

# Electrochromism of Sol-gel Derived Niobium Oxide Films

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Niobium oxide films are promising cathodic electrochromics that in many aspects can compete with the more frequently studied  $\text{WO}_3$  films. The films reported herein were prepared using the sol-gel route from a  $\text{NbCl}_5$  precursor. The electrochromic properties were pronounced for crystalline films that are heat-treated at  $500^\circ\text{C}$  and exhibited transmittance changes between coloured and bleached states of 60 % in the UV and 80 % in the VIS-NIR regions. Improved bleaching and more reversible electrochromism of thick niobium oxide films ( $d > 250\text{ nm}$ ) were obtained by lithiation.

## Introduction

Although anodisation is the most extensively used technique for film deposition<sup>1</sup>, sputtering, chemical vapor deposition (CVD)<sup>2</sup> and the sol-gel route have been also used for preparing niobium oxide films<sup>3,4</sup>. Avellaneda et.al.,<sup>5</sup> following Bradelly's<sup>6</sup> method succeeded in preparing niobium oxide films with excellent electrochromic properties. They showed that the crystalline (TT-phase) niobium oxide films that are heat-treated at  $560^\circ\text{C}$  exhibited pronounced colouring/bleaching changes ( $\Delta T = T_{bl} - T_{col} = 80\% - 20\%$ ), fast kinetics and good stability for cycling in aprotic electrolytes ( $\approx 2000$  cycles). Lithiated niobium oxide films were prepared in an attempt to improve the bleaching characteristics of the thick films. This idea is based on the work of Machida et.al.,<sup>7</sup> who in 1986 showed that bleaching kinetics of amorphous films ( $40\text{Li}_2\text{O} \bullet 35\text{WO}_3 \bullet 25\text{Nb}_2\text{O}_5$ ), obtained by sputtering, exhibited much faster bleaching compared to the unlithiated films.

## Experimental

### Preparation of Sols and Films

Sols were prepared according to the method of Barros Filho et.al.<sup>8</sup>. After dissolving  $\text{NbCl}_5$  (Aldrich, 99%) in propanol (PrOH), acetic acid (HAc) was added to yield a sol with a molar ratio of  $\text{NbCl}_5:\text{PrOH}:\text{HAc}=1:10:0.25$ . Lithium containing sols were prepared with the addition of  $\text{LiCF}_3\text{SO}_3$  (Aldrich 96%) to yield  $\text{NbCl}_5:\text{PrOH}:\text{AcH}:\text{LiCF}_3\text{SO}_3$  with molar ratios of 1:11:0.44:0.1 and 1:11:0.44:0.2 giving a Li/Nb ratio of 0.1 and 0.2. Xerogel films were prepared by pulling the glass slide from the sols with a speed of 1 cm/min. The films

were dried (10 min) with a hot stream of air and then heat-treated at either 300°C or 500°C. Supporting glass electrodes were SnO<sub>2</sub>:F films (Pilkington, U.K.) with a sheet resistance  $R = 10\text{-}12 \Omega$ . These had previously been ultrasonically cleaned and dip-coated with a non-ionic surfactant (Teloxid, Teol, Ljubljana, Slovenia) to improve the optical quality of the films.

