JOURNAL OF MATERIALS SCIENCE **33** (1998) 2181–2185

Two methods of obtaining sol–gel Nb_2O_5 thin films for electrochromic devices

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Nb_2O_5 coatings prepared by the sol–gel route using the dip coating technique with sols prepared from alkoxide or chloroalkoxide (two different methods: sonocatalytic and conventional) precursors are a promising alternative for WO_3 electrochromic coatings. The crystalline films (TT phase) sintered at 560 and 600 °C are transparent and present a deep blue colour under Li^+ ion insertion. Electrochemical stability is excellent as these systems are fully reversible and stable and no change in colour, amount of charge exchanged and corrosion effect could be observed after 2000 voltammetry cycles between 2 and -1.8 V versus Ag. The electrochemical and optical properties of these coatings have been determined as a function of sintering temperature. The superficial structure was visualized by atomic force microscopy (AFM) and scanning electron microscopy (SEM) and the Li^+ diffusion coefficient was determined for both kinds of coatings. © *1998 Chapman & Hall*

1. Introduction

A wide class of materials, called chromogenic materials, change their optical properties (transmission, absorption, etc.) in response to a change in the ambient condition. If their colours change under an applied potential in an electrochemical cell they are called electrochromic materials. This property is observed by a large number of metal oxides, such as TiO_2, WO_3, V_2O_5 and Nb_2O_5. These materials are interesting because of their use in various solid state electrochemical devices, including batteries, and electrodes for photoelectrochemical and electrochromic devices [1, 2]. The electrochemical properties are due to H^+ and Li^+ insertion in the layer, which in the case of TiO_2, WO_3 and Nb_2O_5 cause changes in optical transmissivity from a quasi-transparent state (transmission $T \cong 85\%$) to less than $T \cong 20\%$.

The electro-optical performances of electrochromic coatings are strongly dependent on their structural morphology. Outstanding performances have recently been obtained using materials constituted of aggregates of nanometre-sized particles of CeO_2–TiO_2 [3–6], TiO_2 [7] and Nb_2O_5 [8, 9]. The sol–gel process is a particularly well adapted method for achieving such morphology. Moreover the dip coating technique, a common method of deposition in this field, allows deposition of large area coatings at low cost.

Recently some studies have reported on the electrochromic properties of Nb_2O_5. Blue colouration was found in an opaque Nb_2O_5 layer grown thermally at ~ 500 °C on a niobium metallic disk [10, 11]. Alves [12] has confirmed the possibility of inserting Li^+ ions in a Nb_2O_5 ceramic prepared from a commercial powder sintered at ~ 800 °C. The first attempt to fabricate sol–gel Nb_2O_5 for electrochemical purposes was reported by Lee and Crayston [13], using a sol made of a mixture of $NbCl_5$ dissolved in ethanol. However, the 5–10 μm thick film presented substantial cracking and peeling due to an important shrinkage during drying. More recently, we have obtained homogeneous films without cracks and defects that present good and promising electrochromic properties [8, 9, 14].

In this work we report on the electrochemical and microscopic characterization and electrochromic properties of Nb_2O_5 sol–gel coatings prepared by two different sol–gel methods and deposited by a dip-coating technique on indium-tin oxide ITO-coated glass.

2. Experimental procedure

Two alkoxy methods were used to prepare a transparent and stable niobium alkoxide solution. Sol 1 was prepared by a sonocatalytic process [14, 15] and allowed coatings with good optical qualities and interesting electrochromic properties to be obtained. The starting solution to produce Nb_2O_5 films was prepared by dissolving $NbCl_5$ powder (CBMM, Brazil)

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(1.3 g, 0.005 mol) in butanol (15 ml, 0.16 mol) and acetic acid (3 ml, 0.05 mol). The solution mixture was submitted for a few minutes to the action of ultrasonic irradiation (Sonicator W385 Heat System-Ultrasonic, Inc. at 20 kHz) resulting in a transparent and viscous solution stable for several months at room temperature. The main precursors were probably chloroalkoxides of the type $NbCl_{5-x}(OBu)_x$ [16].

