

DEVELOPMENT OF ELECTROCHROMIC DEVICES WORKING WITH HYDROPHOBIC LITHIUM ELECTROLYTE

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This manuscript report on a new lithium electrolyte, allowing the manufacturing of electrochemical systems, such as electrochromic devices, in ambient atmosphere. It is based on lithium *bis*-trifluoromethane sulfonimide dissolved in the following hydrophobic salt, which was first prepared by M. Grätzel *et al.*: 1-ethyl. 3-methylimidazolium *bis*-trifluoromethane sulfonimide. We have also successfully tested the compatibility of this electrolyte with WO₃ and TiO₂-CeO₂ films acting respectively as efficient electrochromic electrode and counter electrode for smart-window working with Li⁺ ions.

Keywords: Electrochromism; hydrophobic electrolyte

INTRODUCTION

Thin film electrochromic (EC) materials (ECM) and electrochromic devices (ECD) present a basis for light modulators and other electro-optic devices [1–11]. The ECD can be presumed as a system,

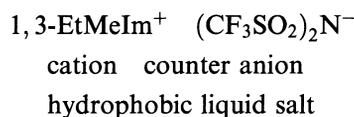
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containing an electrochromic material (ECM_1), a lithium ion conducting electrolyte (Li^+ -IC), and a counter electrode (EMC_2). This assembly is sandwiched between two identical transparent electronic conductors ($\text{ITO} \equiv$ Indium tin oxide) serving as ohmic contacts. EMC_1 switches from the transparent to the colored state during the cathodic process when electrons and Li^+ ions are injected into it. These electrons and cations which are provided by ECM_2 , transit via the external circuit and the electrolyte respectively. The process must be reversible. ECM_2 can either optically switch in a complementary way of ECM_1 or can remain transparent in both the inserted and deinserted states.

The most important problem to solve is the fabrication of efficient Li^+ -IC, EMC_1 and ECM_2 components, which allow the manufacturing process of ECD in open air, i.e., outside the inert atmosphere of the dry-box. The use of the dry-box is indeed unrealistic for obvious practical reasons; it means, for instance, that hydrophobic Li^+ -IC have to be used. This paper report on Li^+ -IC, EMC_1 and ECM_2 components allowing this important aim to be attained.

(i) Li^+ -IC is a hydrophobic electrolyte of high ionic conductivity.

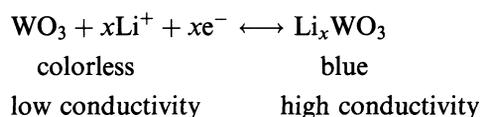
Recently, new hydrophobic ionic liquids with low melting temperature, low vapor pressure and high conductivity have been investigated: they are based on hydrophobic ions. Among these hydrophobic ionic liquids we have focused on the following ionic liquids which was first prepared by M. Grätzel *et al.* [12]:



We have indeed successfully used this hydrophobic liquid salt as a solvent for the solid salt: $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$. That allows us to obtain a new hydrophobic lithium electrolyte of high conductivity, recently patented by some of us [13].

(ii) ECM_1 is a WO_3 film coated, using the sputtering technique, on ITO glass (*ITO glass* \equiv transparent and conducting Indium Tin Oxide deposited in a glass substrate).

Various kinds of inorganic or organic ECM₁ have been proposed and their electrochromic properties have been extensively studied [1–11]. Among them, tungsten oxide is one of the most promising materials for electrochromic devices because of its advantages of a good perceived contrast, memory effect and low switching voltage, when it is in a porous nanocrystalline form.



Several techniques have been used to prepare these porous tungsten oxide films, such as sputtering, evaporation, electrodeposition, chemical vapor deposition, spray pyrolysis and sol-gel methods [1–11]. We have selected, here the sputtering technique which allow us to produce large size films (30 × 30 cm²) meeting, therefore, the industrial needs.

