

## Synthesis of Nb<sub>2</sub>O<sub>5</sub> thin films for electrochromic devices

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A large number of metal oxides such as TiO<sub>2</sub>, CeO<sub>2</sub>, WO<sub>3</sub>, V<sub>2</sub>O<sub>5</sub> and Nb<sub>2</sub>O<sub>5</sub> have been investigated for their use in various solid state electrochemical devices, including batteries, and electrodes for photoelectrochemical and electrochromic devices [1, 2]. One fundamental characteristic of these oxide films is their rapid and reversible coloration when small ions such as H<sup>+</sup> and Li<sup>+</sup> are inserted in the layer lattice, which typically changes their optical transmission from a quasi-transparent state ( $T \cong 85\%$ ) to less than  $T \cong 20\%$  in the ultraviolet (UV), visible or near infrared (IR) range.

The electro-optical performance of electrochromic coatings is strongly dependent on their structural morphology. Outstanding performance has been obtained recently using materials constituted of aggregates of nano-sized particles with CeO<sub>2</sub>-TiO<sub>2</sub> [3–6], TiO<sub>2</sub> [7] and Nb<sub>2</sub>O<sub>5</sub> [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 the deposit of large-area coatings at a low cost and offers advantages in controlling the microstructure of the film.

Very few studies have been reported on the electrochromic properties of Nb<sub>2</sub>O<sub>5</sub>. Reichman and Bard [10] and Gomes *et al.* [11] found a blue coloration in opaque Nb<sub>2</sub>O<sub>5</sub> grown thermally at ~500 °C on niobium metallic disk. Alves [12] has confirmed the possibility of inserting Li<sup>+</sup> ions in a Nb<sub>2</sub>O<sub>5</sub> ceramic prepared from a commercial powder sintered at ~800 °C. The first attempt to fabricate sol-gel Nb<sub>2</sub>O<sub>5</sub> for electrochemical purposes was reported by Lee and Crayston [13] using a sol made of a mixture of NbCl<sub>5</sub> dissolved in ethanol. However, the 5–10 μm thick film exhibited substantial cracking and peeling due to significant shrinkage during drying. More recently, using a sol prepared with niobium pentoxide, we have obtained homogeneous films without cracks and defects, which present good and promising electrochromic properties [8, 9].

In this letter we describe a novel and simpler synthesis of a sol-gel Nb<sub>2</sub>O<sub>5</sub> precursor and report on the electrochromic properties of Nb<sub>2</sub>O<sub>5</sub> coatings deposited by the dip-coating technique on ITO-coated glass.

The preparation of transparent and stable niobium solution was carried out using a sonocatalytic process [14–16], which gives coatings with good optical quality and interesting electrochromic properties. The starting solution to produce Nb<sub>2</sub>O<sub>5</sub> films was

prepared by dissolving NbCl<sub>5</sub> powder (0.2 M) in butanol (0.28 M) and acetic acid (0.05 M). The solution mixture was submitted for a few minutes of 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 are probably chloroalkoxides of the type NbCl<sub>5-x</sub>(OBU)<sub>x</sub> [17].

The coatings were deposited by dipping ITO-coated glass substrate (Asahi-Glass, 14 Ω □<sup>-1</sup>) previously cleaned and rinsed with doubly distilled water and ethanol and then dried at room temperature, into the solution in ambient atmosphere and withdrawing it at a rate of 12 cm min<sup>-1</sup>. The samples were subsequently dried in air at room temperature for 15 min. The uniform gel films were then calcined at temperatures as high as 600 °C using a heating rate of 10 °C min<sup>-1</sup>. The resulting coatings were then kept at the final temperature for 10 min, and were found to be transparent and homogeneous with a thickness of about 100 nm after one dip. The morphology of the films visualized by atomic force microscopy (AFM) consisted of agglomerations of small particles of 30–70 nm size.

X-ray diffraction (XRD) measurements were performed on xerogels obtained from the same sols using a Rigaku model RU200B instrument with CuK<sub>α</sub> radiation.

