

Characterization of an all solid-state electrochromic window

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ABSTRACT

Sol-gel cerium - titanium oxide layers present potential application as transparent counter-electrode (ion storage layer) in electrochromic windows and mirrors using lithium conducting electrolyte and WO_3 electrochromic coating. The precursor sol, prepared by mixing $Ti(OPr^1)_4$ and $Ce(NO_3)_6(NH_4)_2$ in ethanol, is initially dark red and becomes transparent after a few days aging indicating the presence of Ce^{3+} complexes. The layers have been obtained by dip coating technique and heat treated at $450^\circ C$ during 15 minutes. They have been characterized by XRD, SIMS, optical absorption and electrochemical techniques; it is shown that the electrochemical reaction corresponds to a reversible insertion-extraction of lithium ions within a TiO_2 amorphous film containing small CeO_2 crystallites. At low sweep frequencies the process is controlled by a diffusion mechanism ($\tilde{D}_{Li} \approx 6.4 \cdot 10^{-12} cm^2/s$ at $25^\circ C$). Characterizations of an all solid state electrochromic window/glass/ITO/ WO_3 /POE-Li N $(SO_2 CF_3)_2$ / $TiO_2 - CeO_2$ / ITO / glass / are also presented.

1. INTRODUCTION

Considerable attention is being directed to use sol-gel methods for the production of single, multilayer coating as these techniques offer outstanding opportunities over other methods of deposition such as CVD, sputtering or vacuum evaporation¹. Investigations have also been very active in the field of chromogenics to develop and particularly improve electrochromic devices such as all solid state energy efficient windows (smart windows) and reflecting mirrors². These devices have the properties to alter their transmissive or reflective properties by application of an electric field or current and can therefore regulate the heat transfer and the luminous radiation.

Figure 1 shows a typical cross-section of a transmissive device (smart window). It is made of five layers sandwiched between two glass substrates. There are two transparent electrical conductors required for setting up a distributed electric field, an electrochromic layer, an ionic conductor (electrolyte) and an ion storage layer (counter electrode). When a small current is passed through the cell the active electrochromic layer changes its transmittance continuously over a wide range

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(typically 70 - 10%). The electrochromic coating typically switches in a time period of seconds to less than a minute and can maintain its properties when the power is turned off (memory effect). The process is fully reversible and the original bleached state is obtained by reversing the applied voltage.

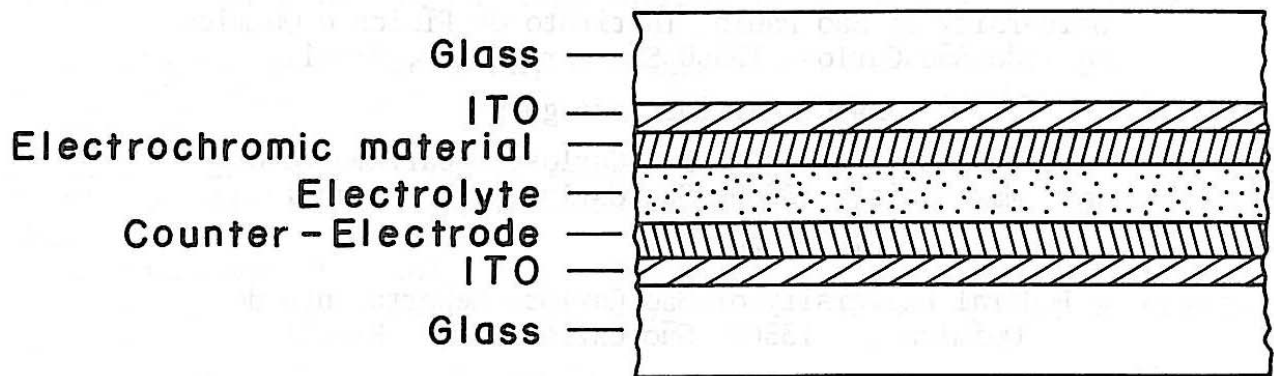
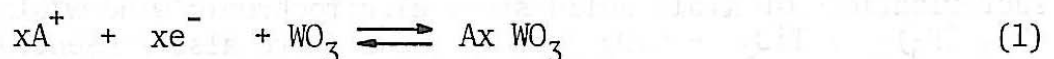


Fig. 1 - Schematic cross-section of a solid state transmissive electrochromic window.

The glass conducting substrates do not present any problem and are readily available on the market. The best electronic conductors are $\text{In}_2\text{O}_3 - \text{SnO}_2$ (ITO) coatings on glass substrates which present today satisfactory electronic conduction (down to $10 \Omega/\text{sq}$) and optical transparency for the realization of small devices³. However, sheet resistance of about $1 \Omega/\text{sq}$ will be needed for large scale electrodes ($1 \times 1 \text{ m}^2$).

Several materials exhibit electrochromic properties. Among them the metal transition oxides such as tungsten and molybdenum trioxides (WO_3 , MoO_3) are modified by the electrochemical insertion of alkali ions or protons. The corresponding reaction is written below for WO_3 :



where $\text{A}^+ = \text{H}^+, \text{Li}^+$

The net result of the insertion reaction is the reduction of the transparent WO_3 host material and its transformation into a blue colored tungsten bronze ($\text{A}_x \text{WO}_3$ or $\text{W}_{1-x}^{6+} \text{O}_{3-x} \text{W}_x^{5+} (\text{OA})_x$); its coloration is due to the presence of a large absorption band in the visible and near infrared region ($E_{\text{max}} \approx 1.4 \text{ eV}$) attributed to electronic transitions from the reduced tungsten ions states W^{5+} toward the conduction band^{4,5}. Both proton and lithium insertion are possible. Although the chemical diffusion coefficient of H^+ in WO_3 is higher than that of Li^+ ,⁶ a complete transmissive or reflective device is easier to realize with lithium conductors than with protonic ones as hydrogen gassing and layer corrosion in acid media limit the life of the protonic based devices.

Many electrolytes have been proposed and tested for the realization of these devices. The advantages of polymeric ion conductor over liquid ones have been recently recognized^{7,8}. Due to their elastomeric properties they provide a good electrolyte/electrode contact, do not present problems of leakage and are easily elaborated in thin film forms. Among them PEO (polyethylene oxide) or PPO (polypropylene oxide) complexed with alkali salts (Li ClO_4 , $\text{Li CF}_3\text{SO}_3$ or $\text{Li N}(\text{SO}_2\text{CF}_3)_2$) exhibit

Li⁺ conductivities in the range 10⁻⁵ - 10⁻⁷ Scm⁻¹ at room temperature suitable for fast switching time.

The electrochromic devices also require the presence of a counter electrode or ion storage layer. Several oxide materials have been proposed recently but none of them exhibit ideal properties of transparence, reversibility and high kinetics of the electrochemical reaction for lithium ions. V₂O₅ is fast enough and reversible but its transmission in the bleached state is too low^{9,10}. Ir₂O₃ retains a good transparency but the insertion of lithium is poor and the reaction is partially irreversible^{11,12}. CeO₂ exhibits a good reversibility, is colourless in both oxidized and reduced states but shows a low reaction kinetics¹³. Recently we have proposed¹⁰ the use of TiO₂ - CeO₂ layers and shown¹⁴ that this new structure allows a better Li⁺ insertion kinetics than pure CeO₂. These films were deposited on ITO coated glasses by sol-gel dip coating technique.

