

Characterization of Tantalum Oxide Films Prepared by Sol-Gel Process for Electrochromic Devices

Nilgun Ozer, Yongxiang He and Carl M. Lampert
Lawrence Berkeley Laboratory, Building Technology Program, Energy & Environment
Division (MS 62-203), University of California, Berkeley CA 94720

Abstract

Tantalum oxide films were prepared by sol-gel process using tantalum ethoxide $\text{Ta}(\text{OC}_2\text{H}_5)_5$. The dependence of deposition conditions (*i.e.* composition of polymeric solutions and spinning rate) on ionic conductivities for tantalum oxide films were studied. The best results achieved for films fabricated by the spin coating technique were from clear polymeric solutions. These films had low packing density $\rho=3.2 \text{ g/cm}^3$ and good proton conductivity (about $10^{-6} \Omega^{-1} \text{ cm}^{-1}$). X-ray photoelectron spectroscopy (XPS) was used for studying the compositions of the tantalum oxide films. We report on the use of tantalum oxide films as ion conductors in devices consisting of $\text{WO}_3/\text{Ta}_2\text{O}_5/\text{H}^+$ ion storage polymer structure. We found tantalum oxide to have very good properties for proton device applications.

1. Introduction

During the last decade several inorganic ion conductors have been investigated for their use in various solid state electrochemical devices including batteries and electrochromic (EC) devices. While crystalline ionic conductors were initially more widely studied, greater efforts have now been directed towards the investigation of amorphous ion conductors. Amorphous ion conductors have advantages of isotropic conduction (due to the absence of grain boundaries), wide composition flexibility, and high ionic conductivity coupled with low electronic conductivity [2-3]. In general practice, inorganic ion conducting layers have been deposited by vacuum evaporation and sputtering [4-5].

Recently, the sol-gel deposition method has been investigated as a new preparation technique for various kinds of ionic conductors [5-6]. The sol-gel method allows for the formation of oxides using low temperatures and very low capital investment compared to vacuum processes. Also deposition rates can be much higher. Since silica gels prepared using the sol-gel method exhibit high protonic conductivity, application of the method to solid state ionics has become a very attractive challenge in recent years [7]. A large number of M-OH (M: Si, Ta, Zr) groups present in the metal oxide-gel system are useful for designing proton conductors [8] composed of metal oxide gels as a host material and appropriate proton conductors as a guest material.

For the development of large area EC devices it is important to have high ionic conductivity of the solid electrolyte [9]. To fabricate EC devices with good response times, the ionic conductivity should be higher than $10^{-7} \Omega^{-1} \text{ cm}^{-1}$, for display devices the ionic conductivity should be at least $10^{-4} \Omega^{-1} \text{ cm}^{-1}$ [1].

Although proton conduction in tantalum oxide is important to the development of EC devices, very few reports have been published on the subject [4, 10-11], none of them used the sol-gel method for deposition.

In our work, we report the preparation of tantalum oxide films by the sol-gel method and the measurement of the proton conductivity for the samples in the film form. In order to

estimate the capability of these sol-gel deposited layers as a solid ion conductor we report the EC properties for cells using tantalum oxide films with sputtered WO_3 films as an active electrochromic layer. The structural properties of the films were investigated by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). Charge balance and coloration characteristics were investigated during voltammetric cycling in a pH 2 electrolyte. Optical analysis were done for colored and bleached films in the visible spectral region.

2. Experimental Methods

2.1 Preparation of solutions

The sol-gel film was prepared according to the process flow chart in figure 1. Solution A was prepared by mixing tantalum ethoxide, $\text{Ta}(\text{O}-\text{C}_2\text{H}_5)_5$ (40 mmol), and absolute ethanol, $\text{CH}_3\text{CH}_2\text{OH}$ (250 mmol), and stirring for 30 minutes. Solution B was prepared by mixing deionized water (200 mmol) and glacial acetic acid CH_3COOH (1.6 mmol). Two cubic centiliters of solution B was then slowly added to solution A with slow stirring. After the exothermic reactions had finished (hydrolysis followed by polycondensation) the solution was covered with a plastic wrap in which pinholes were punched. After stirring the mixture for 2 hours, a clear polymerized solution was obtained.

