

Niobia sol-gel : a new material for electrochromic and photoelectric applications

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ABSTRACT

Nb₂O₅, prepared by a sol-gel process in form of coatings are new materials which have outstanding properties: a) the coatings present electrochromic properties and exhibit a blue coloration under Li⁺ insertion with 100% reversible variation of the optical transmission in the visible and near infrared range between 80% and 20% and have a high chemical stability (tested up to 2000 cycles) b) they are semiconductors and present a photoelectric effect when illuminating in the UV region ($\lambda < 360$ nm). These films are therefore very promising to be used in electrochromic devices and as electrodes for photoelectrochemical purpose and the development of nanocrystalline solar cell.

1. INTRODUCTION

The sol-gel process offers today many advantages over traditional techniques for the preparation of new materials, especially advanced and functional coatings having optical, electronic, chemical and mechanical functions [1] and porous materials. Many sol-gel coatings are presently in practical use, especially for optical purposes.

In this paper, we report on the preparation and physical characteristics of functional Nb₂O₅ films and show how these *new materials* can be used to develop technologically important devices. Up to now niobia has been mainly prepared via conventional technique; however the sol-gel process, thanks to the variety of parameters which can be used and controlled during the sol preparation and gel fabrication, allows to obtain Nb₂O₅ materials with interesting properties for electrochemical and chemical applications. The results indicate that a good understanding of the amorphous and crystalline porous structures, a task for which the sol-gel technique appears today as most promising and unique, should play an important role in the future.

2. Nb₂O₅ ELECTROCHROMIC COATING

A typical electrochromic device consists of five layers sandwiched between two glass substrates. There are two transparent electrical conductors required for setting up a distributed electric field, an electrochromic layer, an ionic conductor (electrolyte) and an ion (H⁺ or Li⁺) 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 in the visible range. The original state is obtained by reversing the applied voltage.

Among the compositions which present an electrochromic behavior the oxides of transition metals such as WO₃, Nb₂O₅, TiO₂, V₂O₅, TiO₂-CeO₂, MoO₃ and some mixed compounds appear to be the best materials; all have been already obtained via sol-gel process [2,3].

1.1 Sol and film preparation

Sol-gel Nb₂O₅ films are new very promising candidate for electrochromic coatings. Very few studies have been reported on the electrochromic properties of Nb₂O₅. Reichman and Bard [4] showed the occurrence of such effects in a 15µm thick coating produced on the surface of a niobium metallic disk by heating at ~500 °C for about 10 min. A coloring effect, chemically stable and with a fast kinetics (1-2s) was seen in reflexion under either H⁺ or Li⁺ insertion. Gomes et al [5] have studied in details the protonic electrochromic properties of 20 µm thick opaque coating prepared in the same way and later Alves [6] has confirmed the possibility to insert Li ions in a 1 mm thick Nb₂O₅ ceramic prepared from commercial CBMM powder sintered at 800°C.

The first attempt to fabricate sol-gel Nb₂O₅ for electrochemical purpose has been reported by Lee and Grayson [7] who have spin coated ITO coated glass electrode with a mixture of NbCl₅ dissolved in EtOH. Hydrolysis and gelation were completed in 1 mol/dm³ H₂SO₄ solution. After drying at room temperature the result was a 5-10 µm thick film with substantial cracking (10 µm islands) and peeling due to important shrinkage. Cyclic voltammograms in LiClO₄-MeCN electrolyte showed a blue coloration with a fast coloration (1-6s) and bleaching (~3s) kinetics and a 6 cm²/C coloring efficiency. However the durability of the electrochromic response was only a few cycles. The quality of the film has been slightly improved by adding 1-malkoxysilane (Glymo) to the precursor sol in order to obtain a Nb-Si Ormocer.