(iii) ECM₂ is a TiO₂-CeO₂ film deposited on ITO glass using RF sputtering.

Some of us have established that cerium doped titanium oxide (TiO₂-CeO₂) is an efficient transparent counter electrode [14–15]: it has been shown that Ce⁴⁺ acts, indeed, as a deep acceptor center for the electrons. It implies that the Ce⁴⁺ ↔ Ce³⁺ reduction–oxidation will take place during the Li⁺ insertion–deinsertion process and will, therefore, inhibit the Ti⁴⁺ reduction, thereby maintaining the film transparency.

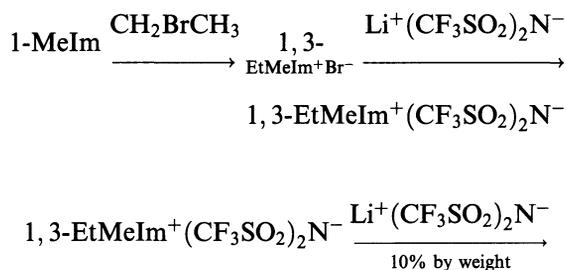
EXPERIMENTAL

Component Preparation

(i) *The Hydrophobic Li⁺-IC*

As quoted above, it is based on lithium *bis*-trifluoromethane-sulfonimide dissolved in hydrophobic 1-ethyl-3-methylimidazolium *bis*-trifluoromethane sulfonimide [12].

The schematic synthesis route is depicted below :



hydrophobic Li^+ -IC (gel type)

In order to synthesize the hydrophobic Li^+ -IC, we first mixed 136 cm³ of 1,1,1 trichloroethane (Prolabo 94%) with 24,3 cm³ of 1-methylimidazole (Aldrich 99%) under vigorous stirring. 100 g of bromoethane (Aldrich 99 + %) were then dropped out, into the solution, for 1 hour. Afterwards, the solution was refluxed for 2 hrs at around 80°C, allowing the reaction to proceed. The so-obtained liquid molten salt was immediately washed 3 times with 100 cm³ of 1,1,1 trichloroethane. Finally, 19 g of the crystallized product, 1,3-EtMeIm⁺Br⁻ (whose melting point is 76°C) was obtained. After drying under primary vacuum for 1 hour, it was dissolved in 45.5 cm³ of distilled water. We separately dissolved 28 g of Li(CF₃SO₂)₂N in 90 cm³ of distilled water. The two solutions were intimately mixed under vigorous stirring, at 70°C for 30 mins. Finally the 2 phases were separated and, after heating at 70°C under primary vacuum for 1 hour, the hydrophobic salt 1,3-EtMeIm(CF₃SO₂)₂N, was obtained (35 g). In order to get the expected hydrophobic Li^+ -IC, we dissolved 3.5 g of Li(CF₃SO₂)₂N into the 35 g of the hydrophobic salt.

(ii) The Electrochromic Material ECM₁: WO₃

The WO₃ films were either provided by Dr. A. Richardt, President of the Society Inland Europe-Paris (France), or deposited in our laboratory using planar magnetron Balzer BAS 450 PM apparatus. We have optimized the sputtering experimental conditions which are listed in Table I.

TABLE I Sputtering Experimental Condition for WO₃ film

<i>Target</i>	<i>Atmosphere</i>	<i>Power</i>	<i>Target to substrate distance</i>	<i>Substrate Temperature</i>
W ($\varnothing = 30$ cm)	O ₂ (50%) + Ar (50%) 10 ⁻² mbar	1000 W	10 cm	70°C 150°C

(iii) The Counter Electrode Material ECM₂: TiO₂-CeO₂

The sputtering conditions for various compositions are listed in Table II.

Film Characterizations

X-ray diffraction measurements were carried out, using CuK α radiation, to investigate the film structure. A JEOLJSM-840 A apparatus, allowing scanning or transmission electron microscopy (SEM or TEM) was used to determine the film texture, thickness and composition.

