

Electrochromic smart windows

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A solid state electrochromic smart window has the configuration glass/TC/EC/IC/IS/TC/glass, where TC is a transparent conductor, EC is an electrochromic coating, IC is an H⁺ or Li⁺ ion conductor and IS is an H⁺ or Li⁺ ion storage layer. Application of a small voltage at the TC electrodes changes optical transmission of the device in a persistent reversible manner. Porous and slightly crystallized sol-gel coatings of TiO₂-CeO₂ composition have the required properties for ion storage counter electrodes. Layers 150 nm thick have 80% optical transmission in the visible range, do not color after H⁺ and Li⁺ insertion and show good electro-chemical stability. These layers have been used as H⁺ or Li⁺ ion storage electrodes, where EC was WO₃. The protonic IC was a cellulose polyacetate polymer and the lithium IC was PEO-LiN(SO₂CF₃). Electro-chemical and optical performances of the cells are reported.

1. Introduction

Development of all solid state electrochromic devices such as smart windows and reflective mirrors is of importance [1]. A typical transmission system is made of five layers sandwiched between two glass substrates as shown in fig. 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).

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 over a wide spectral range and alter the optical transmission of the device. These devices have a time response which varies from seconds to less than a minute and most maintain optical properties for several hours without power. The original state is obtained by reversing the applied voltage. The current collecting layers are usually made of a mixed oxide In₂O₃-SnO₂ (ITO) of low electrical resistivity. The preferred electrochromic layer is WO₃ whose structure and color are modified by electrochemical insertion of ions following the reaction



where A⁺ can be H⁺, Li⁺, Na⁺, etc. The result of the insertion reaction is reduction of transparent WO₃ and transformation into a blue-colored tungsten bronze W_{1-x}⁶⁺O_{3-x}W_x⁵⁺. Coloration is due to a large

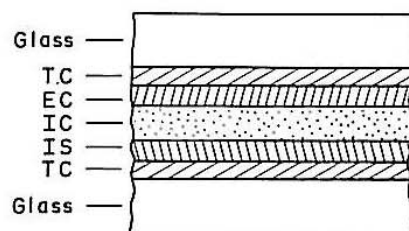


Fig. 1. Schematic cross-section of a typical solid state electrochromic device working in transmission. TC, transparent electronic conductor; EC, electrochromic coating; IC, ionic conductor (electrolyte); IS, ion storage layer (counter electrode).

absorption band in the visible and near infrared region ($E_{\text{max}} \approx 1.4$ eV) attributed to electronic transitions from the reduced tungsten ions states W^{5+} to the conduction band [2,3]. Although the chemical diffusion of Li^+ ions is smaller than that of H^+ , these ions are preferred for devices since hydrogen usually presents a gassing phenomenon and the acid electrolyte media limits the lifetime of protonic-based devices [4].

The advantages of polymeric ion conductors over liquid ion conductors is now recognized [4,5] to provide good electrolyte/electrode contact and low leakage. Among them, polyethylene oxide (PEO) complexed with alkali salts such as $LiClO_4$, $LiCF_3SO_3$ or $LiN(SO_2CF_3)_2$ exhibits Li^+ conductivity in the range 10^{-4} – 10^{-7} S cm^{-1} at room temperature.

V_2O_5 [6,7], Ir_2O_3 [8,9], CeO_2 [10] have been recently proposed for counter electrodes but they do not exhibit required transparency, reversibility and kinetics for reaction with Li^+ ions. We recently proposed TiO_2 – CeO_2 layers prepared by a sol–gel process which allow better Li^+ insertion kinetics than pure CeO_2 [7,11,12].

Sol–gel preparation of TiO_2 – CeO_2 coatings and their optical and electrochemical properties are reported here. The optical and electrochemical properties of two of them are discussed.