In our laboratory, Nb₂O₅ sols have been prepared using an alkoxide route (figure 1a). Pentabutoxide of niobium (Nb(OBu)₅) was first synthesized following the process described by Bradley et al [8] by dissolving niobium chloride (NbCl₅) from CBMM-Brasili in butanol and then mixed with sodium butoxide (Na(OBu)₃) under reflux. During the process a strong exothermic reaction occurs leading to the formation of Nb(OBu)₅ and NaCl. The last compound was then separated by centrifugation and a yellow and transparent precursor sol was obtained. The final sol was prepared by mixing this precursor with glacial acetic acid (CH₃COOH) with molar ratio 1:2 resulting in a sol stable at room temperature for several months. [9,10]. Figure 2 shows the size distribution of the sol particles measured in a light scattering experiment (Malvern 4700). The distribution is bimodal with a z average mean of 16.7 nm and a polydispersion value of 0.267.

The coatings have been deposited by dip coating technique on Donnelly or Asahi Glass ITO coated glass at a withdrawal speed of 12 cm/min, dried at room temperature during 5 min and then densified at 400° C during 15 min. They have typically a thickness of ≈ 80 nm. The process can be repeated to obtain thicker films. The coatings used in this work had 3 layers and a thickness of ~ 250 nm; the final coatings have been finally heat treated in O₂ atmosphere between 400 and 600°C [9,10,11]. Figure 1b shows a block diagram of this procedure.

2.2 Coating characterizations

Figure 3 shows a typical SEM micrograph of a three layers Nb₂O₅ film (250 nm thick) obtained according to the above procedures with a heat treatment at 560°C in O₂ atmosphere during 2 h. The picture shows very good homogeneity of the Nb atoms and excellent microstructure of the surface with no visible crack and defect.

Figure 4 shows a typical DSC scan of a xerogel powder of Nb₂O₅ material obtained after gelification of the sol and taken at a low heating rate of 2°C/min in a O₂ flux. The peaks at low temperature (<350 °C) are related to water and organic materials elimination. The feature around 500 °C corresponds to the onset of crystallization into the TT phase (see below). It is followed by two large exotherms whose peak maximum lies at 630 °C (measured by DTA). This evolution is certainly related to a structural phase transformation.

Fig 252

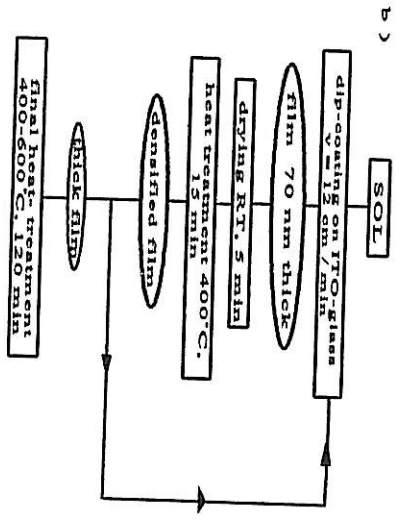
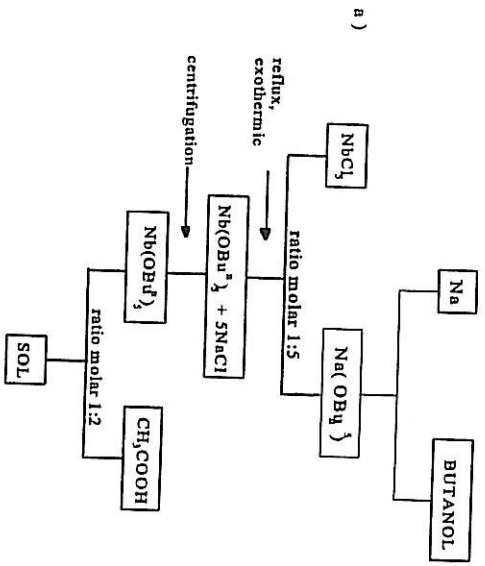


Figure 1. Block diagram of a) Nb₂O₅ sol preparation and b) Nb₂O₅ film preparation.

