

Optical and Electrochemical Properties of Sol-Gel Spin Coated CeO₂-TiO₂ Films

Nilgun Ozer, Selmar DeSouza*, and Carl M. Lampert
Building Technologies Program
Energy and Environment Division
*Materials Science Division
Ernest Orlando Lawrence Berkeley National Laboratory
University of California
Berkeley, CA 94720

June 1995

Optical and electrochemical properties of sol-gel spin coated CeO₂-TiO₂ films

Nilgun Ozer , Selmar De Souza* and Carl M. Lampert

University of California, Lawrence Berkeley Laboratory, Division of Energy and Environment Division and Materials Science Division*, 1 Cyclotron Road, MS. 62-203, Berkeley, CA 94720, USA

ABSTRACT

The optical and electrochemical properties of sol-gel spin coated CeO₂-TiO₂ (50% CeO₂) films were investigated for electrochromic applications. The coating solutions were prepared by using mixed organic-inorganic [Ti(OC₂H₅)₄ and Ce(NH₄)₂ (NO₃)₆] precursors. X-ray diffraction studies showed the sol-gel spin-coated films were composed of an amorphous matrix of titanium oxide containing nanocrystallites of cerium oxide. The coating solar transmission value was T_s=0.8 (250 nm thick). The refractive index and the extinction coefficient were derived from transmittance measurements in the UV-VIS-NIR regions. These films had refractive index value of n=2.18 and extinction coefficient value of k=8x10⁻⁴ at λ=550 nm. Cyclic voltametric measurements showed reversible electrochemical insertion of lithium ions in a CeO₂-TiO₂/LiClO₄-propylene carbonate electrochemical cell. During cycling the films maintain high optical transmittance. Spectrophotometric and electrochemical investigations performed on CeO₂-TiO₂ films revealed that these films are suitable as an optically passive counter-electrode in lithium electrochromic devices.

Key words: sol-gel deposition, counter electrode, cerium oxide-titanium oxide, electrochromic device, optical properties, electrochemical properties.

1- INTRODUCTION

There are numerous literature reports on the fabrication of CeO₂-TiO₂ thin films for use in electrochromic applications¹⁻⁶. As such, CeO₂-TiO₂ have attracted interest as transparent counter electrodes for smart windows. These films are typically made by the sol-gel dip coating process. Sol-gel deposition allows control of the microstructure of the coating and offers a cost effective method to form these coatings⁷. Several precursors have been used for making CeO₂-TiO₂ films. These are based on cerium and titanium alkoxide⁵, cerium-ammonium nitrate and titanium alkoxide^{1,3} and cerium-chlorate and titanium alkoxide^{2,4}. Sol-gel processing allows alteration of the microstructure of the coating. This is achieved by complexing the precursor, changing the pH and viscosity of the solution, modifying the drying conditions and coating technique. By microstructure modification and porosity control, one can enhance the kinetics, durability and ion insertion capability of the CeO₂-TiO₂ film. Although much research has been devoted to electrochemical properties of CeO₂-TiO₂ film prepared by the sol-gel dip-coating method, no investigation has been published on optical properties and ionic conductivity of sol-gel spin-coated films.

In our work we present the preparation of CeO₂-TiO₂ spin coated films by the sol-gel process. These films have high charge intercalation capacity (10 mC/cm²) when the mixed oxide has a CeO₂:TiO₂ ratio of 1:1 . We describe the microstructure, optical and electrochemical properties of sol-gel spin coated films. The structural properties of the films were investigated by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). Electrochemical properties were investigated for lithiated and delithiated films in the CeO₂-TiO₂/LiClO₄ - propylene carbonate (PC) system.

A spectrophotometer was used for measuring spectral transmittance . The optical constants and thickness of the films were derived from transmittance measurements. Film thicknesses were also measured by profilometer for comparison with the spectrophotometric analysis.

2 - EXPERIMENTAL

2.1 - Characterization of the coatings

Structural investigation was performed by a Siemens Kristalloflex X-ray diffractometer (XRD) with Ni filtered $\text{CuK}\alpha$ radiation. The surface morphology of the films were examined using scanning electron microscopy (SEM) with accelerating voltage of 10 kV. A gold coating was applied over the films to avoid the charging of the surface. The chemical compositions and residual carbon content of the films were examined by a Kratos (XSAM 800) X-ray photoelectron spectrometer (XPS) with $\text{MgK}\alpha$ excitation. The background pressure of the system was approximately 5×10^{-9} torr. The spectrometer was calibrated so that the Au (4f 1/2) electron binding energy was at 83.3 ± 0.1 eV and adventitious carbon occurred at 285 ± 0.1 eV. The binding states of cerium and titanium were observed in the XPS data for the Ce 4d , Ti 3p and O 1s photoelectron peaks.

