

Sol-Gel Deposited Amorphous Tantalum Oxide and Niobium Oxide Films as Protonic Conductors

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Abstract

In this work we report on the preparation of tantalum oxide and niobium oxide films by the sol-gel method for use as proton ion conductors in electrochromic devices. Measurement of the proton conductivity was derived from impedance spectroscopy measurements. The proton conductivity for Ta₂O₅ and Nb₂O₅ films was $4.6 \times 10^{-6} \text{ Scm}^{-1}$ and $3.2 \times 10^{-7} \text{ Scm}^{-1}$ respectively. The structural and chemical properties of the films were investigated by X-ray diffraction, X-ray photoelectron spectroscopy and scanning electron microscopy. These films were found to be amorphous and close to the stoichiometry of Ta₂O₅ and Nb₂O₅ respectively. In order to estimate the compatibility of these sol-gel deposited layers as ion conductors for EC devices, we investigated tantalum oxide and niobium oxide films deposited on sputtered WO₃ films. Charge balance and coloration characteristics were investigated during voltammetric cycling in a pH 2 liquid electrolyte. Spectral transmittance was measured for colored and bleached conditions. The photopic weighted transmittance change and solar weighted transmittance change were $T_p=85.2\% - 21.8\%$ and $T_s=75.7\% - 14.2\%$ for tantalum films on tungsten oxide. For niobium on tungsten oxide the values were $T_p=85.3\% - 35.2\%$ and $T_s=75.8\% - 28.1\%$.

1. Introduction

Over the last two decades, much work has been dedicated to develop solid state electrochromic (EC) switching devices for large-area glazing^{1,2}. These devices have the ability to actively control energy flowing in and out of the glazings of buildings and vehicles. The construction of these devices consist of typically a (1) transparent conductor (ITO), (2) electrochromic layer, (3) solid electrolyte or ion conductor, (4) ion storage layer, (5) transparent conductor. One of the most significant development areas is the solid electrolyte of the inorganic type. For large-area EC devices it is important to have an highly ionically conducting solid electrolyte³. Proton conducting amorphous metal oxides are promising materials for use in EC devices. Tantalum (Ta₂O₅), films have been used commercially by Donnelly (Holland, MI) in truck mirrors and by Nikon (Tokyo, Japan) in sunglasses as proton conductors. Niobium (Nb₂O₅), films have been investigated for proton conducting solid electrolyte materials in experimental EC devices⁴⁻⁷. Both these oxides, under specific preparation conditions, have high protonic conductivity and high visible transparency, making them desirable for EC devices. In these materials, the best transport rate of ions is seen in the lower density amorphous phases with some hydration. In general practice, inorganic ion conducting films have been prepared by conventional techniques such as vacuum evaporation, sputtering, and chemical vapor deposition⁴⁻⁹. Recently, the sol-gel deposition method has been adopted to prepare a variety of fast ion conductors, due to ease of fabrication on the large scale^{10,11}. The sol-gel method allows for the formation of ion conductors using low temperatures and very low capital investment compared to conventional thin film forming processes.

2. Experimental

2.1 Preparation of Tantalum and Niobium Films

The sol-gel films were prepared from $\text{Ta}(\text{OC}_2\text{H}_5)_5$ and $\text{Nb}(\text{OC}_2\text{H}_5)_5$ precursors by mixing tantalum and niobium ethoxide with absolute ethanol. Glacial acetic acid, CH_3COOH was used as a catalyzer. The polymerized coating solutions were quite stable and depositions were carried out in air. After deposition, the samples were heat treated in air at 150 C to densify and to remove any remaining solvent. Multiple coating was accomplished by recoating the samples after the heat treatments. The tantalum and niobium films were deposited on both pre-cleaned soda-lime glass coated with indium tin oxide (ITO) and glass coated with ITO and tungsten oxide. All films investigated in this work were deposited using the spin coating technique at a controlled speed of 2500 rpm. The preparative details have been described in previous papers^{11,12}. The fabricated tantalum and niobium films were transparent, hard, durable and chemically stable.

2.2 Characterization of the Coatings

Scanning electron microscopy (SEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS), impedance spectroscopy, and cyclic voltammetry measurements were made on each film. Optical transmission measurements on Ta_2O_5 and Nb_2O_5 films were made over a 350-1800 nm wavelength range using a Perkin and Elmer (Lambda 9) double beam spectrophotometer. In situ UV-VIS spectroelectrochemical properties were examined for the cell equipped with ITO/ $\text{WO}_3/\text{Ta}_2\text{O}_5$ or Nb_2O_5 coated glass working electrode, ITO glass counter electrode, and 0.2 M H_2SO_4 electrolyte. A saturated calomel electrode (SCE) served as a reference electrode. All measurements were performed in the near-normal transmittance configuration relative to air. The surface morphology of the Ta_2O_5 and Nb_2O_5 films was observed by JEOL (JSM 6400) scanning electron microscope. A thin silver coating was applied over the samples to avoid charging of the surface. The structures of Ta_2O_5 and Nb_2O_5 films were investigated using a Philips (PW 1730) X-ray diffractometer with monochromatic $\text{Cu-K}\alpha$ radiation (45 kV, 400 mA). The XPS study was carried out on a Kratos (XSAM 800) spectrometer using $\text{Mg-K}\alpha$ radiation as an excitation source ($h\nu=1253.6$ eV). All spectra were referenced to the C-1s peak for adventitious carbon, which was assigned to the value of 285.0 ± 0.1 eV.