In this paper we first describe in section 2 the techniques used to prepare the electrochromic, electrolyte and ion storage layers. In section 3 we discuss essentially the properties of the precursor sol and the sol-gel TiO₂ - CeO₂ coating which have been characterized by X-ray diffraction (XRD), secondary ions mass spectroscopy (SIMS), optical transmission and electrochemical techniques. In section 4 the basic properties of an all solid state smart window/glass/WO₃/POE-Li N(SO₂CF₃)₂/TiO₂ - CeO₂ /ITO/glass are reported and finally the conclusions are given in section 5.

2. MATERIALS

We describe in this section the procedures used for making thin coatings based on WO₃ and TiO₂ - CeO₂. These layers were backed by a 1.1mm thick glass substrates precoated with transparent and conducting ITO (Baltracon Z20 Balzers). We also report on the procedure used for the preparation and deposition of the polymer electrolyte.

2.1. Electrochromic Coating

WO₃ layers were deposited from the corresponding oxide powder by vacuum evaporation onto 400nm thick indium tin oxide (ITO) coated glasses. The WO₃ films were amorphous to X-ray diffraction and their thickness, measured by a Talystep, was of the order of 200 - 300nm. The films have been characterized electrochemically as deposited without any heat treatment¹⁰. The determination of the chemical diffusion coefficient for lithium $\bar{D} = 2.5 \cdot 10^{-11}$ cm²/s at 25°C has been determined by analysing the low frequency response of the impedance data.

2.2. Electrolyte

The polymer electrolyte was polyethylene oxide- LiX complex with X = ClO₄ or N(SO₂CF₃)₂. They were prepared by dissolving the PEO powder (M.W. = 5.10⁶) and the lithium salt in acetonitril with an O:Li atomic ratio of 8:1 giving rise to the highest ionic conductivity in these systems^{15,16}. The viscous and transparent complex was doctor-bladed on a teflon substrate; the solvent was then evaporated at 70°C during 24 hours. The films having a thickness of 50 to 200 nm were kept in a dry box (< 1ppm H₂O) in order to eliminate any residual solvent or moisture.

2.3. Sol-Gel storage coating (counter-electrode)

TiO₂ - CeO₂ films with various Ti/Ce ratios have been synthesized by the sol-gel

process. The precursor sol was prepared by dissolving $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$ in ethanol to which was added tetraisopropyl orthotitanate $\text{Ti}(\text{O-iso-C}_3\text{H}_7)_4$. The concentration of the cerium salt in ethanol never exceeded 0,25M (limit of solubility). No special care was taken to limit the presence of water in the solution so that the cerium salt acts as an acid which reduces the pH and prevents the $\text{Ti}(\text{OPr})_4$ precipitation. The layers were deposited by dip coating technique on carefully cleaned and dried ITO coated glasses (Baltracon Z20) at a withdrawn speed of the order of 10cm/min. The films were let to dry at room temperature for 15 minutes and then have been partially densified by heat treatment in air at 450°C for 15min. Their thickness was typically 60 to 80nm. The whole procedure was repeated to obtain thicker layers.

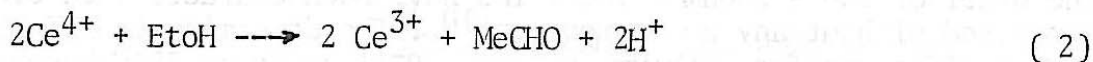
3. PROPERTIES OF THE TiO_2 - CeO_2 ION STORAGE LAYER

The characterization of the WO_3 electrochromic layer and of the polymer electrolyte has been already published elsewhere^{10,17}. In this chapter we shall therefore only report on the characterization of the new TiO_2 - CeO_2 sol-gel ion storage layer using techniques such as optical spectroscopy, X-ray diffraction (XRD), secondary ion mass spectrometry (SIMS), cyclic voltammetry and impedance spectroscopy.

3.1. Physico-Chemical Study of the Sol

The cerium-titanium layers which give the best Li insertion-extraction behavior are those prepared from an aged sol with a ratio $\text{Ce}/\text{Ti} = 1$. These sols are initially clear and dark redish and turn to pale yellow after 6 - 7 days. The gelification that occurs 1 or 2 days after this change of color begins with a phenomenon of flocculation already observed by Kamiya et al¹⁸. The solution is then milky white. In a parallel study, we observed that the solution Ce salt/EtOH is initially clear and dark redish and becomes colorless in about 6 days. This period of time depends on the presence of water which accelerates the clarification. Figure 2 shows the change in optical transmission in the visible region of a 1mm thick Ce salt - ethanol solution 0,25 M as a function of aging time.

E.M.F. measurement of the electrochemical cell $\text{Pt}/0,25\text{M Ce}(\text{NO}_3)_6(\text{NH}_4)_2 - \text{EtOH}/\text{H}^+ - \text{Cl}^-//\text{AgCl}/\text{Ag}$ shows also a decrease of about 700mV during this evolution. The results are in agreement with Ardon¹⁹ who showed that this behavior corresponds to a reduction reaction of Ce^{4+} into Ce^{3+} according to :



The reduction of the Ce^{4+} is preceded by the formation of a dark redish complex $\text{Ce}^{4+}/\text{EtOH}^{20}$. We can therefore consider that the color change of the sol prepared for the dip process is due to the reduction of Ce. Thus, the starting solution contains Ce^{3+} instead of Ce^{4+} as initially presumed. However the use of CeCl_3 instead of $\text{Ce}(\text{NO}_3)_6(\text{NH}_4)_2$ gives coatings with bad electrochemical characteristics¹⁴. This different behavior is presently not understood.

3.2. X-Ray Diffraction

X-ray were carried out on powders obtained from TiO_2 - CeO_2 gels and thin oxide films. The powder was prepared by letting the sol to gel slowly at room temperature until solidification, and followed by a heat treatment in open furnace at different temperatures (230 - 550°C). In this temperature range no difference was observed in the X-ray spectra. Although the gel has been obtained with a sol containing Ce^{3+} complexes the X-ray patterns show the presence of crystalline CeO_2 and small

peaks belonging to the TiO₂ anatase structure (Figure 3).

