

Sol-Gel Electrochromic Device

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M.A. MACÊDO AND M.A. AEGERTER

Institute of Physics and Chemistry of São Carlos, University of São Paulo, Cx. Postal 369, 13560-970 São Carlos (SP), Brazil

Abstract. All solid state electrochromic devices have potential applications in architectural and automotive fields to regulate the transmission and reflection of radiant energy. We present the optical and electrochemical characteristics of two solid state windows having the configuration glass/ITO/TiO₂-CeO₂/TiO₂/TiO₂-CeO₂/ITO/glass and glass/ITO/WO₃/TiO₂/TiO₂-CeO₂/ITO/glass where the three internal layers have been prepared by sol gel methods. The preparation of the individual sols and some physical properties of the different sol gel coatings are reported.

Keywords: electrochromism, electrochemistry, WO₃/TiO₂ layers, films: TiO₂

1. Introduction

The development of all solid state electrochromic devices such as smart windows, displays, automotive rearview mirrors, etc, presents a considerable technological and commercial interest [1]. These devices consist of multiple layers usually sandwiched between two glass layers. A typical device working in transmission has the configuration glass/transparent electron conductor/anode/ionic conductor/cathode/transparent electron conductor/glass. The outermost layers on each side are transparent electron conductors (TC) and are required to set up a distributed electric field. The adjacent layers are the electrochromic layer (EC) and the counter electrode which plays the role of the ion storage layer (IS) for H⁺ or Li⁺ ions. The central layer is an ion conductor (IC). The three inside layers essentially comprise an electro-optically active battery and therefore the (EC) and (IS) layers are mixed electron-ion conductor. When a small current is passed through the cell the ions stored in the (IS) layer diffuse toward the electrochromic layer which has the property to change its spectral transmittance continuously (usually over a wide spectral range) altering the overall optical transmission of the device. The original optical bleached state is obtained by reversing the applied voltage. Such devices have a time response which varies from seconds to minutes and can usually maintain their optical

properties (bleached or colored state) when the power is turned off (memory effect).

Various inorganic materials and processes have been proposed for each specific layer (see [1, 2] for recent reviews). Nowadays indium tin oxide (ITO) is the preferred TC material. WO₃, MoO₃, Nb₂O₅ are typical cathodic EC materials while IrO₂, NiO, Ni(OH)₂ are anodic EC materials and Rh₂O₃ and V₂O₅ were found to color in both states. V₂O₅, Ir₂O₃, CeO₂ and TiO₂-CeO₂ have been proposed for counter electrode, the last material showing better Li⁺ insertion kinetics. Materials such as hydrated Ta₂O₅, ZrO₂, SiO₂, TiO₂ can be used as H⁺ conductor while Li₃N, LiAlF₄, LiNbO₃, LiTiO₃ and LiAlSiO₄ have been proposed for Li⁺. However none of them exhibits the high ionic conductivity as obtained with polymeric or liquid electrolytes which are still the preferred materials used in commercial or prototype devices.

Most of these materials have been already processed by sol-gel methods and a recent review can be found in [2]. Their specific functions to be used as EC or IS layers in electrochromic devices has been demonstrated for WO₃, WO₃-TiO₂, WO₃-MoO₃, Nb₂O₅, TiO₂-CeO₂, V₂O₅, NbVO₅, TaVO₅, MoO₃, oxides of Ir, Ni, Cr, Y, Cu, Co, Fe, Mn, Ni-Co, TiO₂ and CeO₂. Very few works have been reported for transparent IC layers where we can mention TiO₂, Ormosils and for transparent TC layers ITO.

In this paper we present the preparation of the sols used to obtain EC (WO₃), IC (TiO₂) and IS (TiO₂-

CeO₂) layers as well as optical and electrochemical solid properties of two all solid state smart windows built with these layers having the configuration glass/ITO/TiO₂-CeO₂/TiO₂-CeO₂/ITO/glass and glass/ITO/WO₃/TiO₂/TiO₂-CeO₂/ITO/glass.