Cyclic voltammetric measurements were performed with WO_3 coated ITO working electrode. A pH 2, H_2SO_4 solution was used as an electrolyte. Cyclic voltammetric measurements were made using a digital coulometer (PAR) and Hewlett-Packard X-Y chart recorder. For the cyclic voltammetry measurements a potential scan rate of 20 mV/s was used throughout. Single scan or multi-scan cyclic measurements were performed from potentials ranging from +0.5V to -0.6 V. Thickness measurements were performed on a Dektak II surface profiler having a maximum resolution of 5 nm / 100 nm.

3. Results and Discussion

Thickness profile measurements of the sol-gel deposited tantalum and niobia films indicate that the average thickness of a single coating are 88 and 65 nm respectively. The coating used in this study were deposited using six coating cycles. The thickness of the resulting films are about 270 and 380 nm respectively. These films were examined by scanning electron microscopy and exhibited a smooth and adherent surface with very few pinholes or microcracks over a large region of the film. Multiple coating increased thickness, but did not affect the uniformity of the film. XRD patterns of the tantalum and niobia films used in this study were typical of the amorphous state without any diffraction peak characteristics of crystalline Ta_2O_5 or Nb_2O_5 . Figure 1 shows a broad energy scan XPS spectrum of the tantalum and niobia films on a soda-lime glass substrate. The stoichiometry of the films are given as the ratio of oxygen to metal (O:Ta) or (O:Nb) were found to be 4.8 : 2 and 4.9: 2 respectively. This is close to the ratios frequently found for stoichiometric Ta_2O_5 and Nb_2O_5 ¹³. We also observed that the atomic concentration of the films deposited on different substrates were almost the same (within $\pm 2\%$). The high C-1s peak at a binding energy of 285.0 ± 0.1 eV is the usual peak for the sol-gel deposited films and associated with the residual organics and adventitious carbon. When the surface layers were bombarded with Ar^+ ions, only a very small carbon peak remained, indicating a small amount of carbon was present. The amount was difficult to measure.

The peak positions for tantalum films for the Ta-4f core level exhibits two peaks centered at 29.3 ± 0.1 and 27.1 ± 0.1 eV. These peaks can be assigned to the $4f_{5/2}$ and $4f_{7/2}$ core levels of Ta(V) corresponding to Ta_2O_5 ¹³. The bonding states of niobia films were deduced by observing XPS data of Nb-3d core level and O-1s photoelectron peaks. Double peaks are seen for Nb-3d core levels centered at 209.7 ± 0.1 and 207.3 ± 0.1 . They reflect the $3d_{3/2}$ and $3d_{5/2}$ doublets and indicate that the film is close to stoichiometric Nb_2O_5 . The O-1s peaks centered at the binding energies for tantalum are 530.8 ± 0.1 eV and niobia 530.6 ± 0.1 eV. These energies are characteristic of the O^{2-} anion in oxides¹³.

The tantalum and niobia films were voltammetrically tested in the ambient environment in a special test cell. During the cycling procedure transmission data were recorded after 10 cycles. Figure 2 shows the optical switching properties of the two layer metal oxide (Ta_2O_5 or Nb_2O_5 on WO_3) at $\lambda = 550$ nm. It can be seen in Fig. 2 that sputtered tungsten oxide film together with sol-gel deposited tantalum or niobia film gives transmittance change between the colored state and bleached state. The observed transmittance change of tantalum films are higher than the niobia films. The photopic weighted transmittance change and solar weighted transmittance change are $T_p = 85.2\% - 21.8\%$ and $T_s = 75.7\% - 14.2\%$ for tantalum films and $T_p = 85.3\% - 35.2\%$ and $T_s = 75.8\% - 28.1\%$ for niobia films.

Figure 3 shows a cyclic voltammogram for an EC electrode consisting of ITO / WO_3 / Ta_2O_5 or Nb_2O_5 . Shown for reference is an uncoated tungsten oxide film. These results indicate that protons are being intercalated and deintercalated into the tungsten oxide layer. A strong coloration and bleaching is noted with the cyclic potential. Both the tantalum and niobia layers are shown to be transporting ions. Successive cycles are superimposed without any apparent degradation in the change capacity of the film. A nearly single response is observed during cycling of the films. This shows the films are chemically stable and reversible. We also observed that the reversal of the coloration process is at a lower potential for niobia films.