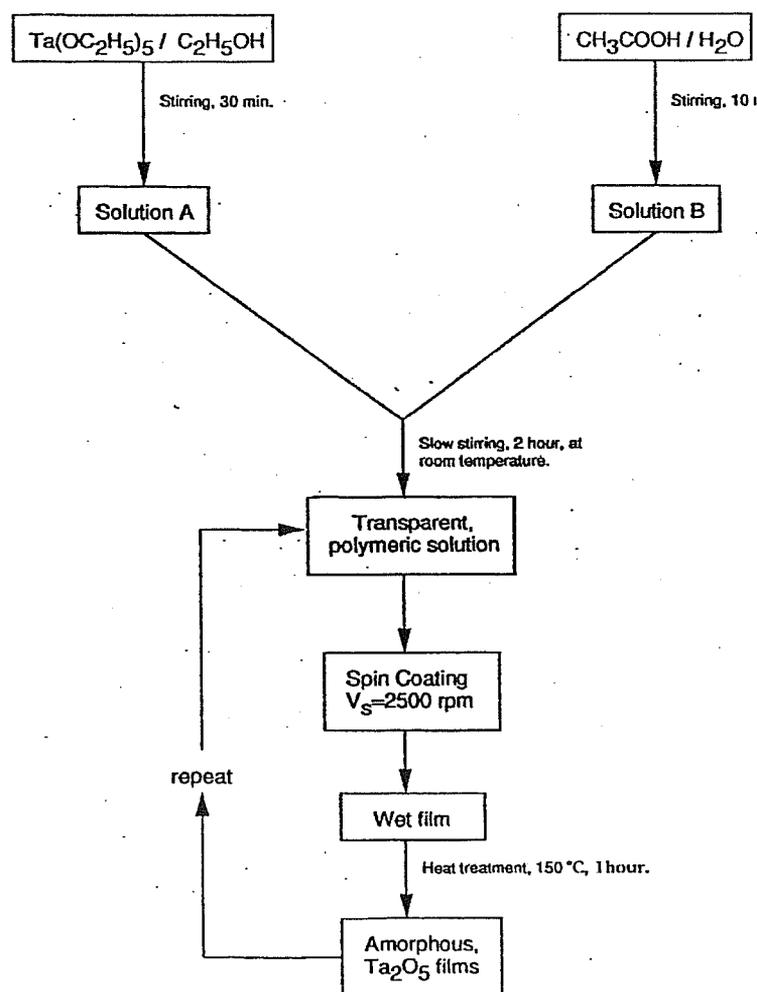


Fig. 1. Flow Chart of Fabrication Process

The viscosity of the solutions were adjusted by adding ethanol. The pH value of the solutions were kept to values below 1.5 in order to maintain the viscosity at a constant amount during 10 to 20 days. The solution was considered stable, as it did not exhibit gelation or precipitation for at least 1 month.

2.2 Preparation of Coatings

Tantalum oxide coatings were deposited by spin-coating with spinning speeds ranging from 1500 to 3000 rpm. The best uniformity was obtained at a spinning rate of 2500 rpm. The supporting substrates ($5.0 \times 3.0 \times 0.1 \text{ cm}^3$) were first washed with very dilute chromic acid and then rinsed with double distilled water. Next the substrates were ultrasonically cleaned with GR grade acetone and dried in air. The substrates employed were soda lime glass, indium tin oxide (ITO) glass (sheet resistance 10Ω), and ITO coated with WO_3 on glass (Donnelley Corp. Holland, MI). The solution was coated uniformly over the substrate surface by spinning the substrate at a controlled speed of 2500 rpm. After coating, the substrate was dried in air at room temperature for 10 minutes leaving a uniform gel film. The coated substrate was then heated at a rate of 4°C min^{-1} up to 150°C for 1 hour in an electrical furnace to form the Ta_2O_5 films. The preparation of thick films required 10-15 repetitions of the procedures described above from spinning through to tempering. The fabricated coatings were transparent, hard, durable, and stable.