## Results and Discussion

### Structural Properties

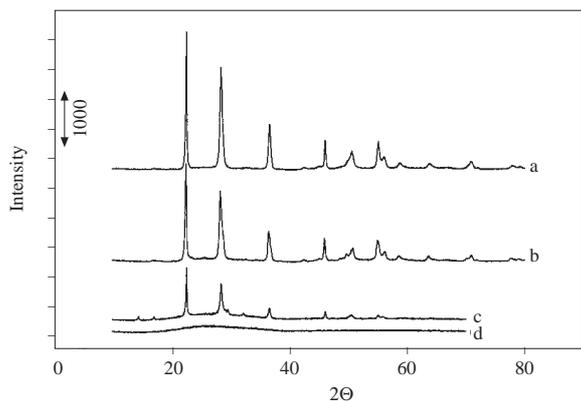
The structure of xerogels, oxide powders and corresponding films were investigated by X-ray diffraction (XRD; Philips PW 1710) and FT-IR spectroscopic measurements (Perkin Elmer Model 2000 Spectrometer with a resolution of 4 cm<sup>-1</sup>). Skeletal modes of the Nb-O stretching vibrations were clearly visible in the FT-IR spectra measured in the whole temperature range (25°C < T < 800°C) showing that the Nb-O oxo-polymer network is established in xerogel films and powders. The band frequencies shift only marginally when films are heat-treated at 300°C and 500°C. These bands were assigned to the Nb-O stretching (800 cm<sup>-1</sup>), Nb-O-Nb bridging (640 cm<sup>-1</sup>) and Nb<sub>3</sub>-O stretching (500 cm<sup>-1</sup> modes according to the vibrational analysis made on crystalline (TT-, T- and H-) phases of Nb<sub>2</sub>O<sub>5</sub> powders<sup>9</sup>. The observed vibrational modes detected for our films correspond to those reported for powders. The small (10-13 cm<sup>-1</sup>) red-frequency shifts of the bands is consistent with the possible shifts which the transversal optical (TO modes) resonances may exhibit, because of the polarization effect in the polycrystalline materials<sup>10</sup>.

XRD spectra (Fig. 1) of niobium oxide and lithiated niobium oxide (with Li/Nb = 0.1) powders and films obtained at 300°C are amorphous while a pseudo-hexagonal (TT- Nb<sub>2</sub>O<sub>5</sub>) phase is formed at 500°C<sup>5,11</sup>.

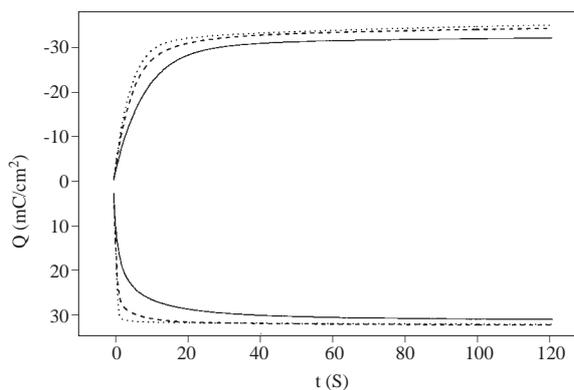
### Electrochemical and Electrochromic Properties of Films

The cyclic voltammetric (CV) response was recorded in 1M LiClO<sub>4</sub>/PC with scan rate 10 mV/s (EG and G PAR model 273 computer controlled potentiostat-galvanostat, driven by 270 Electrochemical Analysis software). All the films showed stabilized CV response after 5 cycles. Crystalline films exhibited well-defined anodic and cathodic peaks. The cathodic current of lithiated niobium oxide films begins to increase at less negative potentials compared with the usual niobium oxide. As can be seen from Figure 2 insertion and extraction of Li<sup>+</sup> ions are faster for lithiated niobium oxide films and increase with the amount of LiCF<sub>3</sub>SO<sub>3</sub> in the sol.

The electrochromic responses of niobium and lithiated niobium oxide films heat-treated at 300°C and 500°C are shown in Figure 3. The amorphous films exhibit a different spectral transmission modulation in the visible spectral range compared crystalline films. The main difference is in the stronger colouring of the crystalline films between 600 nm <math>\langle \lambda \rangle</math> 1100 nm. This observation agrees with similar behaviour reported for amorphous<sup>2</sup> and crystalline niobium oxide films<sup>5</sup>. The lithiated niobium oxide films also exhibit a much higher electrochromic reversibility. The effect of lithiation on bleaching becomes even more pronounced for thicker (2x dipped) films. The bleaching of lithiated niobium oxide films is completed to the same extent within 120 s (Figure 4). In this respect to use of LiCF<sub>3</sub>SO<sub>3</sub> is prerequisite and rules out other possible Li dopants like Li<sub>2</sub>CO<sub>3</sub> and LiCl (Figure 3). Further studies are needed to explain the effect of various dopant precursors. At least in part the improved electrochromism of lithiated films may be because of their increased electrical conductivity ( $\sigma(\text{Li}/\text{Nb}_2\text{O}_5 = 0.2) = 10^{-7}\text{-}10^{-8} \text{ S/cm}$ ,  $\sigma(\text{Nb}_2\text{O}_5) = 10^{-11} - 10^{-12} \text{ S/cm}$ ).