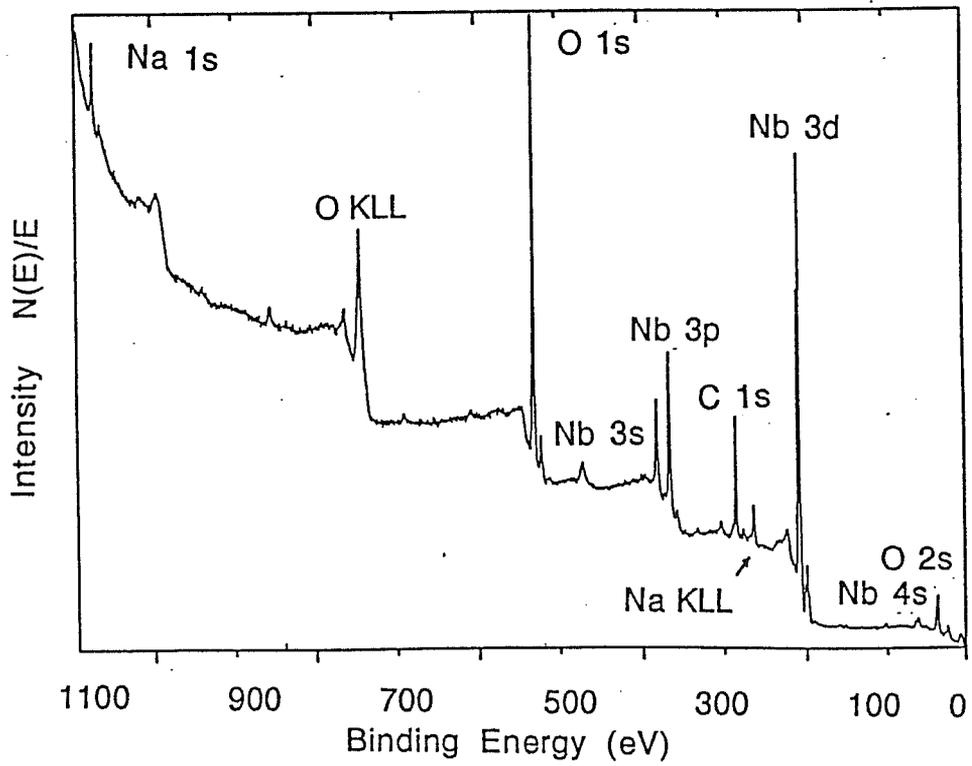
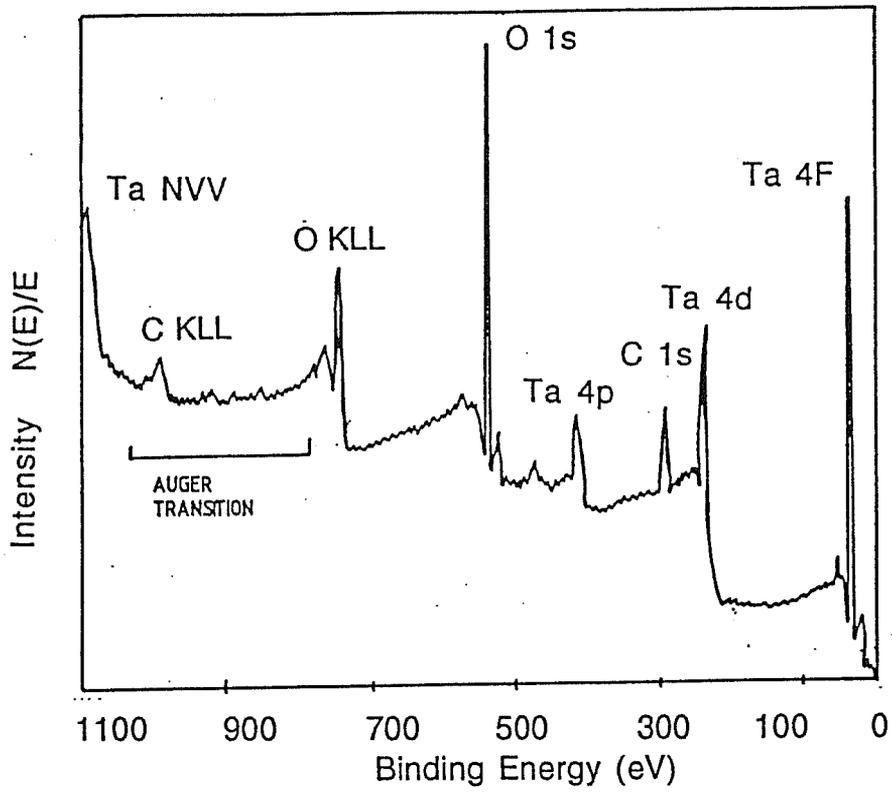


Fig. 1. XPS survey spectrum of tantalum and niobia films.