Thickness measurements were performed on a surface profiler, Dektak II (Veeco Inst. Inc.) having a maximum resolution of 5 nm/ 100 nm. The optical transmittance of the films deposited on quartz substrate were measured in the spectral range 290-2100 nm with Perkin Elmer Lambda 9 spectrophotometer, which was high photometric accuracy (<0.1 %). The refractive index $n(\lambda)$, extinction coefficient $k(\lambda)$, and the thickness d of the films were evaluated from the $T(\lambda)$ values .

Ionic conductivity of the $\text{CeO}_2\text{-TiO}_2$ films were derived using the a-c complex impedance technique. The equipment used was a Schlumberger (model S 11260). Impedance/Gain analyzer with a digital Princeton Applied Research (PAR) model 273 potentiostat, and electrochemical interface. These were programmed by a desktop computer for data collection and analysis.

Cyclic voltametric (CV) measurements were made using a PAR digital coulometer and a Hewlett Packard X-Y chart recorder. The electrochemical cell consisted of a three electrode configuration in a sealed cell. The working electrode was anhydrous 1 M LiClO_4 in propylene carbonate (PC) prepared in a dry box. All potentials in the present work are measured relative to a Ag/AgCl reference electrode. For cyclic voltammetry a potential scan rate of 20mV/s was used throughout. Multi-scan cycling measurements were performed between potentials of 0.4 V (anodic limit) and - 1.1 V (cathodic limit), respectively.

2.2 - Preparation of solutions and coatings

The preparation of the sol-gel coating solution is briefly illustrated in Figure 1. The starting solution was prepared by dissolving $\text{Ce}(\text{NH}_4)_2 (\text{NO}_3)_6$ in ethanol and adding $\text{Ti}(\text{OC}_2\text{H}_5)_4$, while stirring. Then HNO_3 was added to the solution with ethanol. The stirring of the solution was continued for 2 hours. It is well known that titanium ethoxide strongly reacts with water. The presence of the cerium-ammonium nitrate and nitric acid stabilize the solution and prevents this reaction from being too fast. The colloidal solutions were stable up to 4 months when they were kept at 5 °C . The coating solutions from freshly prepared and aged solutions were of different quality. The most transparent and durable coatings were deposited by using the 3 month aged solution. The $\text{CeO}_2\text{-TiO}_2$ films were transparent , slightly yellow, hard , and chemically stable in acid.

Cleaning of the substrate is important for proper adhesion of films⁸. Indium tin oxide (ITO) coated glass substrate (Donnelly Corp, Holland, MI) microscope slides and fused-silica substrates were ultrasonically cleaned with Alconox, rinsed in deionized water,, washed with isopropanol, then dried at 70°C for 1 hour. After cooling , the substrates were used for spin-coating. The coating is deposited by flowing the solution (1 ml) at a viscosity of 1.8 cP onto a substrate and spinning at 1200-3000 rpm. Deposition lasted 3-4 seconds and the total time of spinning after deposition was 60 seconds. The best homogeneity was achieved at spinning rates of approximately 1600 rpm. Single layer coatings were deposited onto the substrates at the spinning speed of 1600 rpm, fired at a temperature of 450 °C for 1 hour . The heating and cooling rate was 2 °C/min. We formed as many as 11 layers to increase the thickness. For multi-layer coatings, the coatings were dried at 150 °C for 30 minutes after each deposition with final firing at a temperature of 450 °C for 1 hour . We found that for the production of high quality multilayer films, a drying cycle for each layer was necessary. Samples dried only in the atmosphere before the application of the next coating were of poor quality, with surface specks that causes scattering of light . Depending on the spinning rate, the thickness of the single layer dried coating varied between 70 and 110 nm.

