SOL-GEL COATINGS FOR ELECTROCHROMIC DEVICES

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ABSTRACT

All solid state electrochromic smart windows with the configuration glass/ITO/WO$_3$/electrolyte/TiO$_2$-CeO$_2$/ITO/glass have been realized. These devices have potential applications in architectural and automotive fields to regulate the transmission and reflection of the radiant energy. The ion storage electrode TiO$_2$-CeO$_2$ have been realized by sol-gel process and its electrochemical properties are studied as a function of various parameters (thickness, heat treatment, etc.). The electrochemical and optical performances of two cells are reported.

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).
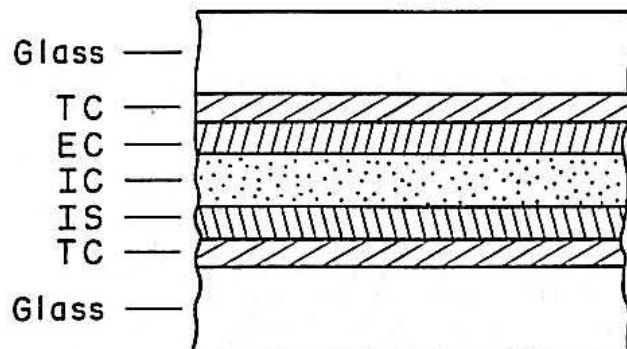

Figure 1. Schematic cross-section of a typical solid state electrochromic device working in transmission. TC=transparent electronic conductor, EC=electrochromic coating, IC=ionic conductor (electrolyte), IS=ion storage layer (counter electrode).

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 turn 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 In$_2$O$_3$-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.

$$x \, A^+ + xe^- + WO_3 \rightarrow A_xWO_3 \qquad (1)$$

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 $W^{6+}_{1-x}O_{3-x}W^{5+}_x$. Its coloration is due to the presence of a large absorption band in the visible and near infrared region ($E_{max}\approx1.4eV$) 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 $LiN(SO_2CF_3)_2$ 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 TiO_2-CeO_2 layers prepared by sol-gel process; this compound allows a better Li^+ insertion kinetics than pure CeO_2 [7,11,12].

In this paper we present an improved sol-gel preparation of the ion storage TiO_2-CeO_2 layer. The Li^+ charge density inserted or extracted 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 two all solid state windows using H^+ and Li ions is presented.

EXPERIMENTAL AND PROCEDURE

The different layers of the electrochromic cells have been obtained or prepared as following: The transparent *electric conductors* (TC) were all ITO layers supplied by Balzers (Baltracon Z20, $\rho=2.6\ 10^{-4}$ Ωcm), Donally (FW 5005, $\rho=2.6\ 10^{-4}$ Ωcm) or Asahi Glass (plasma assisted evaporation $\rho=3.5\ 10^{-4}$ Ωcm). The *electrochromic coating* (EC) was a WO_3 layer 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 = $2,5.10^{-11}$ cm^2/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.=9.10^6) and $LiN(SO_2CF_3)_2$ salt in acetonitrile with an O: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/WO_3 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 choose 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 *ion storage* coating (IS) or counter electrode consisted of TiO_2-CeO_2 layers which were prepared by sol-gel processing. The TiO_2-CeO_2 precursor sols were prepared using $Ce(NH_4)_2(NO_3)_6$ 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 [7,22,12]. 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:

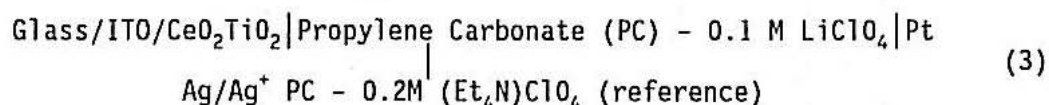$$2\ Ce^{4+} + Pr^iOH \rightarrow 2\ Ce^{3+} + acetone + 2H^+ \qquad (2)$$
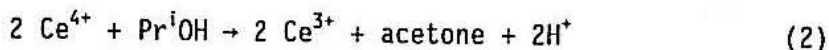
The presence of the acetone is important for the sol stabilization.

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.

