Synthesis of multicolor Nb_2O_5 coatings for electrochromic devices

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Abstract

Thin films of Nb_2O_5 were obtained by a sonocatalytic sol-gel method using chloroalkoxides as precursors. They were deposited using the dip-coating technique and calcined at different temperatures. Precipitates were characterized by X-ray diffraction, DSC, FTIR and the films by SEM. The films of Nb_2O_5 present a good electrochemical response under Li ions insertion. Depending on the treatment temperature, the films change their color from transparent to brown or blue. The efficiency of coloring was estimated to be 22 $cm^2 C^{-1}$ at 600 nm for a 300 nm thick film with a change in optical transmission from 80% to 15%. The cathodic and anodic charges exchanged at a velocity of 50 $mV s^{-1}$ were about 15 $mC cm^{-2}$ and the process is fully reversible. The values measured up to 100 cycles are constant, indicating good chemical stability of the films.

Keywords: Ceramics; Electrochemistry; Niobium oxide

1. Introduction

The electro-optical performance of an electrochromic coating is strongly dependent on its structural morphology. Outstanding performances have recently been reported using materials constituted of aggregates of CeO_2–TiO_2 [1–6] and TiO_2 [7] nanosized particles. The sol-gel process is a particularly well adapted method to achieve such morphology. Moreover, the dip coating technique, a common method of film deposition in this field, allows to deposit large area coatings at a low cost and offers advantages in controlling the microstructure of the film, an asset for eventual technological application.

Very few studies have been reported on the electrochromic properties of Nb_2O_5. Reichman and Bard [8] and Gomes et al. [9] found a blue coloration in opaque Nb_2O_5 grown thermally at ~ 500 °C on a niobium metallic disk. Alves [10] has confirmed the possibility to insert 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 has been reported by Lee and Crayston [11]; they used 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 considerable shrinkage during drying. More recently, using a sol of $Nb(OBu_n)_5$ prepared by synthesis of niobium pentachloride with sodium butoxide under reflux (Na process), we have obtained homogeneous films without cracks and defects presenting good and promising electrochromic properties [12,13]. Also, Ohtani et al. [14] have reported the preparation of Nb_2O_5 films exhibiting good electrochromic properties by using a sol prepared from Nb ethoxide. Nb_2O_5 coatings appear therefore to be promising candidates for use in various solid state electrochemical devices such as photovoltaic solar cells [15] and electrochromic devices [1,2]. One fundamental characteristic of this oxide film is its rapid and reversible coloration when small ions such as H^+ and Li^+ are inserted in the layer lattice which typically change its optical transmission from a quasi-transparent state ($T \cong 85\%$) to less than $T \cong 20\%$ in a large optical range from the near UV to near IR, exhibiting either a blue color when the coating is crystallized, or a brown one when it is amorphous. Such coatings appear therefore as interesting substitutes for the well known and efficient WO_3 coatings.

In this work we report on a preparation of Nb_2O_5 films

dip coated on ITO-coated glass from a sol which is simpler to prepare [16]. Precipitates of Nb_2O_5 have been densified at different temperatures and characterized by X-ray diffraction, differential thermal analysis (DSC) and infrared spectroscopy (FTIR), and the coatings by scanning electron microscopy (SEM), optical and electrochemical techniques.

2. Experiments

The preparation of a transparent and stable niobium solution was obtained using a sonocatalytic process [17–19]. The starting solution to produce Nb_2O_5 films was prepared by dissolving $NbCl_5$ powder (CBMM, Brazil) (1.3 g, 0.005 mol) in butanol (15 ml, 0.16 mol) and acetic acid (3 ml, 0.05 mol) in a small (30 ml) Becker recipient. The solution mixture was submitted for a few minutes ($\sim$ 5 min) to the action of 95 W ultrasonic irradiation from a Sonicator® W385 Heat System-Ultrasonic, Inc. at 20 kHz equipped with a 1/2" Disruptor Horn, resulting in a transparent and viscous solution. This solution was stable for several months at room temperature when kept in a closed glass recipient. It is true that the sonocatalytic process accelerates the chemical reaction of niobium pentachlorate with butanol, resulting in a solution where the main precursors are probably chloroalkoxides of the type $NbCl_{5-x}(OBu)_x$ [20] according to the equation

$$NbCl_5 + BuOH \rightarrow NbCl_{5-x}(OBu)_x + x\,HCl \qquad (1)$$

The coatings were deposited by dipping ITO coated glass substrates (Asahi-Glass, 14Ω/□) previously cleaned and rinsed with bidistilled water, ethanol and then dried at room temperature, into the solution in ambient atmosphere (RH < 60%) and withdrawing it at a rate of 12 cm/min. The samples were subsequently dried in air at room temperature for 15 minutes. The uniform gel films were then calcined in air at different temperatures from 400 to as high as 600 °C using a heating rate of 10 °C min^{-1} and kept at the final temperature for 10 min. The resulting coatings with a thickness of about 100 nm for one dip were transparent and homogeneous without any visual cracking.