**Figure 1.** XRD patterns of powders (a, b) and films (c, d) heat-treated at 300 °C (d) and 500 °C (a, b, c): a, c, d → niobium oxide; b → lithiated niobium oxide (Li/Nb = 0.1)



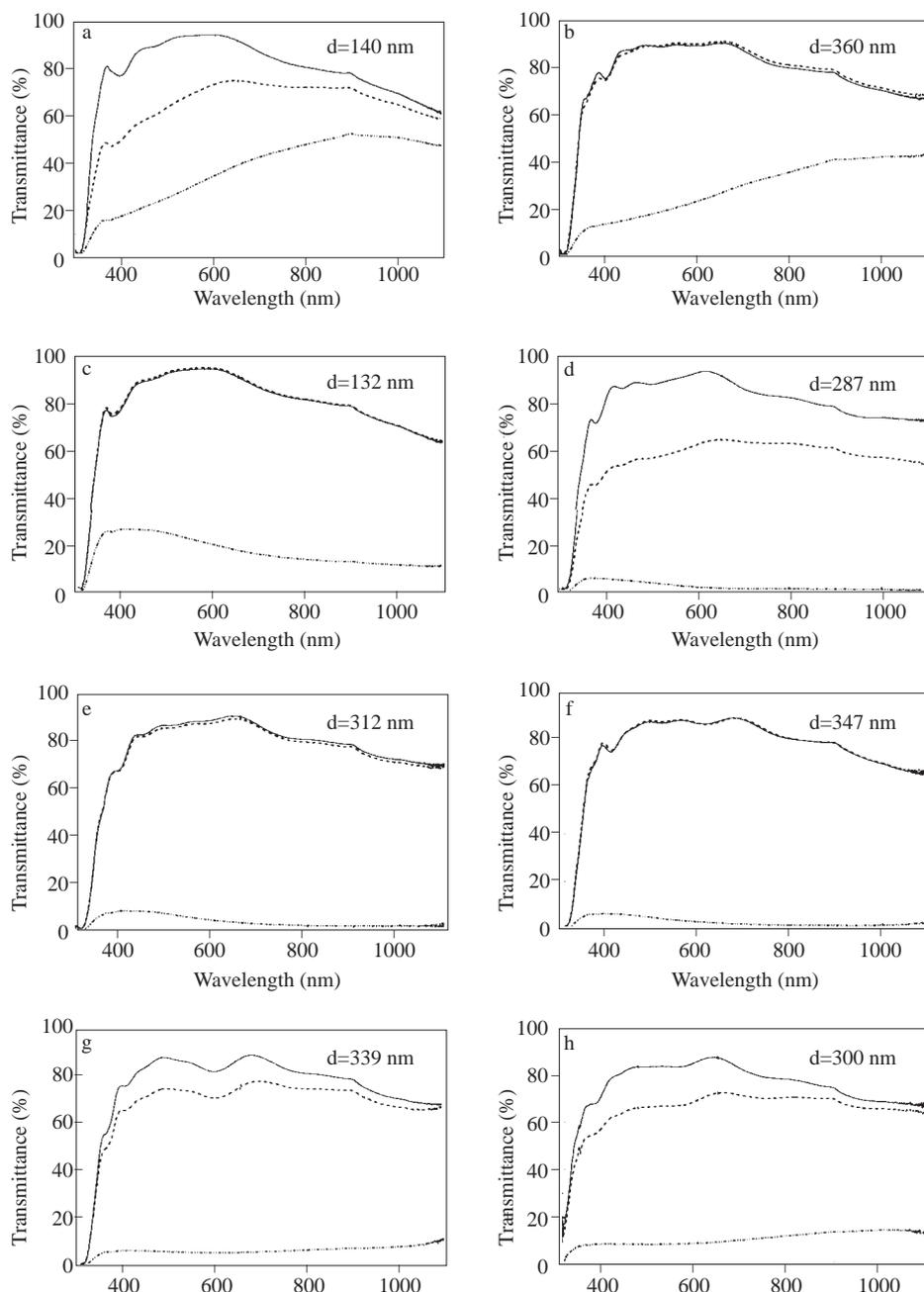
**Figure 2.** Cathodic ( $E = -1.7$  V) and anodic ( $E = 2.0$  V) total charge density ( $Q$ ) of niobium oxide (-) and lithiated niobium oxide films with Li/Nb molar ratios 0.1 (-) and 0.2 (—). Electrolyte was 1M  $\text{LiClO}_4/\text{PC}$