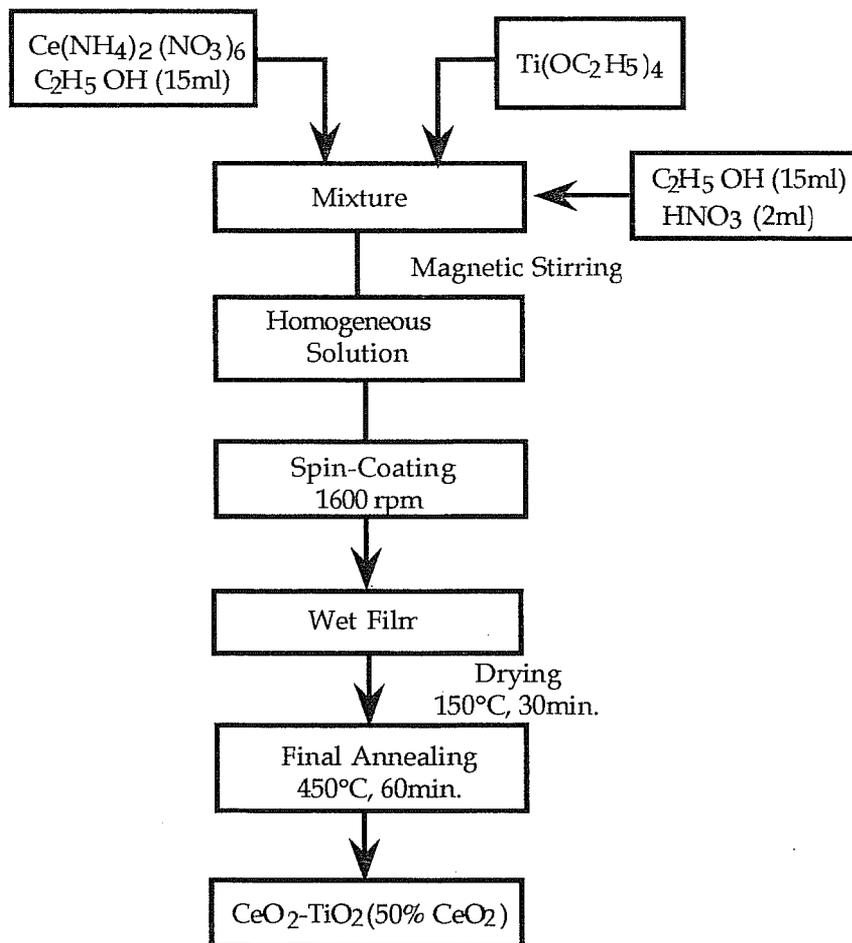


Fig. 1. Flow chart of fabrication process.

2.3 - Optical Measurements

Before fabricating EC devices it is important to know the optical properties of the layers. In this investigation a simple method described by Demiryont et al.^{9,10} was used to determine the optical constants and thickness of the thicker films. The method is based on analysis of the normal spectral transmittance $T(\lambda)$ of a homogeneous weakly absorbing film on a non-absorbing substrate. The optical parameters of $\text{CeO}_2\text{-TiO}_2$ films, the refractive index $n(\lambda)$, the extinction coefficient $k(\lambda)$, and the thickness of the coatings were calculated by this model. The numerical analysis requires construction of the envelope curves of the interference extrema in the transmission spectra. Sample thicknesses were chosen so we could obtain a sufficient number of interference maxima and minima to determine the refractive index and extinction coefficient and thickness accurately. The calculated thickness values were also compared with the Dektak profilometer measurements. The optical constants were evaluated in the wavelength interval of 0.3 to 1.2 μm .

3. RESULTS AND DISCUSSION

Thickness profile measurement of the sol-gel deposited $\text{TiO}_2\text{-CeO}_2$ films indicate that the average thickness of a single coating is 75 nm. The coatings used in this study were deposited with 4 coating cycles. The thickness of the resulting film was about 250 nm as calculated and 250 ± 5 nm measured by the Dektak. These films were examined by scanning electron microscopy and exhibited an 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. Fig. 2 shows the XRD pattern of a coating on soda-lime glass fired at 500 °C. XRD patterns of the $\text{CeO}_2\text{-TiO}_2$ films used in this study showed the peaks of CeO_2 (cerianite) and TiO_2 (anatase) in the fired (> 450 °C) films. No peaks of TiO_2 (anatase) were observed in any of the films fired at lower temperatures. For films fired at 450 °C or above SEM and XRD examinations showed that the film structure consisted of small CeO_2 crystallites imbedded in an amorphous TiO_2 matrix. Fig 3. shows a survey scan XPS spectrum of $\text{CeO}_2\text{-TiO}_2$ films on a soda-lime glass substrate. The stoichiometry of the film are found to be $\text{CeO}_2\text{:TiO}_2$ with a ratio of 1:1.