2. Experimental procedure

Transparent *electric conductor* layers (TC) were Baltracon Z 20 (Balzers) ITO thin films deposited on glass plates 1.5 mm thick and have an electrical resistivity of 200 Ω cm. *Electrochromic coatings* (EC) were WO_3 layers deposited from the corresponding oxide powder by vacuum evaporation on ITO/glass substrate. Films were amorphous to X-ray diffraction and thickness was measured with a Talystep to be 200–300 nm. The chemical diffusion coefficient for Li^+ ions, $\bar{D} = 2.5 \times 10^{-11}$ cm^2/s at 25°C was determined by analyzing low frequency impedance data [7].

For the cells using Li^+ ions, the *ionic conductor* layer (IC) was a polymer electrolyte complex prepared by dissolving polyethylene oxide (PEO) powder (MW) = 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 on the glass/ITO/ WO_3 substrate. The solvent was evaporated at 50°C during 48 h and the substrates were then kept in the dry box for further processing. Polymer films were typically 50–200 nm thick. For the cells using H^+ ions, a cellulose polyacetate protonic gel was prepared by diluting 0.5 g 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 gel obtained was then poured on the glass/ITO/ WO_3 substrate.

The *ion storage* coatings (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 to which tetraisopropyl orthotitanate with atomic ratio Ce:Ti up to 1:1 was added as already described [7,11,12]. The same method can be applied for the preparation of ZrO_2 – CeO_2 sol by mixing zirconium propoxide $Zr(OPr^i)_4$, $Ce(NH_4)_2(NO_3)_6$ salt and ethanol. These sols are stable for only a few days even if they are kept at low temperature. The use of a mixture of $Ti(OPr^i)$ and acetylacetone with $[Ti]/[AcAc]$ ratio varying from 0.5 to 1.25 instead of $Ti(OPr^i)$ slightly improves the sol stability. The use of isopropanol as solvent for the cerium salt (instead of ethanol) leads to a precursor sol stable up to 3 months at 5°C. Dissolution of the cerium salt results in a clear red solution [11] which becomes colorless after about 30 h. This phenomenon is due to a slow reduction of Ce^{4+} according to



The presence of the acetone appears to be important for the long term stabilization of the sol.

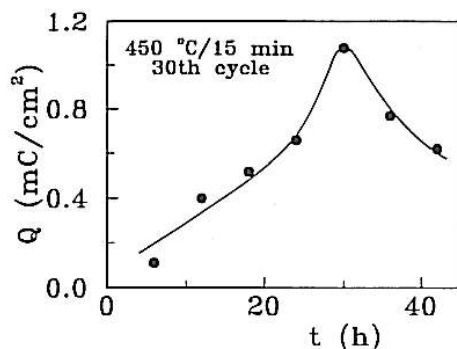


Fig. 2. Li^+ charge density inserted (or extracted) into sol-gel $\text{TiO}_2\text{-CeO}_2$ films during the 30th voltammetry cycle as a function of the aging time of the sol at RT. The films were heat treated at 450°C for 15 min.

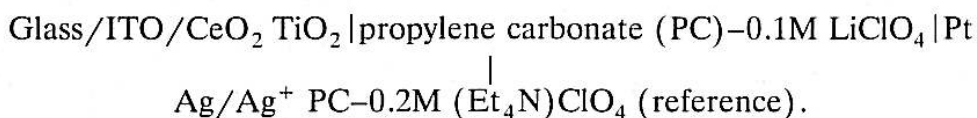
The layers were deposited by dip coating on Baltracon Z 20 ITO coated glass at a 10 cm/min withdrawal speed resulting in good optical quality films of ~ 100 nm thickness. After drying at room temperature for 15 min, the films were partially densified by heat treatment in air up to 550°C . The whole procedure can be repeated to obtain thicker films.

3. Experimental results

3.1. $\text{TiO}_2\text{-CeO}_2$ ion storage coating

Preliminary characterization of $\text{TiO}_2\text{-CeO}_2$ coatings [11–13] have shown that such layers present properties appropriate for use as H^+ or Li^+ ion storage layers in electrochromic devices. Electrochemical ion insertion and extraction is fully reversible and controlled by Li^+ ion diffusion.

