Materials Research, Vol. 5, No. 1, 43-46, 2002.

Electrochromic Properties of Sol-gel Coating of Nb_2O_5 and $Nb_2O_5:Li^+$

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Received: November 13, 2000; Revised: December 29, 2001

Thin solid films of Nb_2O_5 and $Nb_2O_5:Li^+$ were prepared by the sol-gel process using the sonocatalytic method. The films reported here were prepared from a $NbCl_5$ as precursor and butanol as solvent. Through the addition of lithium salt $LiCF_3SO_3$ to the precursor solution, films with different electrochemical performance were obtained. The electrochemical and optical responses of the films were determined from the cyclic voltammetry and chronoamperometry measurements using a 0.1 M $LiClO_4$/PC as electrolyte. The electrochromic properties of the films were investigated using *in situ* spectroelectrochemical method. They exhibit a gray coloration under Li^+ insertion with a reversible variation of the transmittance in the visible and near infrared range between 20% and 80%.

Keywords: *electrochromism, Nb_2O_5, sol-gel*

1. Introduction

In recent years, there has been considerable interest in the good use of solar energy. The development of new technologies in this area has increased over the past years. Such energy is very much applied and one of its utilizations is in electrochromic devices (windows, displays, sunglasses, mirrors). A large class of optically active materials has drawn scientific interest, especially the ones with transmission, absorption and reflectance control. These materials are known as chromogenous as their color change when an external field is applied. Some studies have reported the electrochromic properties of many materials such as TiO_2, WO_3, V_2O_5, Nb_2O_5 etc. The electrochromic properties of these materials are related with the insertion of small ions like Li^+ or H^+ in their structures[1-3].

Pure and doped niobium(V) oxides (Nb_2O_5) are promising cathodic electrochromic materials. Their electro-optical performance depends strongly upon their structural morphology. They can be obtained as films by sol-gel process. This well-know process is a good method to achieve such morphology and combined with dip-coating technique is possible to deposit a large area coating at a low cost as well as to control the microstructure of the films.

Since Richman and Bard's[4] observation on coloring effect in Nb_2O_5 under H^+ or Li^+ insertion, several studies of electrochromic behavior of these materials have been reported. Gomes *et al.*[5] found an opaque blue coloration in Nb_2O_5 grew thermally at ~500 °C on a niobium metallic disk. Alves *et al.*[6] has confirmed the possibility of inserting Li^+ ions into an Nb_2O_5 ceramic prepared from a commercial powder sintered at 800 °C. The first attempt to produce sol-gel films of Nb_2O_5 for electrochromic purpose has been reported by Lee and Crayston[7] using a sol made from a mixture of $NbCl_5$ dissolved in ethanol. Using a sol prepared with niobium pentachloride via Na process, homogenous films without cracks have been obtained, showing good electrochromic properties[8-10]. Faria *et al.*[11] prepared Nb-oxide films from an $NH_4H_2[NbO_4C_2O_4)_3]3H_2O$ precursor dissolved in a solution of citric acid and ethylene glicol. Also Nb_2O_5 films were prepared by the sonocatalytic method[12]. In order to improve the bleaching process, Macek *et al.*[15] have prepared films of Nb_2O_5 doped with lithium salt ($LiCF_3SO_3$) according to Barros Filho *et al.*[16] procedure. These sols were obtained by the solubilization of $NbCl_5$ in propanol for 24 h, and the addition of glacial acetic acid and $LiCF_3SO_3$. These sols resulted in Li/Nb molar ratio of 0.1 and 0.2.

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Trabalho apresentado no 14° CBECIMAT, Águas de São Pedro, Dezembro de 2000.

This paper deals with a study of electrochemical and optical properties of 3 layer coatings of Nb_2O_5 doped with $LiCF_3SO_3$ films utilizing the sonocatalytic sol-gel route and dip coating deposition technique. The sonocatalytic sol-gel route is fast and easy to prepare niobium sol. The films demonstrated excellent bleaching kinetics and gray coloration during the insertion of Li^+. These very good optical quality films can be used probably in architecture applications where the minimum coloration is necessary.

2. Experimental

2.1. Preparation of the sol

The starting solution to produce Nb_2O_5 films was prepared by dissolving $NbCl_5$ powder (1.3 g, 0.005 mol) in butanol (15 mL, 0.16 mol), acetic acid (3 mL, 0.05 mol) and $LiCF_3SO_3$ salt, (10 %mol). The solution mixture was submitted for ~5 min to the action of a 95 W, 20 kHz ultrasonic irradiation from a sonicator resulting in a transparent and viscous solution.