2.3 Characterization of the Coatings

After the films were deposited they were exposed to the ambient atmosphere prior to the optical measurements. Scanning electron microscopy, X-ray diffraction, and X-ray photoelectron spectroscopy, impedance spectroscopy, and cyclic voltammetry measurements were made on each film. Transmission measurements on Ta_2O_5 films were made over a 270-1800 nm wavelength range using a Perkin and Elmer model Lambda 9 double beam spectrophotometer. In situ UV-VIS spectroelectrochemical properties were examined for the cell equipped with ITO/ WO_3 / Ta_2O_5 coated glass working electrode, $\text{SnO}_2:\text{F}$ glass counter electrode, and 0.1 M H_2SO_4 electrolyte. A saturated calomel electrode (SCE) served as a reference electrode. The surface morphology of the Ta_2O_5 films was observed by JEOL model JSM 6400 scanning electron microscope. A Ag coating was applied onto the samples to avoid charging of the surface. The structures of Ta_2O_5 films were investigated by Philips model PW 1730 X-ray diffractometer with monochromatic $\text{Cu-K}\alpha$ radiation (45 kV, 40 mA). The XPS study was carried out on a Perkin-Elmer model ESCA 500 spectrometer using $\text{Mg-K}\alpha$ radiation as an excitation source ($h\nu=1253.6 \text{ eV}$). The electrochemical characterization was performed with a BAS potentiostat/coulometer (model CV 27). A new software program called Electrochromics for Windows (ECW™ Data Preference Dearborn Heights, MI) was used to monitor the I-V characteristics. The ionic conductivity measurements were carried out by an ac-complex impedance technique with an impedance gain-phase analyzer and computer controlled potentiostat-galvanostat, driven by ZPLOT software (Scribner Associates Inc. Charlottesville, VA). The impedance data was obtained in the frequency range of 10 Hz-10 kHz. Ionic conductivity was determined for coatings in the cell configuration shown in figure 2. A working electrode consisted of a roughly 4.8 cm^2 ITO / Ta_2O_5 covered glass slide. A platinum plate served as a counter electrode and SCE as a reference electrode. All potentials are relative to this electrode. In the cyclic voltammetry measurements a potential scan rate of 20 mV/s was used throughout. Single scan or multi scan cycling measurements were performed within and at potentials +0.6 and -0.6 V respectively. Thickness measurements were performed on a Dektak II surface profiler having a maximum resolution of .5 nm / 100 nm

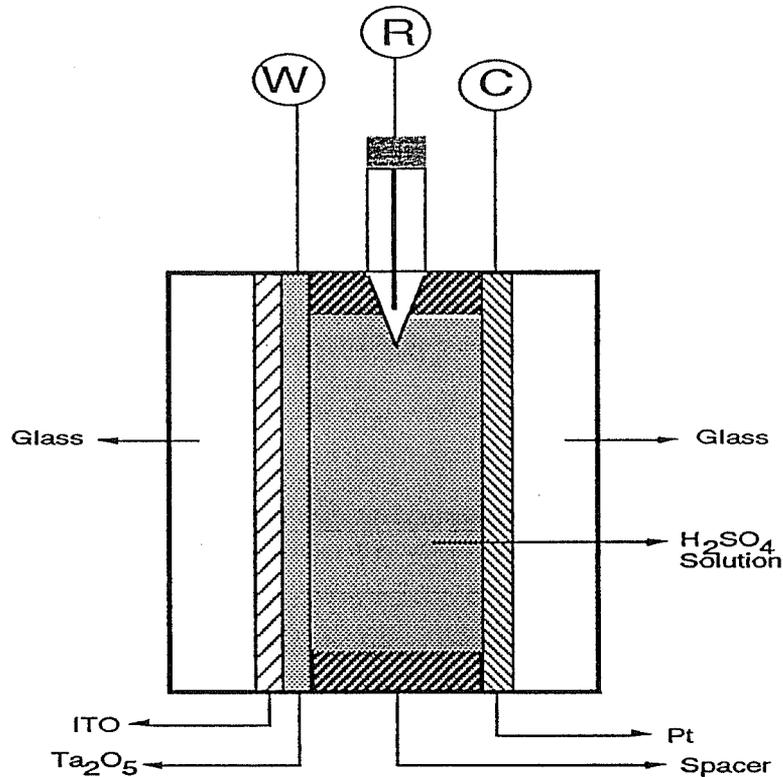


Fig. 2. Schematic Representation of the impedance test cell.

3. Results and Discussion

3.1 Formation of Tantalum Oxide Films

In order to produce transparent and uniform Ta_2O_5 films, the solution used for coating has to be clear. This was achieved by proper chemical formulation and solution preparation procedures. After experimentation with variation in solvent, alkoxide content, and type of catalyst had been done, high quality transparent films were reproducibly deposited onto different substrates. Deposition was conducted by a spin coating technique at a spinning rate of 25000 rpm. Films of sufficient thickness were achievable by multiple coatings of the substrate. The repeated spinning-firing cycles at a spinning speed of 2500 rpm produced a highly transparent thin film with uniform structure. These films were examined by scanning electron microscopy and exhibited very few pinholes or microcracks over a large region of the film. Multiple coating increased changes in thickness, but did not affect the uniformity of the film. Figure 3 shows the change in film thickness as a function of number of coatings or layers for constant firing conditions.