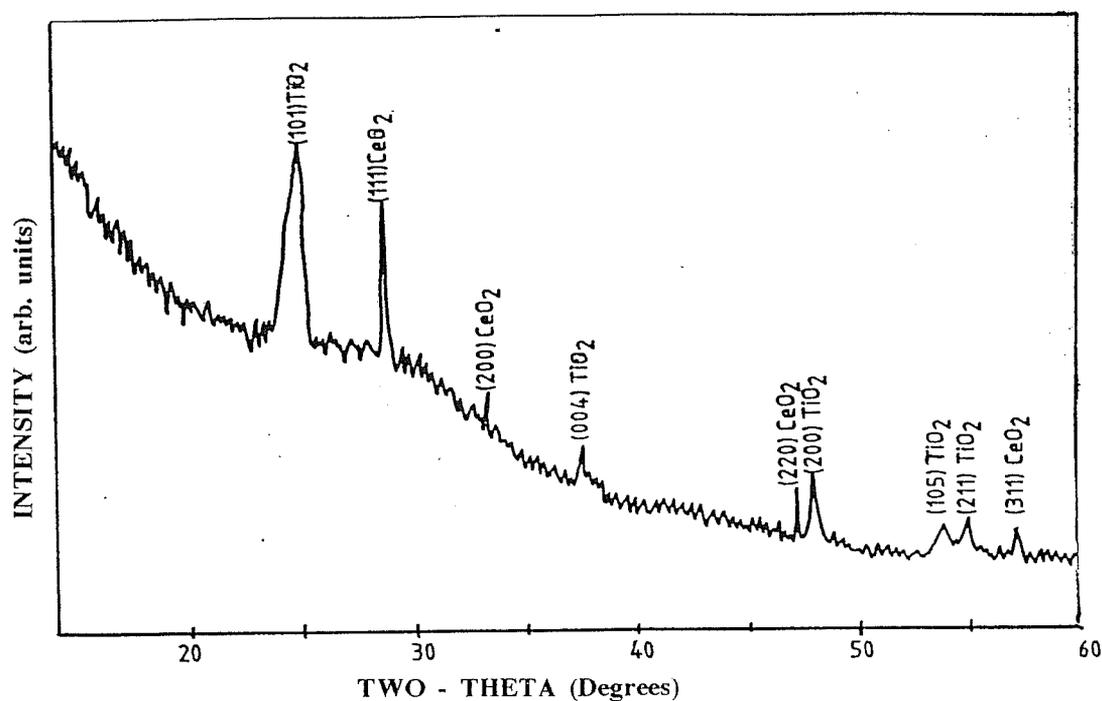


Fig 2. XRD spectra of $\text{CeO}_2\text{-TiO}_2$ films deposited on soda-lime glass ($T > 450$ °C).

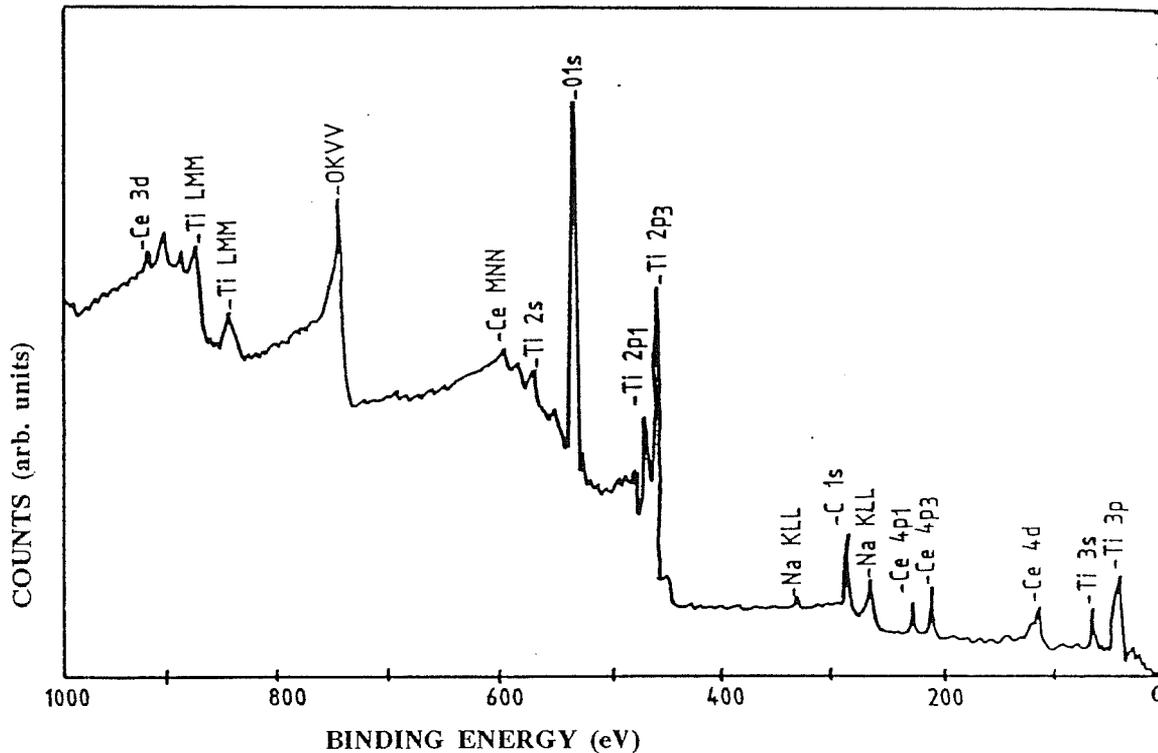


Fig. 3. XPS survey scan of sol-gel deposited $\text{CeO}_2\text{-TiO}_2$ films.