The second precursor, Sol 2, was prepared by synthesizing Nb pentabutoxide, $Nb(OBu_n)_5$, by dissolving $NbCl_5$ (CBMM, Brazil) in butanol, to which was added sodium butoxide under reflux. The process led to the formation of $Nb(OBu_n)_5$ and NaCl. The last compound was separated by centrifugation. The final sol was prepared by mixing this precursor with glacial acetic acid (CH_3COOH) resulting in a sol stable at 20 °C for several months [8, 9]. In this method we did not use ultrasonic irradiation.

The coatings were deposited on an ITO-coated glass substrate (Asahi-Glass, $14\,\Omega_{\square}$) previously cleaned and rinsed with bidistilled water, ethanol and then dried at room temperature. The substrates were dipped into the solution in ambient atmosphere and withdrawn at a rate of 12 cm min^{-1}. The samples were subsequently dried in air at room temperature for 15 min. The uniform gel films were then calcined at temperatures up to 600 °C using a heating rate of 10 °C min^{-1}. The resulting coatings were then kept at the final temperature from 10 min to 3 h and were found to be transparent and homogeneous with a thickness of about 300 nm after three dips.

The surface morphology of the films was visualized by AFM (Topometrix) and SEM (Zeiss 960) analyses.

The electrochemical characteristics (voltammograms) were determined using a Solartron 1286 analyser and a conventional three electrode cell placed in a dry-box under dry N_2. The counter-electrode was a platinum foil of 1 cm^2 area and the quasi-reference electrode was a silver wire. The electrolyte was a 0.1 M solution of $LiClO_4$ dissolved in a propylene carbonate (PC). The cell was previously purged with dry N_2 gas.

The thickness of a film, measured with a Taylor–Hobson Talystep was about 100 nm for a one-dip layer. Optical spectra in the ultraviolet–visual (u.v.–vis) range were recorded *in situ* with a Cary 2315 spectrophotometer. The coated substrate was placed in a special electrochemical cell built with two flat fused quartz windows and the u.v.–vis spectra were measured before and after insertion of Li^+ cations at fixed potentials.

X-ray diffraction measurements of xerogels obtained with the same sols and heat treated at 560 °C for 10 min following the same protocol, indicate that the powder material is crystalline, with a very-low-temperature form TT structure [14, 17].

3. Results and discussion

Fig. 1a, b presents typical cyclic voltammograms of coatings obtained from Sols 1 and 2 measured at a speed of 50 $mV\,s^{-1}$ in the scan range + 2 to − 1.8 V. The increase of the current in the cathodic potential sweep is associated with the Li^+ insertion process. After reversal of the potential scan at − 0.95 V an anodic current peak is clearly observed. This peak is attributed to the extraction of Li^+. An interesting feature of this result is that the coatings show small differences when heated at different temperatures. It was found that the Nb_2O_5 films prepared from Sol 1 were better when calcined at 600 °C (Fig. 1a) while those prepared from Sol 2 were better when calcined at 560 °C (Fig. 1b). Both samples prepared in these conditions were very stable and successive cycles (tested for 2200 cycles for Sols 1 and 2) repeated the original current–potential curve (Fig. 2a, b). The charge exchanged during the insertion–extraction processes decreased only very slightly from 20 mC cm^{-2} to 18 mC cm^{-2} for Sol 1 and increased from 13 to 15 mC cm^{-2} for Sol 2 (Fig. 3). In all cases a cathodic scan to − 1.8 V turned the film dark blue and after an anodic scan to + 2.0 V the film again became transparent (slightly yellow).