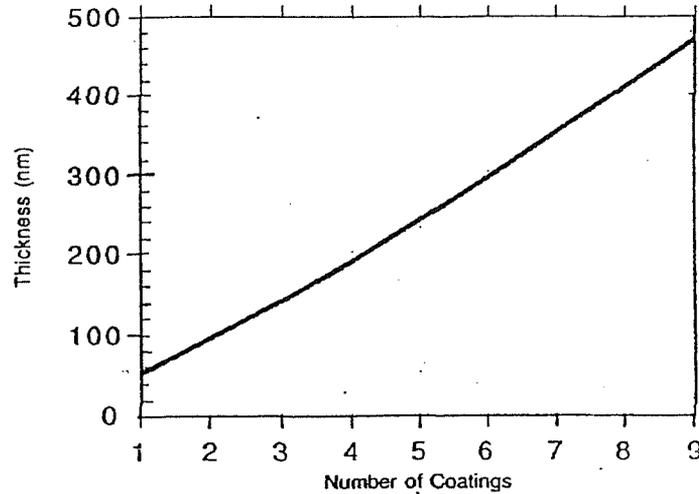


Fig. 3. Variation in film thickness with number of spun on layers. The films are deposited on soda-lime microscope slide glass.

XRD patterns of the tantalum oxide films used in this study were typical of the amorphous state without any diffraction peak characteristics of Ta_2O_5 crystals. Figure 4 shows a broad scan XPS spectrum of a tantalum oxide film on a soda-lime glass substrate. The stoichiometry of the films is given as the ratio of oxygen to tantalum (O:Ta) and was found to be 2:48. We also observed that the atomic concentration of the films deposited on different substrates were almost the same (within 2%). The C1s peak at a binding energy of 285 ± 0.2 eV is the usual peak associated with hydrocarbon surface contamination. This peak is used as an energy reference.

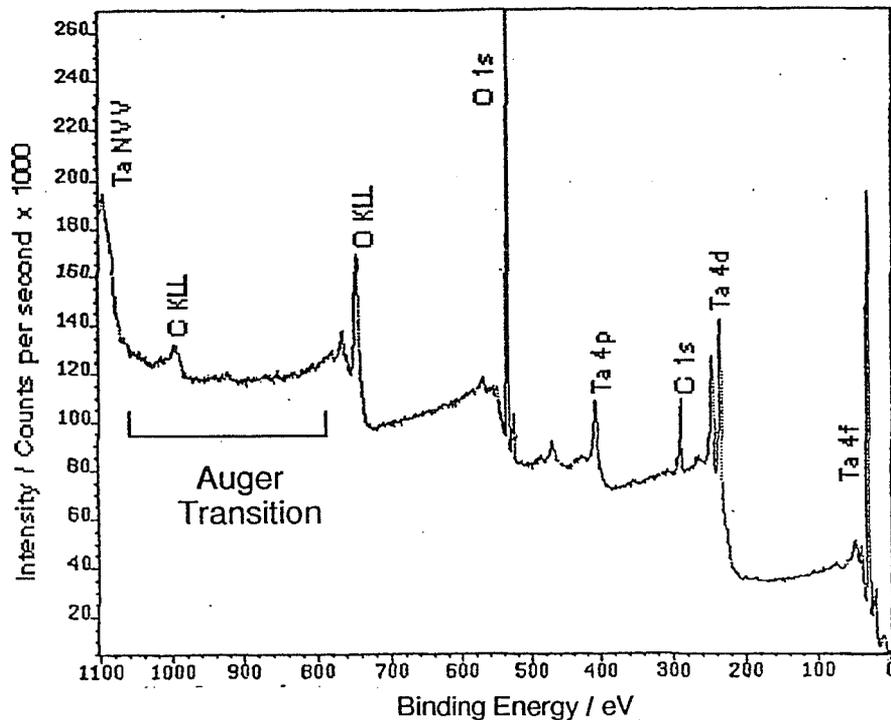


Fig. 4. Wide range XPS spectrum of tantalum oxide films

The corresponding peak positions for tantalum oxide films are listed in Table 1. Figure 5 shows the XPS region around the Ta(4f) core level for Ta₂O₅ films. This region exhibits two peaks centered at 29.3 and 27.1 eV that can be assigned to the 4f_{5/2} and 4f_{7/2} core levels of Ta⁵⁺ [12]. O(1s) peaks of the Ta₂O₅ films, shown in figure 6, always show composite bands indicative of the coexistence of different oxygen chemical bonding. Indeed, curve fitting methods in which the O(1s) spectrum was fitted to a sum of weighted Lorentzian-Gaussian peaks with a linear sloping background by means of a least squares fitting program [13] show two components. Low binding energy (LBE) and high binding energy (HBE) components peak at 530.3 and 531.8 eV respectively. A high binding energy value (523.8 eV) indicates the presence of a low amount of organic remnant contamination. The binding energy of 530.8 eV is characteristic of the O²⁻ anion in oxides [14].