## IR Spectra of Charged Films

IR spectra of thick (5x dipped) as-deposited and cathodically charged niobium oxide films were measured at near normal incidence angle.  $\text{SnO}_2/\text{F}$  coated glass was used as a background for reflection measurements. With the exception of strong interference bands the IR reflection-absorption spectra of as-deposited films reveal mode frequencies identical to the TO modes in transmission spectra of films coated on Si wafers, i.e. Nb-O stretching at  $800\text{ cm}^{-1}$ , Nb-O-Nb bridging at  $649\text{ cm}^{-1}$  and  $\text{Nb}_3\text{O}$  stretching mode at  $500\text{ cm}^{-1}$ . niobium oxide films were charged at  $-1.5$  V for 120 s. After cleaning the surface of the film, to remove the electrolyte, IR near-normal absorption/reflection spectra were measured. As expected absorption increases significantly in the whole IR spectral range, screening the interferences, although the Nb-O modes could still be detected on the steep slope of the strong and broad absorption band. The Nb-O stretching at  $800\text{ cm}^{-1}$  shifts to  $825\text{ cm}^{-1}$  ( $\Delta\nu = +25\text{ cm}^{-1}$ ) while the  $\text{Nb}_3\text{-O}$  stretching mode exhibits the reverse frequency shift from  $500\text{ cm}^{-1}$  to  $460\text{ cm}^{-1}$  ( $\Delta\nu = -40\text{ cm}^{-1}$ ) (Fig. 5). The remaining bridging Nb-O-Nb mode is unaffected due to  $\text{Li}^+$  insertion, though it loses its intensity. The possible  $\text{Li}^+\text{-O}$  modes, that are expected to appear at lower frequencies ( $< 400\text{ cm}^{-1}$ ) cannot be ruled out. A small but distinct blue-frequency shift of the Nb-O stretching ( $\Delta\nu = 25\text{ cm}^{-1}$ ) suggests a partial increase of the Nb-O double bond character that is not compensated for the formation of the Nb-O ...  $\text{Li}^+$  bonding. The IR spectra of the charged films resemble the vibrational changes in the charged amorphous sol-gel derived  $\text{WO}_3$  films, where W = O mode appears at  $950\text{ cm}^{-1}$ .