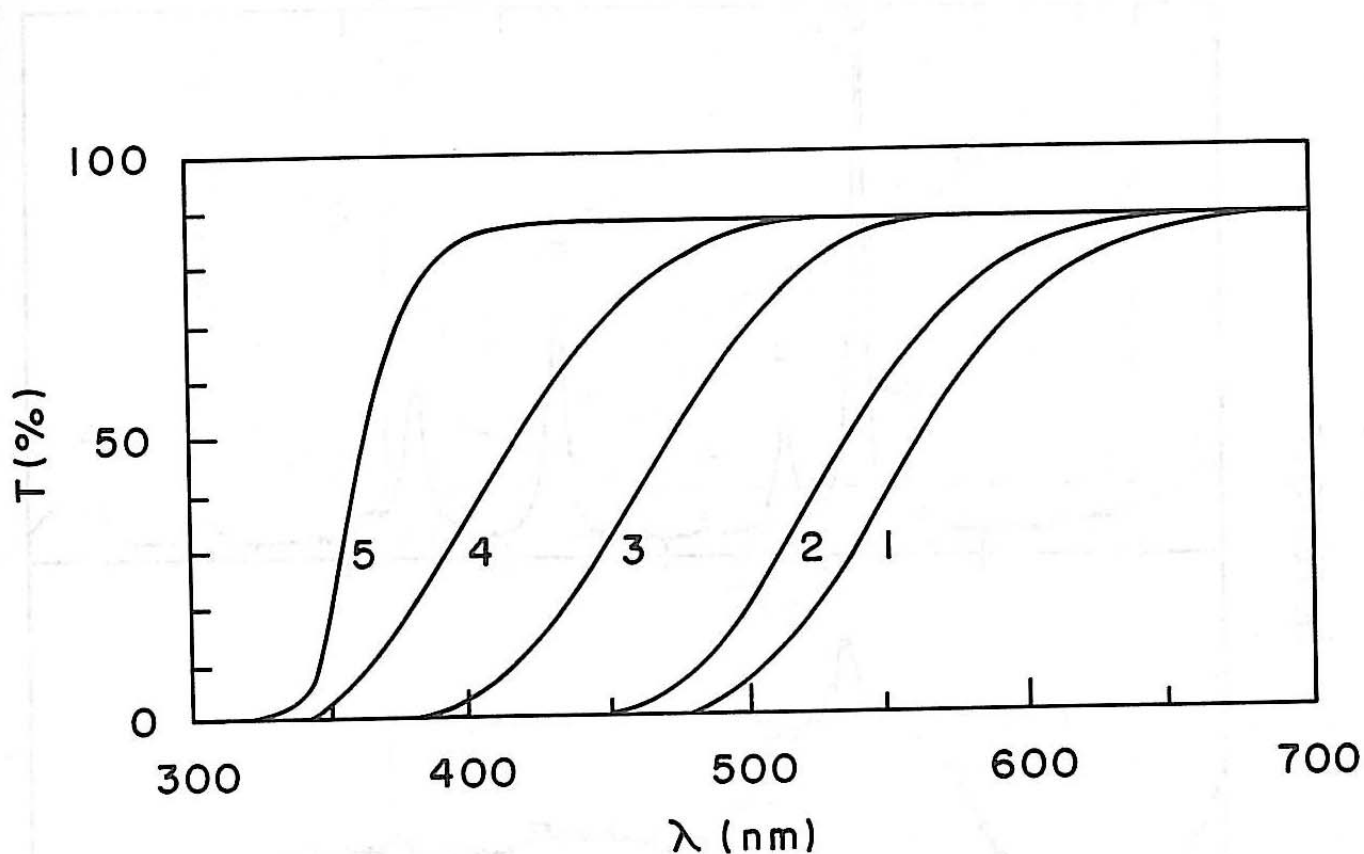
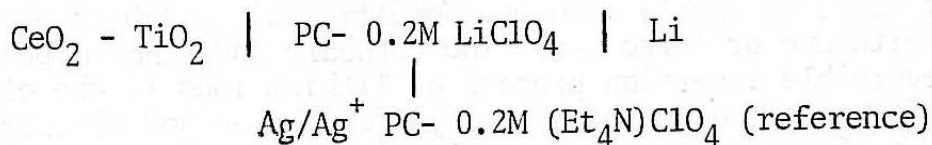


Fig. 2 - Optical transmission of a 1mm thick 0,25M Ce(NH₄)₂(NO₃)₆- ethanol sol as a function of aging time 1, 2, 3, 4 and 5 days.

The thin films obtained after three dips and heat treated at 450°C during 15 minutes have a thickness of about 300nm. They are essentially amorphous under X-ray. Nevertheless, the observation of the main peaks of CeO₂ (Fig. 3b) indicates the presence of very small crystallites. It is worthwhile to mention that the presence of CeO₂ proves that the cerium has been reoxidized during the thermal treatment.

3.3. Electrochemical Characterization

Cyclic voltammetry was employed for surveying the redox process at the TiO₂-CeO₂ film. The automated impedance system consisted of a potentiostat/galvanostat EG&G model 273, and a lock-in analyzer which were both controlled by a computer. Impedance spectra were generated over the frequency range of 10kHz to 0.01Hz using a 10mV peak to peak a.c. excitation. a.c. impedance and voltammetry measurements were made at room temperature and performed in a dry box using a three electrodes cell



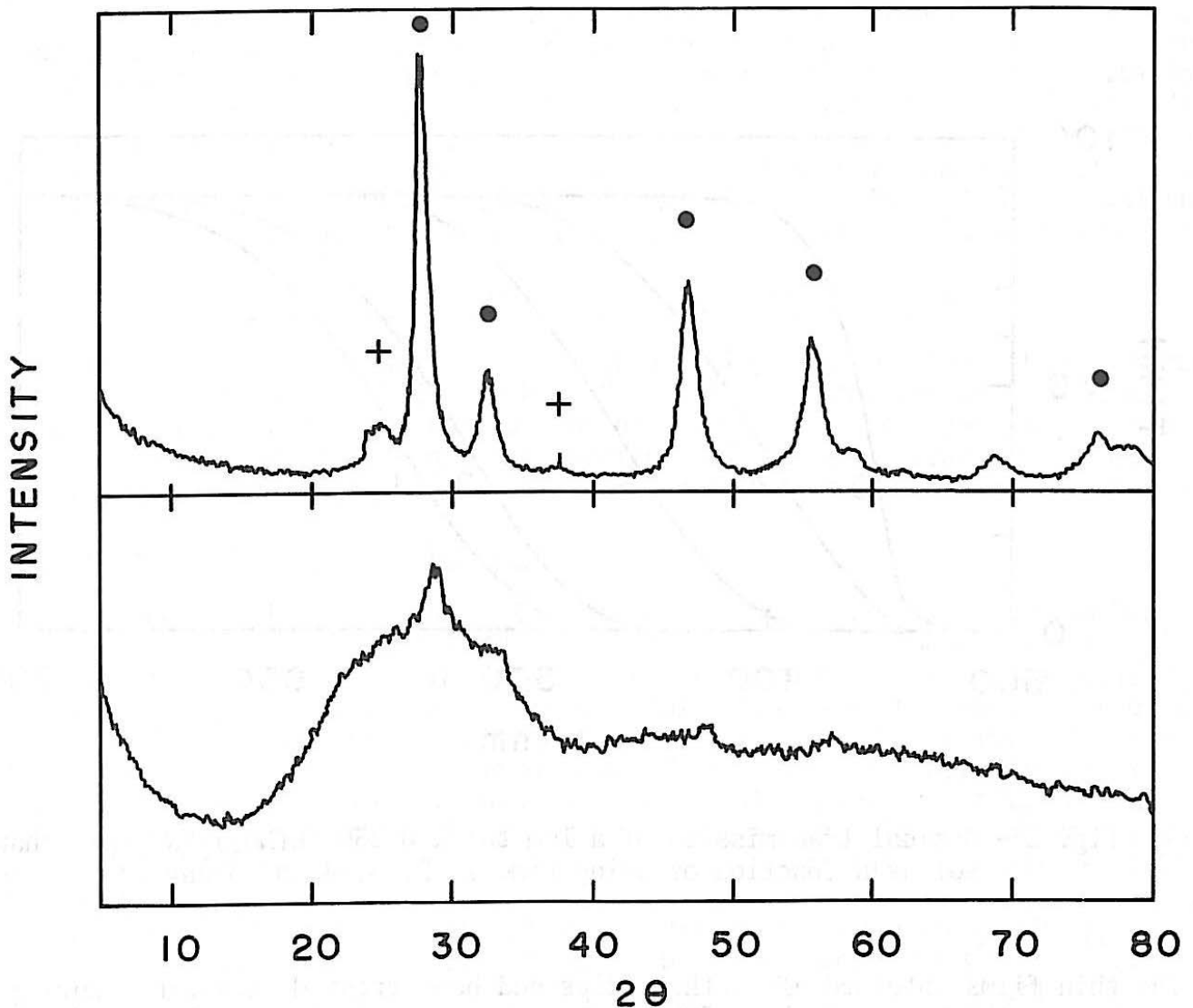


Fig. 3 - X-ray diffractogram of a) TiO₂ - CeO₂ powder heat at 230°C during 14 h. The peaks marked (o) corresponds to CeO₂ and those marked (+) to the TiO₂ anatase structure. b) TiO₂-CeO₂ thin film of about 300nm thickness treated at 450°C during 15 minutes.