X-ray diffraction measurements have been performed on precipitate obtained from the same sols with a Rigaku model RU200B instrument with Kα Cu radiation.

Differential Scanning Calorimetry (DSC) and Differential Thermal Analysis (DTA) were performed with a General V4.1C DuPont 2000 instrument and Thermal Gravimetry (TG) with a Netzsch STA 409. All analyses were executed in an air atmosphere at a heating rate of 10 °C min^{-1}.

The FTIR spectra were obtained using a FTIR Bomem MB-102 operating between 300 and 4000 cm^{-1} and SEM analysis was performed with a Zeiss 960 microscope coupled to an Electronic X-Ray Diffraction (EDX) Link QX2000 with a resolution of 148 eV.

The electrochemical measurements were realized using a Solartron 1286 analyzer 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 propylene carbonate (PC). The cell was previously purged with dry N_2 gas.

The thickness of the films was measured with a Taylor–Hobson Talystep and the optical spectra in the UV–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 UV–Vis spectra were measured before and after insertion of Li^+ cations at fixed potentials.

3. Results and discussion

Fig. 1 shows X-ray diffraction patterns of precipitates obtained with the same sol used for the coatings and heat treated at different temperatures between 400 and 600 °C during 10 min following the same densification protocol. The heat treatment of the samples changes the precipitate structure from amorphous to crystalline. The onset of the crystallization appears at a temperature slightly higher than 400 °C and the intensity of the peaks increase with temperature. The positions of the peaks are compatible with the crystalline phases corresponding to the T or TT structure (low or very-low-temperature form) of Nb_2O_5 as determined by Ko and Weissman [21]. A pseudohexagonal phase with similar d values can also be proposed [22]. The mean interplanar distances obtained from Rigaku RU200B equipment are d = 0.392, 0.312, 0.244, 0.196, 0.180 and 0.166 nm, in good agreement with [21]. According to the authors [21] the TT structure is a less crystalline form of the structure T, stabilized by impurities with the formula $Nb_2(O,Y)_{5+n}$, were Y = OH, Cl, F, etc. and which starts

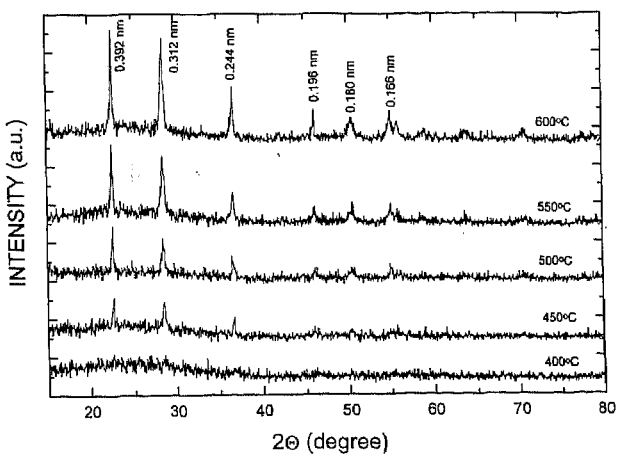

Fig. 1. X-ray diffraction of Nb_2O_5 precipitate heat treated from 400 to 600 °C in air during 10 min showing the TT structure.

