

Sol-gel coatings for electrochromic devices

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ABSTRACT

Electrochromic devices have potential applications in architectural and automotive fields to regulate the transmission and reflection of the radiant energy. Preliminary characteristics of an all sol-gel window with the configuration glass\ITO\WO₃\TiO₂\TiO₂-CeO₂\ITO\glass is presented, and compared with another window where WO₃ was deposited by evaporation. We also present preliminary data of a sol-gel Nb₂O₅ electrochromic layer as well as a thorough evaluation of the properties of a sol-gel TiO₂-CeO₂ ion storage coating where electrochemical properties are studied as a function of various parameters (thickness, heat treatment, etc.).

1. INTRODUCTION

The development of all solid state electrochromic devices such as smart windows and reflective mirrors is of utmost importance [1]. A typical system working in transmission is made of five layers sandwiched between two glass substrates (figure 1). There are two transparent electrical conductors (TC) which are required for setting up a distributed electric field, an electrochromic layer (EC), an ionic conductor (IC) and an ion storage layer (counter electrode) for H⁺ or Li⁺ ions (IS).

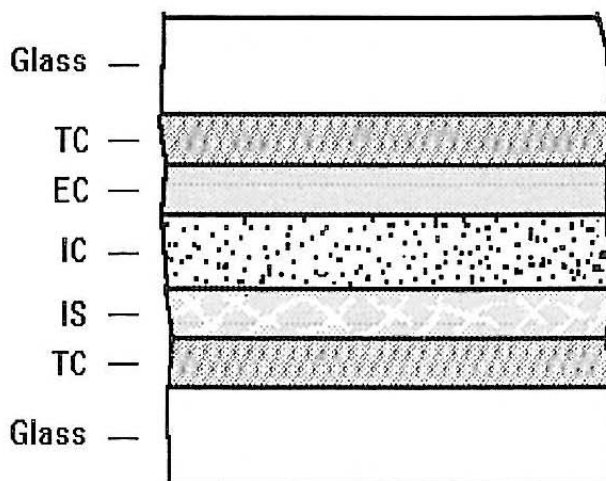


Figure 1. Schematic cross-section of a typical solid state electrochromic device working in transmission. TC=transparent electronic conductor, EC=electrochromic coating, IC=ionic conductor (electrolyte), IS=ion storage layer (counter electrode).

When a small current is passed through the cell the ions stored in the counter electrode diffuse toward the electrochromic layer and change its transmittance continuously over a wide spectral range and consequently alter the overall optical transmission of the device. These devices have a time response which varies from seconds to less than a minute and most of them can maintain their optical properties when the power is turned off for several hours (memory effect). When the process is reversible, the original bleached state is obtained by reversing the applied voltage.

The current collecting layers are usually made of a mixed oxide $\text{In}_2\text{O}_3\text{-SnO}_2$ (ITO) of low electrical resistivity.

Nowadays the preferred electrochromic layer is WO_3 whose structure and color are modified by electrochemical insertion of ions following the reaction



where A^+ can be H^+ , Li^+ , Na^+ , etc. The net result of the insertion reaction is the reduction of the transparent WO_3 host material and its transformation into a blue colored tungsten bronze $\text{W}^{6+}_{1-x}\text{O}_{3-x}\text{W}^{5+}_x$. Its coloration is due to the presence of a large absorption band in the visible and near infrared region ($E_{\text{max}} \approx 1.4\text{eV}$) attributed to electronic transitions from the reduced tungsten ions states W^{5+} toward the conduction band [2,3]. Although the chemical diffusion of Li^+ ions is smaller than that of H^+ , these ions are preferred as hydrogen usually presents degassing phenomenon and the acid media of the electrolyte limits the lifetime of the devices [4].