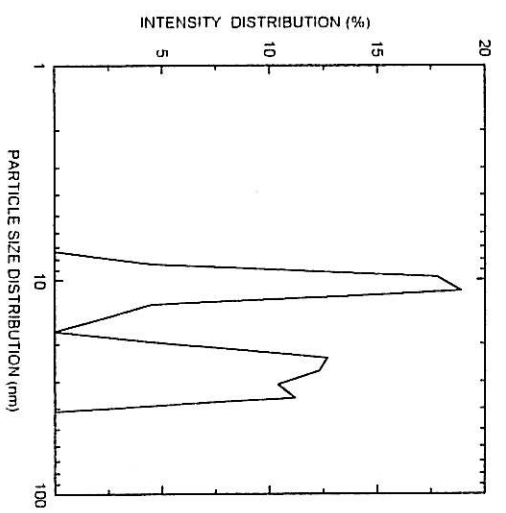


Figure 2. Particles size distribution of the niobia sol

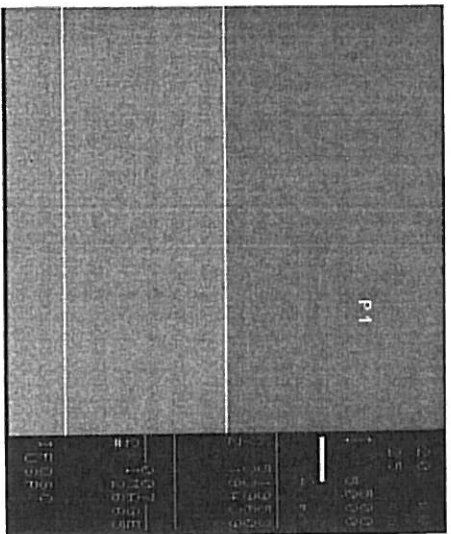


Figure 3. Micrograph of a Nb₂O₅ coating heat treated at 560 °C during 2 h in O₂ atmosphere. The mark is 20 μm in the top part and 2 μm in the lower part of the picture

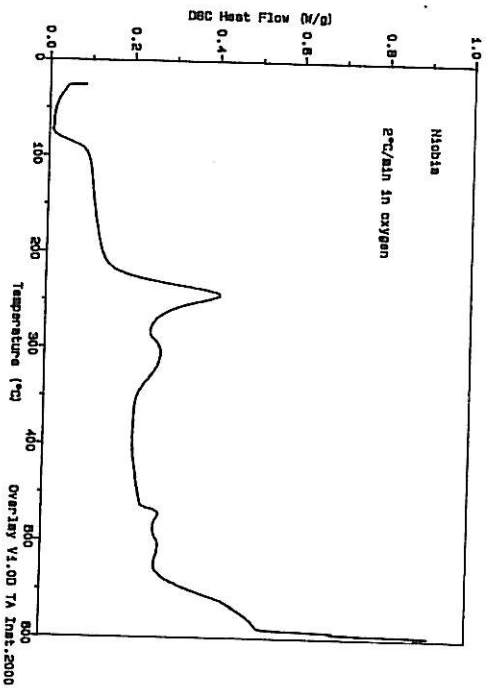


Figure 4. DSC scan of Nb_2O_5 xerogel measured at 2 °C/min in O_2 atmosphere.

probably of the type TT into T.

X-ray diffractograms of xerogels obtained with the same sol have been obtained with a Rigaku model RU200B instrument with a $\text{K}\alpha$ Cu radiation. Figure 5 shows that the gels heat treated up to 500 °C are amorphous. At 560 °C the material is crystalline but the lines are poorly defined. Their position and intensity are compatible with the so-called TT phase as can be seen by comparison with the top part of the figure [12,13]. The width of the principal lines somewhat sharpens at 600 °C but the overall shape of the spectrum does not change. No trace of other phases (T,M,H) has been observed. According to Ko [12], the TT phase is not strictly a niobium pentoxide as some oxygen atoms are replaced by monovalent species such as X = OH, Cl, vacancies, etc and Nb atoms occupy separated but closely-spaced equivalent sites or intermediate positions between them; the compound should be better denoted $\text{Nb}_6\text{O}_{13}\text{X}_1$ or $\text{Nb}_2(\text{OX})_{5\text{TT}}$.