CHARACTERIZATION OF THE TiO_2-CeO_2 ION STORAGE COATING

The sol-gel TiO_2-CeO_2 coating used as ion storage present a fully reversible ion insertion and extraction process controlled by solid state diffusion. The optical transmission of the film is high and remains unaltered during the cyclic process [11,12,13]. 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:

$$Glass/ITO/CeO_2TiO_2 | Propylene \ Carbonate \ (PC) - 0.1 \ M \ LiClO_4 | Pt$$
$$Ag/Ag^+ \ PC - 0.2M \ (Et_4N)ClO_4 \ (reference) \tag{3}$$

using a scanning speed of 50 mV/S and potential limits -1,8 and 0.5 V.

The charge density Q inserted or extracted 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 shows the influence of the heat treatment temperature on Q for films deposited from a sol aged 30h (peak of fig. 1) and heat treated for 15 min. The highest charge is obtained for treatment performed at T=450 ± 20°C.
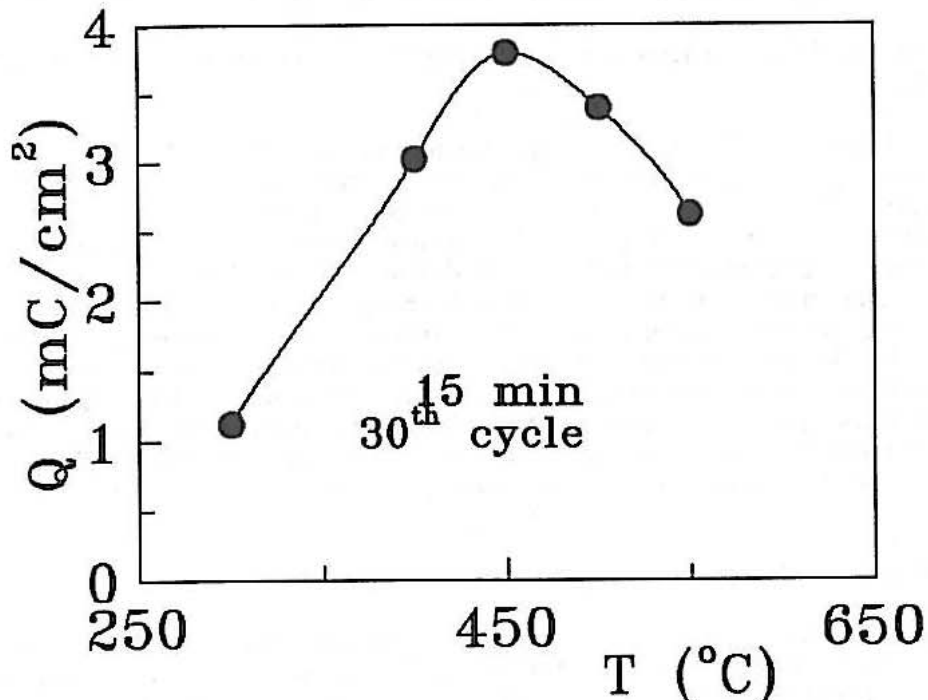

Figure 2. Li+ charge density inserted (or extracted) into sol-gel TiO_2-CeO_2 films deposited on Baltracon ITO coating during the 30th voltammetry cycle as a function of heat treatment temperature (15 min). The films have been prepared from a RT 30 h aged sol.

Figure 3 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 CeO_2 crystallites [11-13]. The charge becomes constant after 20 min.
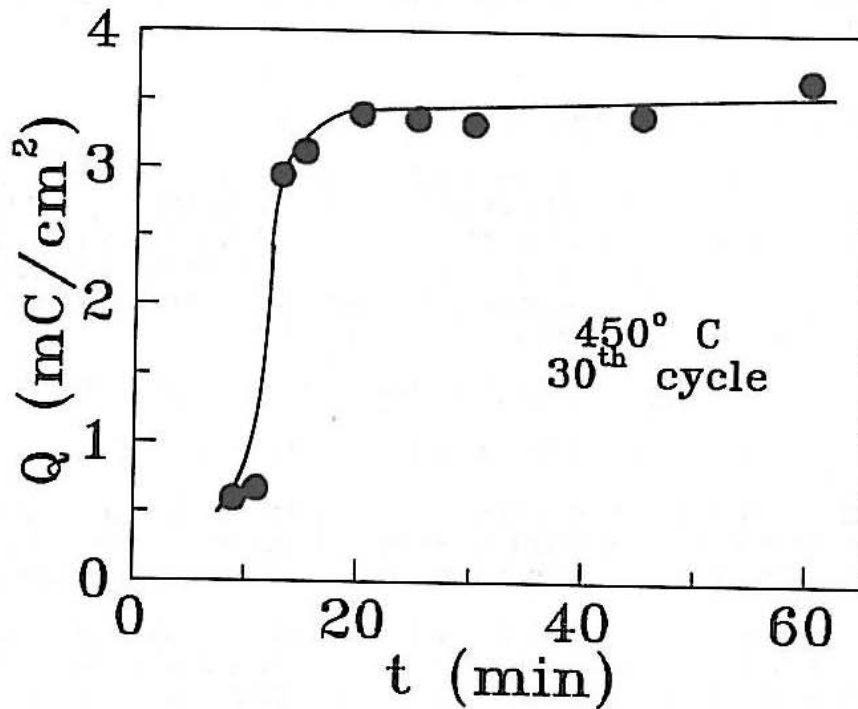