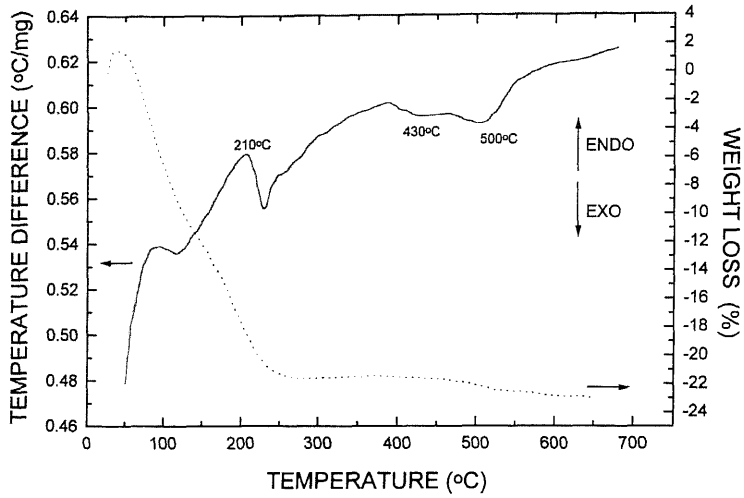

Fig. 2. DTA/TG of niobium precipitate (10 °C min^{-1}, air atmosphere).

to form above 400°C. Around 600 °C the phase TT transforms into the T structure.

The structural change of the niobium precipitates was also followed by DSC (not shown here), DTA and TG (Fig. 2). Endothermic peaks in the DTA curve accompanied by a large weight loss around 100 and 230 °C correspond essentially to water and organic residues elimination [23]. The broad features starting at 390 °C are probably due to the onset of the crystallization of the TT phase, confirming the X-ray diffraction results. The DTA peak and small weight loss (TG) starting at 460 °C correspond to the removal of HCl, CO_2 residues [23].

Infrared spectra were measured for three kinds of samples: solution, wet precipitate at 25 °C and precipitate of Nb_2O_5 heat treated at 600 °C (Fig. 3). The spectrum of niobium solution (curve (a)) shows a very large band at 3300 cm^{-1} corresponding to –OH vibration from butanol solvent. The bands located in the range 2860–2970 cm^{-1} correspond to the CH_3- and $-CH_2-$ stretching vibration of the alkyl groups of butoxy ligands, and those at 1380–1470 cm^{-1} to the deformation vibration of the same species. The bands at 1000–1100 cm^{-1} correspond to the $-COC_4H_9$ stretching vibration of different butoxy ligands bound to niobium atoms. The strong band at 800 cm^{-1} together with other diffused bands in the range from 600 to 950 cm^{-1} are attributed to the Nb–O stretching vibration [24,25]. They are more intense in the wet precipitate sample (curve (b)) and are predominant in the precipitate

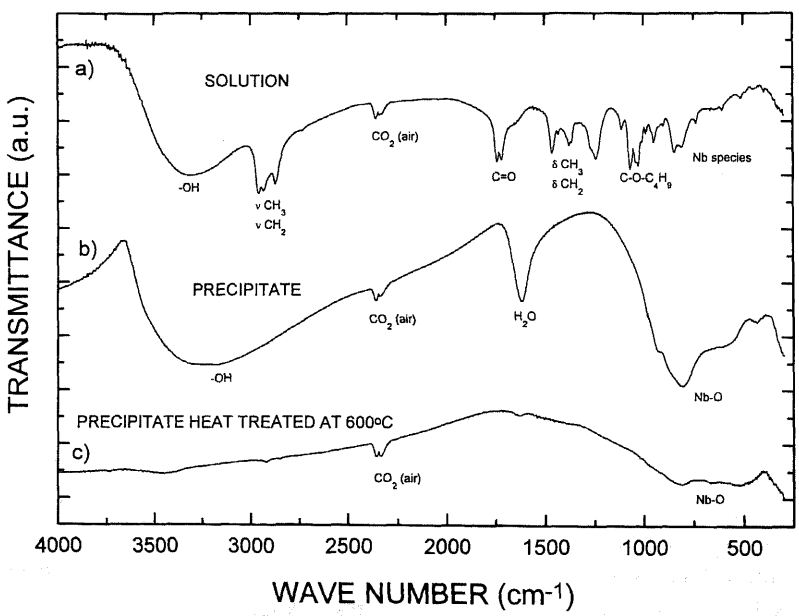

Fig. 3. Infrared spectra of: (a) niobium solution, (b) niobium precipitate at air and (c) Nb_2O_5 precipitate heat treated at 600 °C during 10 min.

sample (curve (c)). The difference of the intensity of these bands is due to the different quantity of the material used for the measurements. In the wet precipitate the very large band in the range 2500–3700 cm^{-1} is due to the –OH groups and at 1630 cm^{-1} to the H_2O vibration. In the precipitate heat treated at 600 °C only Nb–O inorganic bands have been identified in the region of low wave number. The small band at 2360 cm^{-1} that appears in all spectra is due to atmospheric CO_2 [24].