Many electrolytes have been tested. The advantages of polymeric ion conductors over liquid ones is now recognized [4,5] as they provide good electrolyte/electrode contact and present less problems of leakage. Among them polyethylene oxide (PEO) complexed with alkali salt such as LiClO_4 , LiCF_3SO_3 or $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ exhibits good Li^+ conductivity in the range 10^{-4} - 10^{-7}S/cm at room temperature.

Various oxides such as V_2O_5 [6,7], Ir_2O_3 [8,9], CeO_2 [10] have been proposed for counter electrode but none of them exhibits ideal properties of transparency, reversibility and high kinetics for the electrochemical reaction with Li^+ ions. Recently we have proposed the use of $\text{TiO}_2\text{-CeO}_2$ layers prepared by sol-gel process; this compound allows a better Li^+ insertion kinetics than pure CeO_2 [7,11,12,13].

The sol-gel science [14] has now reached a point where it is possible to contemplate the realization of a complete solid state electrochromic cell via such a process. In this paper we present up to date results relative to the preparation and characterization of sol-gel electrochromic coatings of WO_3 and Nb_2O_5 compositions, of a sol-gel protonic conductor based on TiO_2 coating and an improved sol-gel preparation of the ion storage $\text{TiO}_2\text{-CeO}_2$ layer. The Li^+ charge density inserted or extracted in the ion storage layer is studied as a function of various parameters such as aging of sol, temperature and time of densification, thickness of the layer and type of ITO conductor. The optical response of a complete all solid state sol-gel window is presented and compared to a similar device built with coatings prepared by other methods of preparation.

2. EXPERIMENTAL AND PROCEDURE

2.1. Sol-gel coatings

The different layers of the complete sol-gel electrochromic cell have been obtained or prepared as following:

a) The transparent *electric conductors* (TC) were all ITO layers supplied by Balzers (Baltracon Z20, $\rho=2.6 \cdot 10^{-4} \Omega\text{cm}$), Donally (FW 5005, $\rho=2.6 \cdot 10^{-4} \Omega\text{cm}$) or Asahi Glass (plasma assisted evaporation $\rho=3.5 \cdot 10^{-4} \Omega\text{cm}$).

b) Two different electrochromic coatings have been developed. The first one is of WO_3 composition and was prepared by sol-gel process using a colloidal solution (0.5M). This solution was acidified when it passed through an ion-exchange resin[15,16]. The colloidal solution was stabilized by addition of dimethyl sulfoxide $(\text{CH}_3)_2\text{SO}$ in order to avoid the precipitation of $\text{WO}_3 \cdot 2\text{H}_2\text{O}$. The sol was sprayed on ITO coated glass substrates previously heated to a temperature of the order of 150 C. The second one is of Nb_2O_5 composition. Thin films were prepared by the sol-gel process arising by hydrolysis of niobium butoxide $\text{Nb}(\text{OBU}^n)_5$ prepared via the sodium method[17]. Initially niobium chloride NbCl_5 was dissolved in butanol; the solution was then mixed with sodium butoxide $\text{Na}(\text{OBU}^n)$ under reflux. A strong exothermic reaction occurs and leads to the formation of sodium chloride NaCl and $\text{Nb}(\text{OBU}^n)_5$ (0.5M). Sodium chloride was separated by centrifugation resulting in a yellow transparent solution. The final sol was prepared by mixing $\text{Nb}(\text{OBU}^n)_5$ and glacial acetic (CH_3COOH) with a molar ratio 1:2. This sol is stable for several months. The dip-coating method was used to obtain the films. Glass substrates coated with ITO (Asahi Glass) were dipped in this sol and withdrawn at a speed of 4 cm/min, dried at 80°C for 15 minutes and densified by heat treatment at 600°C during 60 minutes. The procedure was repeated to obtain thicker films.

c) The *ion storage* coating (IS) or counter electrode consisted of TiO_2 - CeO_2 layers also prepared by sol-gel processing. The TiO_2 - CeO_2 precursor sols were prepared using $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$ salt dissolved in ethanol and to which was added tetraisopropyl orthotitanate with atomic ratio Ce:Ti up to 1:1 according to a method already described [7,11,12]. The use of isopropanol as solvent (instead of ethanol) leads to a precursor sol stable up to 3 months when kept at 5°C. The dissolution of the cerium salt results in a clear red solution [11] which becomes colorless after about 30 hours. This phenomenon is due to a slow reduction of Ce^{4+} according to:



The presence of the acetone is important for the sol stabilization.