The electrochemical characteristics (voltammogram, chronoamperogram) were determined using a Solartron 1286 analyser and a conventional three-electrode cell placed in a dry-box under dry N<sub>2</sub>. The counterelectrode was a platinum foil of 1 cm<sup>2</sup> area and the quasi-reference electrode was a silver wire. The electrolyte was a 0.1 M solution of LiClO<sub>4</sub> dissolved in propylene carbonate (PC). The cell was previously purged with dry N<sub>2</sub> gas.

The thickness of the films was measured with a Taylor-Hobson Talystep and the optical spectra in the UV-visible 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-visible spectra were measured before and after insertion of Li<sup>+</sup> cations at fixed potentials.

XRD measurements of xerogels obtained with the same sol heat treated at 600 °C for 10 min following the same protocol indicated that the material was crystalline, with TT structure [18], with  $d = 0.0393$ , 0.0313, 0.0244, 0.0196, 0.0175 and 0.0159 nm (Fig. 1).

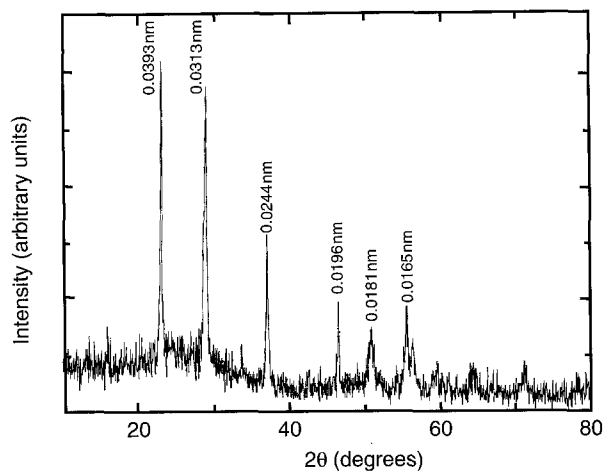


Figure 1 XRD pattern of  $\text{Nb}_2\text{O}_5$  xerogel heat treated at  $600^\circ\text{C}$  in air for 10 min. showing the TT structure.

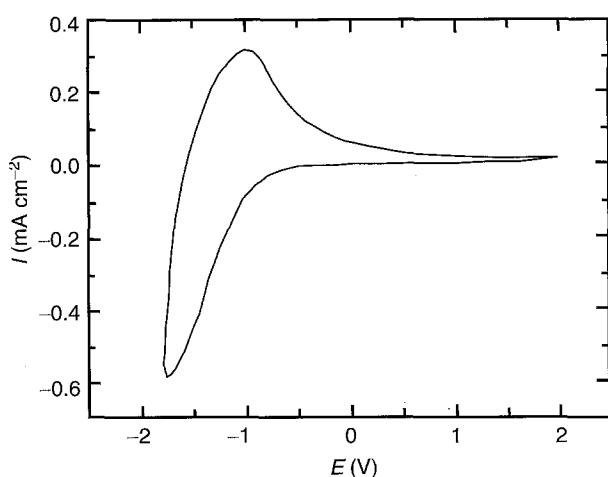


Figure 2 Typical cyclic voltammogram of a  $\text{Nb}_2\text{O}_5$  film deposited on Asahi ITO-coated glass heat treated at  $600^\circ\text{C}$  for 10 min. Electrolyte (0.1 M)  $\text{LiClO}_4/\text{PC}$ , rate  $50\text{ mV s}^{-1}$ .

Fig. 2 shows a typical cyclic voltammogram registered with a one-layer (100 nm thick)  $\text{Nb}_2\text{O}_5$  film heat treated at  $600^\circ\text{C}$  for 10 min. The cathodic peak, just barely observed, is associated with the  $\text{Li}^+$  insertion process. This insertion changes the colour of the film from transparent (slightly yellow) to dark blue at a potential of  $-1.8\text{ V}$ . The anodic peak observed at  $-1.0\text{ V}$  is attributed to the extraction of  $\text{Li}^+$ . The film again becomes transparent at  $+2.0\text{ V}$ . The measurements were done up to 100 cycles, and the insertion and extraction processes were found to be stable and fully reversible after the fourth cycle. The anodic and cathodic charge densities were measured from integration of the cyclic voltammograms. The exchanged charge was equal to  $10\text{ mC cm}^{-2}$  ( $\pm 3\%$ ). The value of the exchanged charge increases with the thickness of the coatings and reaches, typically,  $15\text{ mC cm}^{-2}$  for a three-dip film.