Table 1. Binding energies for Ta₂O₅ samples

Parameter	Film 3 (d=82 nm)	Film 8 (d=190 nm)	MOCVD Ta ₂ O ₅ (12)
Ta 4f _{7/2} (eV)	26.9	27.1	26.9
Ta 4f _{5/2} (eV)	29.2	29.3	29.1
(4f _{5/2} -4f _{7/2}) (eV)	2.3	2.2	2.2
Ta 4d _{5/2} (eV)	230.8	230.9	-
Ta 4d _{3/2} (eV)	232.8	232.9	-
(4d _{3/2} -4d _{5/2}) (eV)	2.0	2.0	-
O 1s LBE (eV)	530.2	530.3	-
O 1s HBE (eV)	532.1	531.8	532.2
Ratio O _{1s} for total O 1s (LBE+HBE)	2.49	2.47	2.5

Ta : O

0.42

0.41

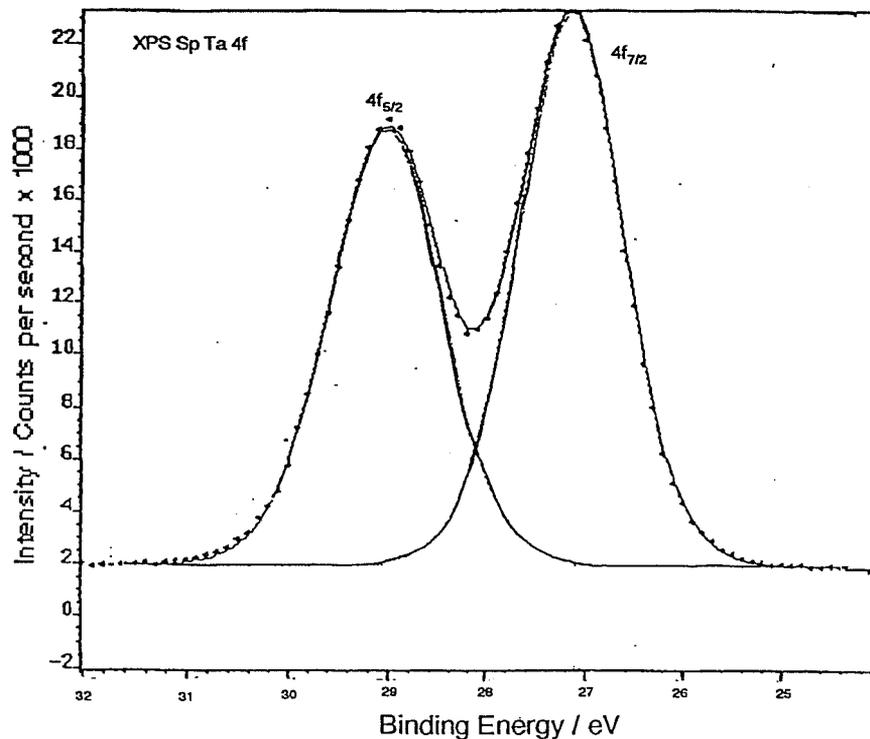


Fig. 5. XPS spectrum of Ta₂O₅ films in the region of Ta(4f).