The layers were deposited by dip coating on ITO coated glass at a 20 cm/min withdrawal speed resulting in films ~50 nm thick. After drying at room temperature for 15 minutes, the films were partially densified by heat treatment in air up to 550°C. The whole procedure was repeated up to 5 times to obtain thicker films.

d) Sol-gel TiO₂ protonic electrolyte was prepared according to the method proposed by Judeinstein et al. [16], where however Ti(OBuⁿ)₄ and glycerol (CH₂OHCH₂OH) were substituted by Ti(OPrⁿ)₄ and ethylene glycol (HOCH₂CH₂OH) respectively.

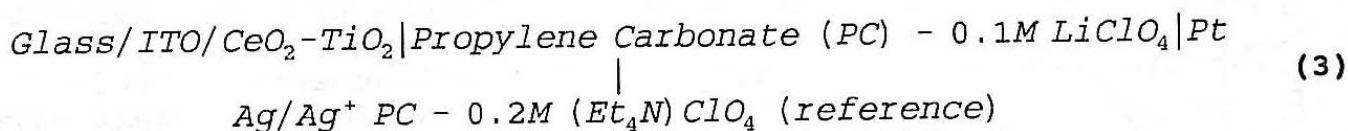
2.2. Other methods of coatings preparation

As it is shown later, the electrochromical and optical properties of a complete sol-gel cell are promising but except for the ion storage coating they are still far from reaching those obtained with other methods of preparation. The best results have been obtained in our laboratory using a WO₃ electrochromic coating (EC) deposited from the corresponding oxide powder by vacuum evaporation onto ITO/glass substrate. The films were amorphous to X-ray diffraction and their thickness measured with a Talystep was of the order of 200-300 nm. The chemical diffusion coefficient for Li⁺ ions is $D = 2,5 \cdot 10^{-11} \text{ cm}^2/\text{s}$ at 25°C [7]. For the cells using Li⁺ ions the ionic conductor layer (IC) was a polymer electrolyte complex prepared by dissolving polyethylene oxide (PEO) powder (M.W.=9.10⁶) and LiN(SO₂CF₃)₂ salt in acetonitrile with an 0:Li atomic ratio of 10:1. The viscous liquid was prepared in a glove box in absence of humidity and was poured onto the glass/ITO/WO₃ substrate. The solvent was evaporated at 50°C during 48h. The films were typically 50 to 200 nm thick. For the cells using H⁺ ions we obtained good results using a cellulose polyacetate protonic gel prepared by diluting 0,5g of cellulose monoacetate (Rhodialite-Rhodia-Brazil) in 2 ml of acetone to which 2 ml of an 80 vol% glacial acetic acid in water was then added. The best ion storage coating (IS) was found to be the sol-gel TiO₂-CeO₂ as described above.

3. CHARACTERIZATION OF THE SOL-GEL COATING

3.1. TiO₂-CeO₂ ion storage coating

The sol-gel TiO₂-CeO₂ coating used as ion storage present a fully reversible ion insertion and extraction process controled by solid state diffusion. The optical transmission of the film is high and remains unaltered during the cyclic process [7,11,12]. The total electric charge inserted or extracted during a cycle was measured at the 30th cycle with a Solartron 1286 Electrochemical Interface in a three electrode cell:



using a scanning speed of 50 mV/S and potential limits -1.8V and 0.5V.

The charge density Q inserted or extrated depends of the aging of the sol. It is maximum after 30 h and corresponds to the state of complete sol optical clearance (figure 2).