2. Experimental and Procedure

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

- a) The transparent electric conductors (TC) were all ITO layers supplied by Donnely (FW 5005, $\rho = 2.6 \cdot 10^{-4} \Omega \text{ cm}$) or Asahi Glass (plasma assisted evaporation $\rho = 3.5 \cdot 10^{-4} \Omega \text{ cm}$) noted D and Ag respectively. Sol-gel processing of these coatings is feasible [3] [4] [5] but the electron conductivity is typically one order of magnitude smaller.
- b) The ion storage coating (IS) or counter electrode consists of a TiO₂-CeO₂ layer deposited by dip-coating technique using a sol prepared from a mixture of Ce(NH₄)₂(NO₃)₆ dissolved in ethanol, isopropanol or glycol ether to which was added tetraisopropyl orthotitanate with atomic ratio Ce:Ti up to 1:1 according to a method already described [6] [7] [8] [9]. These sols are stable up to 3 months when kept at 5°C [10]. The layers deposited on the ITO coated glass at a 20 cm/min withdrawal speed have a thickness of about 70 nm. After drying at room temperature for 15 minutes they have been partially densified by a heat treatment in air at 500°C. The amount of charge which can be inserted in such layers depends on the time and temperature of the heat treatment and the thickness of the layer. As shown below the highest charge density has been obtained with ~250 nm thick layer obtained by repeating the deposition process 3 to 4 times. After each deposition the layers have been fired at 500°C during 5 minutes. After the last coating the whole stack has been heat treated at the same temperature during 120 minutes.
- c) The WO₃ electrochromic coating was deposited by dip-coating on ITO coated glass from a colloidal solution obtained by dissolving tungsten tetrachloride oxide (WOCl₄) in isopropanol (0.1 M) and processed as previously described by Judeinstein et al [11] [12]. Each layer was 50 nm thick and the dip-coating process, done in 30% RH at a rate of 20 cm/min, was repeated 5 times in order to obtain

a final layer 200 nm thick. The densification was performed at 120°C during 24 h. The layers are amorphous.

- d) The TiO₂ sol gel protonic electrolyte was prepared according to a method proposed by Judeinstein et al [11] [12]. Ti(OBuⁿ)₄ was however substituted by Ti(IV) *i*-propoxide. The alkoxide was first mixed with glacial acetic acid in a molar ratio 1:2 and then glycerol (G) or ethylene glycol (EG) was added in a molar ratio G or EG/Ti = 20. According to the literature the reacted mixture gives glycolate derivatives where the organic groups may behave as bridging ligands between Ti metal atoms. No water was added. The resulting material is a viscous organic-inorganic liquid. For these concentrations gels are obtained after 15 and 10 days respectively. The same procedure used with a mixture of acetylacetone and Ti alkoxide (ratio 2:1) leads also to a slightly viscous organic-inorganic liquid whose stability is improved as no gelification has been observed even in presence of water after more than 1 month.

The final assembly of the cell was done by depositing a thin layer of the viscous electrolyte on the IS/ITO/glass stack. The other side of the window was then firmly pressed against it and the whole cell was finally sealed with Torr Seal glue.

3. Characterization of the Coatings, Windows and Discussion

The TiO₂-CeO₂ coating used as ion storage is transparent, slightly yellow and consists of small CeO₂ crystallites embedded in an amorphous TiO₂ matrix [6-10] [13]. Optically a broad unstructured absorption band (OD \equiv 0.25) is observed below $\lambda = 400$ nm peaking at 240 nm; the coating remains totally transparent in the visible-near infrared region during the cycling process. It allows a fully reversible H⁺ or Li⁺ insertion or extraction controlled by solid state diffusion. The amount of charge which can be inserted into the layer measured by integrating voltammetry curves increases almost linearly with the thickness of the layer up to ~250 nm (corresponding to 3 to 4 layers) and then slightly diminishes. For Li⁺ for example using a cell glass/ITO/TiO₂-CeO₂/propylene carbonate (PC)-0.1 M LiClO₄/Pt with reference Ag/Ag⁺/PC-0.2 M(Et₄N)ClO₄ and voltammetry parameters 50 mV/s, +1, 6 V to -1,