All reagents used were of analytical grade. Anhydrous lithium perchlorate was dried under vacuum at 150°C for 24h before use. Propylene carbonate (PC) was purified by distillation. Figure 4 shows typical voltammogram of TiO₂ - CeO₂ electrode heat treated at 450°C during 15 minutes. No difference has been observed for coatings obtained with one or three dips. The cathodic and anodic peaks are characteristics of a reversible insertion process of lithium ions in the electrode material. The stability of these electrodes under repeated charge and discharge conditions has been tested up to 100 cycles and no modification has been observed.

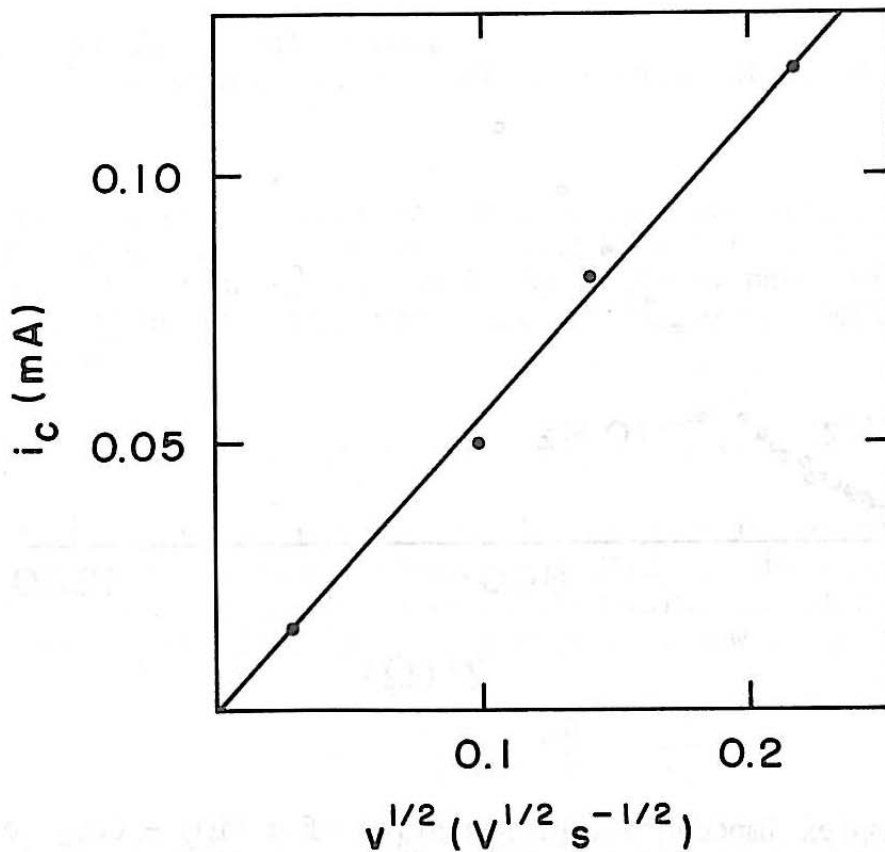
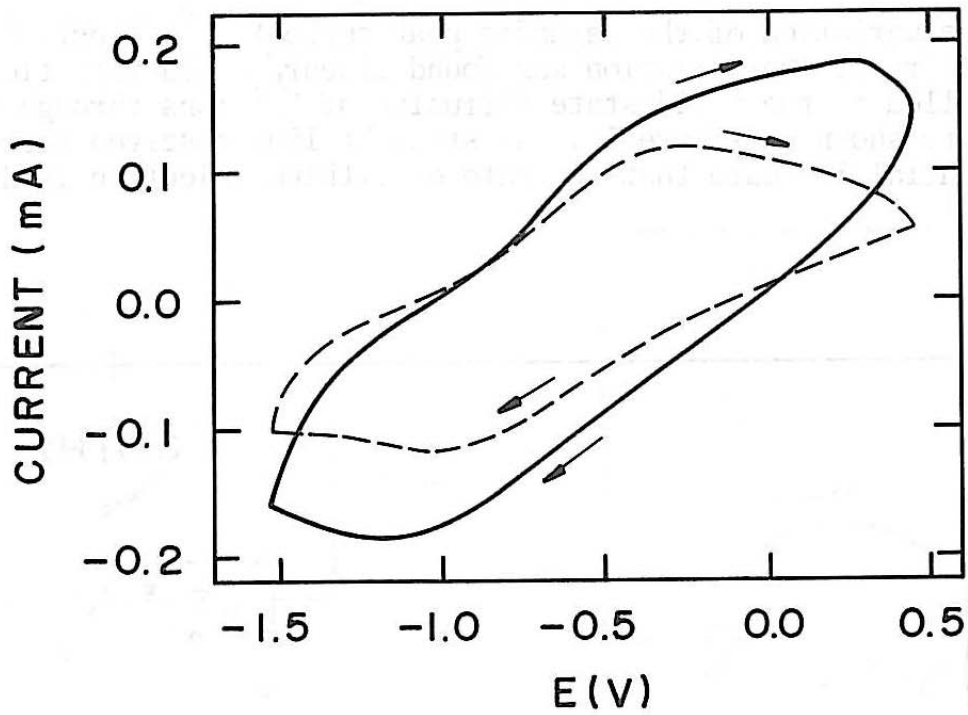


Fig. 4 - a) Cyclic voltammogram of a $TiO_2 - CeO_2$ electrode in PC - 0,2M $LiClO_4$ measured at 50mV/s. (----) and 100mV/s (—) sweep rate.
 b) Variation of the cathodic peak current i_c of the same electrode as a function of the square root of the sweep rate.

Fig. 4b shows the variation of the cathodic peak current as a function of the square root of the sweep rate. The variation was found linear, characteristic of a process which is controlled by the solid state diffusion of Li^+ ions through the film²¹. Impedance data are shown in figure 5. The straight line observed below 10Hz and at equilibrium potential indicate that the rate of lithium injection is diffusion controlled.