Figure 6 presents typical voltammograms measured at speed varying from 2 to 200 mV/s between +2.0 and -1.8 V (vs Ag/AgCl reference) for 3 layers Nb_2O_5 coating deposited on ITO coated glass (Asahi Glass) and sintered 2 h at 560°C in oxygen. The measurements have been performed with a Solartron 1226 electrochemical interface and a cell consisting of three electrodes: a Pt foil (1 cm²) as counter electrode, an Ag wire as a quasi-reference electrode and the "Nb₂O₅" film as working electrode (working area 0.3 cm²). The electrolyte was LiClO_4 dissolved in propylene carbonate with concentration 0.1M and was previously purged with dry N₂ gas. All the electrochemical measurements have been done in a dry box containing N₂ atmosphere with less than 100 ppm H₂O. We must first mention that the voltammograms could not be registered at potential value lower than -2.0 V. Below this value the cathodic current increases very

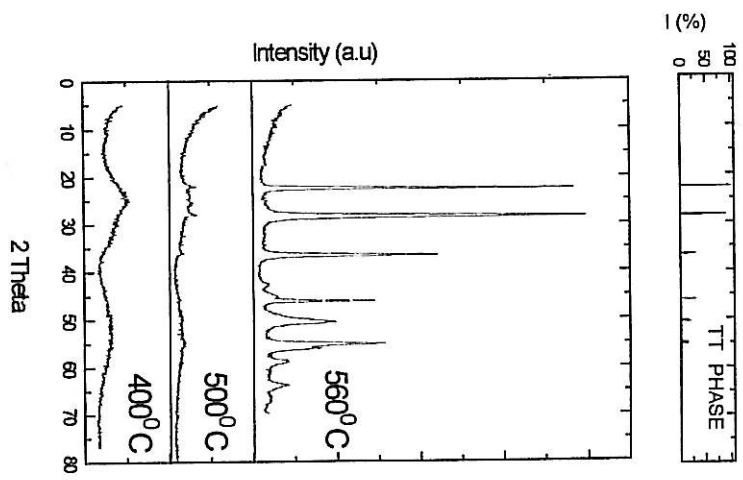


Figure 5. Lower part: X-ray diffraction of Nb_2O_5 xerogels heat treated at 400, 500, 560°C during 2h in O_2 atmosphere. The top part shows the position of the principal peaks of the TT phase

Figure 6. Voltammograms of a 250 nm thick Nb_2O_5 coating deposited on a glass/ITO (Asahi Glass) substrate and heat treated at 560 °C during 2h in O_2 atmosphere. Electrolyte N_2 purged 0.1M LiClO_4/PC ; reference Ag/AgCl ; potential scan +2 V to -1.8 V. Lower part : scan rates 2, 4, 6, 8, 10, 20 mV/s, upper part : scan rates 10, 20, 50, 100, 150 and 200 mV/s.