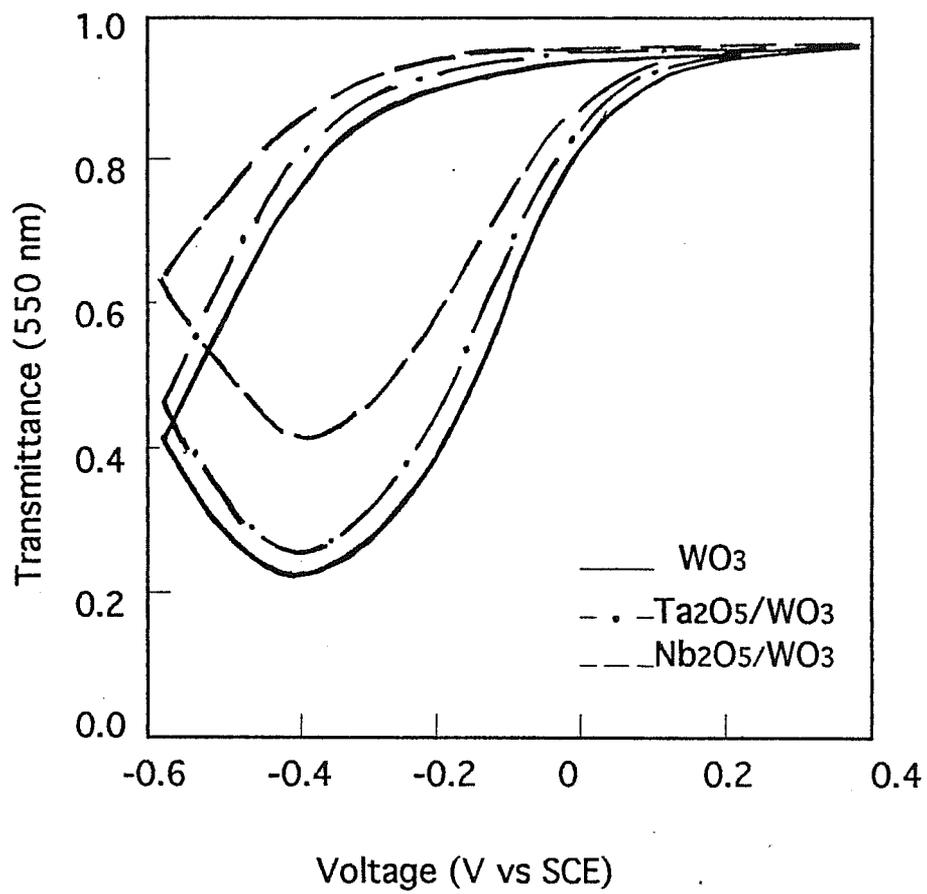


Fig. 2. The monochromatic (550 nm) transmittance - voltage response of tantalum and niobia films on a WO_3 / ITO electrode. For reference, the response for an uncoated WO_3 is shown.