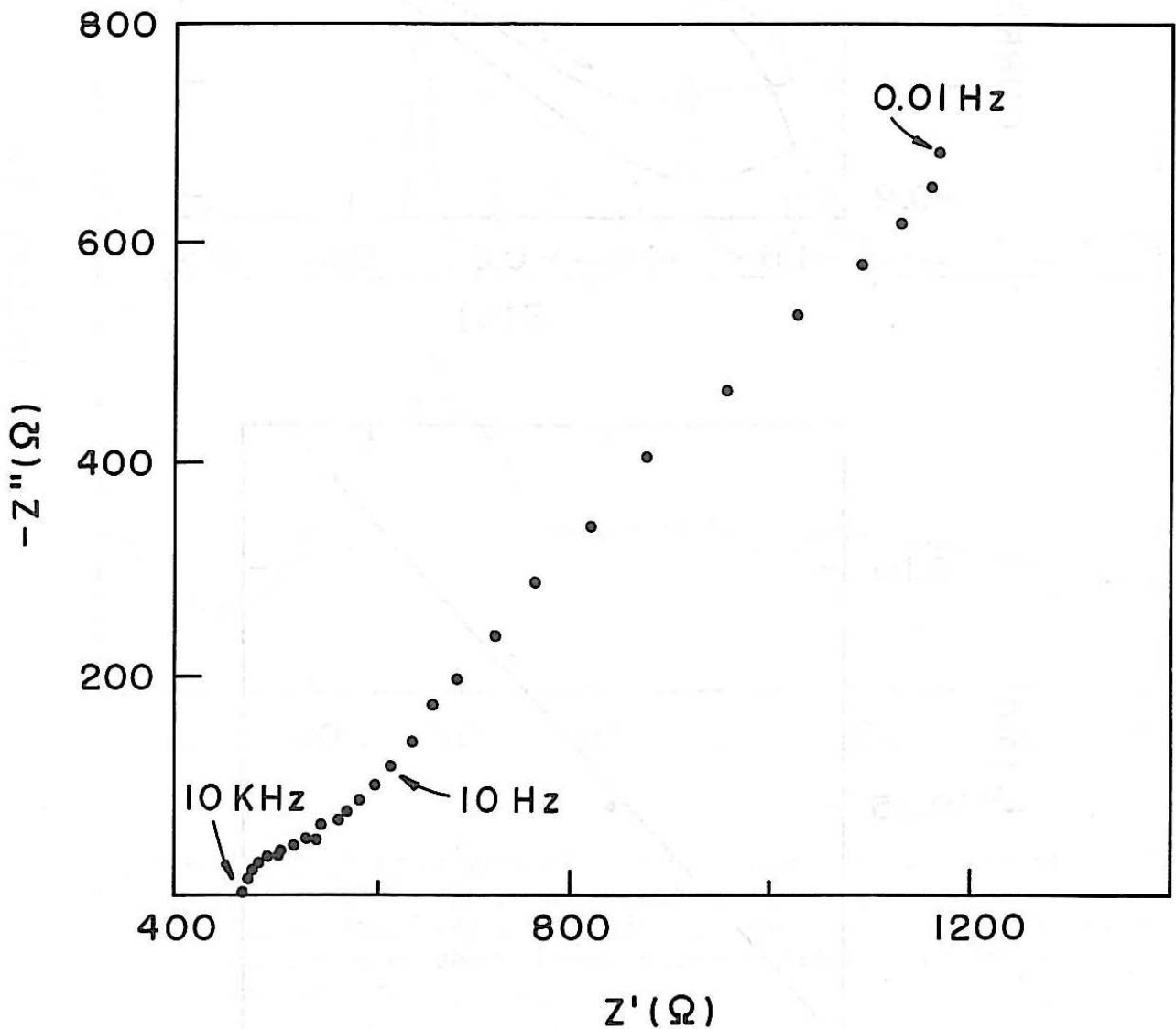


Fig. 5 - Complex impedance representation of a $\text{TiO}_2 - \text{CeO}_2$ electrode in PC - 0.2M LiClO_4 , $E = 0.5\text{V}$ vs Ag/Ag^+ .

The ac response has been analysed by the Randles equivalent circuit²² shown on the left side of figure 6. The circuit elements are the charge transfer resistance θ , the double layer capacitance C_{DL} , the electrolyte resistance R_I and a Warburg

element Z_w . The left side of the figure shows the frequency response of the circuit and is to be compared with the experimental results of figure 5.

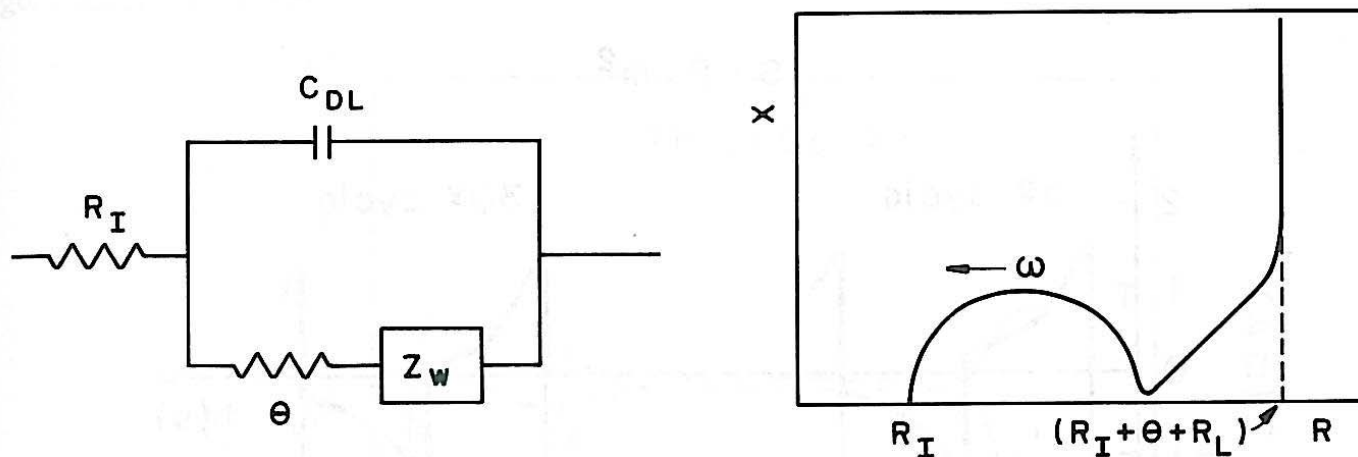


Fig. 6 - a) Equivalent circuit
b) Frequency response of the equivalent circuit (from 22)

The value of the Li diffusion coefficient were obtained either from the straight line region or from the low frequency limiting behavior (vertical line in complex plane not shown in the figure). Both real and imaginary parts of the impedance are proportional to $\omega^{1/2}$ between 10Hz and 1 Hz. The diffusion coefficient was calculated using equation²³ :

$$\bar{D} = (V_m/2FS)^2 (dE/dy)^2 (1/2A^2) \quad (3)$$

where V_m is the molar volume. S the surface area of the electrode, A the slope of Z'' vs $\omega^{1/2}$, F is the Faraday constant and dE/dy is the slope of the coulometric titration curve at a given insertion rate. This value can also be determined from the imaginary part of the impedance diagram at very low frequency (see figure 6b) where

$$R_L = \frac{V_m}{2FS} \left(\frac{dE}{dy} \right) \frac{1}{3\bar{D}} \quad (4)$$

The value of the molar volume used was that of crystalline CeO_2 . For the experimental conditions represented in figure 6, for a film with a thickness $l = 60nm$ and for $E = 0.5V$ vs Ag/Ag^+ , we obtain :

$$\bar{D} = 6.4 \cdot 10^{-12} cm^2/s \quad (5)$$

This value is comparable with those already obtained in WO_3 film²³.

Figure 7 shows a potentiostatic cycling performed on the $\text{TiO}_2 - \text{CeO}_2$ electrode between -1.8 V/Ag and $+0.5 \text{ V/Ag}$. After 30 cycles we see that the loss in the charge passing through the cell is extremely low. This result confirms the voltammetric measurements .