Electrochemical and Spectro Photometric Measurements

Electrochemical experiments were performed with a computer-controlled potentiostat/galvanostat (TACUSSEL, PGS 201 T model)

TABLE II RF-Sputtering Conditions for (TiO₂)-(CeO₂)

<i>Target</i>	<i>Atmosphere</i>	<i>Power</i>	<i>Target to substrate distance</i>	<i>Substrate temperature</i>
(TiO ₂)	O ₂ and O ₂ /N ₂ = 1 5 × 10 ⁻² mbar	60 W	10 cm	50°C
(TiO ₂) _{0.9} ⁻ (CeO ₂) _{0.1}	O ₂ and O ₂ /N ₂ = 1 5 × 10 ⁻² mbar	50 W	10 cm	50°C
(TiO ₂) _{0.66} ⁻ (CeO ₂) _{0.33}	O ₂ and O ₂ /N ₂ = 1 5 × 10 ⁻² mbar	47.5 W	10 cm	50°C
(TiO ₂) _{0.5} ⁻ (CeO ₂) _{0.5}	O ₂ and O ₂ /N ₂ = 1 5 × 10 ⁻² mbar	47.5 W	10 cm	50°C
(TiO ₂) _{0.2} ⁻ (CeO ₂) _{0.8}	O ₂ and O ₂ /N ₂ = 1 5 × 10 ⁻² mbar	42.5 W	10 cm	50°C
(CeO ₂)	O ₂ and O ₂ /N ₂ = 1 5 × 10 ⁻² mbar	40 W	10 cm	50°C

for the electrochemical cell of Pt/LiTFSI + 1,3-EtMelmTFSI/WO₃ (or TiO₂-CeO₂). All the measurements were advantageously performed at room temperature in air owing to the hydrophobic character for the lithium electrolyte (The Pt voltage was standardized versus a Li electrode). The electrochemical lithium insertion/deinsertion was processed under various charge densities which were repeated automatically. Optical properties of the colored and bleached states were investigated using a UV-Vis-NIR spectrophotometer (Varian Cary 2415 Spectrophotometer equipped with DS-15 Data Station). The ionic conductivity of the electrolyte was determined from impedance measurements using a Solartron impedancemeter.

RESULTS

Most interestingly, the hydrophobic Li⁺-IC, -whose water content is less than 3% (Karl Fisher analysis)-, is electrochemically stable over a large electrochemical window (Fig. 1). Moreover, its room tempera-

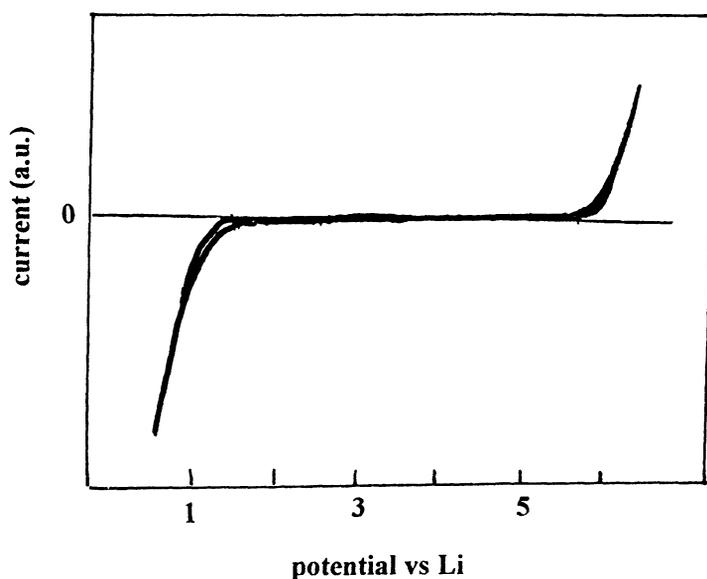


FIGURE 1 Cyclic voltammograms of the hydrophobic Li⁺-IC (anode = lithium metal; cathode = stainless steel).

ture conductivity, which is deduced from impedance measurements using a Solartron impedance meter, is larger than $10^{-3} \Omega^{-1}\text{cm}^{-1}$ (Fig. 2).

