Electrochromic properties of Nb_2O_5 sol–gel coatings

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Abstract

Sol–gel niobium oxide coatings are promising electrochromic materials. The sols have been prepared by a sonocatalytic mixing of $NbCl_5$ powder, butanol and acetic acid. Thermal analysis (DTA/TG) coupled to mass spectrometry has been performed on Nb_2O_5 precipitates to quantitatively analyse the effluents. Transparent and defect-free single and multilayers coatings have been deposited on ITO-coated glass by a dip-coating process and then calcined between 400°C and 600°C. The coatings structure change from amorphous to crystalline (TT form) and the later ones are highly textured. The films present a reversible and fast insertion/extraction kinetics for Li^+ ions. After insertion the amorphous coatings present a grey-brown color, while the crystalline ones are dark blue. The maximum charge density exchanged with a three-layer 200 nm thick coating sintered at 600°C was 16 mC/cm^2 with a corresponding spectral transmission change practically wavelength-independent varying from 80% to 20%. The coloring efficiency determined at $\lambda = 600$ nm was 22 cm^2/C.

Keywords: Sol–Gel; Coatings; Nb_2O_5; Electrochromism

1. Introduction

The electro-optical performance of an electrochromic coating is strongly dependent on its structural morphology. Outstanding performances have been recently reported

using materials constituted of aggregates of CeO_2–TiO_2 [1–5] and TiO_2 [6] 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. Reichmann and Bard [7] and Gomes et al. [8] found a blue coloration in opaque Nb_2O_5 grown thermally at $\sim 500°C$ on niobium metallic disk. Alves [9] has confirmed the possibility to insert Li^+ ions in a Nb_2O_5 ceramic prepared from a commercial powder sintered at $\sim 800°C$. The first attempt to fabricate sol–gel Nb_2O_5 for electrochemical purpose has been reported by Lee and Crayston [10] 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 the drying process. More recently, using a sol prepared with niobium pentachloride via the Na process, we have obtained homogeneous films without cracks and defects presenting good and promising electrochromic properties [11, 12]. Also, Ohtani et al. [13] have reported the preparation of Nb_2O_5 films exhibiting good electrochromic properties by using sol prepared from Nb ethoxide. Nb_2O_5 coatings appear therefore promising candidates for their use in various solid-state electrochemical devices such as photovoltaic solar cells [4] and electrochromic devices [1]. 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. The optical transmission of the coating changes typically 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. It exhibits either a blue color when the coating is crystallized or a grey color when it is amorphous. Such coatings are therefore interesting substitutes for the well-known WO_3 coatings.

2. Experimental

A transparent and stable niobium solution was obtained using a sonocatalytic process described in Ref. [14]. 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) and acetic acid (3 ml, 0.05 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. This solution is stable for several months at room temperature when kept in a closed glass recipient. It is thought that the sonocatalytic process accelerates the chemical reaction of niobium pentachloride with butanol resulting in a solution where the main precursors are probably chloroalkoxides of the type $NbCl_{5-x}(OBu)_x$, according to the equation

$$NbCl_5 + xBuOH \rightarrow NbCl_{5-x}(OBu)_x + xHCl.$$
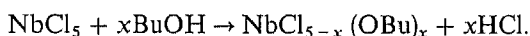
The coatings were deposited by dipping In_2O_3 : Sn (ITO) coated glass substrates (Asahi-Glass, $14\Omega_{\square}$), previously cleaned and rinsed with bidistilled water, ethanol and then dried at room temperature, into the solution in ambient atmosphere (RH < 60%) and withdrawing it at a rate of 12 cm/min. The samples were subsequently dried in air at room temperature for 15 min. The uniform gel films used for electrochemical measurements were then calcined in air or O_2 at different temperatures from 400°C to as high as 600°C using a heating rate of 10°C/min and kept at the final temperature for 10 min. The resulting coatings were transparent and homogeneous with a thickness of about 60 nm for 1 dip.

X-ray diffraction measurements have been performed at glancing incidence with a Siemens D 500 instrument with $CuK_{\alpha 1}$ radiation on multilayer coatings. After dip coating (RH $\cong$ 40%) each layer was directly heat-treated at 400°C during 20 min and then the whole system was directly heated to the final temperature.

Coupled differential thermal analysis and thermogravimetric analysis curves (DTA/TG) were obtained with Nb_2O_5-precipitate prepared with the same sol with a Bähr Thermoanalyse Typ STA 501 instrument coupled to a Thermolab 1165 Fisons instruments mass spectrometer.