Figure 4 shows the spectrophotometric transmittance plot of a 350 nm thick $\text{CeO}_2\text{-TiO}_2$ film. T_0 , T^+ and T^- plots of these figure correspond to the transmittance of bare substrate and maximum and minimum envelopes passing through the transmittance extrema. The number of interference extrema in a given spectral region is proportional to the film thickness and the refractive index. The differences between the T^+ and T^- and the T_0 and T^+ curves are measures of the refractive index and absorption of the film respectively¹¹. They both depend on wavelength. $T(\lambda)$ spectra exhibiting high transparency throughout the wavelength range studied. $\text{CeO}_2\text{-TiO}_2$ films were weakly absorbing beyond 420 nm. Figure 5 shows the spectral dependence of the refractive index and extinction coefficient of spin-coated $\text{CeO}_2\text{-TiO}_2$ films. It can be seen from Fig. 6 that the refractive index has the same characteristics as the extinction coefficient since both of them increase sharply in the strong dispersion region ($\lambda < 400$ nm). The refractive index of sol-gel spin-coated films was $n=2.18$ at $\lambda=550$ nm. The extinction coefficient was $k=8 \times 10^{-4}$ at $\lambda=550$ nm. All deposited films had homogeneous refractive index. No signs of inhomogeneity were observed. The packing densities were calculated from refractive index values of the film, bulk material and the air respectively¹². The calculated packing density values of $\text{CeO}_2\text{-TiO}_2$ films were about 0.64.

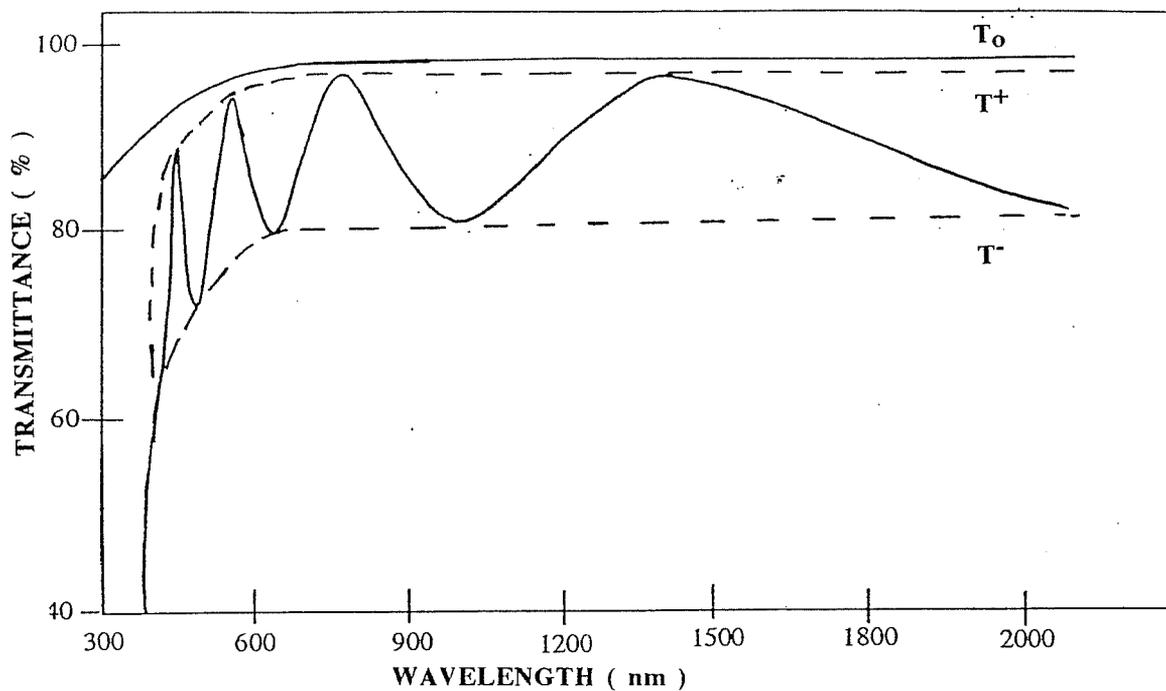


Fig 4. Spectrophotometric transmission spectrum of spin-coated $\text{CeO}_2\text{-TiO}_2$ film (350 nm thick) deposited onto quartz substrate.

