

DIP-COATED $\text{TiO}_2\text{-CeO}_2$ FILMS AS TRANSPARENT COUNTER-ELECTRODE FOR TRANSMISSIVE ELECTROCHROMIC DEVICES

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The dip-coating process is an attractive way for the preparation of thin films used in the field of electrochromism. The scope of the present paper is focused on the $\text{TiO}_2\text{-CeO}_2$ compounds since they exhibit a reversible electrochemical insertion of lithium ions maintaining a high optical transmissivity. These films can be used as transparent counter-electrode in an all solid state electrochromic transmissive device with, for example, WO_3 as electrochromic material and a lithium conductive polymer as electrolyte.

1. Introduction

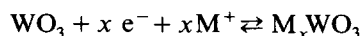
Interest has been increasing during the last years in the preparation of thin films by the sol-gel process. With this method, multicomponent large scale oxide films can be obtained easily and with lower cost than with other methods of deposition such as CVD, sputtering or vacuum evaporation. Investigations are also very active in the field of electrochromism for developing all solid state energy efficient windows. For this purpose, various electrochromic materials such as tungsten trioxide or vanadium pentoxide have already been prepared by the sol-gel method [1,2]. This work presents a new electrode material $\text{TiO}_2\text{-CeO}_2$ deposited by dip-coating onto ITO coated glass and which can be used as transparent counter-electrode in a transmissive electrochromic device.

2. Electrochromic window

The electrochromic phenomenon is the property of some materials to change their optical transmission (reflection) spectrum and especially their colouration by application of an electric field

or current. It has been extensively studied during the past two decades for its application to electro-optic displays and recently for the realization of energy efficient windows [3,4]. This latter kind of device allows the modulation of the window's transmission and reflection properties and, thus, a regulation of the heat transfer rate. The main electrochromic materials are transition metal oxides such as WO_3 or MoO_3 , but organic films can also exhibit the property of electrochromism.

Taking WO_3 as the electrochromic material, the colouration reaction corresponds to an insertion process with electrons and ions injection:



Although the colouration is faster with protonic conduction due to high chemical diffusion coefficient of H^+ in WO_3 , corrosion of the films in acid media occurs limiting the life of the device. Therefore, chemically inactive lithium conductors are preferred.

A schematic cross-section of an electrochromic window is shown in fig. 1. It is a succession of five laminated layers sandwiched between two glass substrates. The two conductive ITO layers are the current collectors. A good compatibility of both

electrochromic material and counter-electrode with the electrolyte is required. Using WO₃ as the electrochromic material, the counter-electrode must be transparent when in the reduced state, i.e. when WO₃ is in an oxidized state. In order to make a solid state device, more convenient than those containing a liquid electrolyte, lithium conductive polymer electrolytes can be used. They provide a good electrolyte/electrode contact due to their elastomeric property and can be elaborated in thin films. With lithium conductors, V₂O₅ [5,6], In₂O₃ [7] and CeO₂ [8] have been proposed as counter-electrodes in a transmissive electrochromic device, but none present all the required properties: transparency, reversibility and high kinetics of the electrochemical reaction. Lithium insertion in V₂O₅ is fast enough and reversible but the transmission in the bleached state is not sufficient. In₂O₃ retains a good transparency but the insertion rate of lithium is poor and the reaction is partially irreversible. CeO₂ exhibits a good reversibility for lithium insertion, is colourless in both oxidized and reduced states but the reaction kinetics are low.

It is generally accepted that the diffusion of lithium into the electrode is the limiting step, determining therefore the kinetics of the insertion reaction. CeO₂ has been studied as the electrode material because it has two stable valences available (+III, +IV) and absorption in the visible region is low due to the presence of f bonding orbitals. However, the size of the insertion sites (1.02 Å) in its fluorine structure is much higher than the lithium ion radius (0.6 Å), and this system is not favourable.

Therefore, starting from the CeO₂ structure, it is suitable to substitute cerium atoms by another element of smaller ionic radius in order to modify the structure.