Fig. 3 shows the variations of the cell current as a function of time during repeated potential steps at intervals of 20 s between  $-1.8$  and  $2\text{ V}$ . The cathodic current, which is responsible for the coloration and is

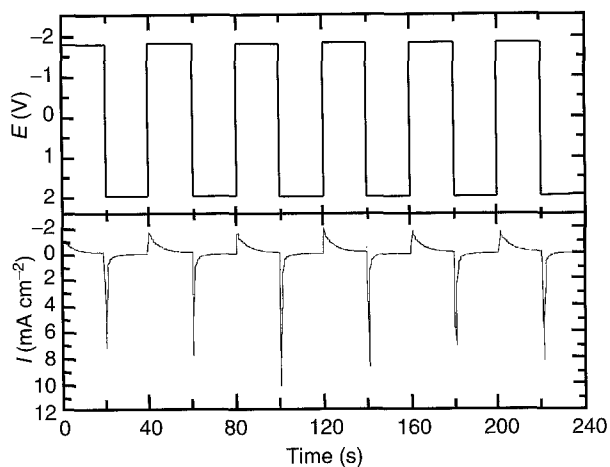


Figure 3 Chronoamperometry with potential steps at every 20 s between  $-1.8\text{ V}$  and  $2\text{ V}$ .

seen after the potential step to  $-1.8\text{ V}$ , has relatively fast kinetics (a few seconds). The  $\text{Li}^+$  extraction is, however, faster. The cyclic variation of the anodic peak intensity observed in Fig. 3 is instrumental.

Fig. 4 shows transmission spectra of  $\text{Nb}_2\text{O}_5$  film deposited onto ITO electrode in the reduced and oxidized state for one- and two-dip layers measured *in situ* at a fixed potential of  $+2.0\text{ V}$  (bleached state) and  $-1.8\text{ V}$  (coloured state). The insertion of  $\text{Li}^+$  changes the transmissivity in the visible-near IR range from about 80% to about 40% for a 100 nm thick  $\text{Nb}_2\text{O}_5$  layer and to less than 20% for a 200 nm thick (two-dip) coating.

All of these results are quite similar to those already obtained using sol-gel  $\text{Nb}_2\text{O}_5$  coatings made with sols prepared from classic Nb alkoxides without sonocatalytic irradiation [8, 9]. However, this new route is much easier and quicker to prepare the sols.

In conclusion, we have shown that films of  $\text{Nb}_2\text{O}_5$  prepared by the sonocatalytic method are promising candidates for electrochromic devices using either protonic or lithium electrolytes. Coatings calcinated at  $600^\circ\text{C}$  in air have a crystalline TT structure and

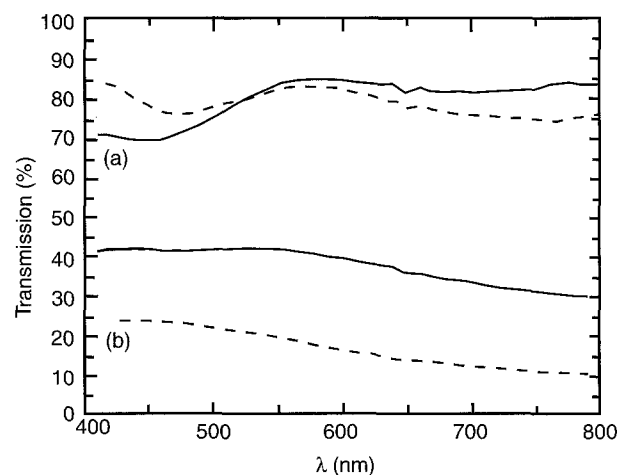


Figure 4 UV-visible spectral variation observed during electrochromic switching of (—) one- and (---) two-dip  $\text{Nb}_2\text{O}_5$  films (a) before (bleached) and (b) after (coloured) polarization at  $-1.8\text{ V}$ .

present a good, reversible and fast insertion/extraction of  $\text{Li}^+$  ions. The charge density inserted in one layer is  $10 \text{ mC cm}^{-2}$ .

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