Cyclic voltammeteries, which allow determination of the total electric charge inserted and extracted during a cycle, were performed in a dry box at room temperature using a Solartron (Schlumberger) equipment consisting of an Electrochemical Interface (model 1286) linked to an Impedance/Gain-Phase Analyzer (model 1260) and a three-electrode cell:



The scanning speed was 50 mV/s and the potential limits were -0.5 and 1.3 V.

Figure 2 shows the influence of the aging time of the sol on the total charge density inserted or extracted during the 30th voltammetry cycle. All coatings were a single layer of ~ 100 nm thickness heat treated at 450°C for 15 min. Maximum charge density occurred after about 30 h and corresponds to complete optical clearance of the sol. For longer times, the sol suffers flocculation and gelation and the charge density diminishes.

Figure 3 shows the influence of heat treatment temperature on total charge density inserted or extracted for films deposited from a sol aged 30 h (peak of fig. 2) and heat treated for 15 min at noted temperatures. The highest charge was obtained for treatment performed at $T = 450 \pm 20^\circ\text{C}$.

Figure 4 shows the influence of the heat treatment at 450°C on the charge density for films prepared with a 30 h aged sol. Rapid variation observed at short times is attributed to nucleation and growth of small CeO_2 crystallites [11–12]. The charge becomes constant after 20 min treatment.

Careful analysis of results indicates that other parameters play an important role as the maximum values shown in each figures vary from batch to batch. The relative humidity of the atmosphere during

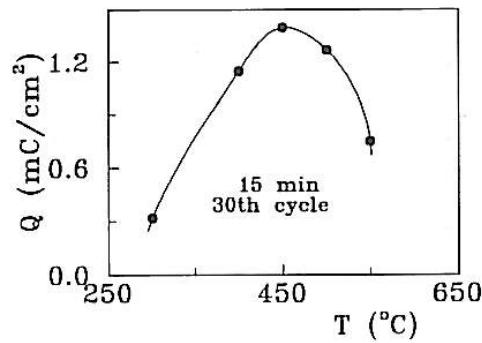
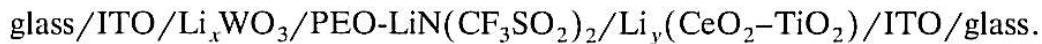


Fig. 3. Li^+ charge density inserted (or extracted) into sol-gel $\text{TiO}_2\text{-CeO}_2$ films during the 30th voltammetry cycle as a function of heat treatment temperature (15 min). The films have been prepared from a RT 30 h aged sol.

film deposition and electric resistivity of the ITO film are probably two of them. Best $\text{TiO}_2\text{-CeO}_2$ films for Li^+ electrochemical insertion and extraction have been realized with films prepared with a 30 h room temperature aged sol having a composition $\text{Ti}:\text{Ce} = 1:1$, heat treated in air at $450 \pm 20^\circ\text{C}$ for 20–60 min.

3.2. Transmissive devices using $\text{TiO}_2\text{-CeO}_2$ electrode

A complete transmissive cell, working with Li^+ ions, was assembled with the configuration



The fabrication of the cell was done in two steps. First, the left and right part of the cell, i.e., $\text{glass/ITO/WO}_3/\text{PEO-LiN}(\text{CF}_3\text{SO}_2)_2$ and $/\text{TiO}_2\text{-CeO}_2/\text{ITO/Glass/}$ were prepared according to section 2. The final cell assembly was carried out in a glove box by firmly pressing the two parts of the device together and sealing the edges with Torr Seal (Varian) glue.