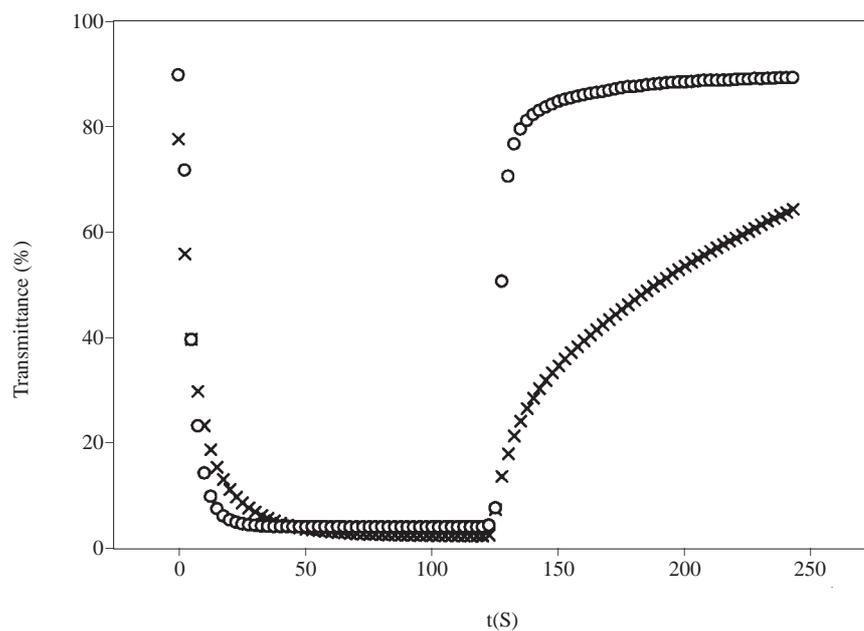
The most salient feature in the IR spectra of the charged films is the broad and strong polaron mode extending from the near IR spectral range and screens the TO modes of niobium oxide. The effect of screening by the polaron absorption could be clearly observed in the LO spectra obtained at near-grazing incidence conditions using p-polarized light. This was tested by charging films at two different levels. At first  $\text{Nb}_2\text{O}_5$  (1x dipped,  $d = 87\text{ nm}$ ) were cathodically charged at only  $-1.0$  V ( $Q_{ins} = -5.7\text{ mC/cm}^2$ , 120 s) which only slightly changed the colour of the films. The LO mode corresponding Nb-O stretching mode already decreases in intensity and becomes shifted from  $965\text{ cm}^{-1}$  (as-deposited films) to  $942\text{ cm}^{-1}$ . Further charging at  $-1.7$  V ( $Q = -42\text{ mC/cm}^2$ ) for 120 s results in complete overdamping of the LO mode of Nb-O stretching and the strong absorption of the polaron mode dominates the IR spectrum. Strong damping of

the LO phonon mode by polaron and phonon interaction with slight frequency shift of the phonon mode has been modelled recently for the substoichiometric  $\text{WO}_3$  and gasochromic  $\text{Pd}:\text{WO}_3$  films<sup>12</sup>.



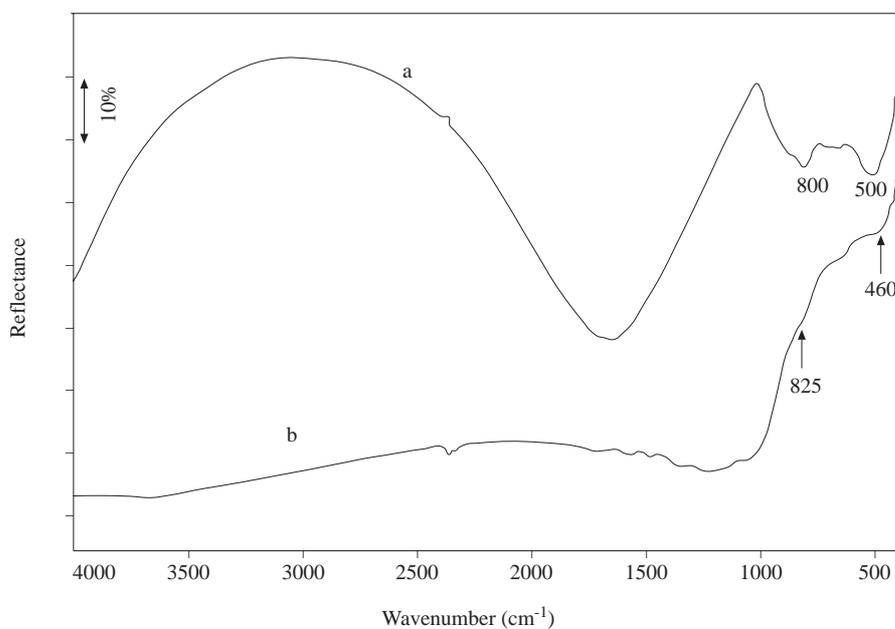
**Figure 3.** In-situ transmittance measurements of films (heat-treated at  $300^\circ\text{C}$  (a, b) and  $500^\circ\text{C}$  (c, d, e, f, g, h)) obtained by charging at  $-1.7\text{ V}$  (120 s) (-.-) and  $2.0\text{ V}$  (120 s) (- - -), as deposited (—). niobium oxide  $\rightarrow$  a, c, d; Lithiated niobium oxide:  $\text{LiCF}_3\text{SO}_3/\text{NbCl}_5 = 0.1 \rightarrow$  b, e;  $\text{LiCF}_3\text{SO}_3/\text{NbCl}_5 = 0.2 \rightarrow$  f;  $\text{LiCl}/\text{NbCl}_5 = 0.2 \rightarrow$  g;  $\text{Li}_2\text{CO}_3/\text{NbCl}_5 = 0.1 \rightarrow$  h