2.2. Preparation of the films

The coatings were deposited by dip-coating method on ITO coated glass substrates (Asahi Glass 14 Ω/□) previously cleaned and rinsed with bidestilled water, ethanol and then dried at room temperature. The ITO glasses were immersed into the solution in ambient atmosphere (RH 60%) and withdrew at rate of 10 cm/min, dried at room temperature for 5 min and then sintered at 450 °C during 5 min. The process was repeated to obtain 3 layer films. The final heat treatment was performed at 560 °C in air atmosphere for 15 min. The resulting coatings were transparent and homogeneous without any visual cracking.

2.3. Measurement technique

Cyclic voltammetry measurements were performed with AUTOLAB 30 equipment and General Purpose Electrochemical System (GPES) for Windows - version 4.7 and the chronoamperometry experiments were performed with an EG&G PAR 273 computer-controlled potentiostat/galvanostat controlled by 270 Electrochemical Analysis software. A conventional three-electrode cell was used, a platinum foil of 1 cm^2 was the counter-electrode and a silver wire was the quasi-reference electrode. The electrolyte was 0.1 M solution of $LiClO_4$ dissolved in propylene carbonate (PC) and the cell was previously purged with dry N_2 gas. The UV-Vis spectra of the films were recorded in situ with a 5G model Varian spectrophotometer and the coated substrate was placed in a special electrochemical cell with two flat quartz windows.

3. Results and Discussion

The cyclic voltammograms for Nb_2O_5 doped and undoped films are depicted in Fig. 1, by sweeping the potential the range of -1.8V to +2.0V. It can be observed that, close to -1.0 V, there is an increase in the cathodic current associated with Nb_2O_5 reduction with simultaneous Li^+ cation insertions. During this process it is observed a change in the optical properties of the films, from transparent to gray color. After changing the potential sweep direction, the lithium deintercalation close to -1.5 V started, followed by a peak at E =-1.2 V. Both films showed the same voltammetric shape, but the Li doped film reached higher current values when compared with non-doped films. The same tendency was observed for the charge densities as a function of time measurements during a potential step at intervals of 30 s between -1.8 V (colored state) and +2.0 V (bleaching state) (Fig. 2). The film doped with lithium showed a better electrochromic performance (42 mC/cm^2) than the undoped one, where the charge density was 29 mC/cm^2.

The transmittance variation as a function of time at λ = 550 nm during a potential step at intervals of 30 s between -1.8 V (colored state) and +2.0 V (bleaching state) is showed in Fig. 3. Doped films exhibited intensive coloring/bleaching changes (T_b - T_c = 59%) where T_b and T_c are transmittances (in %) of bleached and colored films, respectively while undoped film showed T_b - T_c = 33%. In addition doped films exhibited higher reversibility in the coloring/bleaching process when compared with undoped films. They showed an excellent performance where their original transmitting value was restored (approximately 77%). The two curves show that the charge insertions were 30 s, but the lithiated film showed only 20 s for extraction.

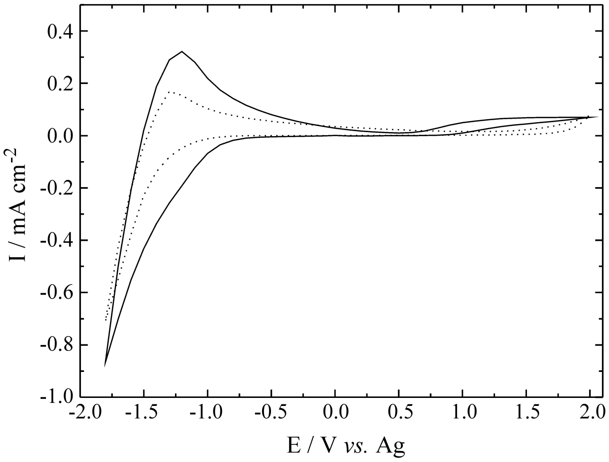

Figure 1. Cyclic voltammogram of niobium oxide films undoped (···) and doped 10 %mol of lithium (-), both with 3 layer coatings deposited on ITO coated glass, thermal treatment at 560 °C in air atmosphere, electrolyte 0.1M $LiClO_4$/PC, scan rate of 50 mV/s.

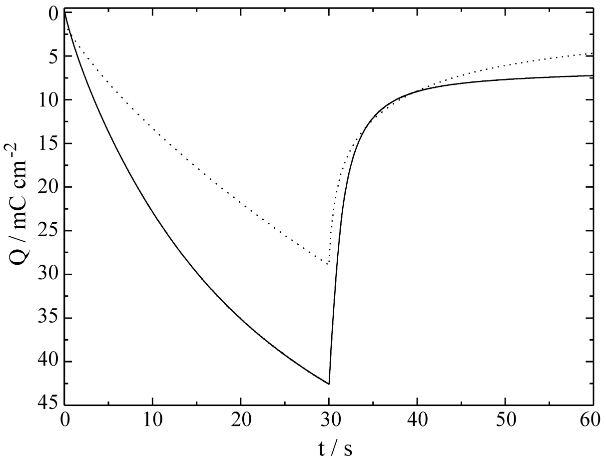

Figure 2. Charge density of the niobium oxide film undoped (···) and doped 10 %mol of lithium (-), interval step of -1.8 V and +2.0 V for 30 s.