Figure 3 shows the influence of the heat treatment temperature on Q for films deposited from a sol aged 30h (peak of fig. 2) and heat treated for 15 min. The highest charge is obtained for treatment performed at

$T=450 \pm 20^\circ\text{C}$.

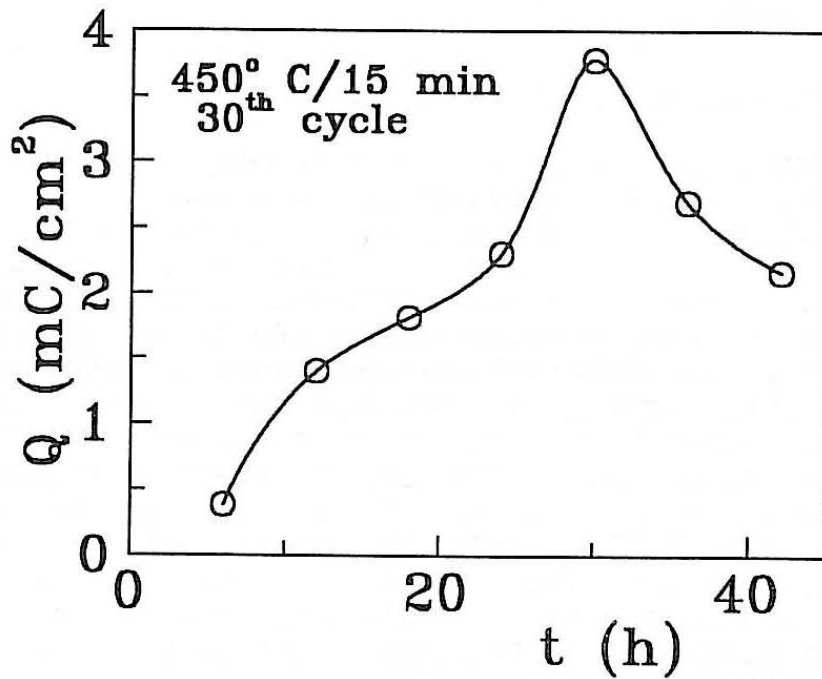


Figure 2. Li^+ charge density inserted in $\text{TiO}_2\text{-CeO}_2$ films at the 30th voltammetry cycle as a function of the precursor sol aging time. The films were dried at 80°C and densified at 450°C for 15 min.

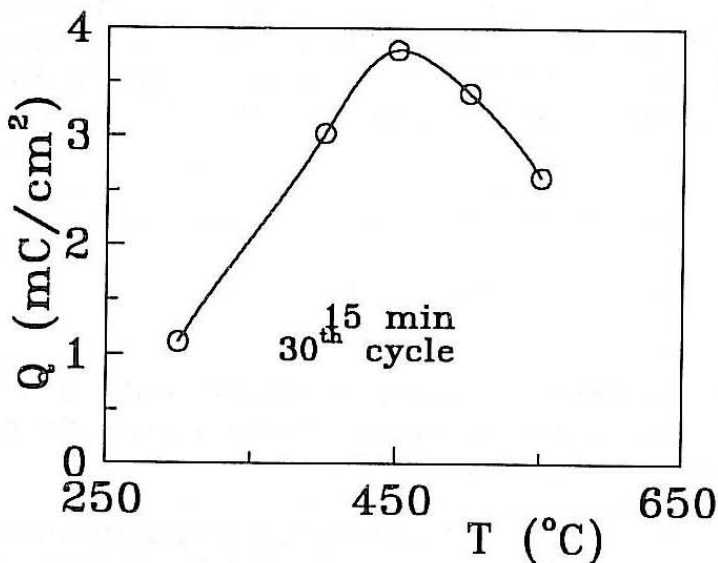


Figure 3. Li^+ charge density inserted (or extracted) into sol-gel $\text{TiO}_2\text{-CeO}_2$ films deposited on Baltracon ITO coating during the 30th voltammetry cycle as a function of heat treatment temperature (15 min). The films have been prepared from a RT 30 h aged sol.