The electrochemical measurements were realized using a Solartron 1286 analyzer and a conventional three-electrode cell placed in an dry-box under dry N_2. The counterelectrode 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 optical spectra in the ultraviolet-visible (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 three-layer Nb_2O_5 films heat-treated at final temperature of 450°C, 500°C and 550°C during 20 min. The heat treatment of the samples changes the structure from amorphous to crystalline. The onset of the crystallization appears at temperature slightly below 500°C. Niobium precipitate crystallizes in the "tief–tief" (TT) structure without texture [11]. However, the films were always found highly textured. For the example shown in Fig. 1 it is impossible to index precisely the diffraction line as at least three different Nb_2O_5 structures are compatible with its position (Powder diffraction standard (JCPDS) 28-317, 30-873, 27-1312). The crystallization process strongly depends on the substrate, the number of deposited layers and the duration of the heat treatment. For instance, no crystallization has been observed for one Nb_2O_5 layer 50 nm thick deposited on ITO up to 550°C, and a single layer deposited on borosilicate glass starts to crystallize with the same textured morphology shown in Fig. 1 also at temperatures slightly lower than 500°C.
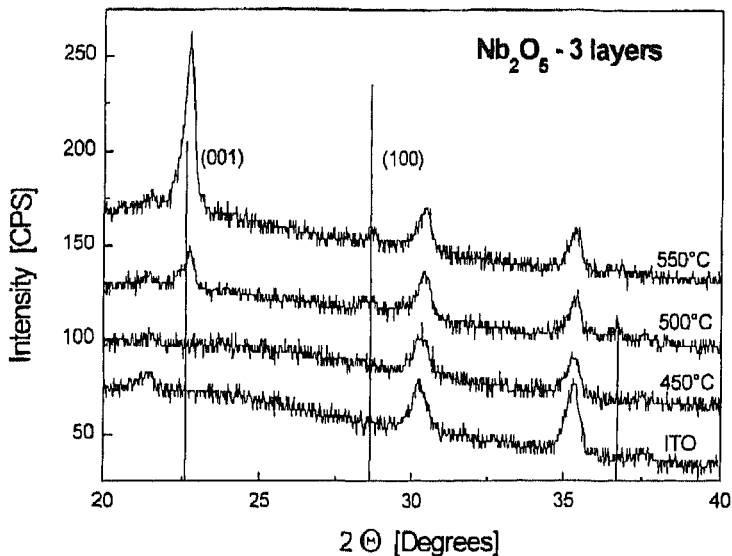
Fig. 1. Glancing angle X-ray spectra of three-layer Nb_2O_5 coating sintered in air at 450°C, 500°C and 550°C and ITO coating (for comparison). The vertical lines indicate the position of the three first main bands of Nb_2O_5 (JCPDS-ICDD 28-317).
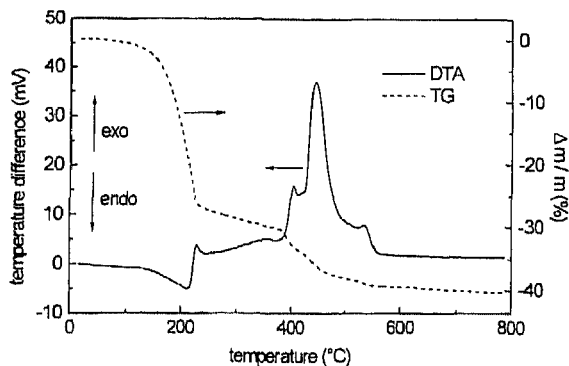

Fig. 2. DTA-TG curves of Nb_2O_5 precipitate at 80°C dried (rate 10°C/min in air).

Fig. 2 shows DTA-TG results of precipitate obtained from the same sol dried at 80°C in air. Two principal features occur at around 220°C and between 400°C and 530°C. These features have been also analysed by mass spectrometry (Fig. 3). The first one at ~ 220°C accompanied by a large weight loss and the slow weight loss between 230°C and 380°C correspond essentially to the removal of C_3H_7, C_4H_8, CH_2OH,
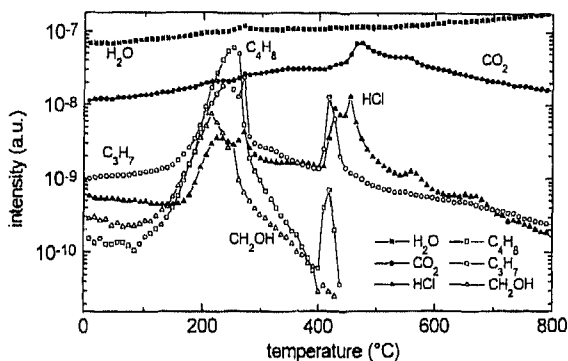
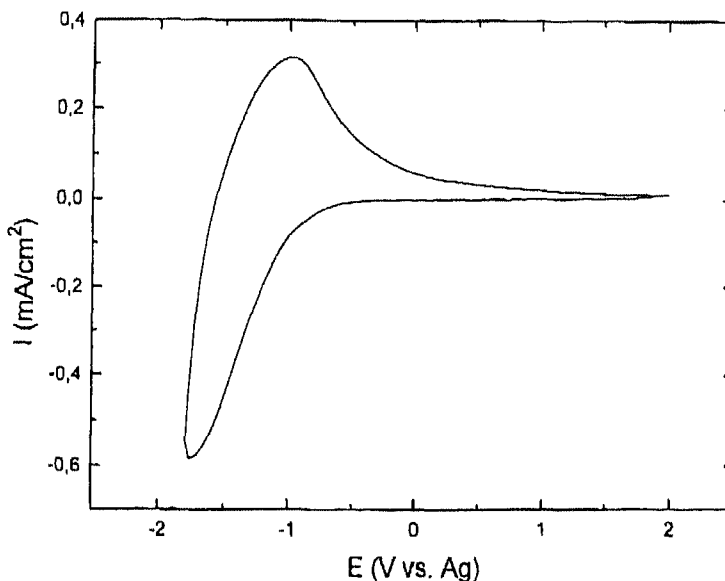Fig. 3. Mass spectrum of Nb_2O_5 precipitate dried at 80°C measured during DTA/TG measurements (rate 10°C/min in air).