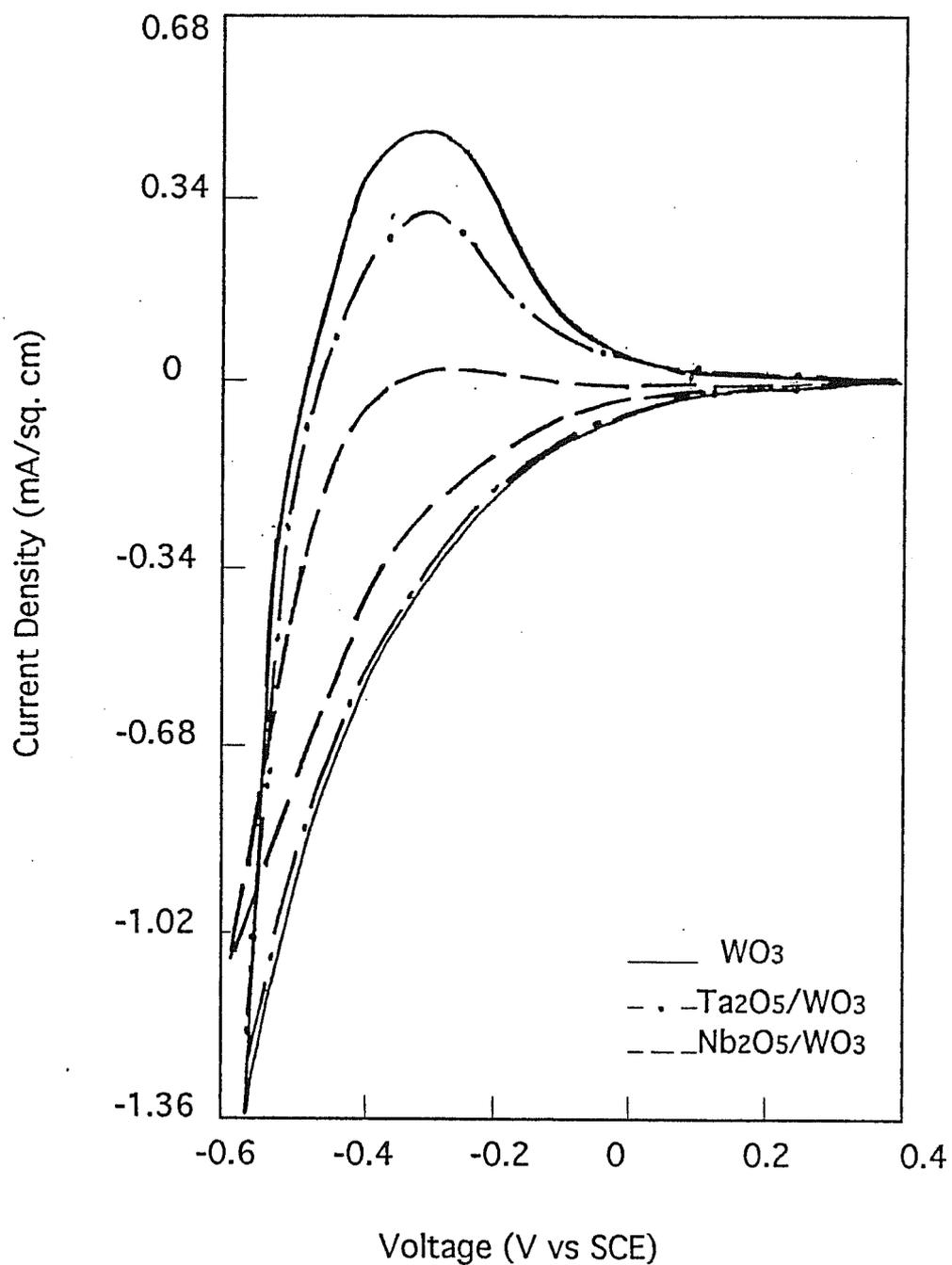


Fig. 3. Cyclic voltammogram for a liquid EC cell using Ta₂O₅ (thickness 210 nm) and Nb₂O₅ (thickness 250 nm) on a WO₃ / ITO as the working electrodes.

Ionic conductivity measurements were determined from A. C. Impedance Spectroscopy, the measurements were made over the frequency range of 100 mHz to 20 Hz. The impedance data was plotted on a complex plane for tantalum and niobia films as shown in Figs. 4 (a) and (b). A simplified equivalent circuit representing the sample was used to calculate ionic conductivity (shown in the inset in Fig. 4) where R_e is the ohmic resistance of the electrodes, C_d is the double layer capacitance of the electrode / electrolyte interface, R_i is the ionic resistance arising from the diffusion of protons, C_g is the geometric capacitance between electrodes. From the impedance analysis, the intersection of the high frequency semicircle with Re (Z) axis represents R_i ionic resistance. These values were used to determine protonic resistance of tantalum and niobia films together with geometric factors (film thickness and the electrode area)¹⁴. The semicircle observed at high frequencies, which is related to the charge transfer process is well separated from the low frequency part of the diagram corresponding to the proton diffusion into the electrode material. The values of protonic conductivity are $4.4 \times 10^{-6} \text{ Scm}^{-1}$ for tantalum films at 0.6 V / SCE and $3.2 \times 10^{-7} \text{ Scm}^{-1}$ for niobia films at 0.7 V /SCE at room temperature. The measured ionic conductivity values agree well with the literature values⁵.

After impedance analysis, the chemistry of the tantalum and niobia films were examined by XPS. Figure 5 shows the XPS spectra for Ta_2O_5 in both the oxidized and reduced states. Figure 6 shows the XPS spectra for a Nb_2O_5 film in the reduced and oxidized states. In the XPS spectra of the reduced Ta_2O_5 , corresponded to $\text{H}_{0.3}\text{Ta}_2\text{O}_5$, and Nb_2O_5 , was $\text{H}_{0.2}\text{Nb}_2\text{O}_5$, a slight shift of the energy levels were observed after insertion of protons. The shift of energy levels are lower by 0.3 eV and 0.4 eV than that observed in as-deposited tantalum and niobia films. After extraction of H^+ the peaks corresponding to Ta-4f and Nb-3d core levels are again observed at the same binding energy values. Also, after proton insertion, the O-1s peaks are shifted from 530.5 ± 0.1 eV to a lower binding energy value of 530.2 ± 0.1 eV in tantalum. A similar shift is observed for niobia where the peaks shift from 530.4 ± 0.1 eV to 530.1 ± 0.1 eV after insertion of protons. After extraction of H^+ , the O-1s peaks are observed at 530.5 ± 0.1 eV (tantalum) and 530.4 ± 0.1 eV (niobia), the same value before H^+ insertion. We also observed a shoulder formation, at higher binding energy, in the O-1s peaks in both oxides after protonation. The shoulder occurred at 532.1 ± 0.1 eV for tantalum and at 531.7 ± 0.1 eV for niobia. This shoulder is associated with OH^- ¹⁵. This could signify a reaction with the water of hydration $\text{Ta}_2\text{O}_5 \cdot x\text{H}_2\text{O}$ in the oxide or the formation of a tantalum hydroxide, $\text{Ta}(\text{OH})_5$ during reduction. At the low applied potentials a water reaction is favored. The results of the XPS and the impedance spectroscopy analysis leads us to conclude that the insertion and extraction process is a diffusion controlled reversible process. It also appears that water plays an important role in the supply and transport of protons.