Figure 4 shows the influence of the heat treatment time realized at 450°C on the charge density for films prepared with a 30h aged sol. The rapid variation observed at short time is attributed to the nucleation and growth of small CeO₂ crystallites [11-12]. The charge becomes constant after 20 min.

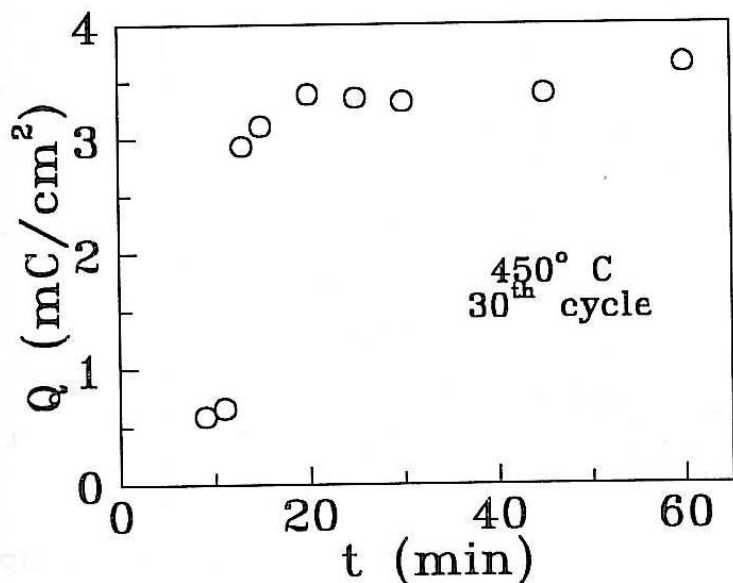


Figure 4. Li⁺ charge density inserted (or extracted) into sol-gel TiO₂-CeO₂ films deposited on Baltracon ITO coating during the 30th voltammetry cycle as a function of the heat treatment time at 450°C. The films have been prepared from a RT 30h aged sol.

The influence of the thickness has been tested by preparing layers using up to five successive coatings (fig. 7). The layers have been deposited on four different ITO coatings. All curves passed through a maximum and the charge inserted or extracted diminishes rapidly for thick coatings. The highest charge (~8.5 mC/cm²) was obtained for ITO supplied by Donally and Asahi Glass. The charge density was found independent of the time of heat treatment (fig. 4) and we conclude that the increase of Q observed when the thickness of the layers increases is due to an increase of the number of sites for Li⁺ insertion. The drop observed for larger thickness is not understood and may come from changes in the electrical characteristics of the ITO layers submitted to heat treatment at 450°C, to a decrease of the Li⁺ diffusion coefficient when its concentration reaches a certain value, or most probably to an increase of the electrical resistance of the ion storage layer as its thickness increases. This will cause a drop of the potential at the electrolyte counter electrode interface and consequently will reduce the amount of charge inserted into the electrochromic layer. This effect may in principle be compensated by increasing the applied potential.