The scanning electron microscopy micrographs (Fig. 4(a)–(d)) show the surface morphology of Nb_2O_5 films heat treated at 400, 450, 500 and 600 °C during 10 min. The amorphous form of the niobium gel found at 450 °C is made of small particles. At 450 °C (Fig. 4(b)) the crystalline particles (~ 70 nm) are already well defined and their size remains constant up to 600 °C (Fig. 4(c)–(d)). All micrographs show that the structure of the film is very uniform. Additional EDX microscopy analysis detects essentially the existence of Nb.

The anodic and cathodic charge densities were measured from integration of cyclic voltammograms between −1.8 and +2 V at a rate of 50 $mV\,s^{-1}$ (Fig. 5), where the cathodic wave maximum corresponding to the insertion of Li ions is visible at −1.8 V and the anodic wave corresponding to the Li extraction occurs at −1 V. Fig. 6 shows the differences in Li charge densities inserted in one-, two- and three-layered films calcined at different temperatures. The exchanged charge increases with the thickness of the coatings and the change is more significant for temperatures above 500 °C. At 600 °C the charge

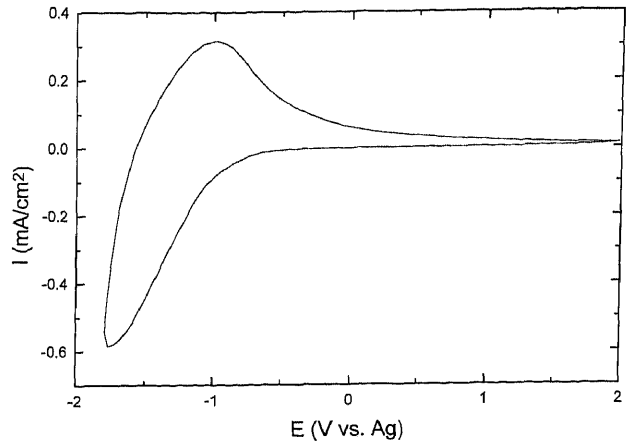

Fig. 5. Typical cyclic voltammetry of an Nb_2O_5 film (~ 100 nm thick) deposited on Asahi ITO coated-glass heat treated at 600 °C/10 min. Electrolyte (0.1 M) $LiClO_4$/PC, rate 50 $mV\,s^{-1}$.