Bleaching of the film by charging at anodic potentials restored the LO modes of Nb-O stretchings, proving the reversibility of the effect of  $\text{Li}^+$  ion insertion/extraction reactions.

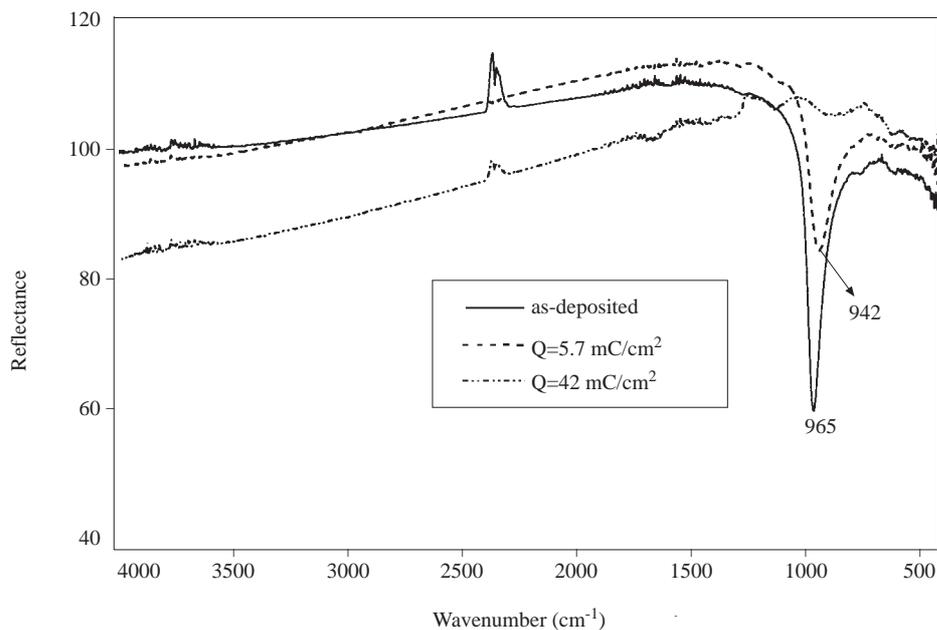


**Figure 4.** Transmittance at  $\lambda = 634$  nm during colouration ( $E = -1.7$  V) and bleaching ( $E = 2.0$  V) of niobium oxide (x) and lithiated niobium oxide ( $\text{Li/Nb} = 0.1$ ) (o)

Future studies of electrical properties in conjunction with their optical and IR spectra are planned to reveal the additional evidence for the existence of the possible free carrier reflection in  $\text{Li}^+$  ion inserted niobium oxide films which could not be ruled out by the represented IR absorption and FT-IR NGIA reflection-absorption spectra of films.



**Figure 5.** FT-IR reflection-absorption spectra of as-deposited niobium oxide film ( $500^\circ\text{C}$ , 5x-dipped) (a) and after charging at  $-1.5$  V for 120 s (b)



**Figure 6.** NGIA FT-IR spectrum of as-deposited niobium oxide film (500 °C, 1x dipped) (—) and spectra obtained after charging at -1.0 V (- - -) and -1.7 V (-.-.-)

## Conclusions

The sol-gel route based on alcoholic sols prepared from  $\text{NbCl}_5$  precursor was found to be suitable for making dip-coated niobium oxide amorphous (300 °C) and crystalline (500 °C) films. Lithiation was found to increase the electrochemical reversibility and the reversibility of bleaching of amorphous and crystalline films.

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