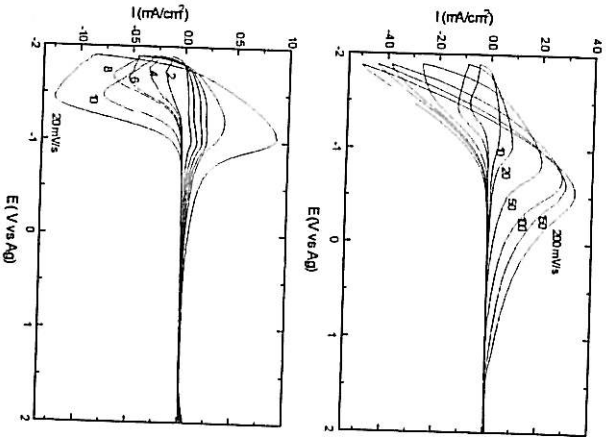
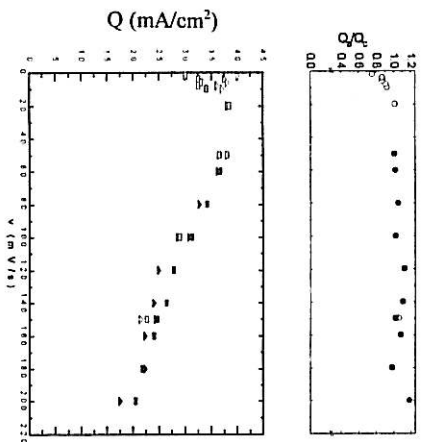


Figure 7. Lower part : Inserted charge Q_C (\blacktriangle) and extracted charge (\blacktriangle , \blacktriangle) integrated from the voltammograms obtained with two films prepared in the same conditions versus scan rate. Upper part : ratio Q_A/Q_C versus scan rate.



rapidly and the coating turns black and permanently damaged. Electrochemical measurements made with uncoated but heat treated ITO substrates shows that this effect is due to the reduction of this material. Within the safe range of -1.8 to 2.0 V, two different regimes can be observed.

At low speed ($v < 10$ mV/s) the curves are rather complex and appear as a superposition of at least two insertion phenomena, one into the niobate coating and the other into the ITO coating to which belong the cathodic and anodic waves observed at -1.7 and -1V respectively (figure 6 lower part). BET measurements (not shown here) indicate that xerogels at 560 °C have still a relatively high porosity $S=60\text{m}^2\text{g}^{-1}$. As the charge inserted is high and constant ($Q_C \approx 20$ mC/cm 2), as shown in figure 7, it seems, at these low scan rates, that the Li^+ ions have time to reach the ITO electronic coating. On the other hand, as shown in the upper part of the same figure, the cycles are not reversible: the total charge extracted, Q_A , is smaller than the total charge inserted and consequently the ratio Q_A/Q_C is smaller than 1. The color of the coating after Li^+ insertion is blue-black and after bleaching the system remains slightly colored.

For scan rate higher than 10 mV/s the voltammograms are totally different (figure 6 upper part). At lower speed the Li^+ insertion peak is clearly visible at ~ -1.5 V, but shifts rapidly to lower and out of range potentials when the speed is increased. The extraction peak can be observed in the whole scan range and also shifts but to higher potential values. Although the value of the charge inserted or extracted diminish with the speed, their ratio Q_A/Q_C remains now constant and approximately 1 (figure 7) indicating that the process is fully reversible in this speed range.

The variation of the maximum intensity of the cathodic and anodic currents with the scan rate is practically impossible to measure as at low speed it would be necessary to make a careful deconvolution of the insertion processes and at high speed, the maximum of the insertion peak is not observed in the safe

potential range used and the values of I_{max} of the extraction peak should be measured from the base line of the cathodic part at low negative potential, a task which is impossible to realize without a better knowledge of the chemical processes occurring at the electrode. Therefore it is not possible to argue if the process is limited by the Li diffusion or is due to a superficial phenomenon. Measurements are underway with coatings deposited on metallic substrate in order to avoid the ITO reduction occurring at ~ -2.0 V and extend the potential range to lower values.

In the high speed range the color of the coating after Li insertion is deep blue. Figure 8 shows the optical transmission spectrum measured in situ with a Cary 17 spectrophotometer in the range 300 to 1100 nm at different applied potentials either during the insertion or the extraction process. A small hysteresis is observed but the good superposition of the curves in the bleached state at $+2.0$ V shows that the system is totally reversible.

