

Characterization of Sol-Gel Deposited Niobium Pentoxide Films for Electrochromic Devices

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Abstract

Niobium pentoxide films, fabricated by the sol-gel process, were spin coated onto conductive indium tin oxide (ITO)/glass, and microscope slides. These films were cycled in a 1M LiClO₄ propylene carbonate (PC) solution, and exhibited electrochromic behavior upon the electrochemical insertion (reduction) and extraction (oxidation) of lithium. In-situ optical transmittance measurements were investigated in the ultra-violet/visible/near-infrared wavelength regions (250-2100 nm). Niobium pentoxide films showed reversible optical switching from 320 to 870 nm, but were found electrochromically inactive in the infrared region. Surface analysis using X-ray photoelectron spectroscopy (XPS) indicated little difference in the chemistry of Nb₂O₅ films as deposited and lithiated Li_xNb₂O₅ films, as XPS binding energies of Nb and O showed no appreciable shifts. These films were found to be amorphous by X-ray diffraction. Optical transmittance measurements combined with cyclic voltamograms and XPS spectra, revealed that the electrochromic behavior of these films occurs due to the insertion of Li⁺ cations into niobium pentoxide films. The bronze coloration of the niobium pentoxide films could make them useful as an electrochromic counter electrode for electrochromic devices.

1. Introduction

During the past few decades there has been great interest in electrochromic materials, this is due to their many potential applications in electro-optical devices such as chromogenic glazing in windows and large-scale electronic information displays [1-2]. Inorganic materials that promise good electrochromic properties are in the class of transition metal oxides and hydroxides [3-5]. Examples are WO₃, MoO₃, V₂O₅, Nb₂O₅, CoO₂, Mn₂O₃, and hydrated NiO_x. Also, materials such as rare earth oxides have been researched [7-8].

The most promising electrochromic materials for use as working electrodes are Li_xWO₃ [4] and H_xWO₃ (0 ≤ x ≤ 0.5), whose chemical, optical, and structural properties have been thoroughly investigated. There has been continued interest in finding suitable working and counter electrode couples that can compliment each other. Many materials, such as V₂O₅, IrO₂, Nb₂O₅, and CoO have been investigated as counter electrodes to compliment tungsten bronzes [9-11]. But, in the case of Nb₂O₅ it is best to use it with an anodically coloring material such as NiO. Counter electrode materials involving IrO₂ would not be cost effective in window applications, although V₂O₅ and CoO have shown promise.

Another possible material for use as a working electrode is NiO_x. It has been demonstrated that NiO_x is a potential candidate for use as a working electrode in large

area windows applications [1, 12-13]. As with WO_3 , finding a suitable counter electrode is a challenge. Nb_2O_5 could be a potential counter electrode to compliment NiO_x . Nb_2O_5 films are readily fabricated by rf sputtering [14], anodic oxidation [15-16], synthetic routes [17], and with sol-gel chemistry [18]. NbO_x films are of particular interest as a counter electrode in NiO_x devices.

In this paper we present characterization of sol-gel deposited Nb_2O_5 films, which has received little attention in the literature. Major advantages of the sol-gel process are ease of microstructure control, potential for a homogeneous coating over a large area, high porosity, and good chemical and mechanical stability [19]. These factors can influence the kinetics, durability, coloring efficiency, and charge storage in electrochromic device components [20-21]. The aim of this investigation is to deposit Nb_2O_5 by sol-gel spin coating technique for use as a potential counter electrode material. Included in this study is the analysis of switching properties using voltammetry, spectroscopy, and identification of chemical species by X-ray photoelectron spectroscopy.

2. Experimental Procedure

2.1 Preparation of Solutions

The sol-gel film was prepared according to the process flow chart in fig 1. Niobium ethoxide ($\text{Nb}(\text{OC}_2\text{H}_5)_5$, 99.95%, Aldrich Chem. Co., Milwaukee, WI) was used to prepare polymeric solutions by hydrolysis and polymerization reactions. The starting solution was prepared by mixing niobium ethoxide, absolute ethanol ($\text{C}_2\text{H}_5\text{OH}$), and glacial acetic acid (CH_3COOH) while stirring. Stirring of the solution was continued for 30 minutes. Absolute ethanol was then added slowly to the first solution by stirring.