The Figure 3 shows the TEM photographs of the WO_3 films prepared at 70°C (A) and 150°C (B). The photo A evidences crystallites of about 10 nm diameter in a rather porous texture. A more dense film is observed on the photo B, and the crystallites have an average diameter of 30 nm.

When the substrate temperature is higher than 150°C , 300°C for instance, the films are highly dense with an average crystallite size of 100 nm. We are then dealing with the orthorhombic variety of WO_3 . The color changes are less marked in these film due to the too high crystallinity. That is the reason why we have finally used the two substrate temperatures which are quoted in the table (70°C and 150°C).

The Figure 4 represents the evolution of the inserted charge (Li^+) as a function of the film thickness for the two types of films. A forming process, accounting for the inserted charge difference between the first

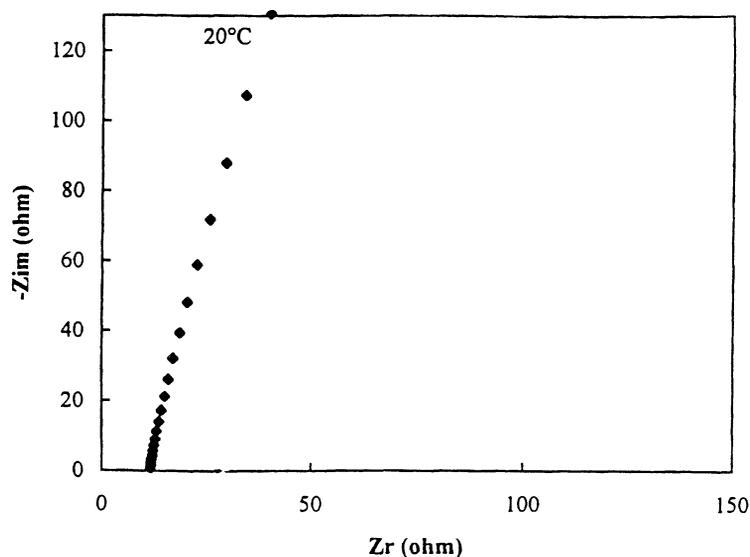
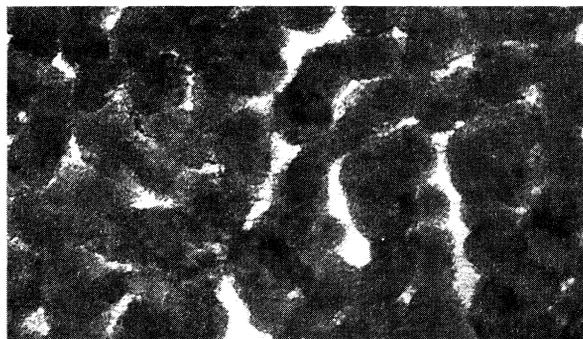
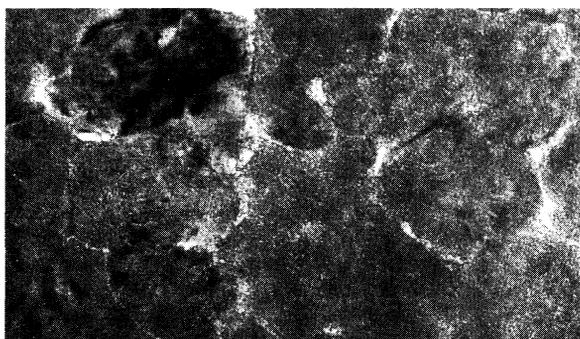


FIGURE 2 Impedance data (from 1 Hz to 1 MHz) of the hydrophobic Li^+ -IC (the electrolyte is sandwiched between two stainless steel electrodes).