Fig. 4. Typical voltammetry of a Nb_2O_5 film deposited on Asahi ITO coated glass, heat-treated at 600°C/20 min. Electrolyte 0.1 M $LiClO_4$/PC, rate 50 mV/s.

H_2O and HCl. The exothermic peaks obtained in the second feature are due to the removal of C_3H_7, C_4H_8, HCl (410°C) and HCl, CO_2 (450°C and 530°C).

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 (Fig. 4). 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. 5 shows the Li
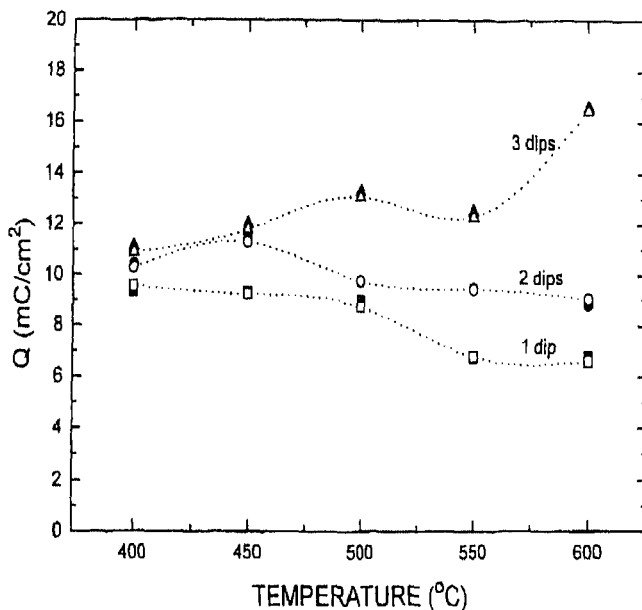
Fig. 5. Charge densities for 1, 2 and 3 layers films calcined at different temperatures calculated from integration of cyclic voltammogramms for Li^+ insertion (full symbols) and extraction (open symbols).

charge densities inserted in 1, 2 and 3 layered films calcined at different temperatures. The exchanged charge increases with the thickness of the coatings and varies from $7 mC/cm^2$ for 1 layer (60 nm thick) to $16 mC/cm^2$ for a 3 layers coating (200 nm thick).

Fig. 6 shows the transmission spectra of Nb_2O_5 film deposited onto ITO substrate in the reduced and oxidized state for a one dip layer 60 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°C 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^+ ions changes the transmissivity from the near UV up to the near-infrared range. At the lowest densification temperature, 400°C, the film is amorphous and the Li^+ insertion process changes the color of the film from transparent (slightly yellow) to grey. For 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 60 nm thick Nb_2O_5 layer densified at 600°C. The transmissivity of thicker films (120 nm), densified at 600°C, is less than 20%. The possibility of thin films of niobium oxide to change their color from transparent to grey or blue under the same applied potential can be very interesting for future application. Both systems show excellent electrochemical stability.