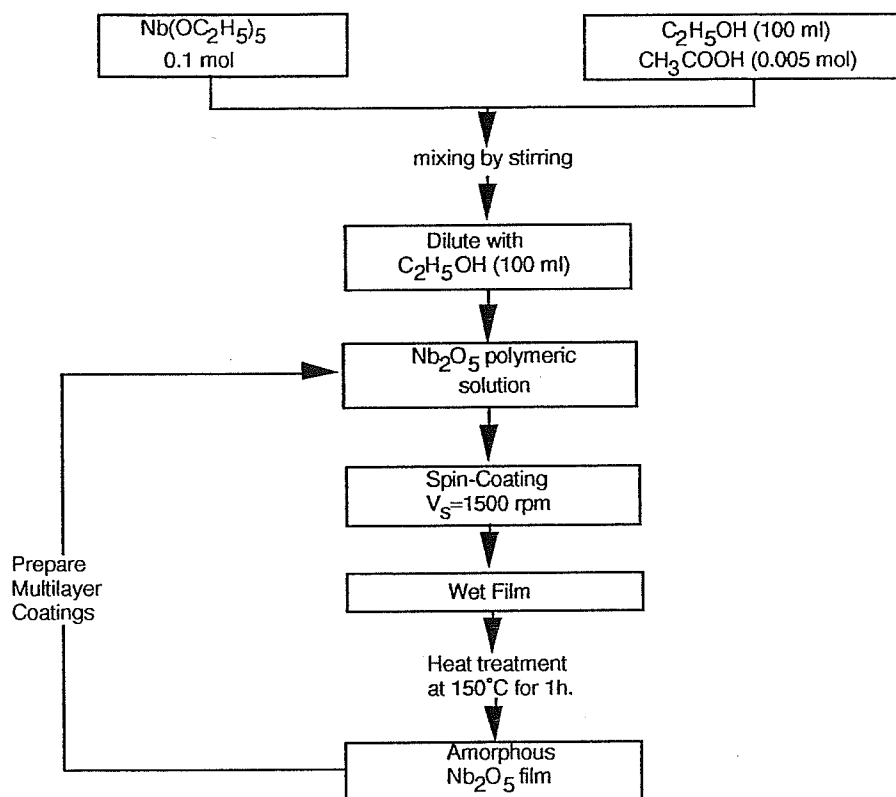


Fig. 1. Flow Chart of Fabrication Process

A clear solution was obtained after stirring for 2 hours. This solution was used to spin coat the substrates. The viscosity of the solution (1.4 cP) was adjusted by adding ethanol. The solution was found to be stable for at least two months.

2.2 Preparation of Nb₂O₅ Coatings

Cleaning of the substrate is important for proper adhesion of coatings [22]. Microscope slides and In₂O₃:Sn (ITO) coated glass substrates (9 Ω/cm², Donnelly Corp. Holland, MI) were ultrasonically cleaned in acetone, rinsed in deionized water, washed with methanol, dried at room temperature, and then stored in a desiccator. The coatings were deposited by allowing (0.5 ml) of solution to flow onto a substrate spinning at 1200-3000 rpm. Deposition took 4 - 5 s, and the total time of rotation after deposition was 40 s. As many as 15 coatings on a single substrate were done to increase the film thickness. Heating of the coatings between spinning was necessary, because the gel films dried very slowly in air. The coatings were tempered at 150 °C for one hour. The fabricated coatings were transparent, hard, durable, and stable.

2.3 Characterization of the Coating

Prior to the optical and structural investigations, the deposited films were exposed to the ambient atmosphere. Scanning electron microscopy, X-ray photoelectron spectroscopy, UV-VIS-NIR spectroscopy, and cyclic voltammetry measurements were made on each Nb₂O₅ film.

Scanning electron microscopy (SEM, Jeol model JSM 6400) was used to examine the surface morphology of the films. A silver coating was deposited on the samples to avoid charging of the surface. The structure of Nb₂O₅ films were investigated by X-ray diffraction (XRD). The XRD study was carried out on a Philips model PW1730 X-ray diffractometer using CuKα excitation (45 kV, 40 mA).