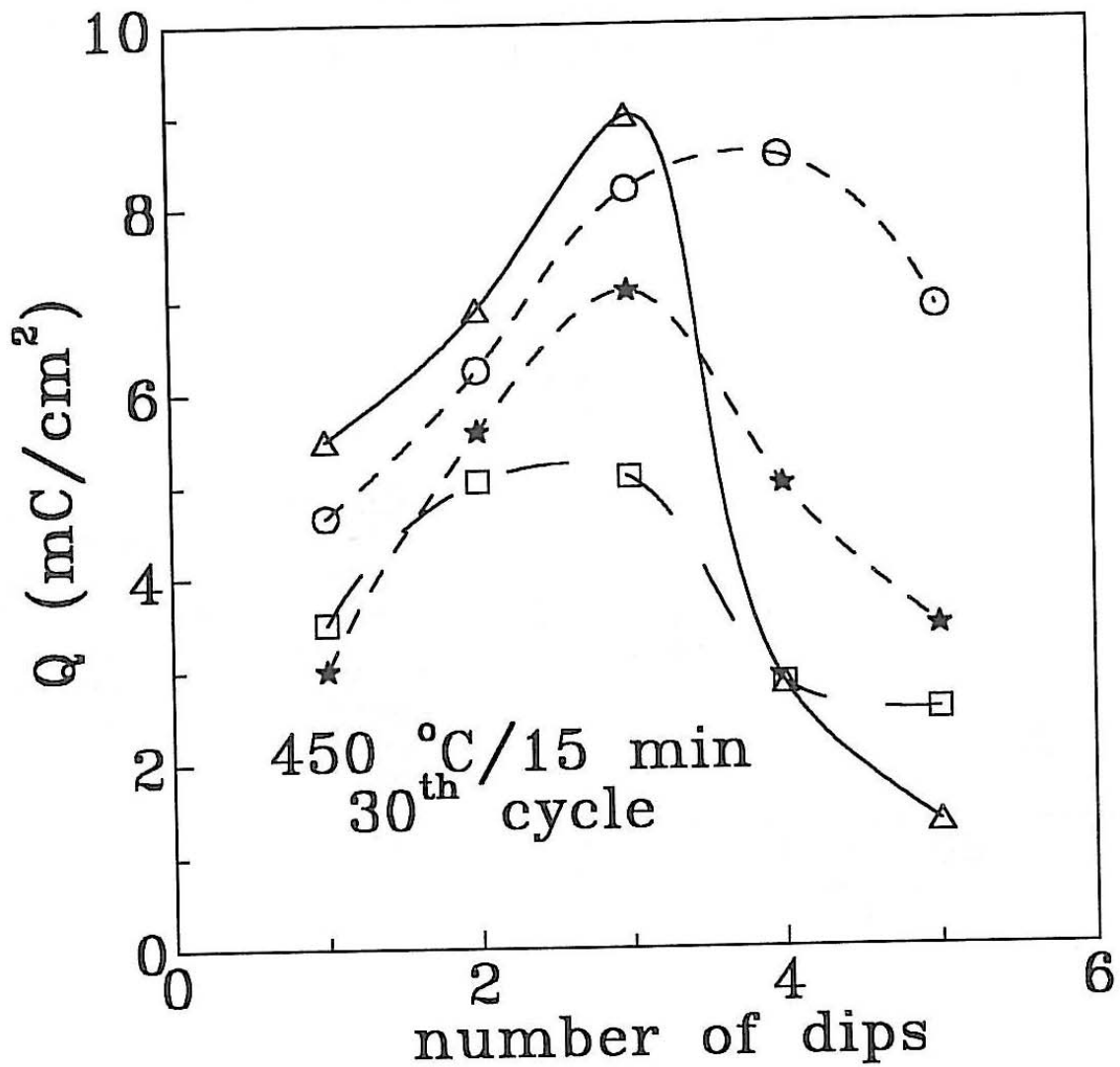


Figure 5. Li^+ charge density inserted (or extracted) into sol-gel $\text{TiO}_2\text{-CeO}_2$ as a function of the number of dips. The films have been deposited on ITO supplied by (□) Balzers, (★) Asahi Glass, (O) Asahi Glass previously heat treated at 450°C during 15 min in air and (Δ) Donally.

3.2 Nb_2O_5 electrochromic coating

The optical transmissions of a Nb_2O_5 thin coating are shown in figure 6. These spectra were measured after applying potential from -2.8V (Li^+ insertion) and -0.5V (Li^+ extraction). The transmission in the visible range is superior to 70% in the bleached state, and drops to less than 20% in the colored state. The good electrochemical reversibility and optical density indicate that Nb_2O_5 could be used as an electrochromic layer in EC devices.