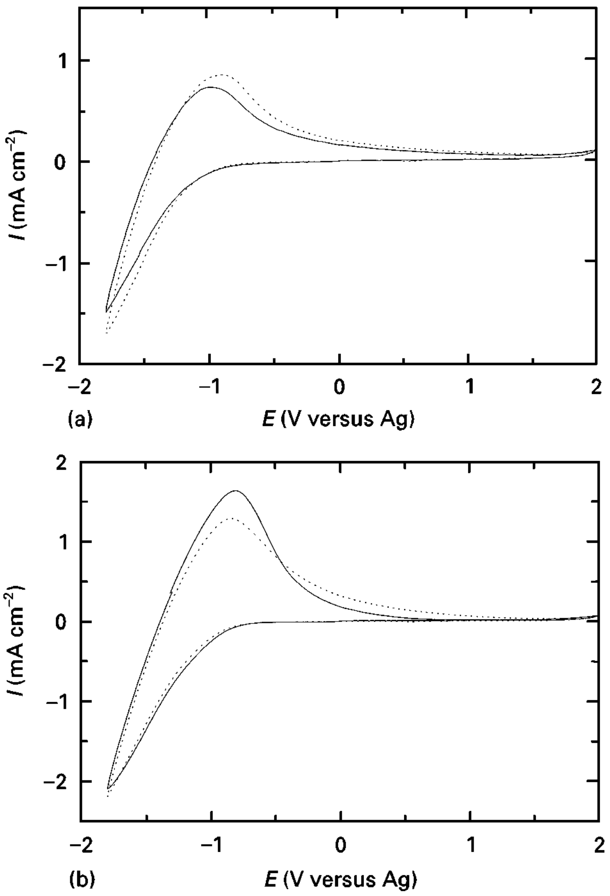

Figure 1 Typical cyclic voltammetry of an Nb_2O_5 film prepared from Sols 1(a) and 2(b), deposited on Asahi ITO-coated glass, heat treated at (- - -) 600 and (——) 560 °C for 2–3 h in an O_2 atmosphere. Electrolyte (0.1 M) $LiClO_4$–PC, rate 50 $mV\,s^{-1}$.

Fig. 4a,b shows typical cyclic voltammograms registered by a three-layer Nb_2O_5 film heat treated at 600 and 560 °C for 2–3 h in an O_2 atmosphere for three different scanning rates 50, 100 and 200 $mV\,s^{-1}$. The maximum value of the anodic peak increases with scanning rate, and the quantity of charge inserted decreases from 19 ($v = 50\,mV\,s^{-1}$) to 6.9 mC cm^{-2} ($v = 200\,mV\,s^{-1}$) for Sol 1 and from 20 ($v = 50\,mV\,s^{-1}$) to 8.8 mC cm^{-2} ($v = 200\,mV\,s^{-1}$) for Sol 2.