Figure 3. Li^+ charge density inserted (or extracted) into sol-gel TiO_2-CeO_2 films deposited on Baltracon ITO coating during the 30th voltammetry cycle as a function of the heat treatment time at 450°C. The films have been prepared from a RT 30h aged sol.

The influence of the thickness has been tested by preparing layers using up to five successive coatings (fig. 4). 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/cm^2) was obtained for ITO supplied by Donally and Asahi Glass. The charge density was found independent of the time of heat treatment (fig. 3) 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 characteristic of the ITO layers submitted to heat treatment at 450°C or to a decrease of the Li^+ diffusion coefficient when its concentration reaches a certain value.

CHARACTERIZATION OF TRANSMISSIVE DEVICES.

We present the optical transmission of two all solid state cells Glass/ITO(Balzers)/WO_3/electrolyte/TiO_2-CeO_2/ITO(Balzers)/glass where the electrolyte is PEO-$LiN(CF_3SO_2)_2$ and a cellulose-polyacetate for Li^+ and H^+ ion conduction respectively. The optical transmission spectrum of the windows in the visible-near IR range is shown in figure 5. In the bleached state the window presents an optical transmission of the order of 60% between 500 and 1000 nm. This value is reduced to about 20% when the window polarization is inverted (colored state). The window using H^+ ions conduction presents identical electrochemical properties. However as $D_{H+} > D_{Li+}$ the time optical

response is faster but its lifetime is considerably reduced because of the corrosion of the WO_3 and/or ITO layers by the acidic electrolyte.
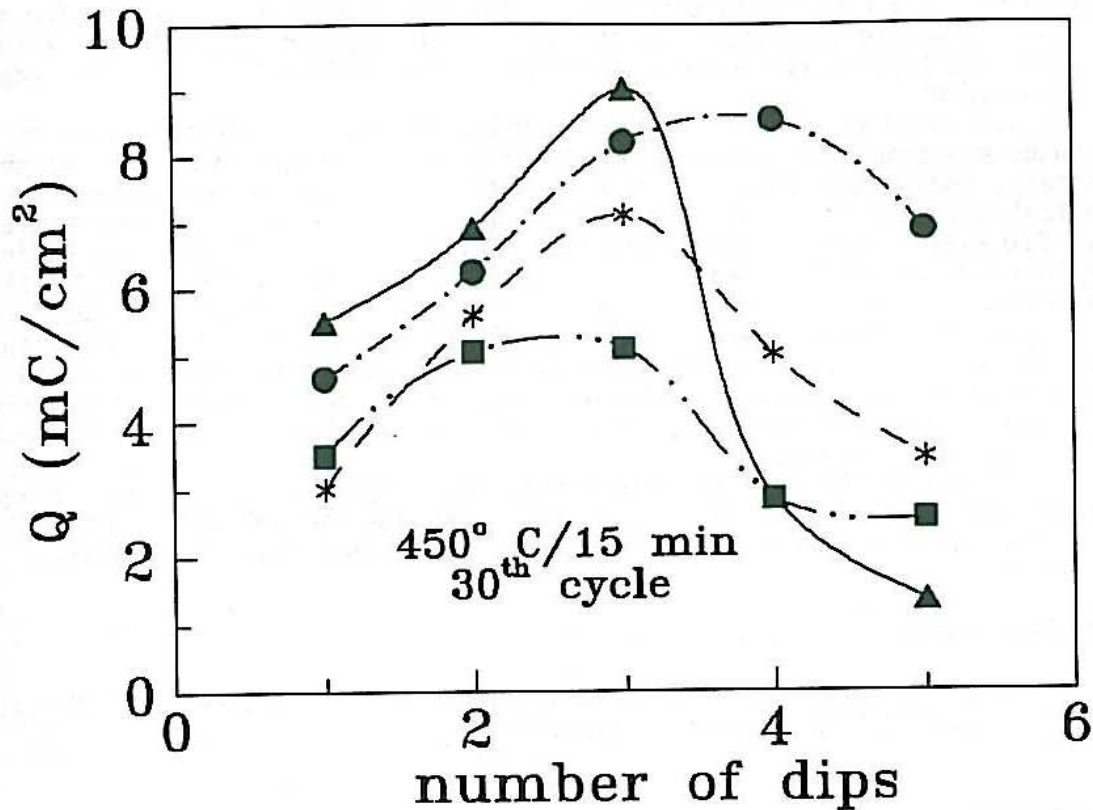