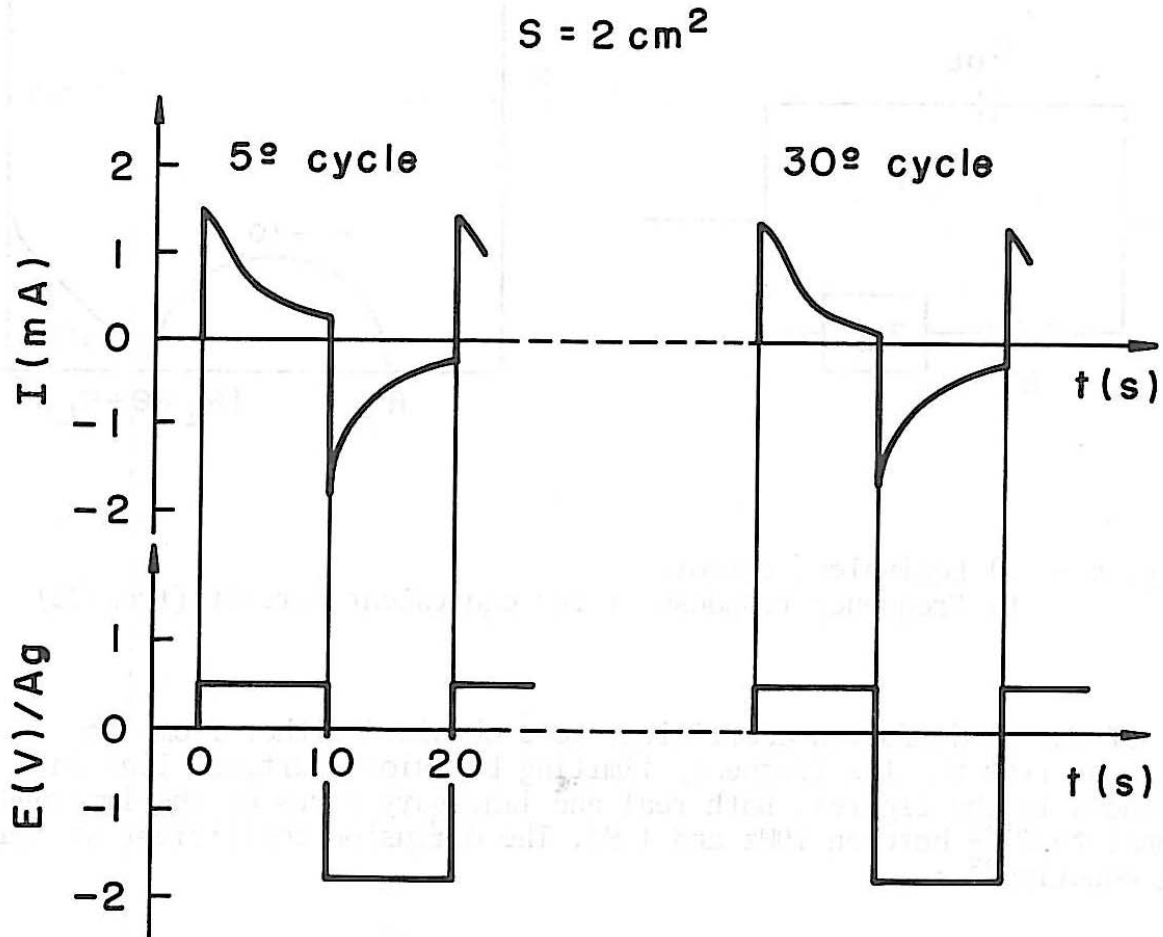


Fig.7 - Potentiostatic cycling of a three dip $\text{TiO}_2 - \text{CeO}_2$ electrode ($\text{Ti/Ce} = 1$) in a 0.2M propylene carbonate - LiClO_4 .

3.4. SIMS Characterization

SIMS profiles have been obtained at the Center for Microanalysis of Materials , University of Illinois at Urbana Champaign using a Camera IMS 3 f instrument²⁴ . Figure 8 shows the profiles of Ti, Ce, Li, Na, K, O, Si, Sn¹¹⁸ and In for a two dip layer $\text{TiO}_2 - \text{CeO}_2$ film deposited on an ITO coating and heat treated at 450°C for 15 minutes. Lithium was electrochemically inserted into the oxide film. A thin gold layer was also deposited on the top surface to eliminate the ion beam charging

effects. As no standard was available the height of each curve cannot be related to the elements concentration. We see that the concentration of these elements is constant throughout the layer and that diffusion of Sn and In of the ITO coating does not affect the composition of the ion storage layer. The figure 8 also proves that Li⁺ ions have been inserted into the layer and that its concentration is homogeneously distributed.

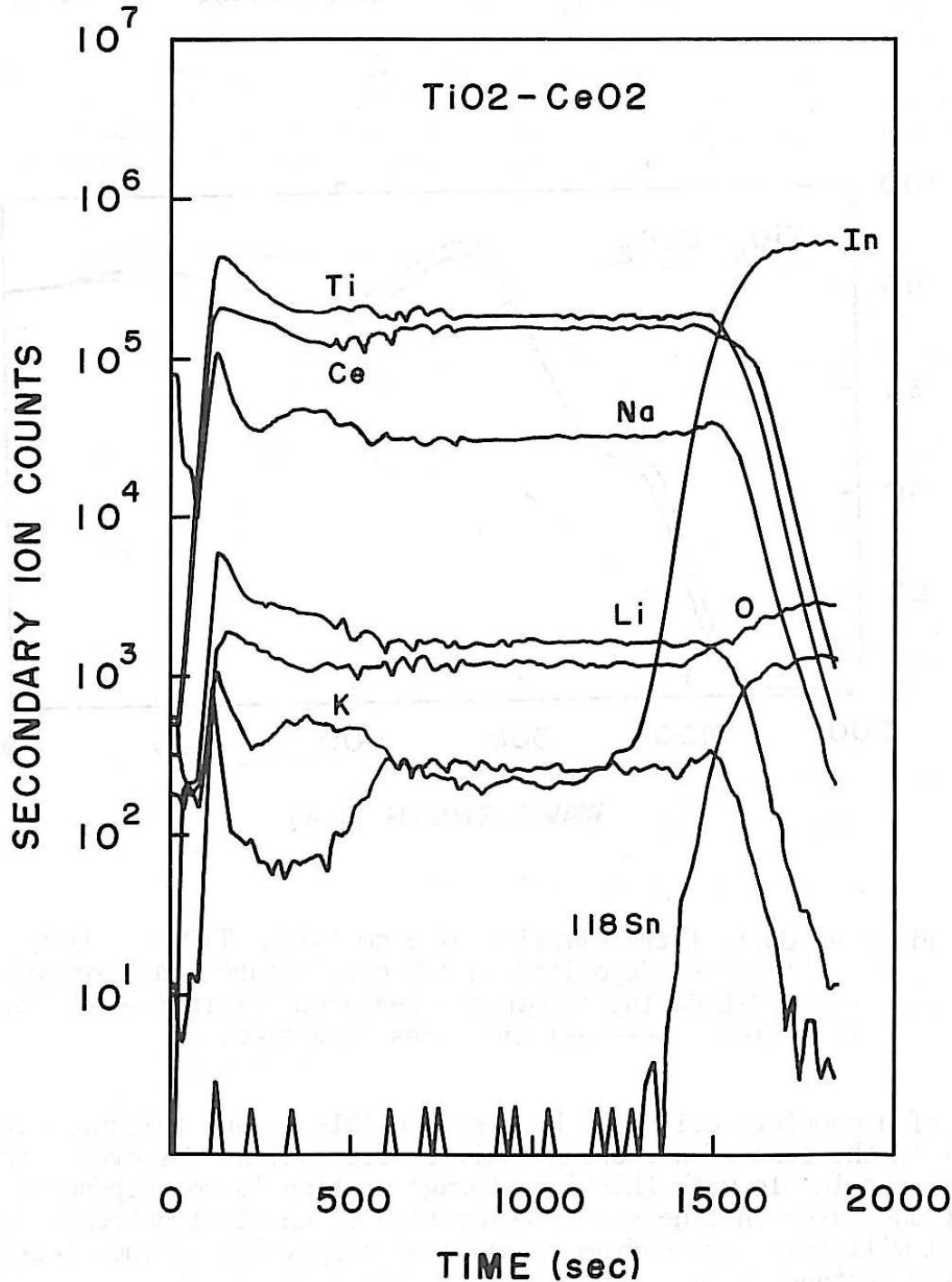


Fig. 8 - SIMS profiles of Ti, Ce, Li, Na, K, O, Si, In and ¹¹⁸Sn of a 2 dip layer TiO₂ - CeO₂ film deposited on ITO coated glass and heat treated at 450°C for 15 minutes measured after Li⁺ ions insertion.