Figure 5 (right) shows the cell current and the optical transmission at $\lambda = 750$ nm measured as a function of the potential difference (linear time variation) applied between the working and reference electrodes. The maximum of the peak insertion of Li into WO_3 lies at a potential higher than $E = 3$ V but the extraction peak is clearly seen at $E = -2$ V. Transmission in the bleached state is 60% (for $E = 0$) and drops to 25% when Li^+ ions are transferred from the IS ($\text{TiO}_2\text{-CeO}_2$) electrode toward the EC (WO_3) electrode. The process is totally reversible. The left side shows the potentiostatic response of the cell with the optical transmission at $\lambda = 750$ nm. The time variation of the current is different when Li^+ ions are inserted into the WO_3 layer or the $\text{TiO}_3\text{-CeO}_2$ layer. It presents a rapid curvature change around $t = 20$ s for cathodic polarization $E = -2.5$ V, i.e., when the Li^+ ions are transferred from the

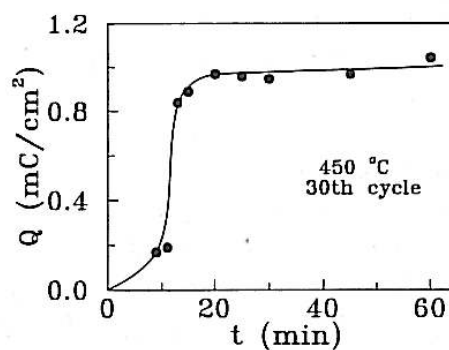


Fig. 4. Li^+ charge density inserted (or extracted) into sol-gel $\text{TiO}_2\text{-CeO}_2$ films during the 30th voltammetry cycle as a function of the heat treatment time at 450°C . The films have been prepared from a RT 30 h aged sol.

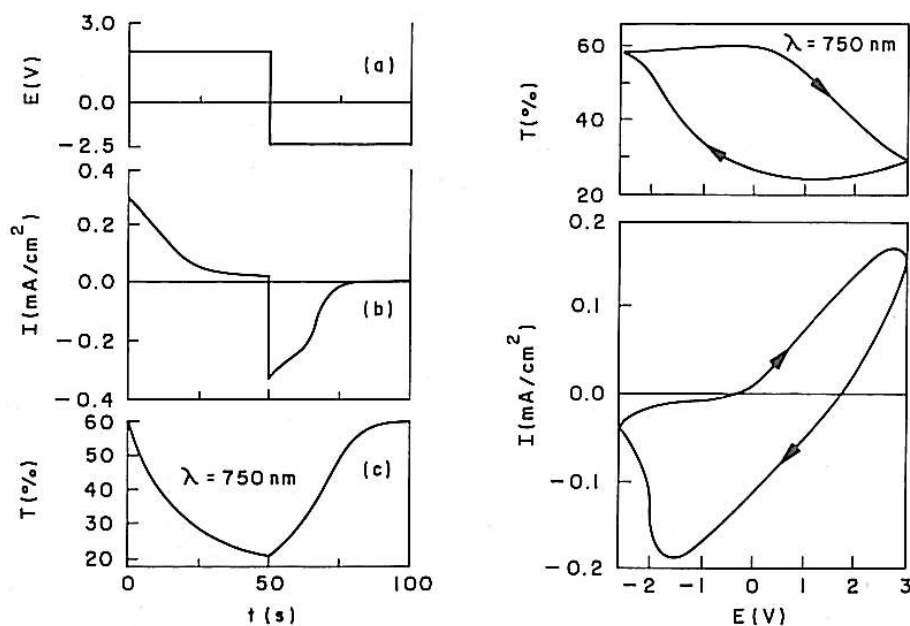


Fig. 5. (right) Cyclic voltammetry and optical transmission variation ($\lambda = 750$ nm) of a complete transmissive window glass/ITO/ WO_3 /PEO-LiN(CF₃SO₂)₂/CeO₂-TiO₂/ITO/glass. Speed 50 mV/s, E vs. WO_3 . (left) Potentiostatic and time variation of the optical transmission of the same window. (a) applied voltage (vs WO_3). (b) current I . (c) optical transmission at $\lambda = 750$ nm.

electrochromic WO_3 layer toward the storage coating. A similar behavior was also observed using 0.1M LiClO_4 electrolyte [11], indicating that this phenomenon is related to the insertion of Li^+ into the CeO₂-TiO₂ layer. We believe that this rapid variation is due to a decrease of the Li^+ diffusion coefficient when its concentration reaches a certain value.