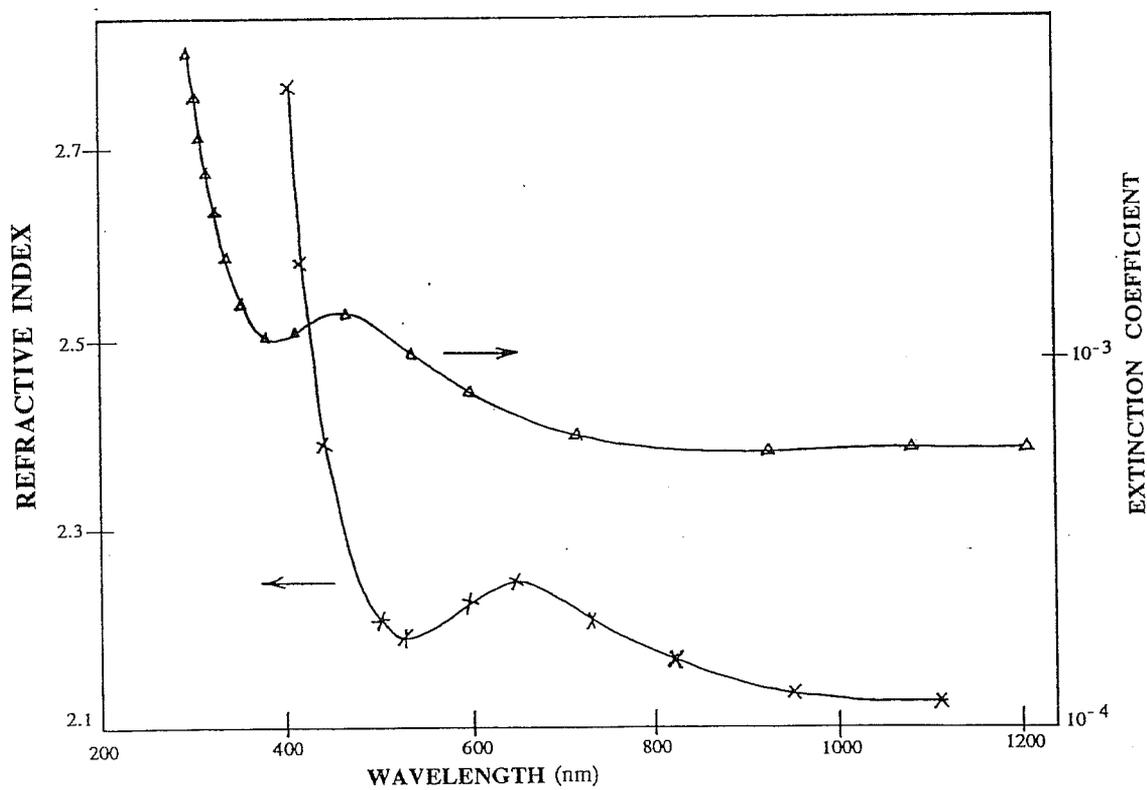


Fig.5. Wavelength dependence of the refractive index and extinction coefficient of spin coated films.

The cyclic voltammetry shown in Fig. 6 was obtained from a four layer $\text{CeO}_2\text{-TiO}_2$ film (250 nm thick). The anodic and cathodic peaks appeared at 0.21 and -1.08 V, respectively. The cathodic and anodic peaks are characteristic of a reversible insertion process of lithium ions in the electrode material. The charge inserted and extracted from electrode material at a scan rate of 20 mV/s was 10 mC/cm². During the insertion no visible coloration could be observed. Potentiostatic cycling was performed on the same $\text{CeO}_2\text{-TiO}_2$ electrode between -1.1 and 0.4 V versus Ag/AgCl for 50 reduction and oxidation cycles. The cycling showed good stability with no charge loss, demonstrating the reversibility of Li^+ insertion / extraction. The cycle lifetime of the $\text{CeO}_2\text{-TiO}_2$ layers were tested and no degradation in the charge capacity was observed electrochemically or by visual inspection of the cell up to 25000 cycles.