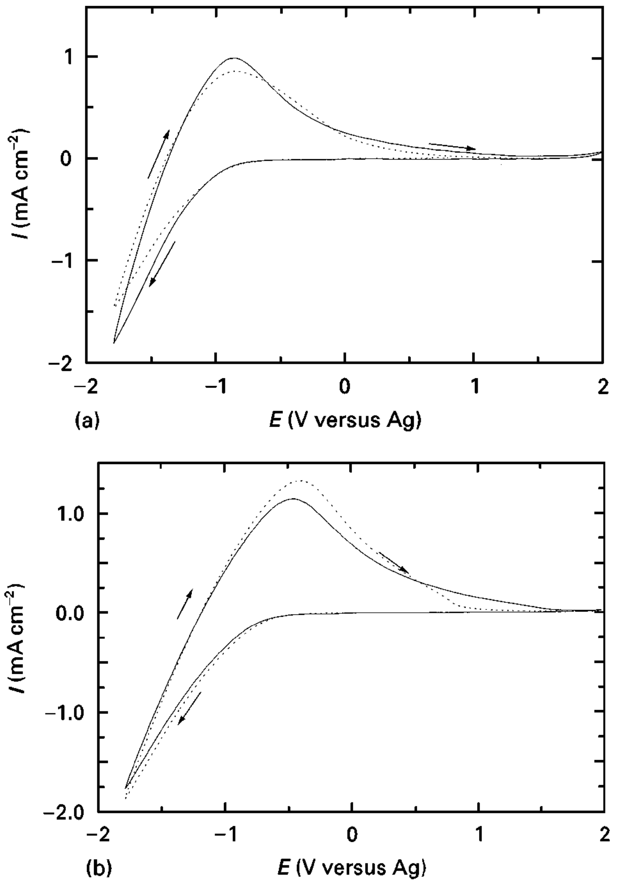

Figure 2 Voltammograms of an Nb_2O_5 film as a function of number of cronoamperometric cycles. Nb_2O_5 prepared from: (a) Sol 1 (heat treated at 600 °C) and (b) Sol 2 (heat treated at 560 °C) for 2–3 h in an O_2 atmosphere. Electrolyte (0.1 M) $LiClO_4$–PC, rate 50 mV s^{-1}. (——) 1°, (- - -) 1100°.

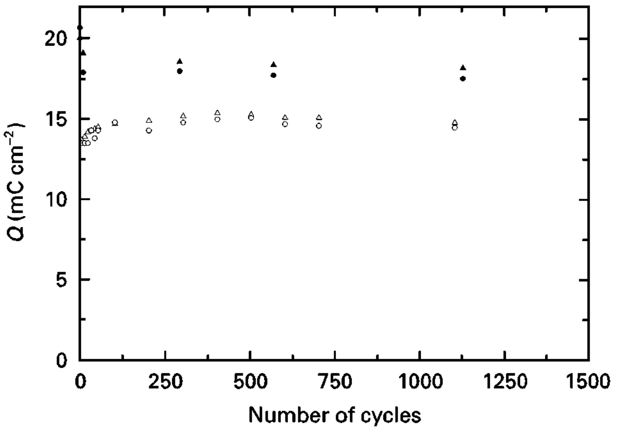

Figure 3 Cathodic (●, ○) and anodic (▲, △) charge density, Q as a function of the number of chronoamperometric cycles with potential steps at every 10 s between − 1.8 and 2 V. Closed symbols, Sol 1; open symbols, Sol 2.

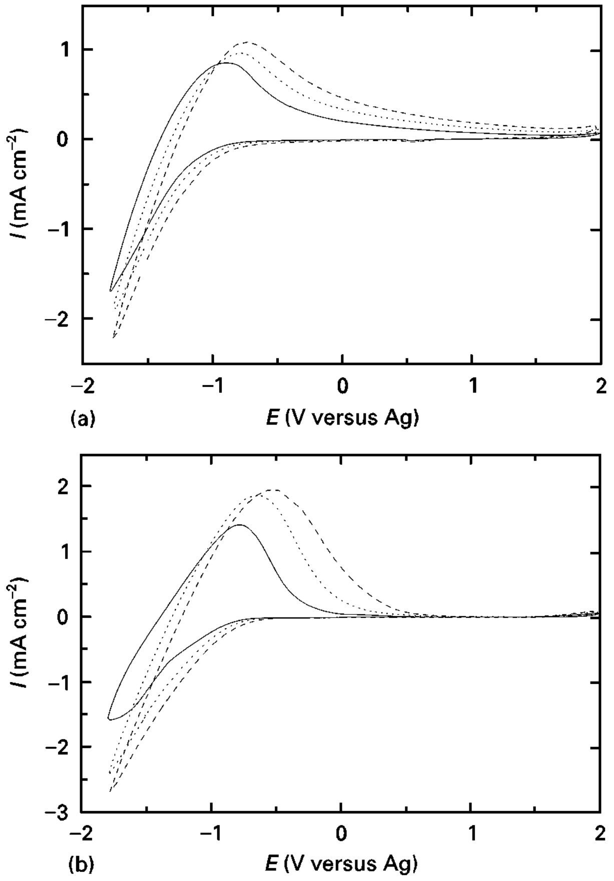

Figure 4 Voltammograms of Nb_2O_5 coatings deposited on Asahi ITO-coated glass heat treated at 560 and 600 °C for 2–3 h in an O_2 atmosphere. Electrolyte (0.1 M) $LiClO_4$–PC, scan rate (——) 50, (- - -) 100, (— — —) 200 mV s^{-1}; (a) Sol 1 and (b) Sol 2.