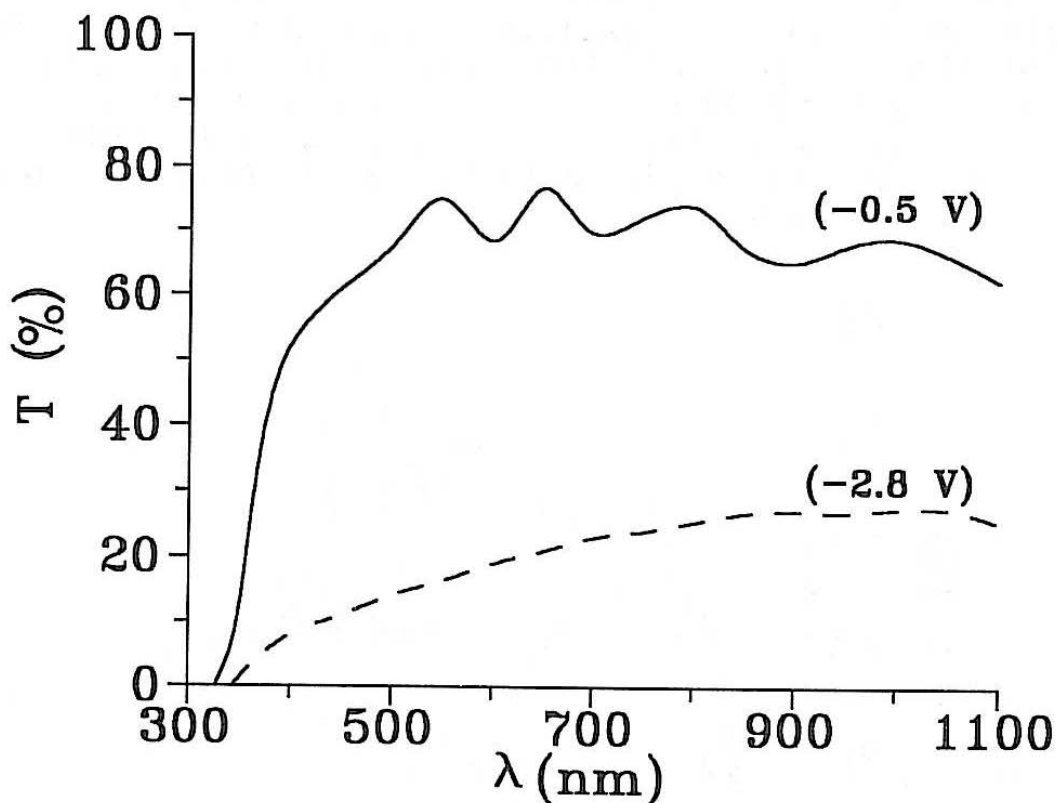


Figure 6. Optical transmission of sol-gel Nb_2O_5 coating (3 dips) in bleached (—) and colored (---) states.

4. CHARACTERIZATION OF TRANSMISSIVE DEVICES.

We present the optical transmission of two all solid state electrochromic windows

Glass/ITO/ WO_3/H^+ electrolyte (sol-gel)/ $\text{TiO}_2\text{-CeO}_2$ (sol-gel)/ITO/Glass (4)