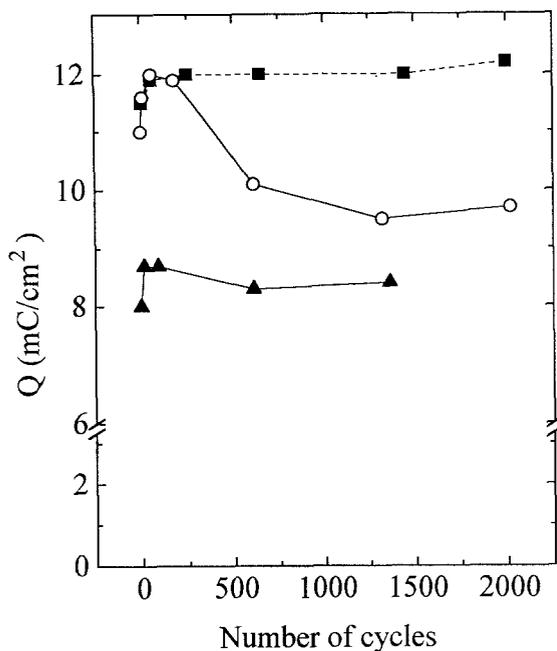


Fig. 1. Total H^+ and Li^+ charge inserted or extracted in a 210 nm thick sol gel TiO_2-CeO_2 layer as a function of the number of cycles showing a stable long term behavior. The plain curves refer to coating prepared with glycol ether (\blacktriangle), or isopropanol (\circ) and tested with Li^+ . The dashed curve is obtained with isopropanol (\blacksquare) and tested with H^+ . Voltammetry parameters for H^+ : cell glass/ITO/ $TiO_2-CeO_2/TiO_2/gel/Pt$ with reference SCE; rate 50 mV/s; potentials: +3.4 V to -2.0 V. Voltammetry parameters for Li^+ : see text.

6 V, the increase is typically $50 \mu C/cm^2$ up to $\sim 11 mC/cm^2$. The new heat treatment protocol has definitively improved the charge values, reflecting a corresponding increase of the number of sites for Li^+ insertion. The slight decrease observed for thicker layer is not completely understood; analysis of voltammetry curves shows a continuous shift of the insertion and extraction peak toward higher or lower potential respectively suggesting a gradual increase of the electric resistance of the coating causing a drop of the effective potential at the electrolyte/electrode interface. Figure 1 shows typical long term behavior of the total H^+ and Li^+ charge inserted (or extracted) in a TiO_2-CeO_2 three layers coating. After an initial rise followed by a slight decrease, the values of the charge stabilizes typically between 8.5 and $12 mC/cm^2$.

The long term response of the IC/IS/ITO glass stack has been tested for protonic conduction by submitting all solid state symmetric cells having the configuration glass/ITO/ $TiO_2-CeO_2/TiO_2/TiO_2-CeO_2/ITO/glass$ to extended potentiostatic and/or voltammetry cycles. The protonic electrolyte has been prepared with a ra-

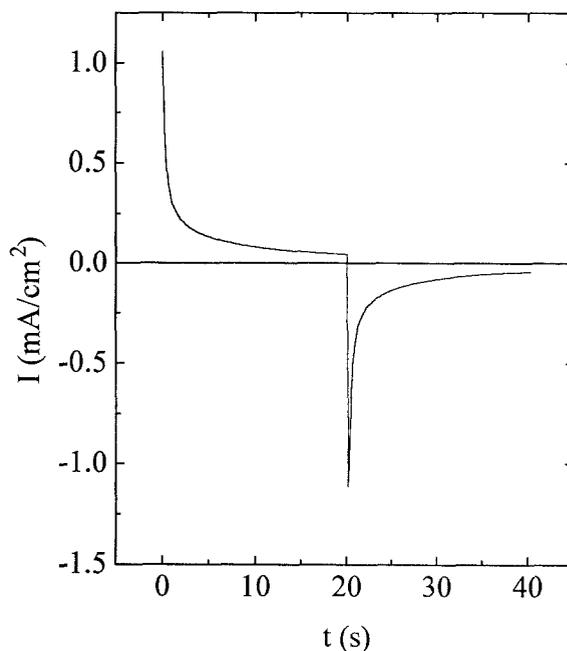


Fig. 2. Time response of a glass/ITO/ $TiO_2-CeO_2/TiO_2-CeO_2/ITO/glass$ to square wave voltage of ± 0.8 V, period 40 s. The protonic IC layer was prepared with a ratio acetic acid/Ti = 4. No extra charge has been inserted.

tio acetic acid/Ti varying between 4 and 16. Such cells do not exhibit any coloration during the cycling. The voltammetry curves were found practically symmetric and no degradation has been observed electrochemically or by visual inspection of the cell up to 30000 cycles or when kept on the shelf in open circuit for several weeks (test are still in progress). The time response of the current density flowing through the cell to square wave voltage of ± 0.8 V applied with a period of 40 s is shown in Figure 2 for the 29340th cycle. A fast switching time ($\sim 2, 5$ s) is observed for both the insertion or extraction process showing that the sol gel stack $TiO_2/TiO_2-CeO_2/ITO/glass$ performs perfectly well for the proposed purpose. It is worth while to note that the cell configuration employed in this test is of no use for optical devices but other applications such as all sol gel thin solid state battery can be foreseen.