Fig. 7 shows the relationship between the variation of the optical density (ΔOD) measured at 600 nm and the charge inserted during the coloration process at various cathodic potential for a 200 nm thick Nb_2O_5 coating (3 dips; heat-treated at 600°C).
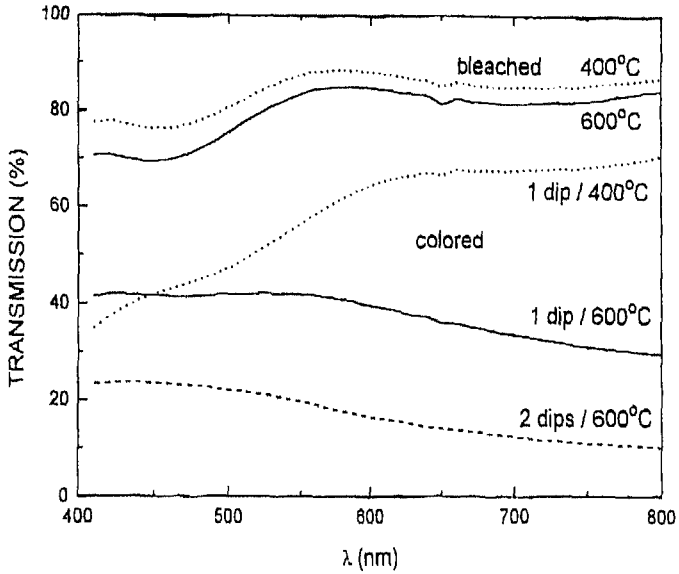
Fig. 6. UV-VIS spectra observed during electrochromic switching in the bleached (2.0 V) and colored state (− 1.8 V) of one layer Nb_2O_5 films ($\sim$ 60 nm thick) calcined at 400°C ($\cdots$), 600°C (—) and a 2 layers film calcined at 600°C (- - -).
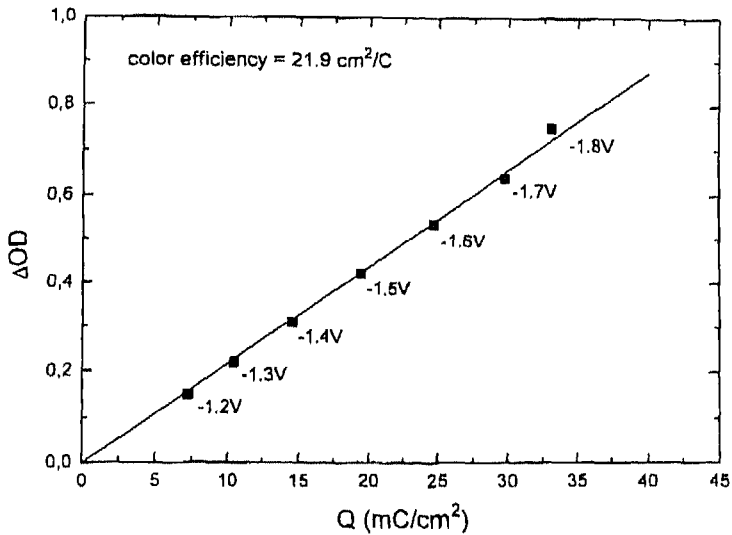

Fig. 7. Variation of the optical density ΔOD versus the Li^+ charge inserted during the coloration process at various cathodic potential for a 200 nm thick Nb_2O_5 film heat-treated at 600°C.

The linear relation shows that the electrochemical property of Nb_2O_5 can be attributed to a reversible electrochemical reaction. From the slope of the linear plot, the coloring efficiency is equal to $22 \, cm^2/C$ (at 600 nm). This value is larger than that reported by Lee et al. [10] for Nb_2O_5 thin film prepared via sol–gel process ($6 \, cm^2/C$) but comparable to the $38 \, cm^2/C$ reported by Ohtani et al. [13], determined for a 10 layers 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 sol–gel process (about $167 \, cm^2/C$ at 800 nm) [15].

The preparation of the sol by simply mixing $NbCl_5$ with ethanol without sonocatalysis as reported by Lee and Crayston [10], does not allow to obtain homogeneous crack-free Nb_2O_5 films. The use of sonocatalysis, for the preparation of chloralkoxides-based sols leads, however, to the obtention of homogeneous Nb_2O_5 films presenting excellent reversible electrochromic properties similar to those obtained by using pure alkoxide reported by Ohtani et al. [13] or Nb-butoxide reported earlier by us [11, 12]. However, these routes are either time-consuming when prepared in the laboratory or very expensive if the precursors are bought in 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 are of fundamental importance for eventual industrial development.

4. Conclusions

A 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 to be used in devices using either protonic or lithium electrolytes [16]. Nb_2O_5 coatings calcined in air at different temperatures from 400°C to 600°C change their structure from amorphous to crystalline with probably a TT structure. They are highly textured. The films present a reversible and fast insertion/extraction kinetics of Li^+ ions. The maximum charge density inserted into a three-layer 200 nm thick coating was $15 \, mC/cm^2$ and the efficiency of coloring was $22 \, cm^2/C$ at 600 nm. After insertion, the amorphous films present a grey color while the crystalline ones are dark blue. Consequently their optical absorption or transmission spectra are different.

These results are similar to those already obtained by us [11, 12] and Ohtani et al. [13] using sol–gel Nb_2O_5 coatings made with sols prepared from classic Nb alkoxide routes without sonocatalytic irradiation. However, this new route is easier and cheaper and the preparation of the sols is quicker.

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