Chronoamperometry measurements (not shown here), where the current was registered during the application of a square pulse of $+2.0$ to -1.8 V, show that the insertion process has a time response of about 10 s while the extraction process is faster, about 4 s.

For coatings deposited either on Asahi Glass or Donnelly ITO and heat treated in O_2 atmosphere the inserted charge is constant since the first cycles and its time behavior, tested up to 2000 full voltammetry cycles shows an excellent chemical stability (figure 9). When the coatings are amorphous (i.e. for heat treatment at $T \leq 500$ °C), the inserted (or extracted) charge first increases up to about 500 cycles and then decreases; this behavior suggests some structural evolution of the amorphous oxide network. The shape of the voltammograms measured at 50 mV/s are similar to that shown in figure 6 (upper part) but the color of the layer is brown and the amount of charge involved in the process is smaller. When the coatings are heat treated in air instead of O_2 at temperature between 400 and 560 °C, we found that the amount of charge slightly decreases with the number of cycles for both type of substrates.

It is also possible to insert proton in these coatings. The cycles are also reversible but the lifetime of the coatings is short and does not exceed a few cycles. We believe that the bad performance is due to corrosion problems similar to the phenomenon observed with WO_3 coating.

In conclusion we can state that "niobate" coating can now be prepared by the sol-gel process with excellent optical quality without cracks and good homogeneity. These coatings show reversible electrochromic properties when measured at scan rate higher than 10 mV/s and exhibit a deep blue coloration similar to that of WO_3 coating. The variation of the optical transmission is high for a 250 nm thick layer and the kinetics of the insertion and extraction processes are quite adequate to use these coatings as electrochromic layer to built smart windows or mirrors, a research which is presently underway in our laboratory.

3. Nb_2O_5 AS PHOTOELECTRICAL COATING

Recently a new photovoltaic solar cell concept has been developed by Graetzel et al [14]. The device is based on the use of small (~ 20 nm) colloidal semiconductor particles of TiO_2 prepared by a sol-gel process and sintered at low temperature and whose surface has been sensitized by a monolayer of transition metal complex in order to shift the absorption spectrum of TiO_2 ($\lambda < 380$ nm) toward the visible solar range. Contrary to conventional semiconductor cells, the nanocrystalline device separates the function of light absorption (charge creation) and charge transport. The light is first absorbed by the sensitizer whose absorption spectral range can be adapted to the solar spectral range by a careful choice of its composition. The excited electrons are then transferred to the conduction band of the TiO_2 where they rapidly diffuse through the thin coating ($\sim 2\mu\text{m}$) and are collected by a conducting electrode. The cycle is then closed by returning the electrons to a counter electrode and through an adequate electrolyte which allows the regeneration of the

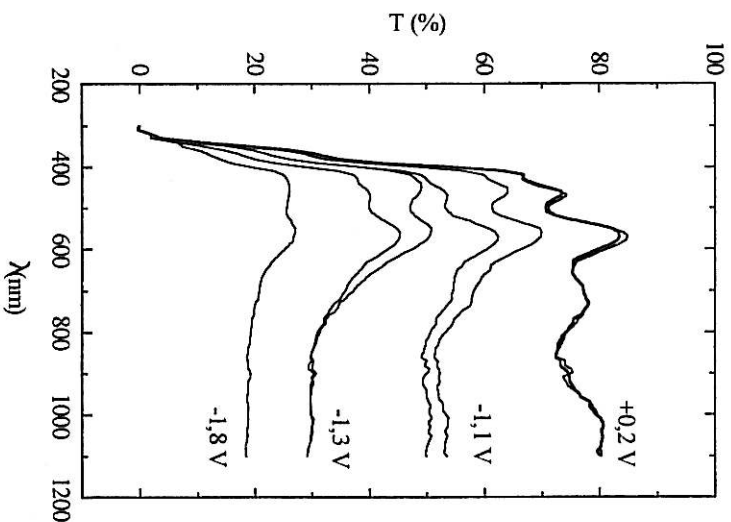
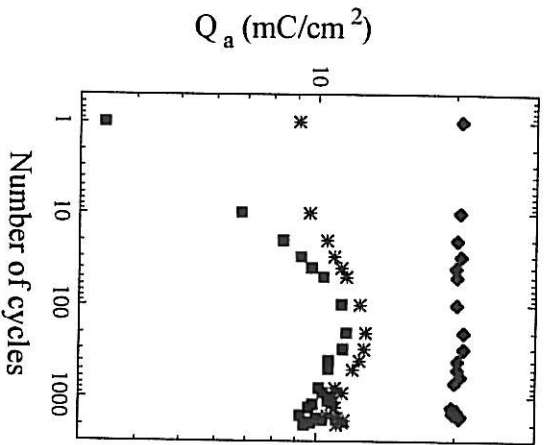