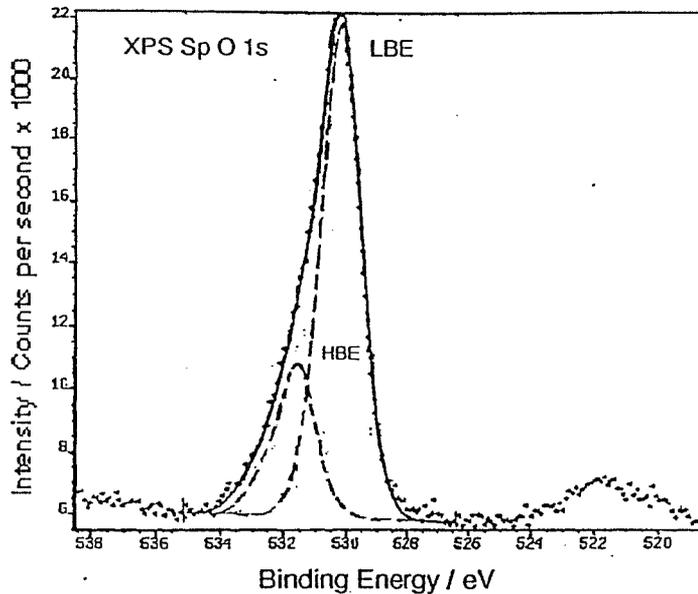


Fig. 6. Typical O(1s) spectra of a Ta_2O_5 film. The continuous curve represents experimental data. Fitted component and their sum are represented by broken curves and dots respectively.

3.2 Electrochemical Characterization

Sol-gel deposited Ta_2O_5 films were voltammetrically examined in the ambient environment in a special test cell; a pH=2 H_2SO_4 solution was used as an electrolyte. Voltammetric cycling was performed with computer-controlled equipment. During the cycling procedure transmission of the samples was measured at $\lambda=550$ nm. Voltage, current, charge, and transmission data were recorded during ten cycles before and after and aging period of 3600 cycles under conditions as described in section 2.3. Figure 7 shows the optical switching properties of the two layer metal oxide (Ta_2O_5 on WO_3) at $\lambda=550$ nm. It can be seen in figure 7 that the sputtered tungsten oxide film together with sol-gel deposited tantalum oxide film gives a strong transmittance change between the colored state and bleached state. The photopic weighted transmittance change and the solar weighted transmittance change are $T_p=85.1\%-21.9\%$ and $T_s=75.6\%-14.2\%$ respectively.

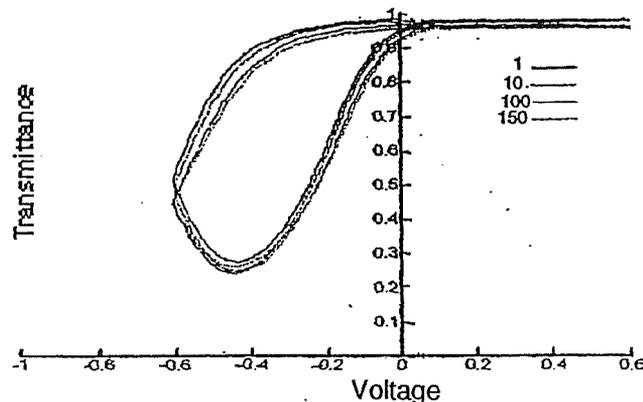


Fig. 7. The monochromatic (550 nm) transmittance-voltage response of sol-gel spin coated Ta_2O_5 film on a WO_3/ITO electrode. Cycles 1 through 150 are show at selected intervals.

Figure 8 shows a cyclic voltammogram for an EC electrode consisting of ITO/ $\text{WO}_3/\text{Ta}_2\text{O}_5$. Figure 9 shows the charge density as a function of time for Ta_2O_5 film (thickness 190 nm) deposited on ITO/ WO_3 glass substrates. These examinations suggest that application of a cathodic potential against calomel electrode results in electrochemical proton insertion from the Ta_2O_5 layer to the WO_3 layer and is associated with the coloration process. Anodic current corresponds to the bleaching processes. Successive cycles are superimposed without any apparent degradation in the charge capacity of the film. A nearly single wave is observed during both processes. Showing that the electrochemical insertion is reversible.