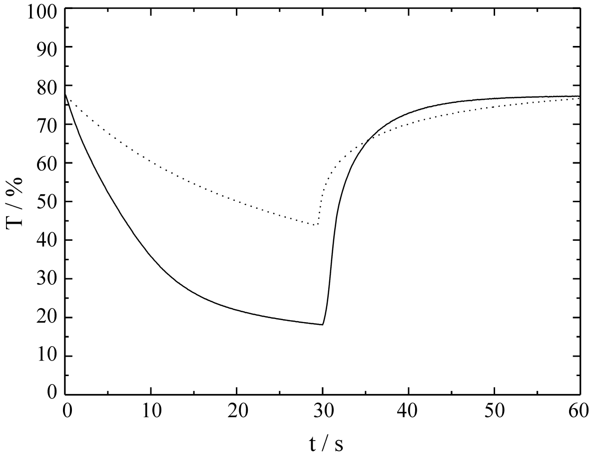

Figure 3. The variation of transmittance at λ = 550 nm as a function of time during a potentiostatic step between -1.8 V and +2 for 30 s, undoped (···) and doped 10%mol of lithium (-).

This fact can explain the influence of Li^+ present in the structure of the film. This was assumed to be due to the increased ionic conductivity of films originated from the presence of lithium[14]. It probably facilitates the exit of the charges inserted when an anodic potential is applied.

The color changes for doped and undoped Nb_2O_5 films were performed by *in situ* visible measurements from 350 nm to 800 nm (Fig. 4). The results show that the films exhibit a different spectral transmission, where the lithiathed film exhibits much higher transmission difference values between colored and bleached states. For the doped films it was observed a transmission of 18% for colored and 72% for the bleaching state and for undoped film, 40% for colored and 75% for bleaching state.

The importance of using doped films with Li^+ is the improvement of the bleaching kinetics, which helps their electrochromic properties[15].

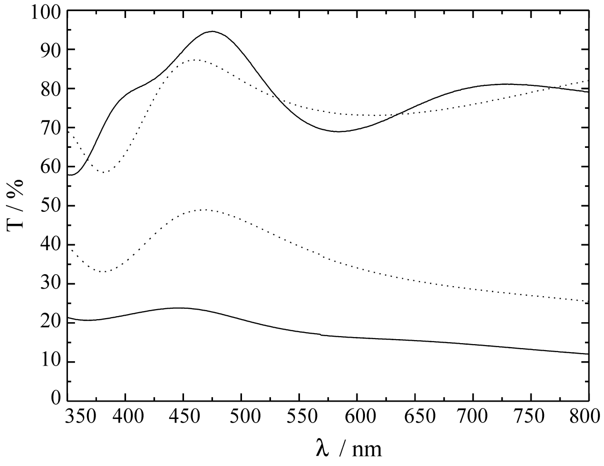

Figure 4. *In situ* UV-Vis spectra observed during electrochromic switching in the bleached (+2.0 V) and colored states (-1.8 V) of niobium oxide films, undoped (···) and doped 10 %mol of lithium (-).

The analysis of the optical density variation and transmittance versus density charge for Nb_2O_5 films unlithiathed and lithiathed is shown in Figs. 5 and 6. It can be observed that, for all cases, the films were transparent with an initial transmission about of about 80%. As the charge was inserted, there was an initial linear increase in ΔOD, followed by saturation. The initial linear increase is to be expected from the Beer-Lambert law, and the slope of this gives the electrochromic efficiency (η) of 9.5 cm^2/C and 19 cm^2/C for undoped and doped films respectively.

4. Conclusions

A sonocatalytic method was used for the preparation of stable, cheap and easy to prepare niobium oxide sol. Sol-gel doped Nb_2O_5 films have shown better electrochromic properties evidenced by a larger transmittance difference between colored and bleached states than undoped films. The difference between both states was about 59% for doped

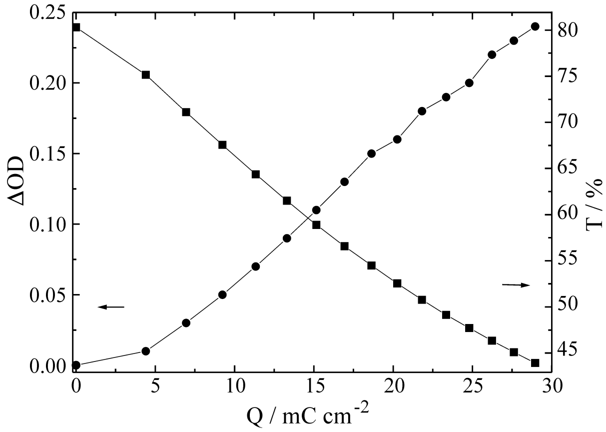

Figure 5. Optical density (●) and transmittance (■) v*s.* charge density for the films of Nb_2O_5 film unlithiathed.