The optical transmission spectrum in the visible-near IR range is shown in fig. 6. In the bleached state, an optical transmission of the order of 60% between 500 and 1000 nm is observed. This is reduced to about 20% when the window polarization is inverted (colored state).

Another transmissive cell, working with H^+ ions, has been assembled in air using the same procedure with the configuration

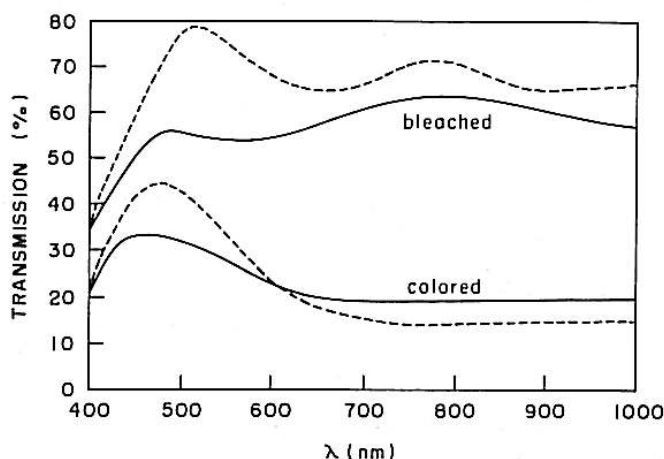
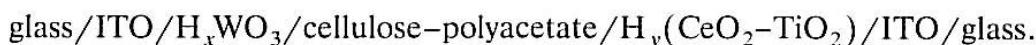


Fig. 6. Optical transmission of two all solid state windows having the configuration: —, glass/ITO/ Li_xWO_3 /PEO-LiN(CF₃SO₂)₂/CeO₂-TiO₂/ITO/glass; ---, glass/ITO/ H_xWO_3 /cellulose-polyacetate/CeO₂-TiO₂/ITO/glass. Respective polarization vs. WO_3 : -2.5 V and -1.1 V (bleached state); 3 V and 1.4 V (colored state).

This window presents identical electrochemical properties as with Li^+ ions but as $\bar{D}_{\text{H}^+} > \bar{D}_{\text{Li}^+}$ the optical time response is faster but lifetime is reduced because of corrosion of WO_3 and/or ITO layers by electrolyte. The overall optical transmission variation appears slightly larger (fig. 6).

Windows built with electrochromic polymeric films such as polytoluidine and polyanisidine in substitution of WO_3 have also been tested with success for H^+ or Li^+ ions up to 250 cycles with a loss in charge smaller than 5% [13,14].

4. Conclusion

Solid state electrochromic windows have been realized using as counter electrode (ion storage) a $\text{CeO}_2\text{-TiO}_2$ coating prepared by the sol-gel process. This compound can store either H^+ or Li^+ ions. Good optical and lifetime behavior is obtained using WO_3 as an electrochromic layer and $\text{PEO-LiN}(\text{CF}_3\text{SO}_2)_2$ as an electrolyte. Optical transmission varies from 60 to 20% and 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 in the $\text{CeO}_2\text{-TiO}$ layer. The Li^+ chemical diffusion coefficient appears to decrease when a critical Li^+ concentration is reached. The H^+ conducting window shows similar behavior, with faster time response but drastically reduced lifetime because of corrosion. The substitution of WO_3 by polymeric layers such as polytoluidine opens new opportunity particularly for protonic based electrochromic devices.

We believe that the good electrochemical properties of these ion storage layers come in part from the possibility, through the sol-gel process, to tailor an optimum porous texture of the layers via a controlled heat treatment. In this respect, sol-gel made electrochromic layer, such as WO_3 [15] and electrolyte, such as Ta_2O_5 (for proton) or ormosils [16] (for Li^+) are good candidates for future realization of fully sol-gel made smart windows or mirrors.

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