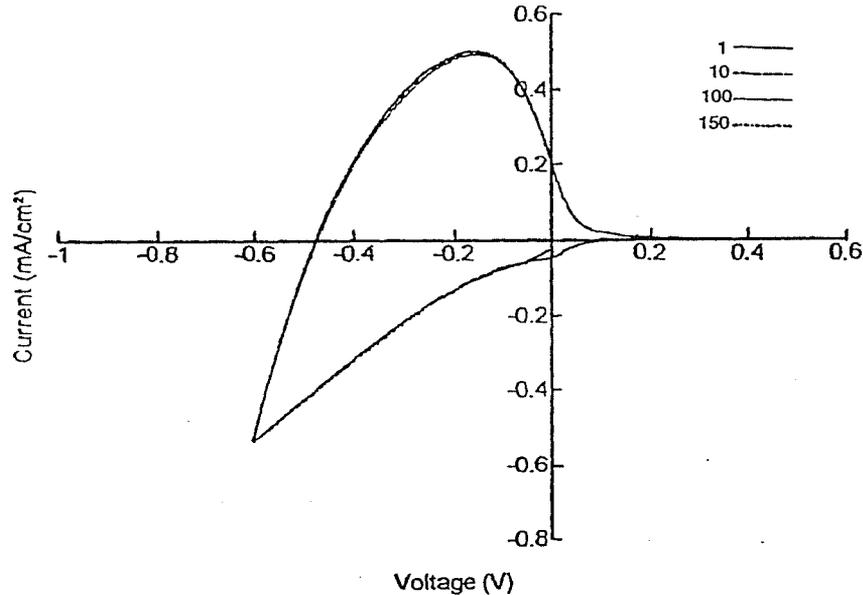


Fig. 8. Cyclic voltammogram for the EC cell using sol-gel deposited Ta_2O_5 film (thickness 190 nm) on a WO_3/ITO electrode. Shown are selected cycles from 1-150.

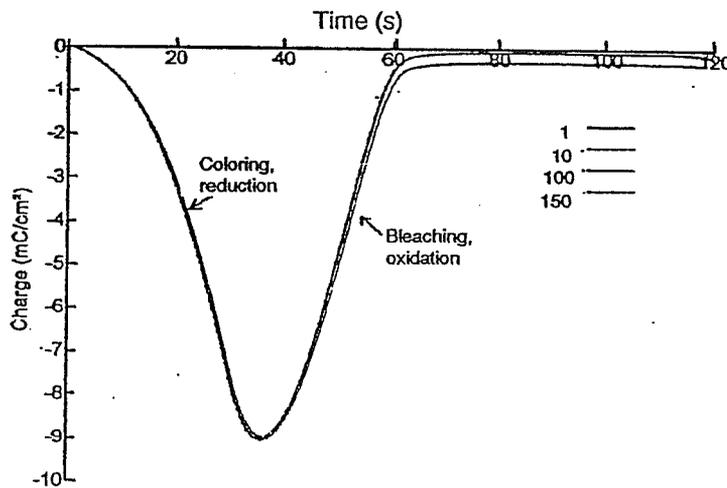


Fig. 9. The charge time response of sol-gel spin coated Ta_2O_5 film on WO_3/ITO electrode. Shown are selected cycles from 1-150.

Ionic conductivity measurements were determined from A.C. Impedance spectroscopy, the measurements were made over a frequency range of 10 Hz to 10 kHz. The impedance data was plotted on a complex plane and is shown in figure 10a. All samples tested gave nearly the same characteristics. The equivalent electric circuit is shown in fig. 10b; where R_e is the ohmic resistance of the electrolyte and electrode, C_d is the geometric capacitance between electrodes, and R_i is the charge transfer resistance.

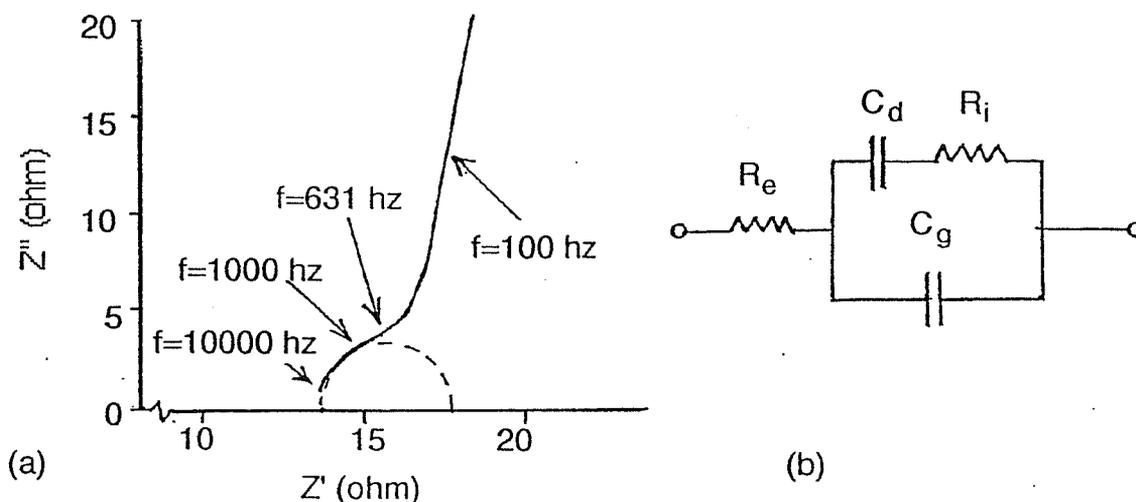


Fig. 10. a) Typical impedance plot of tantalum film ($0.4 \mu\text{m}$ thick, electrode area is 4.8 cm^2 , at room temperature).
 b) Modeled electric equivalent circuit for the electrochromic cell with charge transfer and diffusion of the electroactive species.