X-ray photoelectron microscopy (XPS, Kratos model XSAM 800) was used to identify chemical composition of the films. The background pressure of the system was approximately 5x10⁻⁹ torr. The ion-pumped ultra-high vacuum chamber was equipped with a MgKα X-ray source, a double pass CMA (including an internal electron gun for Auger electron spectroscopy), and a sample introduction cell. During XPS experiments, a pass energy of 40 eV between the inner and outer CMA cylinders was employed. The spectrometer was calibrated so that the Au(4f_{7/2}) electron binding energy was at 83.3 eV and adventitious carbon occurred at 284.5±0.1 eV.

Electrochemical experiments were done using a potentiostat/galvanostat (Princeton Applied Research Model 273), digital coulometer (Princeton Applied Research Model 179), and a X-Y chart recorder (Helwlett Packard 7035 B). The electrochemical cell consisted of a three-electrode configuration. Nb₂O₅ on ITO glass substrate was used as a working electrode, with a lithium metal counter-electrode and reference electrode. The electrolyte was 1 M LiClO₄/propylene carbonate (PC).

For the potentiostatic experiments a potential scan rate of 10 mV/s was used throughout. Single or multi-scan cyclic measurements were performed within and at the potentials 1.2 and 4.0 versus Li. All work took place in an argon filled glove-box.

Optical transmittance measurements on Nb_2O_5 films were taken over a 250-1800 nm wavelength range. A Perkin and Elmer model Lambda 9 double beam spectrophotometer was used.

The thickness of the films were measured by a Dektak II (Veeco Inst. Inc., Santa Barbara CA) surface profiler having a maximum resolution of 0.5 nm/100 nm. Film thickness ranged from 80 to 180 nm for single layer coatings.

3. Results and Discussion

3.1 Formation of Nb_2O_5 Coatings

To produce transparent and uniform Nb_2O_5 coatings the polymeric solutions used for spinning must be clear and homogeneous. After studying variation in solution alkoxide content, type of catalyst, and solvent we deposited high-quality coatings onto both glass and ITO coated glass substrates by using the method given in subsection 2.1. The thickness of Nb_2O_5 coatings was affected by the spinning rate (v_s) as shown in fig. 2. Lower spinning rates for solutions with the same viscosity produced thicker films. Film thicknesses between 83 and 178 nm were obtained by varying the spinning rate from 3000 to 1000 rpm. The most homogeneous films were produced at a spinning rate of approximately 1500 rpm.

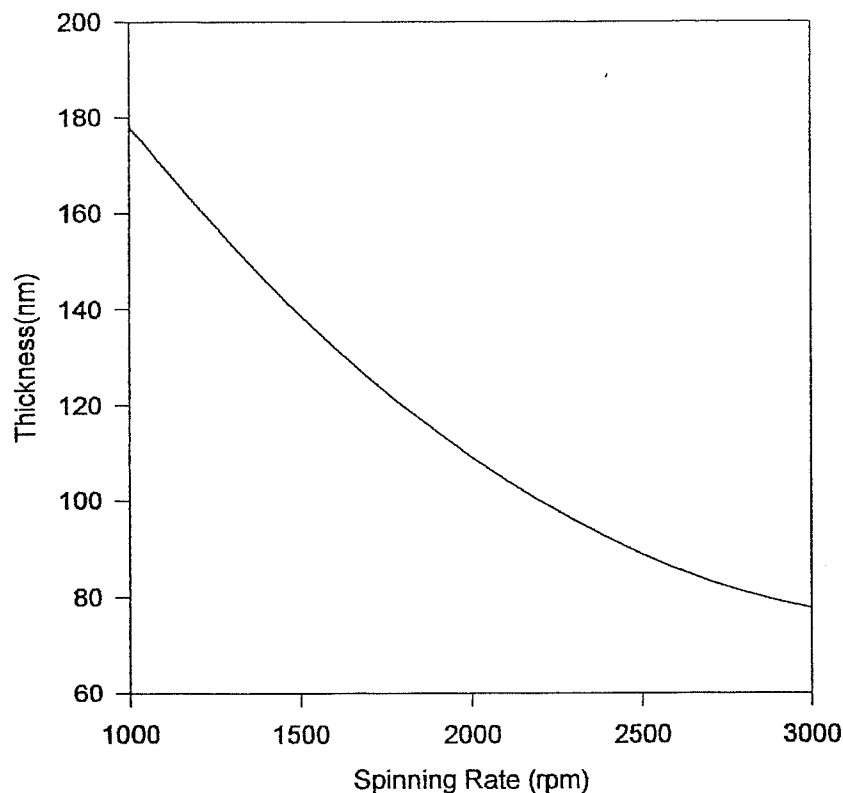


Fig. 2. Variation in film thickness as a function of spinning rate.

