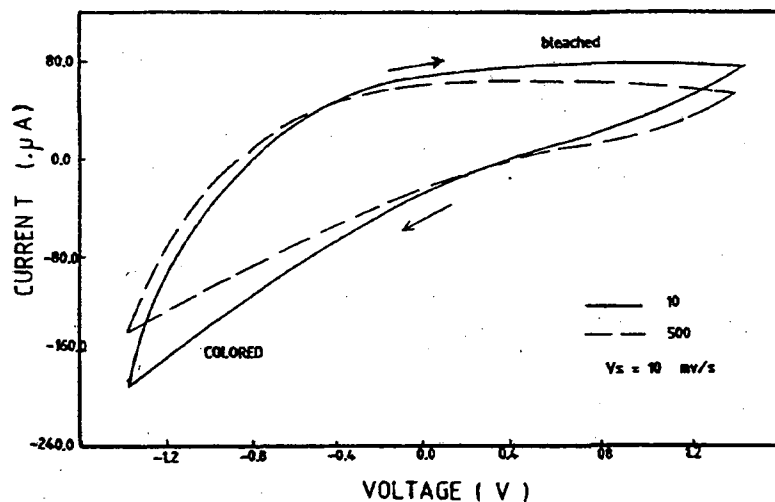


Fig. 2. Cyclic voltammogram of the prototype ( F: SnO<sub>2</sub> / WO<sub>3</sub> / α-PEO-LiClO<sub>4</sub> / Li<sub>2</sub>NiO<sub>x</sub>H<sub>y</sub> / F: SnO<sub>2</sub> ), laminated window at room temperature.

The electrochromic response of WO<sub>3</sub> / α-PEO-LiClO<sub>4</sub> / Li<sub>2</sub>NiO<sub>x</sub>H<sub>y</sub> window is further demonstrated by Figure 3 and Figure 4 which show changes in current and transmittance with time under a constant potential of ± 1.4 V. Figure 4 reveals a good charge reversibility, with a total transmittance variation at 556 nm of ΔT=30 % and an acceptable switching time of the order of 50 sec . The solar optical transmittance spectra of the WO<sub>3</sub> / α-PEO-LiClO<sub>4</sub> / Li<sub>2</sub>NiO<sub>x</sub>H<sub>y</sub> window is shown in Figure 5. The window becomes dark blue by the cathodic scan and becomes transparent by anodic scan. The window was observed for more than 1200 cycles and little detectable change in their optical and electrochemical properties could be observed.

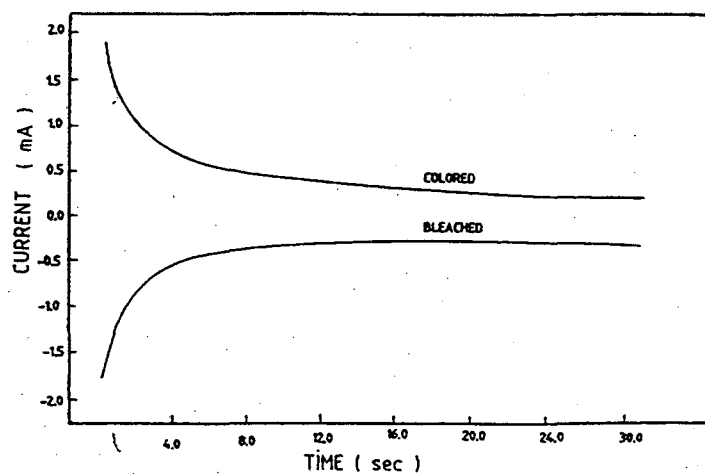


Fig 3. Transmittance change of the glass-F:SnO<sub>2</sub> - Li<sub>2</sub>NiO<sub>x</sub>H<sub>y</sub> / α PEO - LiClO<sub>4</sub> / WO<sub>3</sub> - F: SnO<sub>2</sub> - glass window, upon application of a voltage of ±1.4 V.



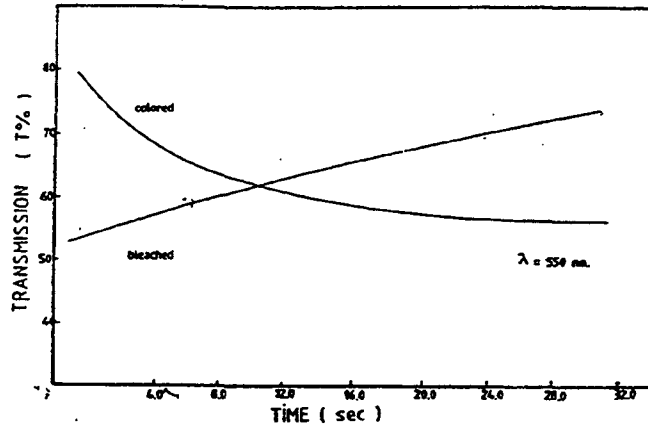


Fig. 4. Charge reversibly exchanged during the coloring - bleaching process of the window.

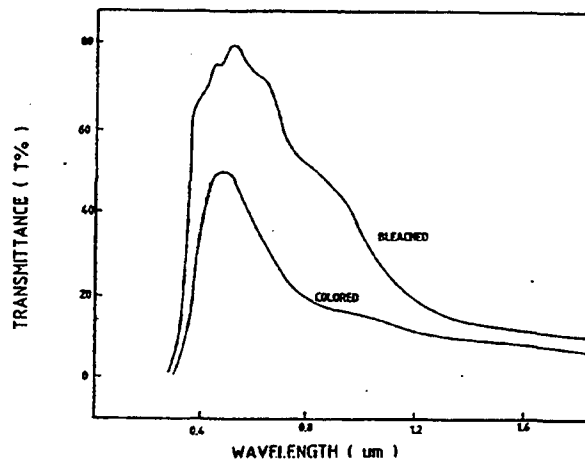


Fig. 5. Optical transmittance of sol-gel deposited smart window having the configuration: glass - F:  $\text{SnO}_2$  -  $\text{LiNiO}_x\text{H}_y$  /  $\alpha$  PEO -  $\text{LiClO}_4$  /  $\text{WO}_3$  - F:  $\text{SnO}_2$  - glass.

#### 4. CONCLUSION

Sol-gel deposited electrochromic layers can be used for the fabrication of electrochromic smart windows. A prototype of smart window glass employing sol-gel deposited layers has been successfully fabricated. In the prototype device, a  $\text{WO}_3$  film was used as a working electrochromic layer, and a  $\text{Li}_2\text{NiO}_x\text{H}_y$  film as the counter electrode, and amorphous oxymethylene linked poly (oxyethylene) -  $\text{LiClO}_4$  as an ion conducting layer. The polymeric ion conducting layer was transparent and showed a high ionic conductivity of the order of  $10^{-5} \text{ Scm}^{-1}$  at room temperature. Potentiostatic cycling ( $\pm 1.4 \text{ V}$ ) was performed on the electrochromic window and reversible transmittance variance from 50 % to 80 % was observed at 550 nm. The device cycled unchanged for 1200 cycles.

## ACKNOWLEDGMENT

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