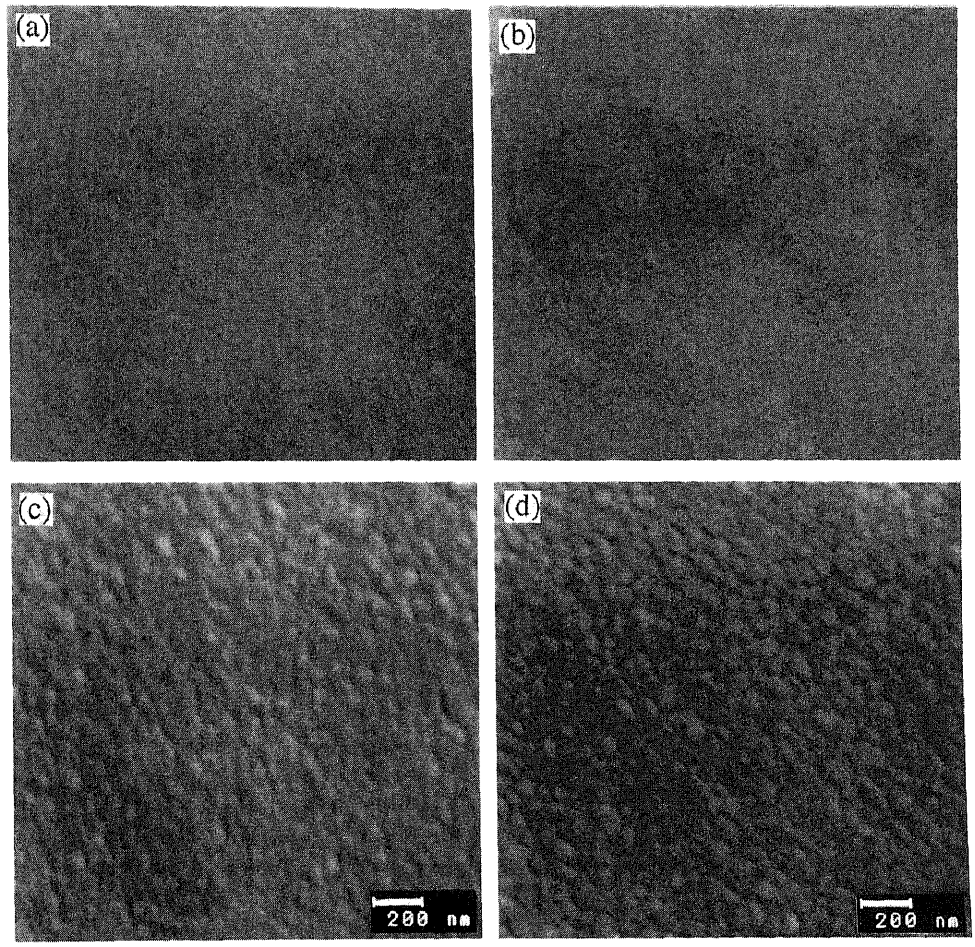

Fig. 4. SEM micrographs of Nb_2O_5 films heat treated at (a) 400 °C, (b) 450 °C, (c) 500 °C and (d) 600 °C.

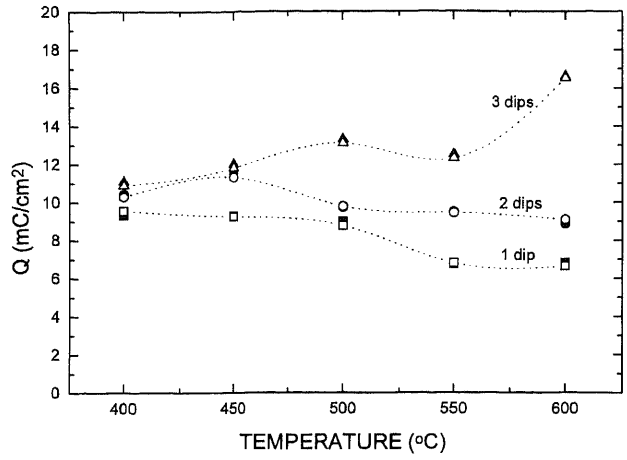

Fig. 6. Charge densities for one-, two- and three-layered films calcined at different temperatures calculated from integration of cyclic voltammograms for insertion and extraction process. The full symbols represent insertion and the other ones extraction process.

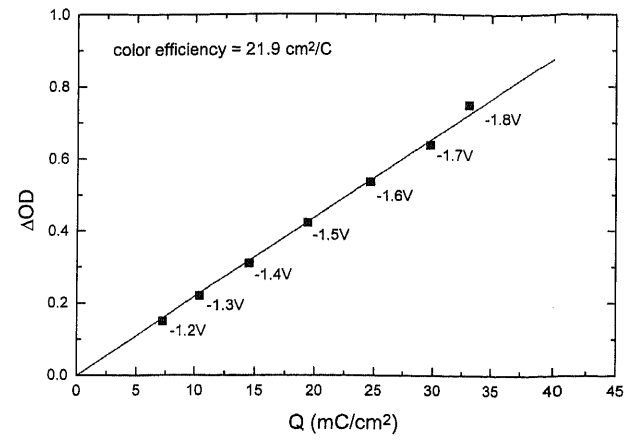

Fig. 8. Relationship between ΔOD, measured at $\lambda = 600$ nm, and inserted charge during the coloration process of a crystalline Nb_2O_5 300 nm thick film heat treated at 600 °C.

inserted and extracted increases from 7 $mC\,cm^{-2}$ for 1 layer (100 nm thick) to 16 $mC\,cm^{-2}$ for a three-layer coating (300 nm thick).

Fig. 7 shows the transmission spectra of Nb_2O_5 film deposited onto an ITO electrode in the reduced and oxidized state for a one dip layer 100 nm thick measured in situ at a fixed potential of +2.0 V (bleached state) and −1.8 V (colored state). The films were densified at 400 and 600 °C. All measurements have been performed up to 100 cycles and the insertion and extraction processes were found stable and fully reversible after the fourth cycle. The insertion of Li^+ changes the optical transmission from the near UV to the near infrared range. At the lowest densification temperature, 400 °C, the film is practically amorphous and the Li^+ insertion process changes the color of the film from transparent (slightly yellow) to brown. For