SEM micrographs of the surface of such films show relatively few pinholes or micro cracks over a large area. Successive single layer additions were made for as many as 15 layers. For this purpose it was desirable to have a solution that was stable over a long time period. The samples were fired after each deposition procedure at a temperature of

150 °C for one hour. The resulting films were highly transparent, and were clear yellow in color. The thickness of the films as a function of the number of spinning cycles is shown in fig. 3. A nearly linear relationship was found from this plot. Furthermore, the thickness increment per layer was approximately 124 nm. XRD patterns of the tantalum oxide films used in this study were typical of the amorphous state without any diffraction peak characteristics of Nb₂O₅ crystals.

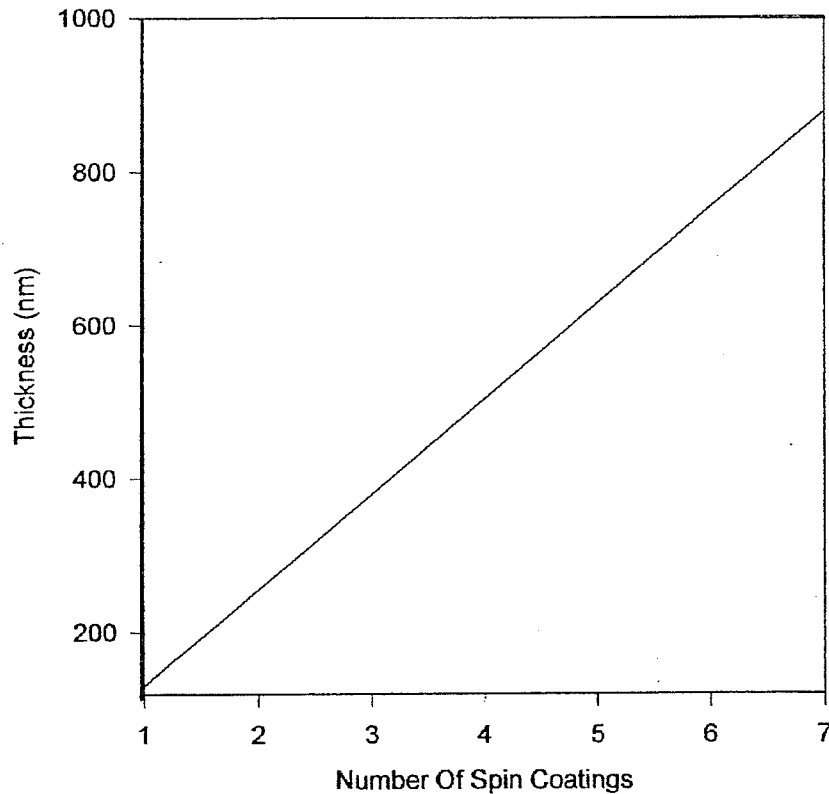


Fig. 3. Variation in thickness with number of spin coatings. The films were deposited on soda-lime microscope slides ($v_s=1500$ rpm).

Figure 4 shows a wide range XPS spectrum of niobium oxide film on a soda-lime glass substrate. The only impurities seen in the film are sodium and carbon. All films showed peak energies for niobium and oxygen within normal experimental error. The measured binding energies agrees very well with standard Nb₂O₅ [23].