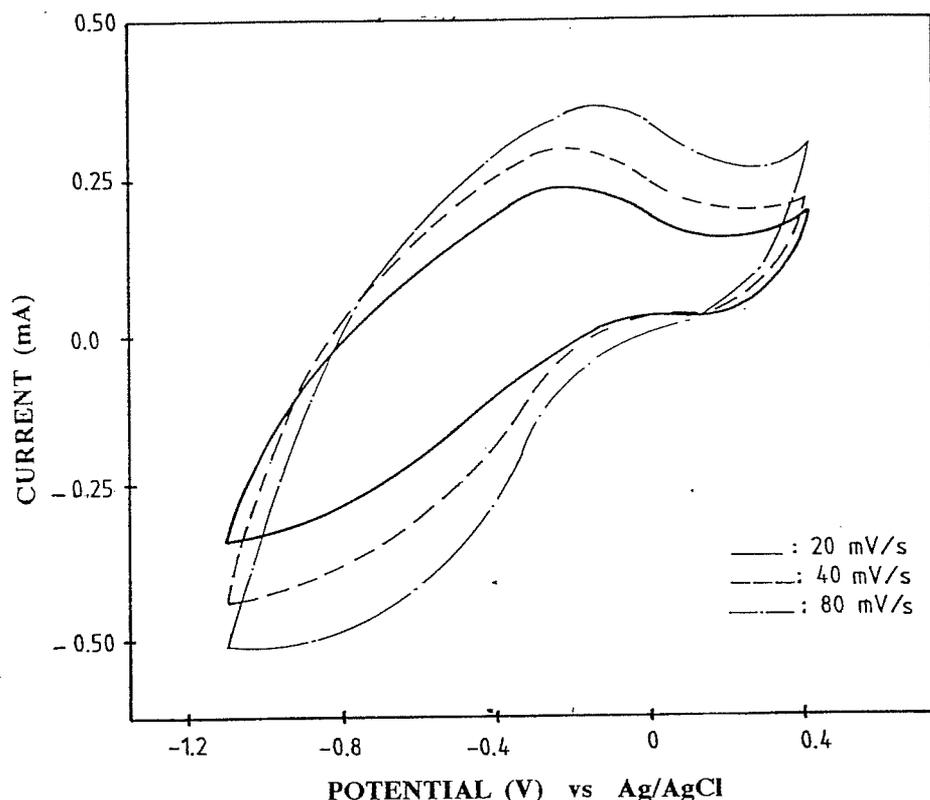


Fig. 6. Cyclic voltammogram of a sol-gel deposited $\text{CeO}_2\text{-TiO}_2$ film electrode after 10 switching cycles in 1 M LiClO_4/PC (electrode area= 2.8 cm²).

Ionic conductivity measurements were determined from a-c impedance spectroscopy. The measurements were made over the frequency range of 100 mHz to 20 Hz. Fig. 7 shows a typical complex impedance plane diagram which consists of a slightly depressed semi-circle at the high frequency region and straight line in the low frequency region. A simplified equivalent circuit representing the sample was used to calculate ionic conductivity (shown in the inset in Fig.7) where R_e is the ohmic resistance of electrode, C_d is the double layer capacitance of the electrode / electrolyte interface, R_i is the ionic resistance arising from the diffusion of lithium ions, C_g is the geometric capacitance between electrodes. From impedance analysis, the intersection of the high frequency semicircle with $\text{Re}(Z)$ axis represents R_i the ionic resistance. These values were used to determine ionic conductivity of $\text{CeO}_2\text{-TiO}_2$ films together with geometrical factors (film thickness and the electrode area)¹³. The semi-circle observed at the high frequency part of

the diagram corresponds to the lithium diffusion into the electrode material. The value of lithium conductivity is 1.3×10^{-6} S/cm for $\text{CeO}_2\text{-TiO}_2$ films at 0.8 V vs Ag/AgCl at room temperature.