The diffusion coefficient, D, of Li^+ ions in the electrolyte was calculated from the formula [18]

$$D = \left(\frac{i_p}{2.72 \times 10^5 \, n^{3/2} \, C_0 \, v^{1/2}} \right)^2$$

where D is the diffusion coefficient in centimetres squared per second, C_0 the concentration of active ion in solution (moles per cubic centimetre), v the sweep rate (volts per second), n the number of Electron 1, and i_p the anodic peak of current density (amps per centimetre squared) that is read from the cyclic voltammograms (Fig. 1a, b). The values were for Sols 1 and 2, respectively, $D = 1.4 \times 10^{-8}$ and 3.6×10^{-8} cm^2 s^{-1}. In both cases the values obtained were higher than those reported for WO_3 films i.e. $D = 2.93 \times 10^{-11}$ cm^2 s^{-1} [18], but similar to the value $D = 5 \times 10^{-9}$ cm^2 s^{-1} reported by Mohapatra [19] obtained from potentiostatic measurements.

Fig. 5a,b presents micrographs of films of Nb_2O_5 prepared in the two ways and deposited on glass. The structure of the film, Sol 1 (Sol 2 not presented here), visualized by the AFM picture, is formed by a uniform agglomeration of small particles with an average size of about 30–70 nm (Fig. 6). These particles are not visible in the SEM micrographs, but they confirm that the surface of the films prepared by the two different methods have excellent microstructure without visible cracks and defects.

Fig. 7 shows transmission spectra of Nb_2O_5 films prepared from Sols 1 and 2 and deposited onto an ITO electrode. The u.v.–vis spectra were registered *in situ* in the reduced and oxidized state for three-dip layers at a fixed potential of + 2.0 (bleached state) and − 1.8 V (coloured state). The insertion of Li^+ changes the transmission in the visible–near infrared range from about 80 to less than 20% for ~ 300 nm thick (three-dip) coatings prepared by the two different routes (Sols 1 and 2).

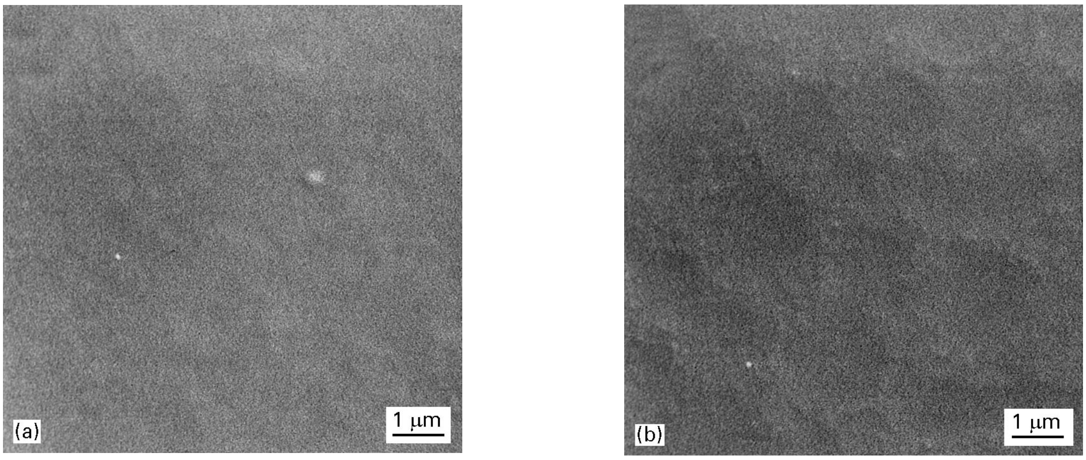

Figure 5 SEM micrographs of Nb_2O_5 films: (a) film prepared from Sol 1 heat treated at 600 °C, and (b) film prepared from Sol 2 heat treated at 560 °C.