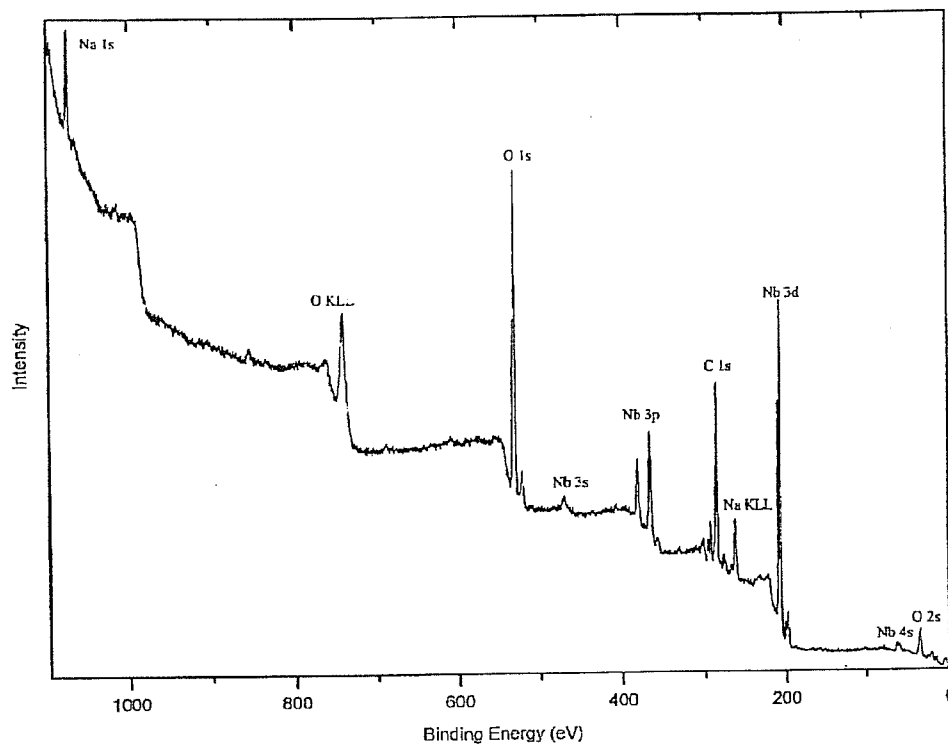


Fig. 4. XPS scan of Nb_2O_5 films.

Figure 5 shows the XPS region around the Nb(3d) core levels for Nb_2O_5 films. This region exhibits two peaks centered at 209.7 ± 0.2 and 207.3 ± 0.2 eV that can be assigned to $3d_{3/2}$ and $3d_{5/2}$ core levels of Nb^{5+} . The film was uncolored.

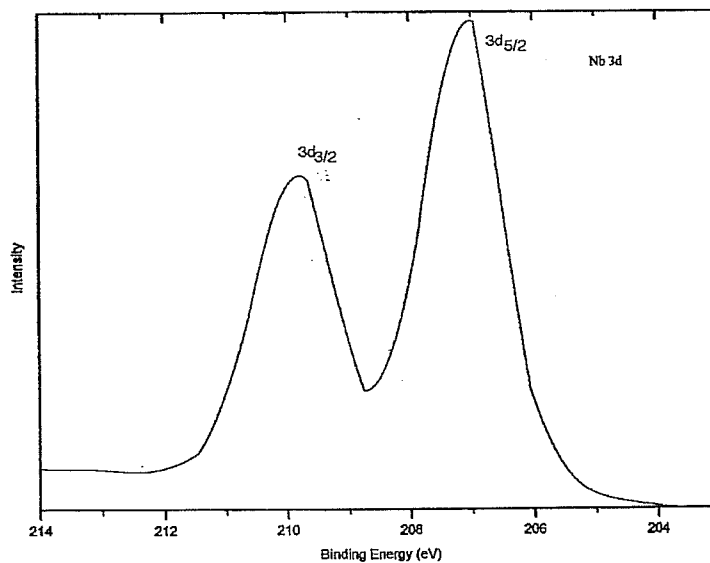


Fig. 5. XPS spectrum of Nb_2O_5 films in the Nb(3d) region. These peaks correspond to Nb_2O_5 .

The corresponding O 1(s) spectra is shown in figure 6. The spectrum exhibits a single peak centered at 530.5 that can be assigned to O^{2-} . The binding energy of 530.5 eV fits well with the data in the literature, and corresponds to the O^{2-} anion in oxides [24].