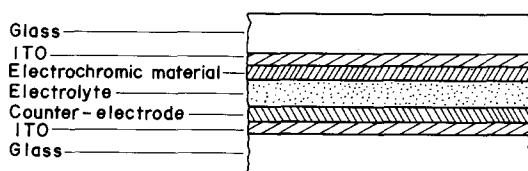


Fig. 1. Cross-section of an electrochromic window.

3. Experimentals

3.1. Film preparation

TiO₂-CeO₂ films with various Ti/Ce ratios have been synthesized by the sol-gel process using the dip-coating method. The starting solution was prepared by dissolving Ce(NH₄)₂(NO₃)₆ in ethanol, then adding tetraisopropyl orthotitanate Ti(O-iso-C₃H₇)₄. The concentration of Ce(NH₄)₂(NO₃)₆ never exceeded 0.25M, which is the limit of solubility of this salt in ethanol at room temperature. It is well known that titanium alkoxides strongly react with water. The presence of the cerium-ammonium nitrate stabilizes the solution and prevents this reaction being too fast.

The ITO coated glasses were carefully cleaned, rinsed with bidistilled water and ethanol, then dried at 70°C for 1 h. After being cooled, the samples were dipped into the solution and withdrawn vertically at a speed of 10 cm/min, dried for 15 min and densified at 450°C for 15 min. The procedure was repeated to increase film thickness.

3.2. Electrochemical measurements

An EE&G PARC173 potentiostat/galvanostat was used for voltametric and chronoamperometric measurements. The measurements were made in a 0.1M LiClO₄-propylene carbonate solution in a dry box. Both propylene carbonate and lithium perchlorate were previously dried. The counter-electrode, a platinum foil, and the reference, a silver wire, were immersed in a 0.01M AgClO₄-propylene carbonate solution. The reference was separated from the principal compartment by a fritted glass.

An all solid state transmissive electrochromic device was realized using amorphous evaporated WO₃ as the electrochromic material and the complex polyethylene oxide (PEO)-LiN(SO₂CF₃)₂ with O/Li = 10 as the polymer electrolyte. The counter-electrode in this device was a TiO₂-CeO₂ film (Ti/Ce = 1) deposited onto ITO coated glass by dipping three times. The WO₃ electrode was reduced potentiostatically in liquid electrolyte at $E = -2$ V/Ag before assembling the cell. The

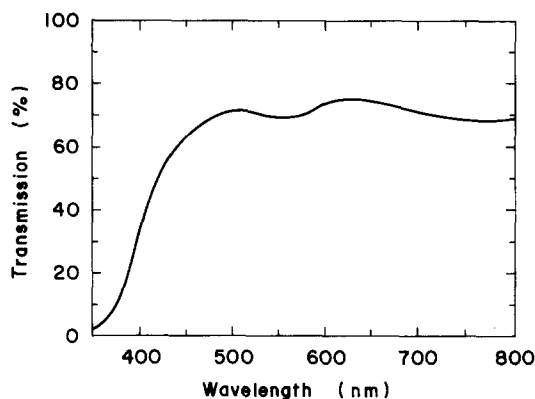


Fig. 2. Transmission spectrum in the visible region of a CeO₂-TiO₂ electrode (Ti/Ce = 1) dipped twice onto an ITO coated glass.

polymer electrolyte was prepared by mixing and stirring PEO powder ($MW = 6 \times 10^5$) and the lithium salt in acetonitrile. Then, it was doctor-bladed on the counter-electrode, heat treated at 80 °C to evaporate the solvent and dried under vacuum. Finally, the entire cell was hot pressed at 80 °C and sealed.

4. Results

The sol prepared for the dip process was dark red and stable during at least one week at room temperature. As the sol was heated, it gelled and became milky white. The films obtained after densification were yellowish and transparent. A typical transmittance spectrum in the visible region is presented in fig. 2.

The cyclic voltammetry shown in fig. 3 was obtained with a CeO₂-TiO₂ (Ti/Ce = 1) film dipped three times. 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 the electrode material at a sweep rate of 10 mV/s is 10 mC/cm², corresponding to an optical density of approximately 0.5 for amorphous WO₃. The cathodic threshold potential was limited to -1.8 V/Ag to avoid any side reaction on the ITO layer. During the insertion, no visible colouration could be observed.