3.5. Optical Characteristics

Figure 9 shows the transmission spectrum of a ~300nm thick $\text{TiO}_2\text{-CeO}_2$ oxide prepared with a sol aged 3 days and subsequently heat treated at 450°C for 15 minutes and measured before and after Li^+ ions insertion. The optical transmission remains practically unaltered. This exceptional behavior is technologically of great importance as no coloration will appear at this electrode during the cycles.

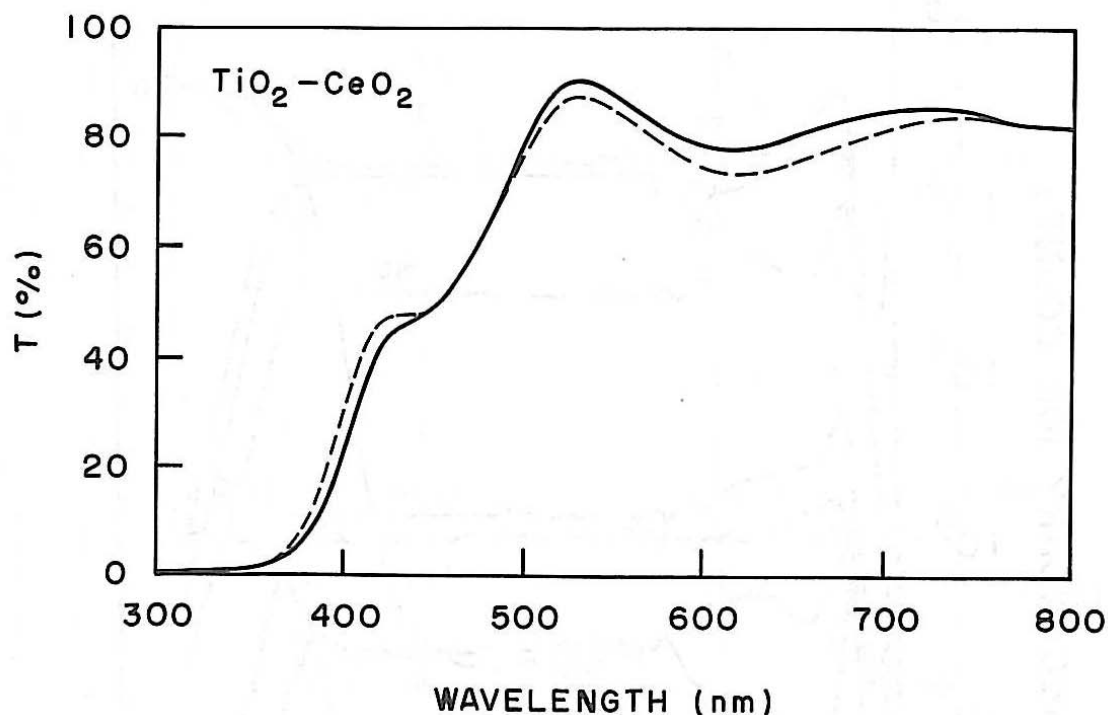


Fig.9 - Optical transmission of a nm thick $\text{TiO}_2 - \text{CeO}_2$ (3 dips) deposited on ITO coating and heat treated at 450°C during 15 minutes measured before (—) and after (-----) Li^+ ions insertion.

The contrast of a complete cell will be less sensible to any thickness variation of the layer, as in the case of a rocking chair configuration. Moreover the higher transmittivity obtainable with this ion storage coating is not dependent of the counter electrode layer thickness. The coloration of an electrochromic device (window or mirror) will only arise from the optical properties of the electrochromic layer (WO_3 for instance).

4. PROPERTIES OF THE ELECTROCHROMIC LAYER AND THE WINDOW

As discussed in the previous section, the coloration of a complete device which uses a $\text{TiO}_2 - \text{CeO}_2$ ion storage layer is only governed by the properties of the

electrochromic layer. The window which is presently tested has the configuration shown in figure 1. The sandwich is composed of the following elements :

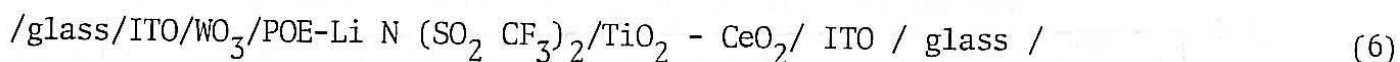


Figure 10 shows the optical response of the electrochromic layer WO_3 250nm thick deposited by evaporation technique on an ITO coated glass substrate before and after a partial Li^+ ions insertion corresponding to a charge of 10.5mC/cm^2 . It shows a reduction of the optical transmission already reaching 50% at 600nm. A complete window is presently under test. It is built by assembling three separate components : glass / ITO / WO_3 , electrolyte and $\text{TiO}_2\text{ - CeO}_2$ / ITO / glass. After their assembling the complete cell is hot pressed at 80°C in a dry box and sealed with a low vapor pressure resin (Varian Torr - seal).