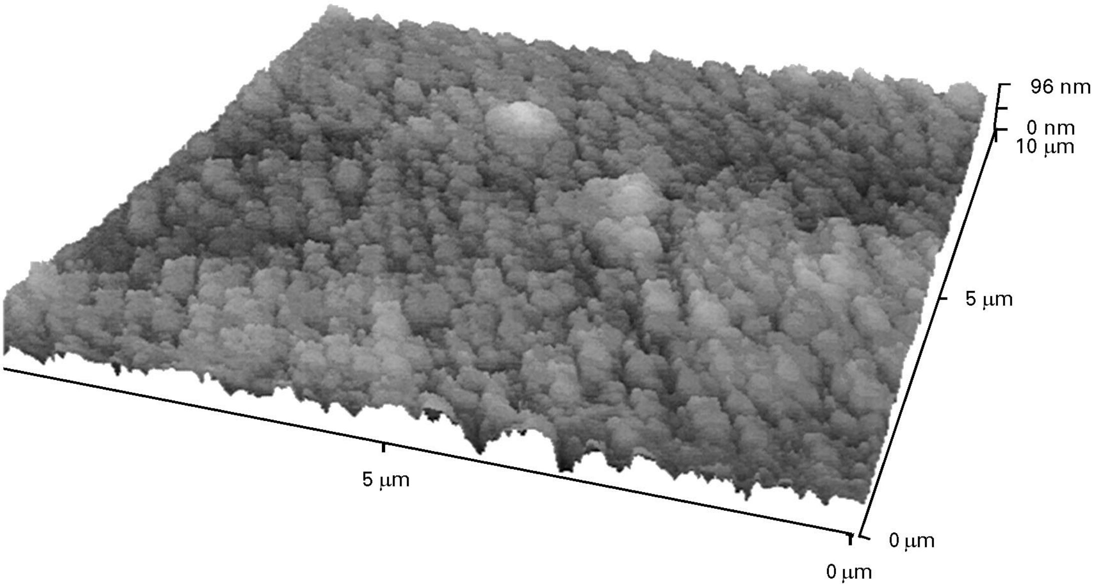

Figure 6 AFM picture of a film prepared from Sol 1 heat treated at 600 °C for 1 h. Imaging mode AFM super-tip topography (forward) with three-dimensional perspective.

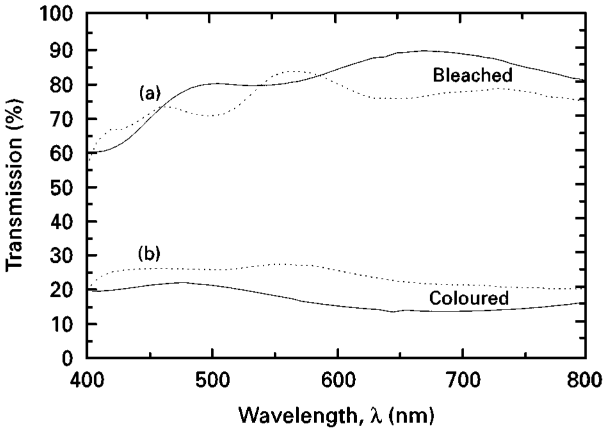

Figure 7 U.v.–vis spectral variation observed during electrochromic switching of thrice dipped Nb_2O_5 films of Sols 1 (——) and 2 (- - -) before (a) and after (b) polarization at 1.8 V.

4. Conclusions

We have shown that films of Nb_2O_5 prepared either by sonocatalytic or conventional methods are promising candidates for electrochromic devices using lithium electrolytes. The powders calcined at 560–600 °C in an O_2 atmosphere have a crystalline TT structure. The coatings present good, reversible and fast insertion–extraction for Li^+ ions. AFM measurements show that the films are formed by uniform agglomeration of nanometre-sized particles (20–70 nm). The charge density inserted at a voltammetric scanning rate of $50\,mV\,s^{-1}$ in the films prepared from Sol 1 (about $18–20\,mC\,cm^{-2}$) is similar to the charge inserted in the film prepared from Sol 2 ($15–20\,mC\,cm^{-2}$). Small differences were found in the value of the Li^+ diffusion coefficient, where the D value from Sol 2 coatings was about 2.6 times superior than that for coatings prepared from Sol 1. However, the sonocatalytic route was easier and quicker in preparing sols than the classic method and this route avoided the possibility of Na residue.