4. Conclusions

We found that the sol-gel spin coated films could make acceptable ion conductor films for use in electrochromic devices. Films of about 300 nm could be made from 8 spin coatings. These films were found to be amorphous and close to the stoichiometry of Ta_2O_5 and Nb_2O_5 respectively. From impedance measurements we conclude that the tantalum films have higher ionic conductivity than amorphous niobia films. Ta_2O_5 films had room temperature proton conductivities of $4.6 \times 10^{-6} \text{ Scm}^{-1}$ and Nb_2O_5 had $3.2 \times 10^{-7} \text{ Scm}^{-1}$. Although the protonic conductivity of sol-gel deposited tantalum and niobia films is two orders of magnitude lower than ionic conducting polymer films it is still adequate for devices. In order to estimate the compatibility of these ion conductors for EC devices, we deposited tantalum oxide and niobium oxide films deposited on sputtered WO_3 films. Charge balance and coloration characteristics were investigated during voltammetric cycling in a pH 2 liquid electrolyte. The photopic weighted transmittance change and solar weighted transmittance change were $T_p=85.2\% - 21.8\%$ and $T_s=75.7\% - 14.2\%$ for tantalum films on tungsten oxide. For niobia on tungsten oxide the values were $T_p=85.3\% - 35.2\%$ and $T_s= 75.8\% - 28.1\%$. In view of EC device application sol-gel deposited Ta_2O_5 and Nb_2O_5 are both promising candidates as proton conductors.

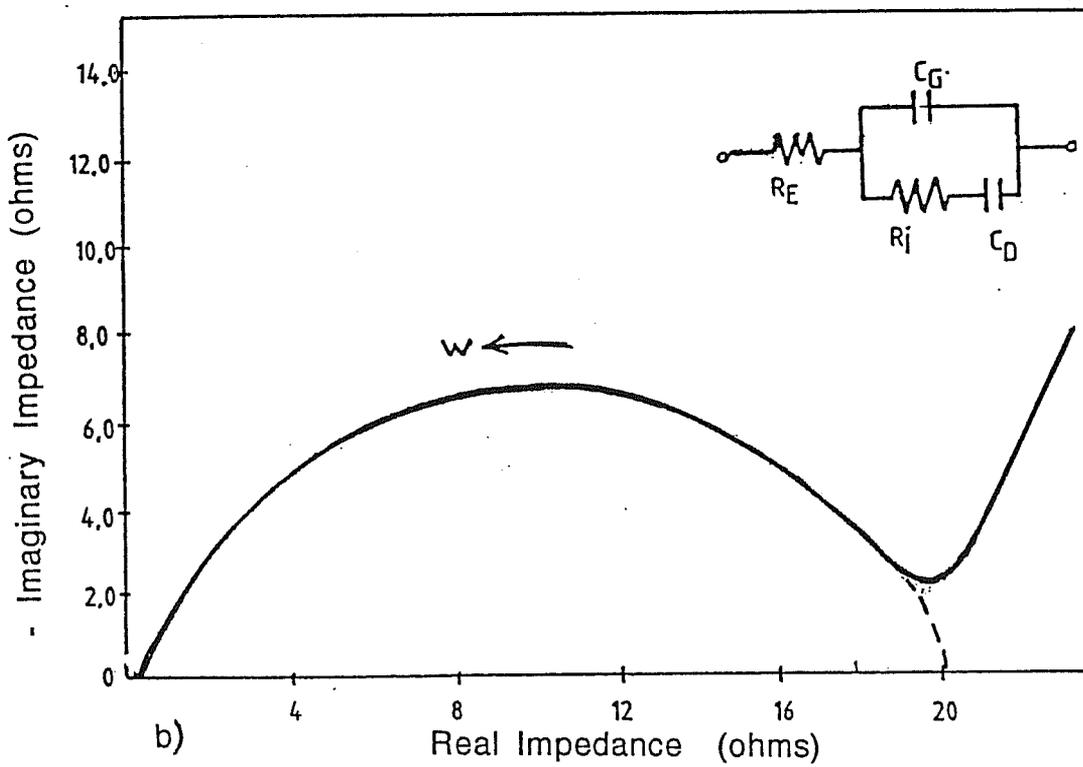
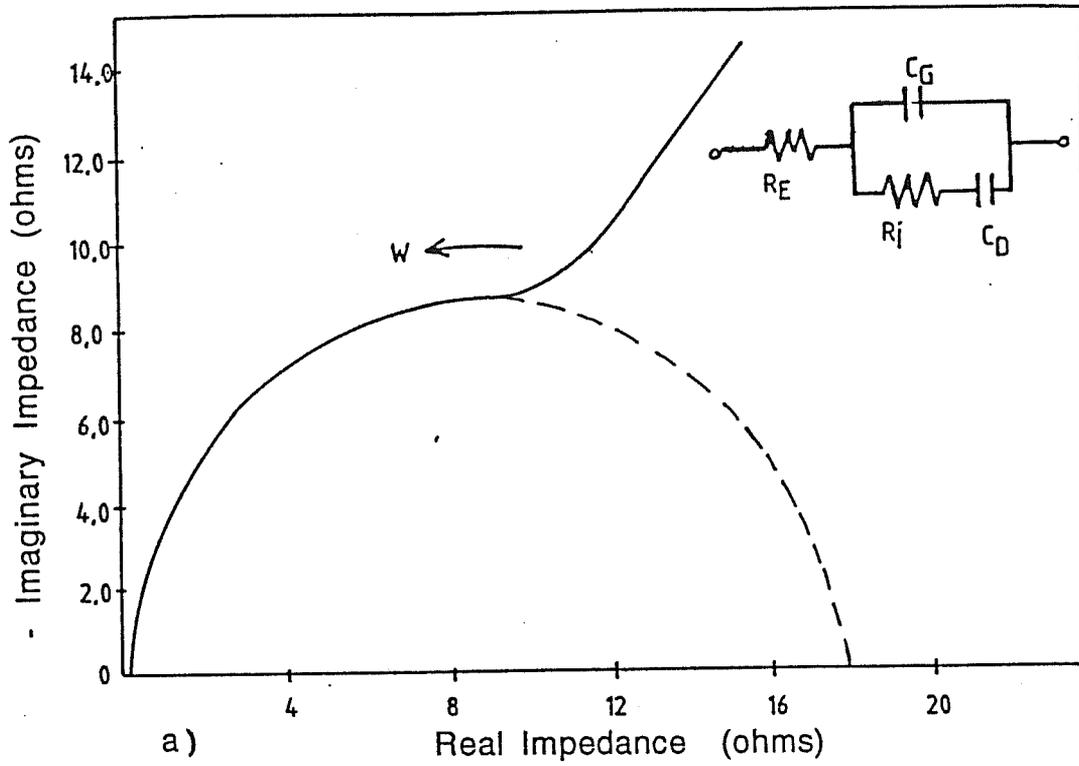