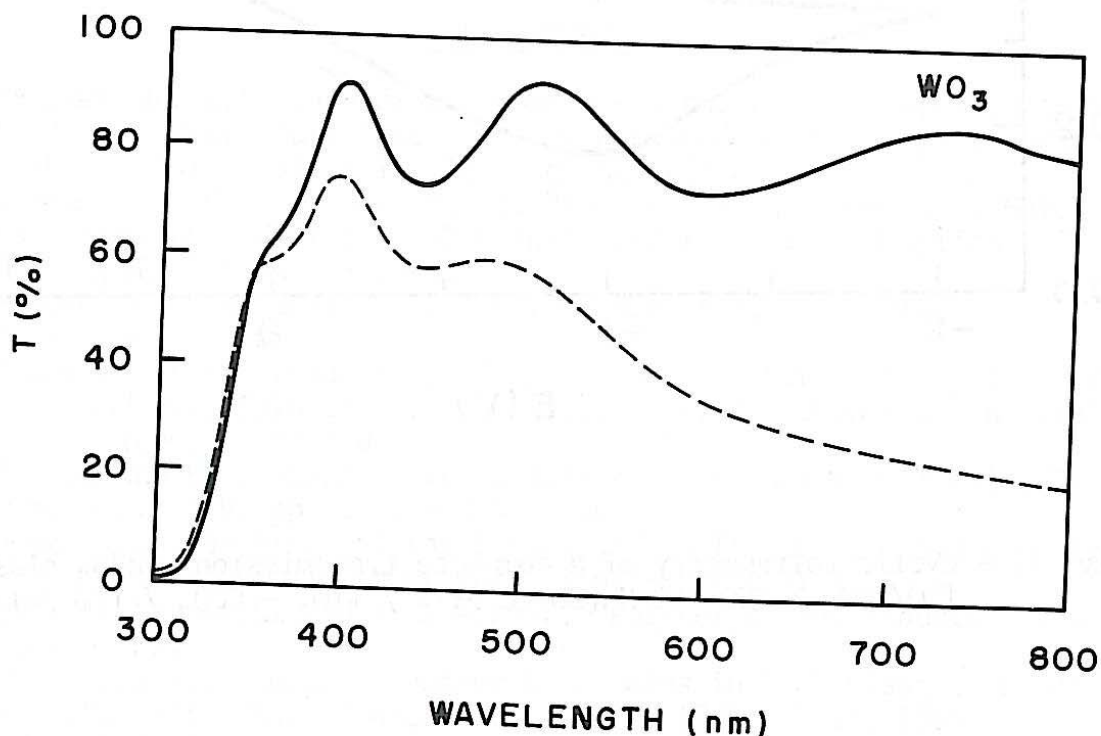


Fig. 10 - Optical transmission of an 250nm thick WO_3 deposited by evaporation technique on ITO coated glass substrate measured before (—) and after (----) Li^+ ions insertion.

Fig. 11 shows the cyclic voltammetry of such a device. The $\text{TiO}_2\text{ - CeO}_2$ counter electrode is used as a reference electrode. The coloration of this cell changes reversibly by applying a suitable voltage between the two electronic electrodes. It is blue when WO_3 is reduced and transparent and colourless when it is oxidized. Complete optical characterizations are underway.

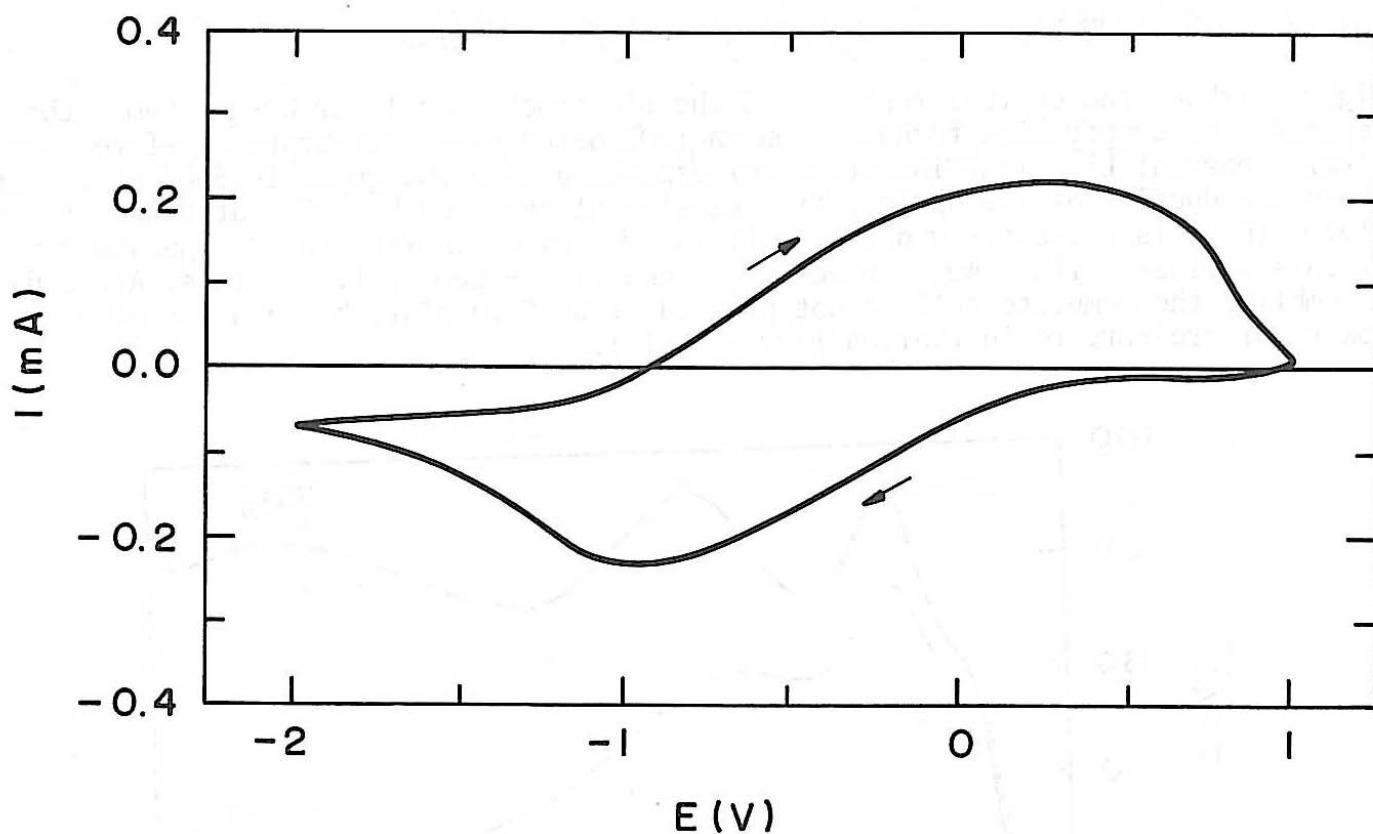


Fig. 11 - Cyclic voltammetry of a complete transmission window glass / ITO/ WO_3 / PEO- Li N $(\text{SO}_2 \text{ C F}_3)_2$ / TiO_2 - CeO_2 / ITO /glass.

5. CONCLUSIONS

This paper presents an investigation of the physical properties of TiO_2 - CeO_2 thin films prepared by the sol-gel process using the dip coating technique. This material presents an outstanding behavior as Li^+ ion storage electrode and its use is quite promising for electrochromic devices such as smart windows or mirrors²⁵. The lithium insertion is reversible and the electrode kinetics is acceptable. The process is controlled by solid state diffusion. No coloration is observed during the electrochemical cycles which should improve the uniformity of the optical contrast of such devices. The chemical diffusion of Li at room temperature is $\bar{D} = 6.4 \cdot 10^{12} \text{ cm}^2/\text{s}$ ($E = 0.5\text{V}$ vs Ag/Ag^+). This value is comparable to those obtained in WO_3 electrochromic film. The detailed mechanism of the lithium insertion is still not very well understood.

The best electrochemical results have been obtained with a 5 to 7 days aged sol. Physico chemical studies show that in such a sol the cerium is present almost as Ce^{3+} . It is however oxidized into Ce^{4+} during the heat treatment of densification and very small crystallites of CeO_2 are observed in a still amorphous TiO_2

matrix. The presence of these crystallites seems to be fundamental as well as the choice of the cerium precursor. The use of CeCl_3 for instance, which is also found as Ce^{3+} in the precursor sol, gives poor electrochemical reaction.

Complete transmissive and reflective devices are presently under extensive tests in order to determine their optical properties, long term reversibility and general performances under different ambient conditions. The feasibility of preparing other components by the sol-gel process such as the electrochromic coating (WO_3) and a solid state electrolyte is also underway.

ACKNOWLEDGMENTS

This research was financially supported by CNPq, FAPESP and FINEP (Brazil). P.B. and B.V. acknowledge the Ministère des Affaires Étrangères (France) for a scholarship to realize this research.

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