A

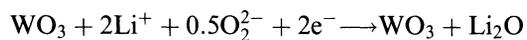


B

1 cm = 10 nm

FIGURE 3 TEM photographs of the films prepared at 70°C (A) and 150°C (B).

insertion step (i) and the following insertion-deinsertion steps (ii), is more pronounced for the more porous films, A. This forming process corresponds, very likely, to the reduction of the adsorbed oxygen such as O_2^- in the nanoscale structure (surface contamination):



The Figure 5 gives the evolution of the change in optical density (ΔOD), defined here as $\ln(T_{\text{bleach}}/T_{\text{color}})$, as a function of the reversible inserted charge (Li^+), for the films A and B. We see that

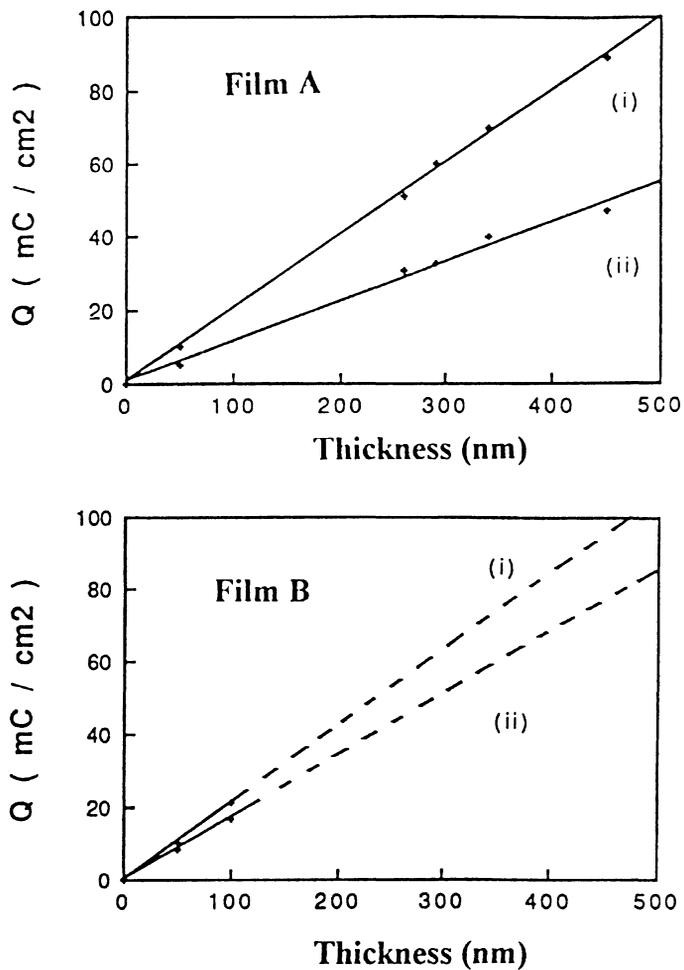


FIGURE 4 Evolution of Q , which is the inserted charge (Li^+), as a function of the film thickness (WO_3 films A and B; $V = 2V$ vs. Li , (i) first insertion, (ii) following insertions and deinsertions).