Fig 4. Impedance plots of amorphous (a) Ta_2O_5 (270 nm thick), and (b) Nb_2O_5 (380 nm thick) films on ITO. The inset shows the equivalent circuit used for analysis.

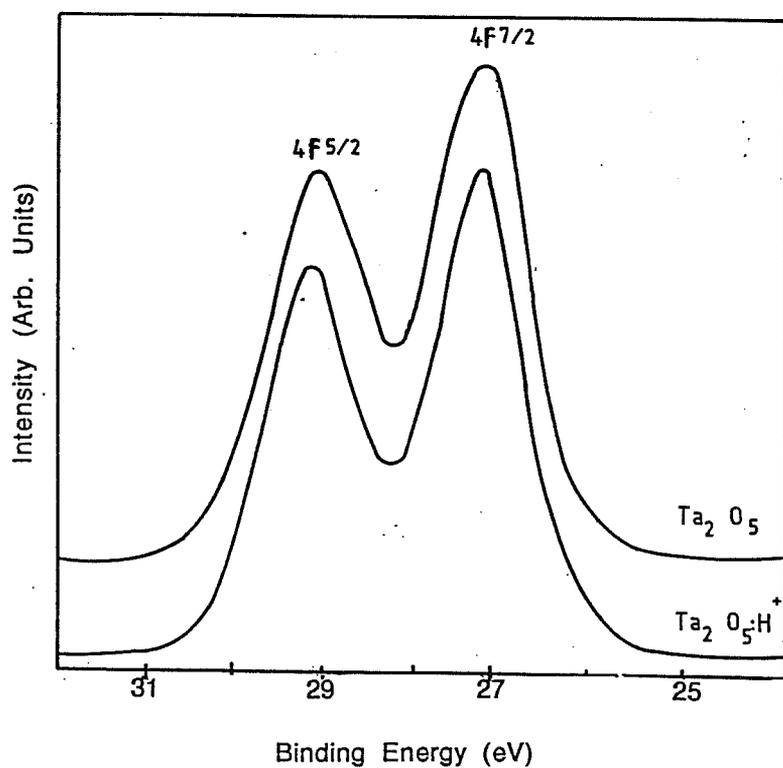
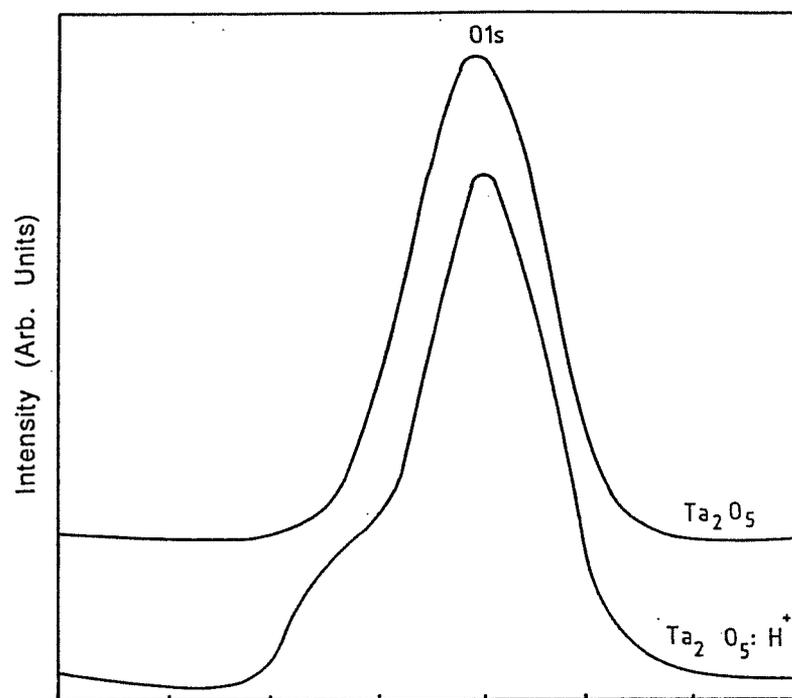