Acknowledgements

The authors are indebted to Dr Ulf Werner (INM-Saarbrücken) for assistance with the AFM measurements and acknolwedge financial support from FAPESP and CNPq (Brazil).

References

1. M. A. AEGERTER, in "Sol–gel chromogenic materials and devices, structure and bonding," Vol. 85, edited by R. Reisfeld and C. K. Jorgensen (Springer Verlag, Berlin, 1996) p. 149.
2. C. M. LAMPERT and C. G. GRANQUIST (eds), "Large-area chromogenics: materials and devices for transmittance control," Vol. IS4, (SPIE, Bellingham, WA, 1990) p. 2.
3. P. BAUDRY, A. C. M. RODRIGUES, M. A. AEGERTER and L. O. S. BULHÕES, *J. Non-Cryst. Solids* **121** (1990) 319.
4. J. C. L. TONAZZI, B. VALLA, M. A. MACÊDO, P. BAUDRY and M. A. AEGERTER, in "Proceedings on sol–gel optics," Vol. 1328, edited by J. D. Mackenzie (SPIE, Bellingham, WA, 1990) p. 375.
5. M. A. MACÊDO, L. H. DALL'ANTONIA and M. A. AEGERTER, in "Proceedings on sol–gel optics II", Vol. 1758, edited by J. D. Mackenzie (SPIE, Bellingham, WA, 1992) p. 320.
6. D. KÉOMANY, J.-P. PETIT and D. DEROO, in "Proceedings on optical material technology for energy efficiency and solar energy conversion XIII", Vol. 2255, edited by V. Wittwer, C. G. Granquist and C. M. Lampert (SPIE, Bellingham, WA, 1994) p. 363.
7. A. HAGFELDT, N. VLACHOPOULOS and M. GRÄTZEL, *J. Electrochem. Soc.* **141** (1994) L82.
8. C. O. A. AVELLANEDA, M. A. MACÊDO, A. O. FLORENTINO and M. A. AEGERTER, in "Proceedings on optical materials technology for energy efficiency and solar-energy conversion XIII," Vol. 2255, edited by V. Wittwer, C. G. Granquist and C. M. Lampert (SPIE, Bellingham, WA, 1994) p. 38.
9. C. O. AVELLANEDA, M. A. MACÊDO, A. O. FLORENTINO, D. A. BARROS FILHO and M. A. AEGERTER, in "Proceedings on sol–gel optics III", Vol. 2288, edited by J. D. Mackenzie (SPIE, Bellingham, WA, 1994) p. 422.
10. B. REICHMAN and A. J. BARD, *J. Electrochem. Soc.* **127** (1980) 241.
11. M. A. B. GOMES, L. O. S. BULHÕES, S.C. CASTRO and A. J. DAMIÃO, *ibid.* **137** (1990) 3067.
12. M. C. ALVES, MSc thesis, Federal University of São Carlos, São Carlos, Brazil (1989).
13. G. R. LEE and J. A. CRAYSTON, *J. Mater. Chem.* **1** (1991) 381.
14. A. PAWLICKA, M. ATIK and M. A. AEGERTER, *J. Mater. Sci. Lett.* **14** (1995) 1568.
15. M. ATIK and J. ZARZYCKI, *ibid.* **13** (1994) 1301.
16. G. R. LEE and J. A. CRAYSTON, *J. Chem. Soc. Dalton Trans.* (1991) 3073.
17. E. I. KO and J. G. WEISMANN, *Catalysis Today* **8** (1990) 27.
18. M. A. HABIB and D. GLUECK, *Solar Energy Mater.* **18** (1989) 127.
19. S. K. MOHAPATRA, *J. Electrochem. Soc.* **125** (1978) 145.
20. SPIE The International Society for Optical Engineering.

Received 13 September 1996
and accepted 5 December 1997