From the impedance analysis, the intersection of the high frequency semicircle with Z' axis represents R_i , the ionic resistance. This value was used to determine the ionic resistance of Ta_2O_5 film together with geometric factors (film thickness and electrode area) [15]. The values of ionic resistivities varied from 2.0×10^5 to $>10^6 \Omega \text{ cm}$ depending on the deposition conditions (spinning rate, viscosity of polymeric solution). The ionic conductivity of a material is the inverse of ionic resistivity. The ionic conductivity varied from 5×10^{-6} to $10^{-7} \Omega^{-1} \text{ cm}^{-1}$ for Ta_2O_5 films. Sol-gel deposited films are known to be less dense than the films deposited by different techniques [16]. This decreased film density leads to an increase in film ion conductivity by providing larger surface area for absorbed protons. It has been shown that absorbed water on the surface of tantalum oxide thin films strongly influences proton conduction [4]. Since protons are believed to be the conducting species in Ta_2O_5 films, a high amount of absorbed water means more protons will be available for conduction and therefore the ionic conductivity will be higher. Our examinations have shown that sol-gel spin coated films have higher conductivity ($5 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$) compared to films deposited by rf sputtering ($3.3 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$) [10].

4. Conclusions

From impedance and electrochemical measurements we can conclude that sol-gel spin-coated amorphous Ta₂O₅ films have higher ionic conductivity and better properties than Ta₂O₅ films obtained by other methods. Transparent Ta₂O₅ films deposited by sol-gel process had ion conductivities as high as $5 \times 10^{-6} \Omega^{-1}\text{cm}^{-1}$. The coloring and bleaching cycles for the EC cells using Ta₂O₅ layers coated onto WO₃ substrates with 0.1 M H₂SO₄ as an electrolyte were very similar to cycles using WO₃ alone with 0.1 M H₂SO₄. Electrochemical examinations show that Ta₂O₅ films are promising candidates for solid inorganic thin film ion conductors. Our next of area of study will be to examine the electrical and optical characterization of sol-gel Ta₂O₅ films when integrated into full electrochromic devices.

5. Acknowledgments

The authors wish to thank Dr. Temel Büyüklımanlı, Material Characterization Laboratory, Penn State University, for performing XPS measurements. This research was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Building Technologies, Building Systems and Materials Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

6. References

1. V.V. Truong, F.E. Girouard, and P.S. Ashrit, in *Large Area Chromogenicis*: eds. C. Lampert and G.G. Granqvist, SPIE, Bellingham, WA (1990), p.386.
2. D. Ravaine, *J. Non-Cryst. Solids*, 73, 286 (1985).
3. T. Minami, *J. Non-Cryst Solids*, 95&96, 107 (1987).
4. T. Saito, Y. Ushio, M. Yamada, and T. Niwa, *Solid State Ionics*, 40/41, 499 (1990).
5. L.C. Klein, *Solid State Ionics*, 32 & 33, 638 (1989).
6. M. Tsai, S.P. Szu, B. Wang and M. Greenblatt, *J. Non-Cryst Solids* 136, 227 (1991).
7. J. Livage, *Solid State Ionics* 50, 307 (1992).
8. M. Tatsumisago, K. Kishida, and T. Minami, *Solid state Ionics*, 59, 171 (1993)
9. J. Nagain, *Hyomen Kagaku* 9, 259 (1988).
10. M. J. Duggan, T. Saito, T. Niwa, *Solid State Ionics*, 62, 15 (1993).
11. A. Kishimoto, T. Nanba, and T. Kudo, *Solid State Ionics*, 40/41, 903 (1990).
12. C.H. An and K.Sugimoto, *J. Electrochem. Soc.*, 141, 853(1994).
13. E.E. Kahawaga, F. Bouramrane, A.B. Hallak, M.A. Daous, M.A. Salim, *J. Vac. Sci.Tech. A* 11(3) 580 (1993).
14. P.H. Holloway and G.C. Nelson, *J. Vac. Sci. Technol.*, 16, 793 (1979).

15. C. Ho, I.D. Raistrick and R.A. Huggins, *J. Electrochem. Soc.* Vol., 127, 343 (1980).
16. J. Brinker and G. Scherer, *Sol-Gel Science*, Academic Press, San Diego, 1990.