ΔOD and therefore the optical coulombic efficiency $\Delta OD/\Delta Q$, i.e., coloration efficiency, is higher for the film A. Consequently, we believe that the film A is the most interesting one (for an application point of view) in spite of the above mentioned formatting process. Moreover, the cyclic voltammogram of the film A, reported on the Figure 6,

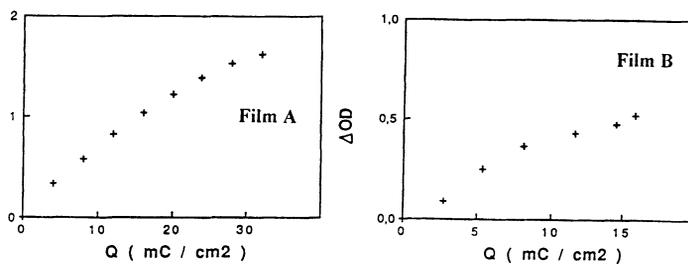


FIGURE 5 Evolution of the optical density, ΔOD , as a function of Q , which is the reversible inserted charge (WO_3 films A and B; film thickness = 3000 Å; $\lambda = 550$ nm).

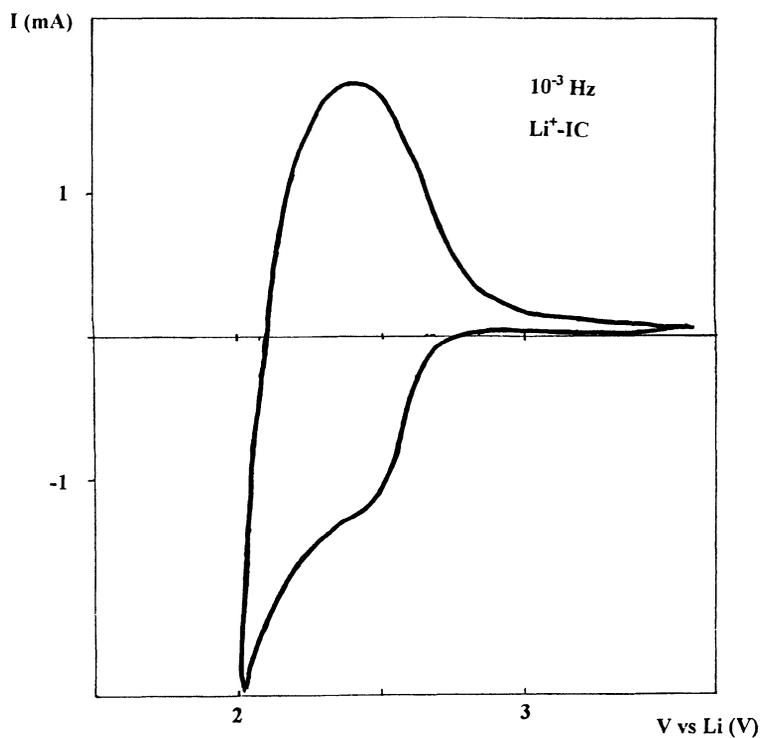


FIGURE 6 Cyclic voltammograms, in Li^+ -IC, of WO_3 : film A (anode = lithium metal; cathode = glass + ITO + WO_3).

shows that the insertion potential is larger than $2V$: it is, hopefully, within the stability domain of the hydrophobic Li-IC (Fig. 1).

Concerning the $\text{TiO}_2\text{-CeO}_2$ films, the achievement of a good transparency in both inserted and deinserted states is illustrated on the Figure 7 for the composition $(\text{TiO}_2)_{0.9}(\text{CeO}_2)_{0.1}$: indeed, the absorption coefficient does not change in the whole visible range upon Li^+ insertion. The reversible $\text{Ce}^{4+} + e \leftrightarrow \text{Ce}^{3+}$ redox process occurring during the Li^+ insertion process is evidenced on the Figure 8, showing the voltammogram for the composition $(\text{TiO}_2)_{0.9}(\text{CeO}_2)_{0.1}$; as shown in this figure, the electrode potential must remain larger than $\sim 2V$ vs. Li, in order to avoid the Ti^{4+} reduction and thereby maintain the film transparency.