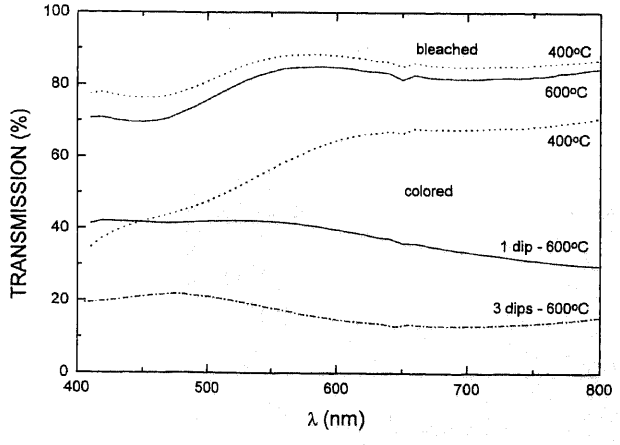

Fig. 7. UV–VIS spectral variation observed during electrochromic switching before and after polarization at −1.8 V of one-layered Nb_2O_5 films (~100 nm thick) calcined at 400 °C (---) and at 600 °C (————) and three-layered Nb_2O_5 film (~300 nm thick) calcined at 600 °C (– · –).

coatings calcined above 500 °C the film becomes dark blue after insertion at a potential of −1.8 V. The change in transmission is practically uniform in the whole spectral range, varying from about 80% to about 40% for a 100 nm thick Nb_2O_5 layer densified at 600 °C. The optical transmission of thicker films (300 nm) densified at 600 °C is less than 20%. The possibility of thin films of niobium oxide to change their color from transparent to brown or blue under the same applied potential can be very interesting for future application. Both morphologies show excellent electrochemical stability.

Fig. 8 shows the relationship between the variation of the optical density (ΔOD) measured at 600 nm and the charge inserted during the coloration process for a 300 nm thick Nb_2O_5 coating (three dips; heat treated at 550 °C). The linear relation at various cathodic potential shows that the electrochemical property of the Nb_2O_5 film can be attributed to a reversible electrochemical reaction. From the slope of the linear plot the coloring efficiency is equal to 22 $cm^2\,C^{-1}$ (at 600 nm). This value is larger than that reported by Lee et al. [11] for a Nb_2O_5 thin film prepared via a sol-gel process (6 $cm^2\,C^{-1}$) but comparable to the 38 $cm^2\,C^{-1}$ reported by Ohtani et al. [14], a value measured for a 10-layer film (thickness not reported) obtained with a sol prepared by partial hydrolysis of niobium (V) ethoxide [$Nb(OEt)_5$] with concentrated hydrochloric acid (HCl). However, the coloring efficiency is smaller than that of WO_3 film prepared by a sol-gel process (about 167 cm^2/C at 800 nm) [21].

The preparation of the sol by simply mixing $NbCl_5$ with ethanol without sonocatalysis, as reported by Lee and Crayston [11], does not allow to obtain homogeneous, crack free Nb_2O_5 films. The use of sonocatalysis for the preparation of chloroalkoxides based sols leads however to obtaining homogeneous Nb_2O_5 films that present excellent and reversible electrochromic properties similar to those obtained from pure alkoxide reported by Ohtani et al. [14]

or Nb-butoxide reported earlier by us [12,13]. However these routes are either time consuming when prepared in the laboratory or very expensive if bought on the market. The Nb chlorobutoxide precursor prepared under sonocatalysis is however easier and cheaper to prepare and allows to prepare sols which can be kept unaltered during several months, these parameters being of fundamental importance for eventual industrial development.

4. Conclusion

The sonocatalytic method was used for the preparation of stable, cheap and easy to prepare niobium oxide sol based on chlorobutoxide precursors. Sol-gel Nb_2O_5 films obtained from this sol present excellent electrochromic properties and are promising candidates for being used in devices using either protonic or lithium electrolytes. Nb_2O_5 coatings calcined in air at different temperatures from 400 to 600 °C change their structure from amorphous to crystalline with TT structure. The films present a reversible and fast insertion/extraction kinetics of Li^+ ions. The maximum charge density inserted into a 300 nm thick, three-layer coating was 15 $mC\,cm^{-2}$ and the efficiency of coloring was 22 $cm^2\,C^{-1}$ at 600 nm. After insertion the amorphous films present a brown color while the crystalline ones are dark blue and consequently their optical absorption spectra are different.

All these results are similar to those already obtained by us [8,9] and Ohtani et al. [14] using sol-gel Nb_2O_5 coatings made with sols prepared from classic Nb alkoxides routes without sonocatalytic irradiation. However, this new route is easier and cheaper and the preparation of the sols is quicker.

Acknowledgements

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