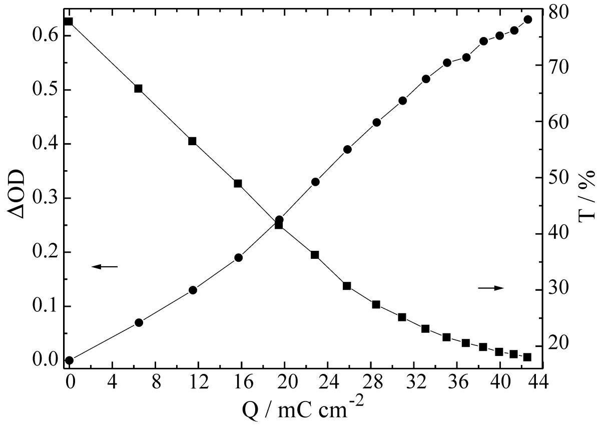

Figure 6. Optical density (●) and transmittance (■) *vs.* charge density for the films of Nb_2O_5 film lithiathed.

films and 33% for undoped one. It probably occurs because Li^+ in its structure improves the bleaching kinetics. Both films showed high charge density inserted, but the doped ones showed best coloration and reversibility behavior reaching the bleaching state faster than undoped films. The maximum charge density inserted into a tree-layer coating was 42 mC/cm^2. The sonocatalytic route is easy and cheap and the preparation of the sols is quick, giving promising results.

Acknowledgment

The authors would like to acknowledge the financial support given by FAPESP.

References

1. Granqvist C.G. *Handbook of Inorganic Electrochromic Materials*, Elsevier, Amsterdam, 1995.
2. Monk, P.M.S.; Mortimer, R.J.; Rosseinsky, D.R. *Electrochromism Fundamental and Applications*, VCH Weinhein, 1995
3. Aegerter, M.A. *Sol-Gel Chromogenic Materials and Devices*, Structure and Bonding, v. 85, p. 149-194, Springer, Berlin Heildelberg, 1996
4. Reichman, B.; Bard, A.J. *J. Eletrochem. Soc.*, v. 127, n. 1, p. 241-242, 1980.
5. Gomes, M.A.B.; Bulhões, L.O.S.; Castro, S.C.; Damião, A.J. *J. Eletrochem. Soc.*, v. 137, n. 10, p. 3067-3070, 1990.
6. Alves, M.C. *Msc. Thesis,* Federal University of São Carlos, São Carlos, Brazil, 1989.
7. Lee, G.R.; Crayston, J.A. *J. Mater. Chem.,* v. 1, n. 3, p. 381-386, 1991.
8. Avellaneda C.O.; Aegerter M.A; Pawlicka A. *Química Nova*, v. 21, n. 3, p. 365-367, 1998.
9. Avellaneda C.O.; Pawlicka A.: Aegerter M.A. *J. Mater. Sci.*, v. 33, n. 8, p. 2181-2185, 1998.
10. Aegerter M.A.; Avellaneda C.O.; Pawlicka A.; Atik M. *J. Sol-Gel Sci. Techn.*, v. 8, n. 1-3, p. 689-696, 1997.
11. Faria R.C.; Bulhões L.O.S. *J. Electrochem. Soc*, v. 141, n. 3, p L29-L30, 1994.
12. Pawlicka A.; Atik, M.; Aegerter, M.A. *Thin Solid Films*, v. 301, n. 1-2, p. 236-241, 1997.
13. Ohtani B.; Iwai, K.; Nishimoto, S.; Inui, T. *J. Electrochem. Soc.*, v. 141, n. 9, p. 2439-2442, 1994.
14. Ozer, N.; Chen, D.G.; Lampert, C.M. *Thin Solid Films*, v. 277, n. 1-2, p. 162-168, 1996.
15. Macek, M.; Orel, B.; Krasovec, U.O. *J. Electrochem. Soc.*, v. 144, n. 9, p. 3002-3010, 1997.
16. Barros Filho, D.A.; Abreu Filho, P.P.; Werner, U.; Aegerter, M.A. *J. Sol-Gel Sci. Technol.*, v. 8, n. 1-3, p. 735-742, 1997.

FAPESP helped in meeting the publication costs of this article