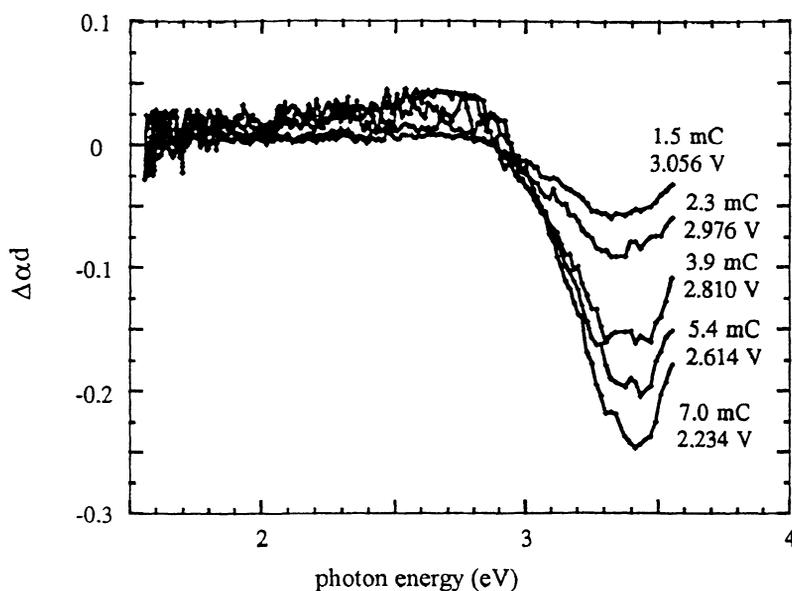


FIGURE 7 Variation of the absorption coefficient as a function of the inserted charge of a $(\text{TiO}_2)_{0.9}(\text{CeO}_2)_{0.1}$ film (film thickness = 3000 \AA , $S = 1 \text{ cm}^2$), deposited on glass + ITO).

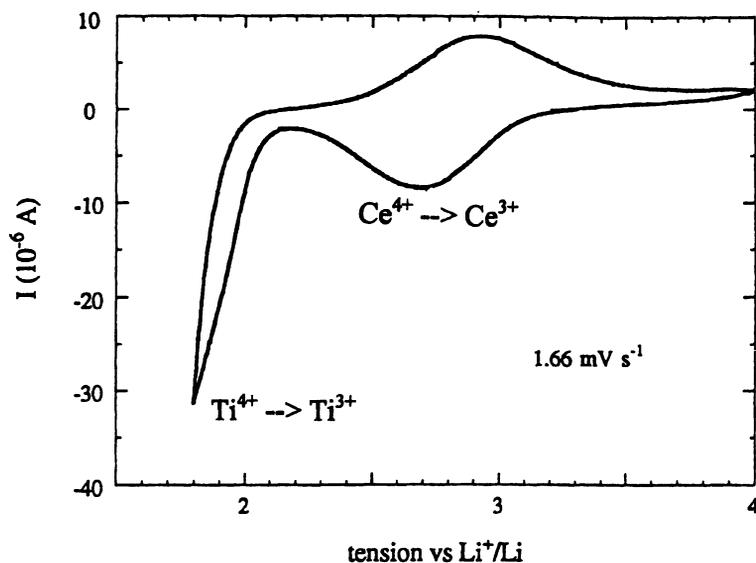


FIGURE 8 Voltammogram for the composition $(\text{TiO}_2)_{0.9}(\text{CeO}_2)_{0.1}$.

CONCLUSIONS

All the above mentioned results allow us to manufacture cheap and new electrochromic displays, ECD, which are based on the components presented in this manuscript. Let us quote that the ECD use Li^+ ions and not H^+ ones, so that they will have an efficient memory effect (over several days). They are easily manufactured in “open-air”, and not in inert and costly atmosphere of a dry box as it generally occurs for other ECD(Li^+), those which are very sensitive to water contamination due to the hydrophilic character of the ionic conducting electrolyte, Li^+ -IC. We have solved this problem by manufacturing new hydrophobic Li^+ -IC having also a high ionic conductivity and a low vapor pressure.

Acknowledgement

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