Similar measurements (not reported here) are in progress in order to test the symmetric configuration glass/ITO/ $WO_3/TiO_2/WO_3/ITO/glass$.

Finally complete $10 cm^2$ electrochromic windows having the configuration glass/ITO/ $WO_3/TiO_2/TiO_2-CeO_2/ITO/glass$ have been built with the three internal active layers prepared by sol gel methods. Figure 3 shows typical optical transmission measured in

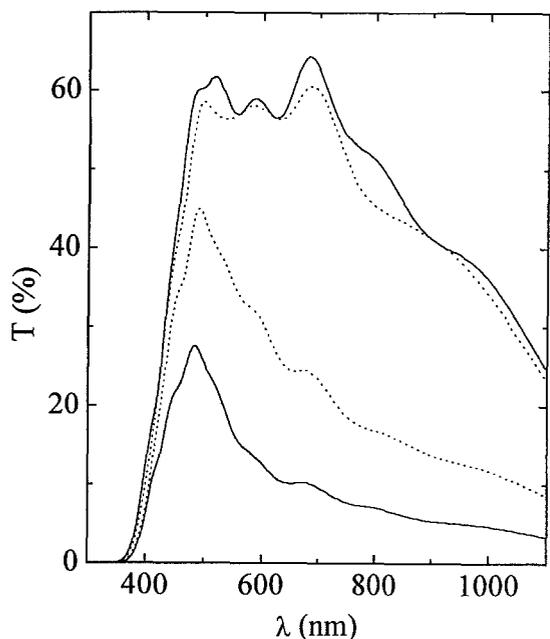


Fig. 3. Visible-near infrared transmission of a cell glass/ITO/WO₃/TiO₂-CeO₂/ITO/glass in the bleached and colored state; —1st cycle, --- 360th cycle.

the visible-near IR region in the bleached and colored states. The results obtained with the 1st cycle are totally comparable with those obtained with windows built with layers prepared by other coating methods [14] [15]. Figure 4 shows the time response of the current density flowing through the device to square wave voltage held at ± 1.5 V limits for 60 s. The coloring and bleaching kinetics are fast (< 10 s). The bleaching response reflects a curvature change around 20 s; such a behavior was already observed in a window.../Li_xWO₃/polymer electrolyte/TiO₂-CeO₂... [13] and attributed to a decrease of the ion diffusion coefficient during its insertion into the IS electrode when its concentration reaches a certain value.

The main problem which remains to be solved is the lifetime of the present device. Figures 3 and 4 show also the results obtained at the 360th cycle. They clearly indicate a degradation. Visual inspection of the devices shows a lack of adherence between two layers as seen by the presence of interference patterns. The origin of the phenomenon is not known yet. As no degradation has been reported in the first window (up to 30000 cycles) it is highly probable that the problem lies at the WO₃/TiO₂ interface. Chemical reactions between the materials may provoke stresses or evolve gases at the interface forcing the layer to separate. Coating of the WO₃ layer by a thin layer of

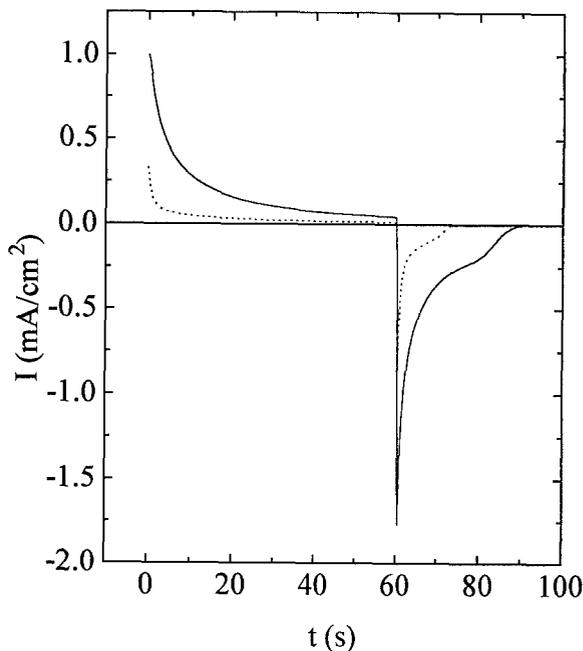


Fig. 4. Current variation to square wave voltage (± 1.5 V, period 60 s) of the cell of Figure 3; —1st cycle, --- 360th cycle.