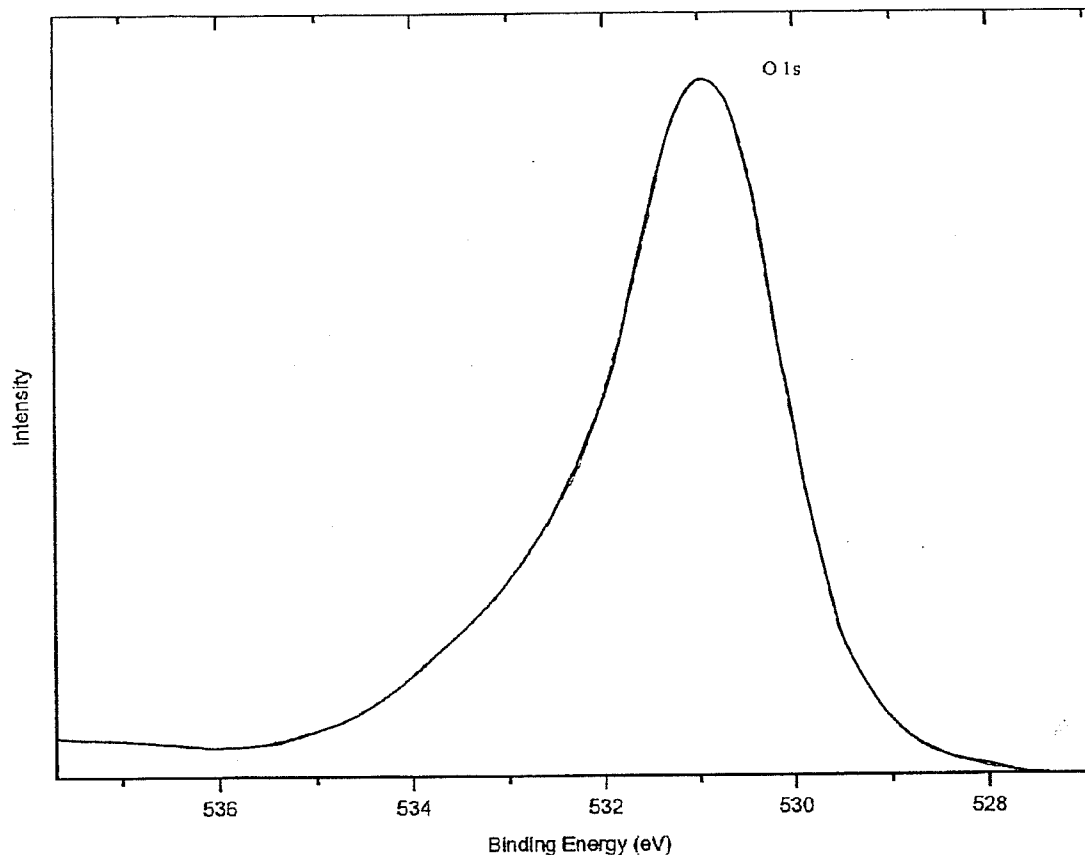


Fig. 6. Typical O(1s) spectra of Nb₂O₅ films.

Electrochemical coloration caused a small downward shift of the binding energy levels. The shift in binding energy levels for the XPS spectra of the reduced form of Nb₂O₅ (Li_xNb₂O₅) is shown in Table 1. The small shift in the binding energies, and the change in electronic structure of the oxide film, are due to the insertion of Li⁺ during electroreduction.

Table 1. Binding Energies of Nb₂O₅ Samples

Parameter	Nb ₂ O ₅	Li _x Nb ₂ O ₅
Nb 3 _{3/2} (eV)	209.7	209.2
Nb 3 _{5/2} (eV)	207.3	206.8
O 1s (eV)	530.5	530.1
Ratio of Nb/O	0.45	0.36

3.2 Electrochemical Characterization

Cyclic voltammetry (CV) was performed at room temperature on deposited films of Nb₂O₅/ITO/glass. Figure 7 shows the cyclic voltamogram of Nb₂O₅ in 1 M LiClO₄ propylene carbonate, which is similar to that reported previously for dip-coated Nb₂O₅ [17]. As can be seen from fig 7, the cathodic current increases without a peak being observed at the inversion potential (1V). In the positive voltage sweep an anodic current peak appears. The cathodic and anodic charge obtained at a sweep rate of 20 mV/s are approximately 2×10^{-2} C/cm². Long term cycling experiments at room temperature show that Nb₂O₅ films were quite stable to cycling, undergoing reduction /oxidation reactions for over 1000 cycles without significant change or degradation. The amount of charge transfer did not differ significantly (no more than 1 mC/cm²) between cycle numbers 500-1000.