Figure 8. Optical transmission spectrum of Nb_2O_5 coating heat treated at 560 °C during 2h in O_2 atmosphere and measured after different step potentials during a complete cycle.

Figure 9. Time dependence of the charge extracted as a function of the number of voltammetry cycles (+2V to -1.8 V) measured at a scan rate of 50 mV/s. The coatings have been heat treated for 2h in O₂ atmosphere at (♦) 560 °C (crystalline), (■) 500 °C (amorphous) and (✱) 400 °C (amorphous).



sensitizer cations by electronic transfer. In such device, the TiO₂ coating has therefore two functions and act as a support for the sensitizing molecules and for the electronic charge transport.

Several other oxides present semiconducting properties including BaTiO₃, WO₃, Nb₂O₅, SrTiO₂, KTaO₃, Ta₂O₅, etc. Nb₂O₅ can be obtained in form of small colloidal particles. The material has a band gap slightly larger than TiO₂, and the flat band potential vs SHE is 0V [15], slightly smaller than TiO₂ (0.2V).

The fabrication of 250 nm thick Nb₂O₅ coating and the electrochemical test have been realized as described in section 2.1. However UV light from a 100 W Xe lamp was coupled to a Bausch and Lomb UV-Visible high intensity monochromator and focussed on the sample through a quartz window adapted on the side of the electrochemical cell. Preliminary measurements [16] show that niobate coatings present a photoelectric effect whose wavelength maximum lays at slightly smaller values than TiO₂ particles. Figure 14 shows a comparison of the absolute action spectrum of two films of both materials measured in a cell using an aqueous solution of 0.2N LiClO₄ as electrolyte at 1V vs SCE potential. The peak maximum of Nb₂O₅ lies at slightly higher energy than TiO₂, as this material has a wider energy gap. For those experimental conditions of coating preparation, which have not yet been optimized for this application, the current intensity of the niobata appears smaller than TiO₂. These new coatings may be of interest to substitute TiO₂ coatings for the realization of nanocrystalline solar cell similar to those developed by Graetzel et al [14]. Research is under way in our laboratory.

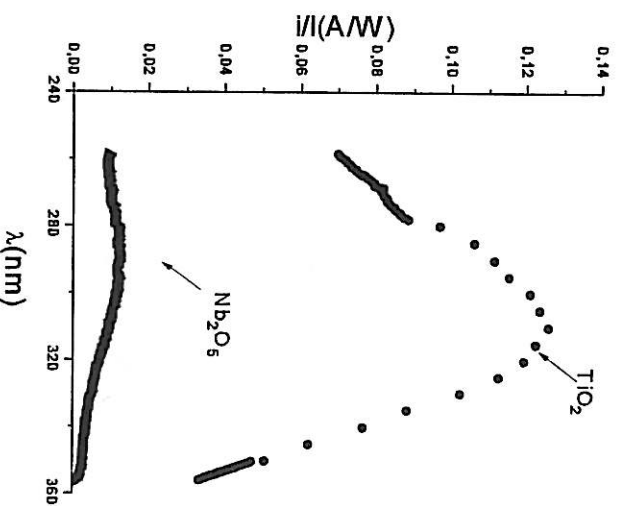


Figure 10. Absolute electric response of Nb₂O₅ and TiO₂ coatings heat treated at 560 °C during 2h, as a function of the wavelength of optical irradiation