All the coatings of the first cell were realized by the sol-gel process as described above (2.1). The second cell was mounted using a better WO_3 layer developed in our laboratory (see 2.2). The optical transmission spectra of both windows in the visible-near IR range is shown in figure 7. Both systems can be cycled and present stages of coloration and bleaching. The sol-gel window has still a low transmission variation. This is due to the fact that the parameters of the electrochromic coating WO_3 have not been optimized (thickness, temperature of densification, etc). The second cell has a transmission of about 75% in the bleached state which is reduced to about 25% at 600 nm in the colored state. This window has a fast optical response. However both cells have a relatively short

life time because of the corrosion of the WO_3 and/or ITO layers by the acidic electrolyte. Nevertheless we have shown that a complete electrochromic cell can be realized using the sol-gel process. The preparation of the sol-gel $\text{CeO}_2\text{-TiO}_2$ coating has been optimized and the results presented indicate that it can be used with advantages as H^+ and Li^+ storage layer in such devices. Considerable work should be done now to optimize the electrochromic sol-gel layer (WO_3 or Nb_2O_5) and the protonic TiO_2 electrolyte.

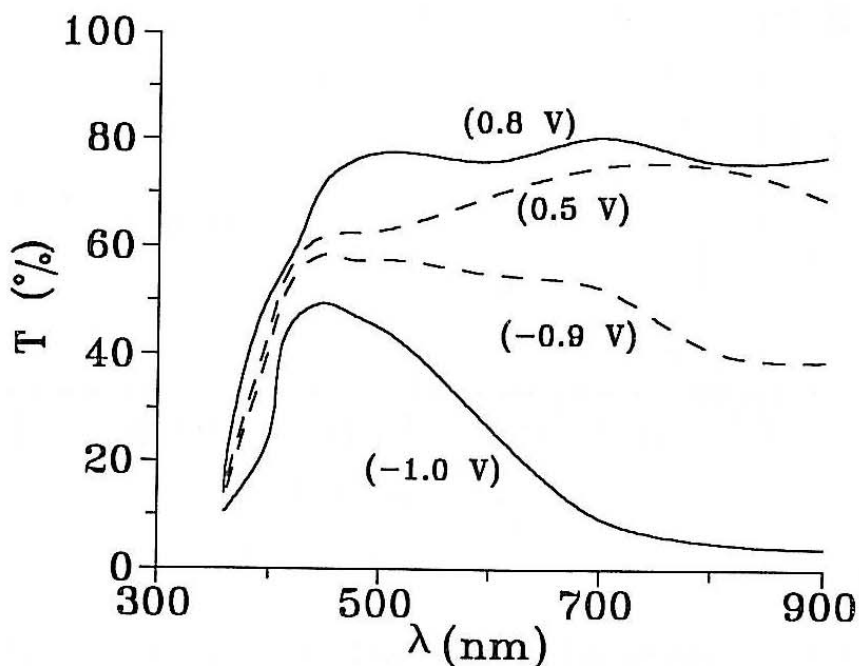


Figure 7. Optical transmission of two electrochromic windows having the configuration: glass/ITO/ H_xWO_3 / $\text{TiO}_2\text{-sg}$ / $\text{CeO}_2\text{-TiO}_2\text{-sg}$ /ITO/glass where (—) is a vacuum evaporated WO_3 and (---) is a sol-gel (sg) WO_3 .

5. CONCLUSION

An all solid state electrochromic window has been realized using sol-gel coatings such as WO_3 (electrochromic layer), TiO_2 (proton electrolyte) and $\text{CeO}_2\text{-TiO}_2$ (ion storage layer). Its optical transmission in the colored and bleached states has been measured and compared to similar window whose WO_3 coating has been prepared by evaporation. Although its performance are still far from the best device built in our laboratory, we have shown that the realization of an all sol-gel electrochromic device is feasible. However considerable work should be performed to optimize its performance. This has already been done for the sol-gel $\text{CeO}_2\text{-TiO}_2$ ion storage layer for which the electrochemical properties have been determined as a function of different preparation parameters such as aging of the sol, time and temperature of the densification process, thickness of the coating and type of ITO coating. The highest charge density was of the order of 8.5

mC/cm².

We believe that the good electrochemical properties of the ion storage layer come in part from the possibility, through the sol-gel process, to tailor an optimum porous texture of the layers via controlled heat treatment.

6. ACKNOWLEDGMENTS

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7. REFERENCES

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