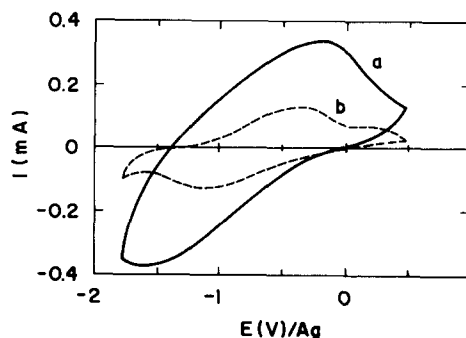


Fig. 3. Cyclic voltammetry of a CeO₂-TiO₂ electrode (Ti/Ce = 1) dipped three times in a 0.1M propylene carbonate-LiClO₄ solution. a, 50 mV/s and 9.1 mC; b, 10 mV/s and 14.5 mC.

Other CeO₂-TiO₂ films have been prepared by the same method using CeCl₃ · 7H₂O as cerium salt. The electrochemical response was much lower than with the ammonium cerium nitrate. We suggest that the valence of the cerium atoms in the films when using the chloride cerium is three. Moreover, the low vapour pressure of TiCl₄ might provoke titanium evaporation during the densification step. In the case of the ammonium-cerium nitrate, there is a mixed valence (III, IV) on the cerium atoms, allowing the reduction from valence IV to III.

A potentiostatic cycling performed on the same CeO₂-TiO₂ electrode between -1.8 V/Ag and +0.5 V/Ag is shown in fig. 4. After thirty reduction/oxidation cycles, the loss in the charge passing through the cell every cycle is very low, demonstrating the reversibility of the electrochemical reaction.

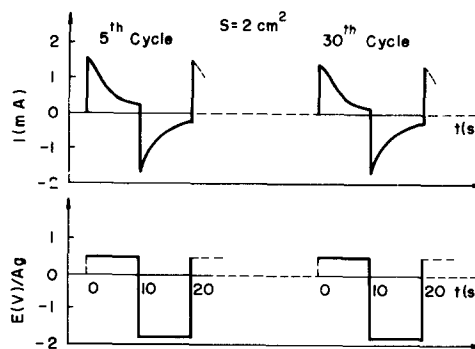


Fig. 4. Potentiostatic cycling of a CeO₂-TiO₂ electrode (Ti/Ce = 1) dipped three times in a 0.1M propylene carbonate-LiClO₄ solution.

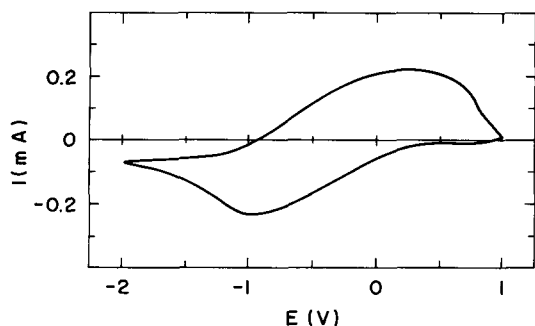


Fig. 5. Cyclic voltametry of a complete transmissive device: glass/ITO/ WO_3 /PEO-TFSI/ CeO_2 - TiO_2 /ITO/glass (PEO = polyoxyethylene oxide; TFSI = $\text{LiN}(\text{SO}_2\text{CF}_3)_2$).

The cyclic voltametry shown in fig. 5 was realized with a complete transmissive electrochromic device. A CeO_2 - TiO_2 electrode was used as reference electrode and counter-electrode. The colouration of this device changed reversibly by applying a voltage between the two electrodes. It was blue when the tungsten trioxide electrode was polarized cathodically, transparent and colourless when it was polarized anodically.

5. Conclusion

This paper presents the first investigation on the electrochemical study of CeO_2 - TiO_2 thin films prepared by the sol-gel process. This new electrode material, working via lithium insertion, ap-

pears to be very attractive as a transparent counter-electrode in a transmissive electrochromic device using lithium conductors. The lithium insertion is reversible and the electrode kinetics are promising. Further experiments are being performed in order to evaluate the influence of the sol composition, number of dips and temperature of densification on the electrochemical behaviour.

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