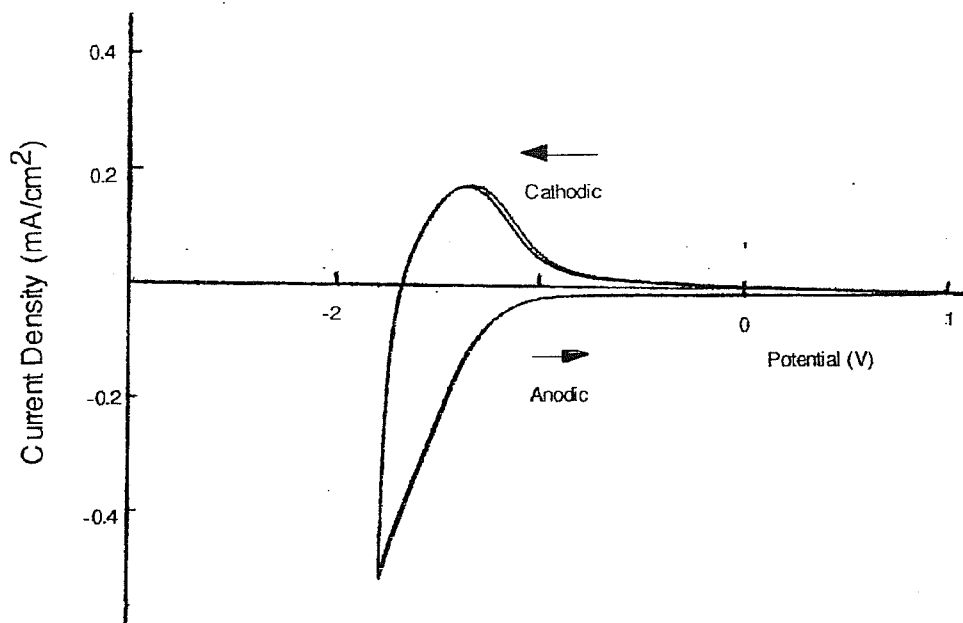


Fig. 7. Cyclic voltamogram at a sweep rate of 20 mVs^{-1} for a 230 nm thick Nb₂O₅ film on ITO coated glass electrode in 1M LiClO₄ propylene carbonate solution.

The optical transmittance of Nb₂O₅ films was measured on ITO substrates. The UV/VIS/NIR transmittance spectra of a Nb₂O₅/ITO/glass electrode in the reduced and oxidized state are shown in figure 8. The Nb₂O₅ film is bronze under the applied potential of -1.9 V. A decrease in transmittance between 350 and 800 nm occurs when the electrode is under applied potentials of +0.8 V. Using the weighted ordinate method, the photopic response for the colored and bleached state were found to be $T_p=0.46$ and $T_p=0.79$ respectively. Deeper coloration can be obtained at -2.0 V, then $T_p=0.32$. The film became transparent again when a bleaching potential of 0.8-0.5 V was applied for a few seconds.