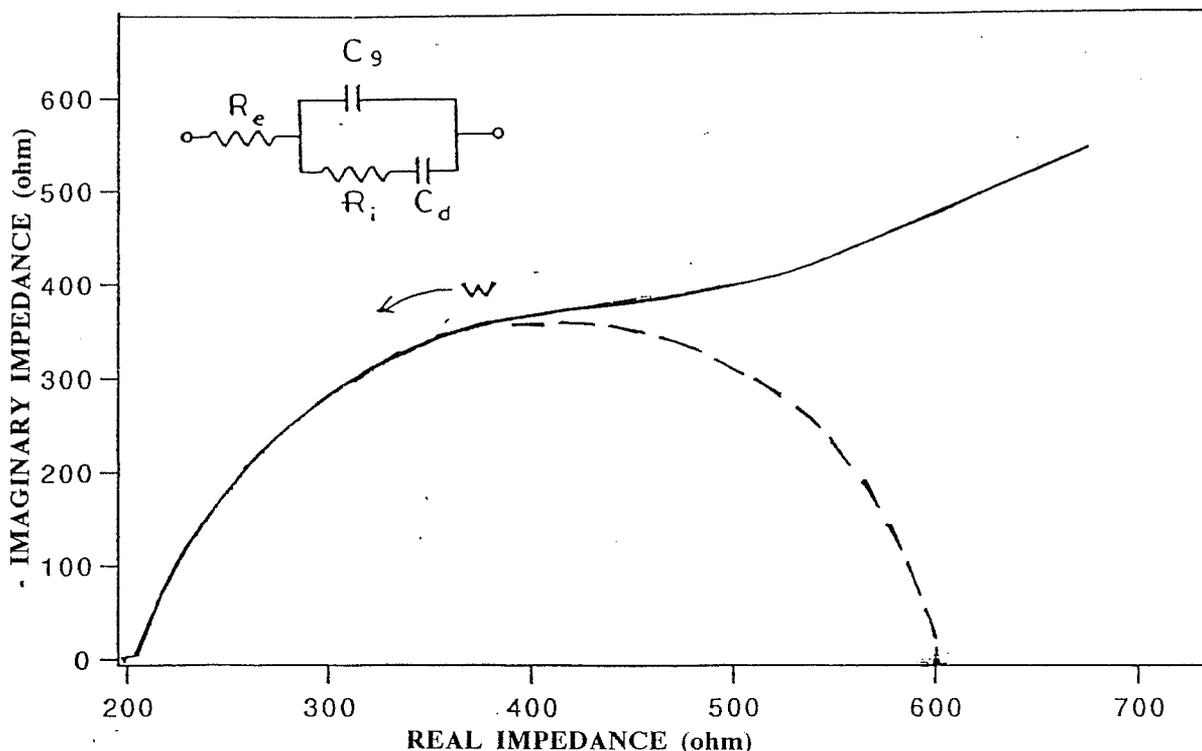


Fig. 7. Impedance plots of $\text{CeO}_2\text{-TiO}_2$ (250 nm thick) film on ITO. The inset shows the equivalent circuit used for the analysis.

CONCLUSION

We found that the sol-gel spin coated $\text{CeO}_2\text{-TiO}_2$ films could make acceptable transparent counter electrode film for use in lithium base devices. Films of about 250 nm thick could be made from 4 layers. These films consisted of small CeO_2 crystallites imbedded in an amorphous TiO_2 matrix. From impedance measurements we conclude that $\text{CeO}_2\text{-TiO}_2$ films had room temperature lithium conductivity of 1.3×10^{-6} S/cm. These films had refractive index value of $n=2.18$ and extinction coefficient value of $k=8 \times 10^{-4}$ at $\lambda=550$ nm. We also examined that $\text{CeO}_2\text{-TiO}_2$ films have reversible lithium insertion and promising electrode kinetics. As a result sol-gel spin coated $\text{CeO}_2\text{-TiO}_2$ films are promising candidates as transparent counter electrodes in electrochromic devices.

ACKNOWLEDGMENTS

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

REFERENCES

1. P. Baundry, A. C. M. Rodrigues, M. A. Aegerter and L. O. Bulloes, " Dip-coated TiO_2 - CeO_2 film as a transparent electrode", J. Non-Cryst. Solids 121, 319-321, 1990.
2. A. Makishima, M. Asami and K. Wada, " Preparation and properties of TiO_2 - CeO_2 coatings by sol-gel process", J. Non-Cryst. Solids 121, 310-314, 1990.
3. B. Valla, J. C. L. Tonazzi, M. A. Macedo, L. H. Dall'Antonia, M. A. Aegerter, M. A. B. Gomes and L. O. Bulloes, "Transparent storage layers for H^+ and Li^+ ions prepared by sol-gel technique", SPIE Proc. V 1536, 44-62, 1991.
4. U. Lavrencic Stangar, B. Orel, I. Grabec, B. Ogorevc and K. Kalcher, " Optical and electrochemical properties of CeO_2 and TiO_2 - CeO_2 coatings", Sol. Energy Mater. and Sol. Cells, 31, 171-185, 1993.
5. D. Keomany, J. P. Petit and D. Deoroo, "Structure of sol-gel made CeO_2 - TiO_2 and relation with electrochemical insertion of lithium", SPIE Proc. V2155, 165-179, 1994
6. P. Baundry, M. A. Aegerter, D. Deroo and B. Valla, " Electrochromic window with lithium conductive polymer electrolyte", J. Electrochem. Soc., 138, 460-465, 1991.
7. C. J. Brinker and G. W. Sherer, *Sol-Gel Science* , ch. 4, Academic Press, London, 1990.
8. D. M. Mattox, " Surface cleaning in thin film technology", Thin Solid Films 53, 81-96, 1978.
9. H. Demiryont and J. R. Site, "Effect of oxygen in ion beam sputter deposition of titanium oxides", J. Vac. Sci. Technol. A2, 1457-1460, 1984.
10. N. Ozer, H. Demiryont and J. H. Simmons, "Optical properties of sol-gel spin coated TiO_2 films", Appl. Opt., V30 , 3661-3666, 1991.
11. E. Aktulga, " A method for the determination of the optical parameters of thin films", Ist . Univ. Bulletin 48 , 17-35, 1983.
12. G. Atanassov, R. Thielsch and D. Popov, "Optical properties of TiO_2 , Y_2O_3 and CeO_2 films deposited by electron beam evaporation", Thin Solid Films 223, 288-292, 1993.
13. C. Ho. I. D. Raistrick and R. A. Huggins, "Application of a-c techniques to study of lithium diffusion in WO_3 films", J. Electrochem. Soc. 127, 343-350, 1990.