Fig.5. XPS spectra of a 250 nm thick Ta₂O₅ film . Shown are the O-1s peaks and the Ta-4f peaks. Note the hydroxyl shoulder during reduction.

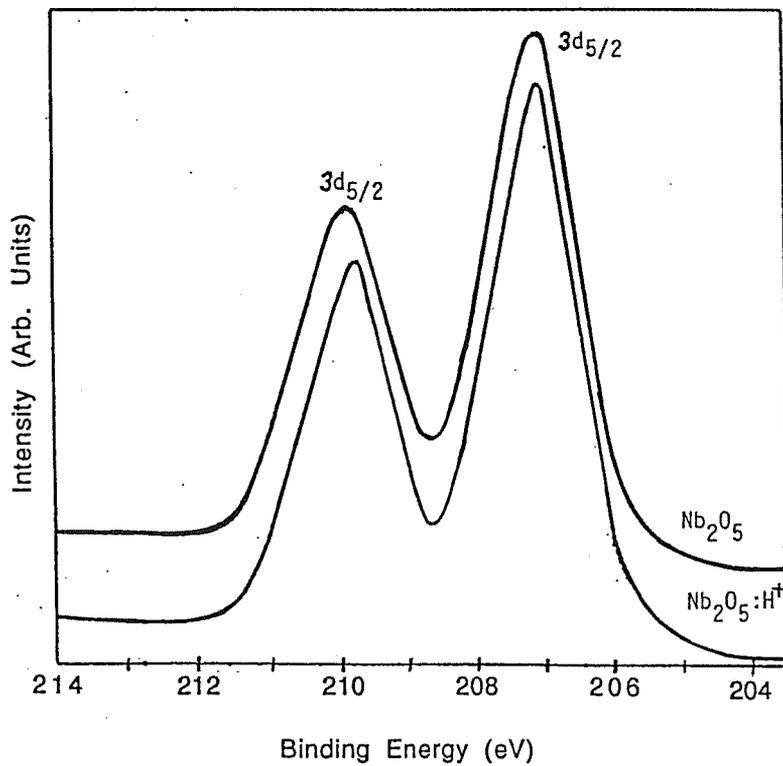
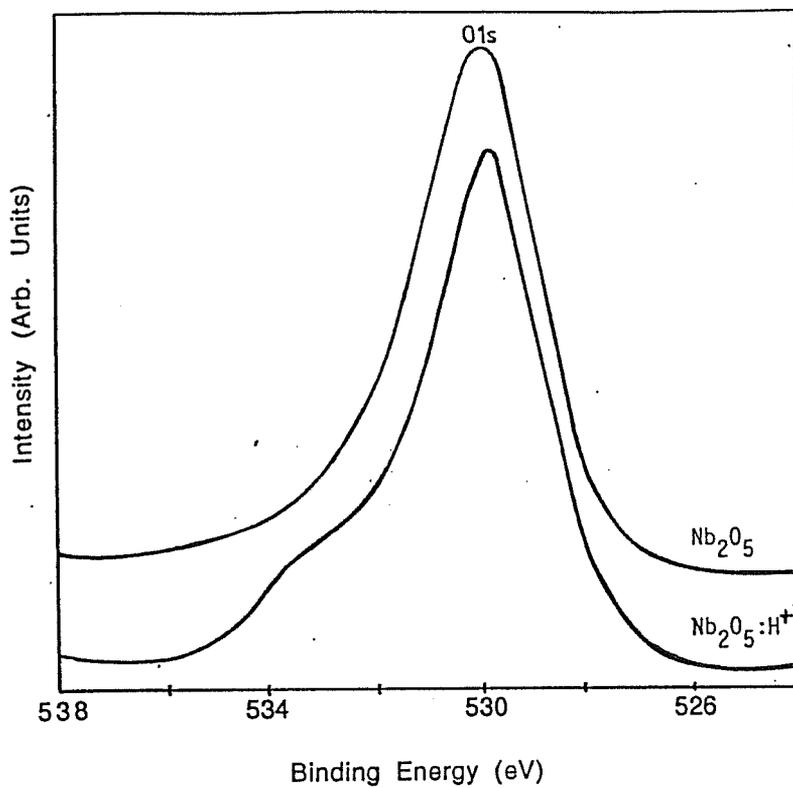


Fig. 6. XPS spectra of a Nb_2O_5 film (280 nm thick). Shown are the O-1s peaks and the Nb-3d peaks. Note the hydroxyl shoulder formation during reduction.

5. Acknowledgments

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