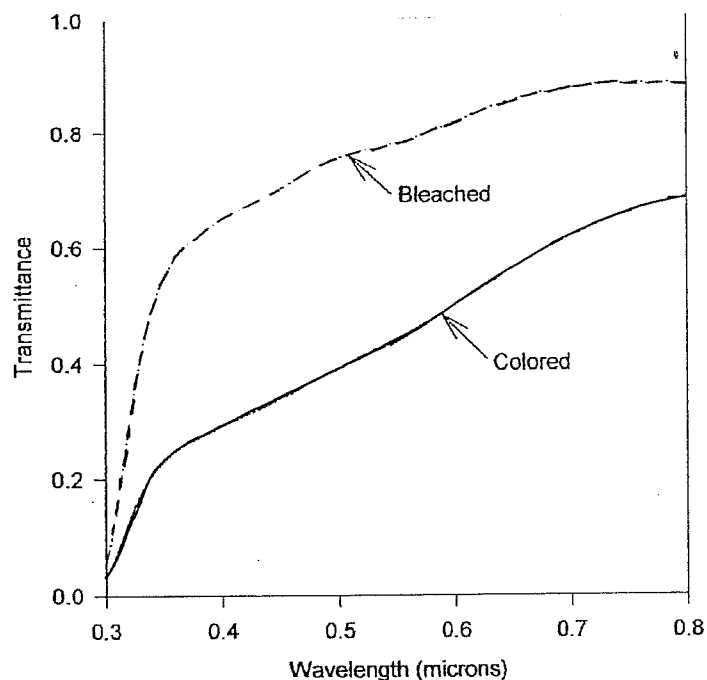


Fig. 8. Transmittance spectra of Nb_2O_5 films on ITO coated glass electrodes; oxidized (bleached) at + 0.8 V and reduced (colored) at -1.9 V.

The typical transmittance-time response of Nb_2O_5 films in the reduced and oxidized state are shown in fig. 9. A decay time of 30 s for coloring and rise time of 3 s for bleaching are observed. Indicating that Nb_2O_5 films bleach faster than they color.

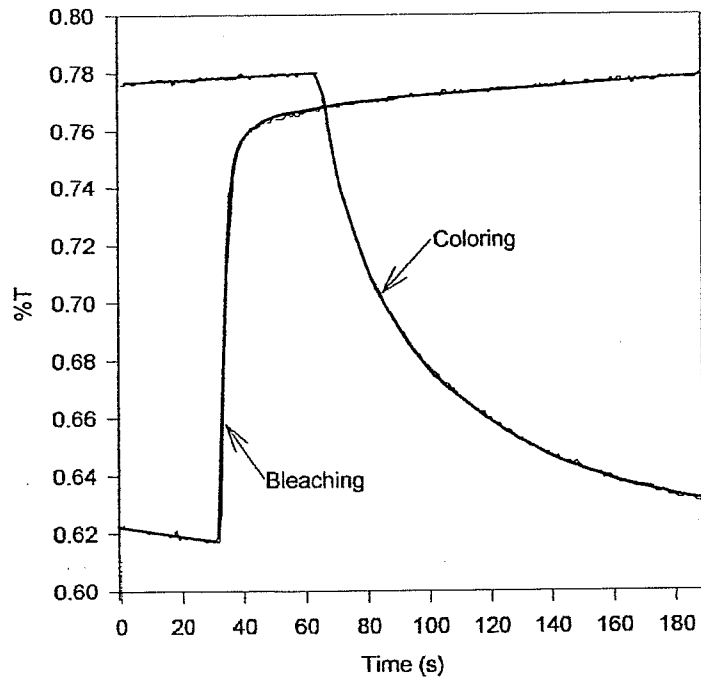
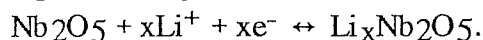


Fig. 9. Transmittance-time response of a Nb_2O_5 film on ITO coated glass electrode at 550 nm.

The electrochemical measurements combined with the optical transmittance study proves that the electrochromic effect of the Nb₂O₅ films is associated with an Li⁺ insertion-extraction process. Li_xNb₂O₅ is the lithiated (colored) form and Nb₂O₅ the delithiated (bleached) form. From these results the possible cathodic and anodic reaction can be represented by:



The lithiation-delithiation processes occurring in the Nb₂O₅ system enables it to serve as a good counter electrode for NiO_x devices.

4. Conclusion

Amorphous electrochromic Nb₂O₅ films were prepared successfully by a sol-gel spinning technique. The best film uniformity was observed at a spin rate of 1500 rpm. Reduction and oxidation of these films in 1 M LiClO₄ propylene carbonate solution resulted in desirable changes in optical transmittance. XPS examination suggest the film consist of Li_xNb₂O₅ in the colored state. Electrochemical experiments have shown that the material was reversible and stable for at least 1000 cycles. The optical characterization of Li_xNb₂O₅ films demonstrated that transmittance modulation was evident in the visible and near-infrared regions. Nb₂O₅ films were found electrochromically inactive in the infrared region. Nb₂O₅ is transparent, while the reduced (Li_xNb₂O₅) form is brown. Nb₂O₅ films may be useful in anodically coloring electrochromic applications as a counter electrode, particularly in nickel-oxide devices.

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