Figure 4. Li^+ charge density inserted (or extracted) into sol-gel TiO_2-CeO_2 as a function of the number of dips. The films have been deposited on ITO supplied by (■) Balzers, (★) Asahi Glass, (●) Asahi Glass previously heat treated at 450°C during 15 min in air and (▲) Donally.
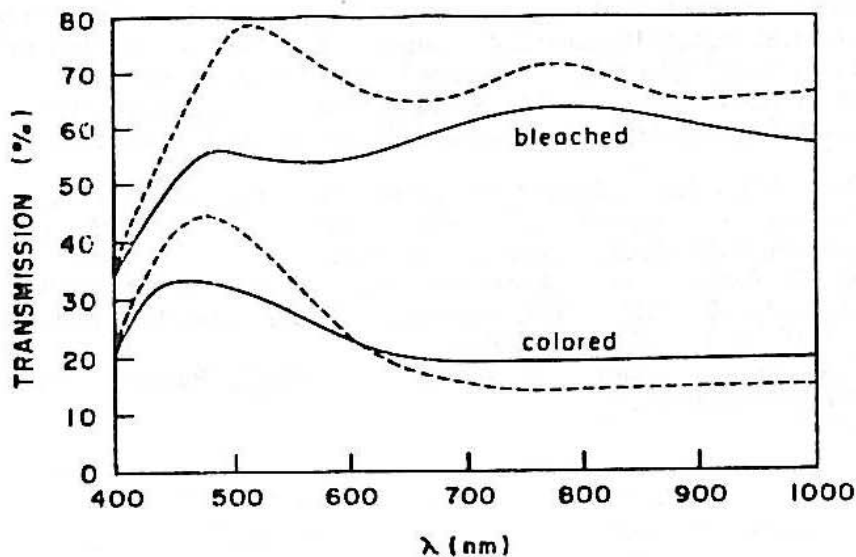

Figure 5. Optical transmission of two all solid state windows having the configuration: ── glass/ITO/Li_xWO_3/PEO-LiN(CF_3SO_2)$_2$/CeO_2-TiO_2/ITO/glass, ─── glass/ITO/H_xWO_3/cellulose-polyacetate/CeO_2-TiO_2/ITO/glass. Respective polarization vs WO_3: -2.5V and -1.1V (bleached state); 3V and 1.4V (colored state).

CONCLUSION

The electrochemical properties of TiO_2-CeO_2 sol-gel coating 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/cm^2.

All solid state electrochromic windows have been realized using as a counter electrode (ion storage) a CeO_2-TiO_2 coating prepared by the sol-gel process, which can store either H^+ or Li^+ ions. For Li^+ conduction good optical and lifetime behavior is obtained using WO_3 as an electrochromic layer and PEO-$LiN(CF_3SO_2)_2$ as an electrolyte. The optical transmission varies typically from 60% to 20% and the time response from the bleached state to the colored state is of the order of 25 s. The speed limitation of the response is due to the insertion process of the Li^+ ion into the CeO_2-TiO_2 layer; the Li^+ chemical diffusion coefficient appears to decrease when a certain concentration is reached. The H^+ conducting window shows a similar behavior. Its time response is faster but its lifetime is drastically reduced because of corrosion phenomena.

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 layer via a controlled heat treatment.

ACKNOWLEDGMENTS

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