4. CONCLUSION

We have shown that it is possible to prepare Nb_2O_5 material by a sol-gel process either in the form of coating with excellent optical and electrochromic properties, xerogel or aerogel. The coatings heat treated at 560 °C in O_2 atmosphere present interesting electrochromic properties and turn blue under Li^+ ions insertion. The process is reversible for scan rate higher than 10 mV/s. Therefore these new coatings are very promising to substitute WO_3 coatings for the realization of smart windows and mirrors. Small colloidal particles can also be obtained and preliminary measurements show that this material presents a photoelectric effect when illuminating in the UV region similar to TiO_2 particles. This material is consequently promising to be used for photoelectrochemical applications such as the realization of nanocrystalline solar cells.

This research was financially supported by grants of FAPESP, CNPq, FINEP and CBMM (Brazil).

4. REFERENCES

1. Sakka, S.; Yoko, T., *Chemistry, Spectroscopy and Applications of Sol-Gel Glasses*, Reisfeld, R., Jorgensen, C. K., ed., Springer-Verlag, Berlin, p. 89-118, 1992
2. Agrawal, M.; Cronin, J.P.; Zhang, R., *SPIE Sol Gel Optics II*, San Diego, v. 1758, p. 330, 1992
3. Lyman, N.R.; Moser, F. H.; Hichwa, B.P., *SPIE Optical Materials Technology for Energy Efficiency Solar Energy Conversion II*, v. 823, p. 130-7, 1987
4. Reichman, B.; Bard, A. J., *J. Electrochem. Soc.*, v. 127, p. 241-2, 1979.
5. Gomes, M. A. B.; Bulhões, L. O. S.; Castro, S. C.; Danião, A. J., *J. Electrochem. Soc.*, v. 137 (10), . 3067-70, 1990.
6. Alves, M. do C., *MSc Thesis*, Federal University of São Carlos (Brazil), 1989.
7. Lee, R. G.; Craston, J. A., *J. Mater. Chem.*, v. 1, p. 381-6, 1991.
8. Bradley, D. C.; Chakravarti, B. N.; Wardlaw, W., *J. Am. Chem. Soc.*, v. 7, p. 2381-4, 1956.
9. Avallaneda, C.O.; Macedo, M. A.; Aegerter, M. A., *Proceedings 38th. Congresso Brasileiro de Cerâmica*, Blumenau, SC, Brazil, 18-21/06/94.
10. Avallaneda, C.O.; Macedo, M. A.; Florentino A.O.; Aegerter, M. A., *SPIE Optical Materials Technology for Energy Efficiency and Solar Energy Conversion XIII*, accepted 1994
11. Macedo, M. A.; Dall'Antonia, L. H.; Aegerter, M. A., *SPIE Sol-Gel Optics II*, v. 1758, p. 320-9, 1992.
12. Ko, E. I.; Weismann, J. G., *Catalysis Today*, v. 8, p. 27-36, 1990.
13. Weismann, J. G.; Ko, E. I.; Wynthatt, P.; Howe, J. M., *J. Chem. Mat.*, v. 1, p. 187, 1989.
14. Graetzel, M., *MRS Bulletin XVII*, v. 10, p. 61, 1993.
15. Kung, H. H.; Jarret, H. S.; Sleight, A. W.; Ferretti, A., *J. Appl. Phys.*, v. 48, p. 2463, 1977.
16. Barros Filho, D. A.; Florentino, A.; Aegerter, M. A., *Proceedings of 38th. Congresso Brasileiro de Cerâmica*, Blumenau, SC, Brazil, 18-21/06/94.