Ta₂O₅ as proposed by Cogan et al [15] as an effective protection from the degradation against reaction of this material with a poly AMPs electrolyte may be useful. However as Judeinstein et al [11, 12] claimed a lifetime longer than 40000 cycles for a symmetric always colored cell SnO₂/WO₃/TiO₂/WO₃/SnO₂ whose active layers have been realized with the same sol gel methods, we believed that the problem lies in the adequate composition of the electrolyte. However failure due to hydrogen embrittlement or generation is not discarded [16].

4. Conclusion

We have presented two all solid electrochromic windows whose three internal active layers have been realized by sol gel methods and using protons as ionic carriers. The first one had the symmetric configuration glass/ITO/TiO₂-CeO₂/TiO₂/TiO₂-CeO₂/ITO/glass and does not show any visible coloration during the cycling since TiO₂-CeO₂ does not color. This device can be useful for other application such as solid state battery. This configuration was used to test the lifetime of the TiO₂/TiO₂-CeO₂/ITO/glass side of the optical device. This part performed perfectly up to 30000 cycles with no apparent opti-

cal and electrochromic degradation (longer time test still in progress). The non-symmetric optical window having the configuration glass/ITO/WO₃/TiO₂/TiO₂-CeO₂/ITO/glass shows optical transmission change between the colored and bleached state and kinetics totally comparable to similar devices whose layers have been processed by other techniques. The lifetime of our sol-gel device is however shorter. This is due to a lack of adherence between the EC and IC electrodes. It is suggested that this failure can be eliminated by choosing an adequate composition in the preparation of the TiO₂ electrolyte. Nevertheless, if we discard this lifetime problem, we have shown that it is possible now to obtain complete sol-gel electrochromic devices showing comparable optical properties as those obtained using other methods of preparation.

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References

1. Lampert, C.M. and Grandqvist, C.G., Large-area chromogenics: materials and devices for transmittance control, SPIE, Bellingham, (1990) **IS4**.
2. Agrawal, M., Cronin, J.P., and Zang, R., Sol gel optics II, SPIE (1992), **1758**, p. 330.
3. Ogiwara, S. and Kinugawa, K., Yogyo-Kyokai-Shi (in Japanese) **90**, 157 (1982).
4. Gonzalez-Oliver, G.J.R. and Kato, I., J. Non-Cryst. Solids **82**, 400 (1986).
5. Dislich, H., J. Non-Cryst. Solids **57**, 371 (1983).
6. Tonazzi, J.C.L., Valla, B., Macedo, M.A., Baudry, P., and Aegerter, M.A., SPIE (1990), **1328**, p. 375.
7. Baudry, P., Aegerter, M.A., Derro, D., and Valla, B., J. Electrochem. Soc. **138**, 460 (1991).
8. Valla, B., Tonazzi, J.C.L., Macedo, M.A., Dall'Antonia, L.H., Aegerter, M.A., Gomes, M.A.B., and Bulhoes, L.O., SPIE (1991), **1536**.
9. Aegerter, M.A., *Patent pending No. WO 91/02282 (PCT/BR90/00006)*, (1991).
10. Macedo, M.A., Dall'Antonia, L.H., and Aegerter, M.A., MRS (1992), **276**, p. 125.
11. Judeinstein, P., Livage, J., Zarniansky, A., and Rose, R., Solid State Ionics **28-30**, 1722 (1988).
12. Judeinstein, P. and Livage, J., Sol-gel Optics, SPIE (1990), **1328**, p. 344.
13. Macedo, M.A., Dall'Antonia, L.H., Valla, B., and Aegerter, M.A., J. Non-Cryst. Solids **147/148**, 792 (1992).
14. Goldner, R.B., Seward, G., Wong, K., Haas, T., Foley, G.H., Chapman, R., and Schulz, S., Solar Energy Materials **19**, 17 (1988).
15. Cogan, S.F. and Rauch, R.D., Reference 1, 482.
16. Czanderna, M.W. and Lampert, C.M., *SERI/TP-255-3637*, (1990).