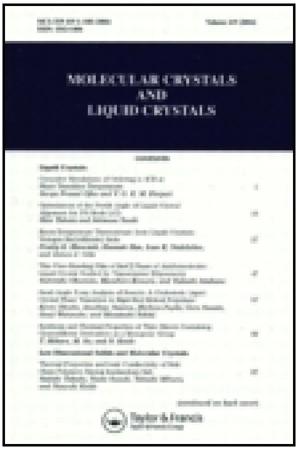

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Thin Film Sol-Gel of CeO_2-ZrO_2: The Candidate for Counter Electrode in Electrochromic Devices

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Thin Film Sol-Gel of CeO_2-ZrO_2: the Candidate for Counter Electrode in Electrochromic Devices

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Thin films of mixed oxides of CeO_2-ZrO_2 with molar ratio Ce/Zr = 0.73 have been prepared by sol-gel method. The precursor sols were obtained from a mixture of $Ce(NH_4)_2(NO_3)_6$, titanium alkoxide ($Zr(OPr^i)_4$) and isopropanol and then submitted to ultrasonic irradiation. The films were deposited using the dip-coating technique on ITO-Asahi glass and densified at 80° C during 15 min and calcined at 450°C during 15 min in oxygen atmosphere. Xerogels were characterized by thermal analysis (DTA-TG) and X-ray diffraction. Their possible use as ion storage (counter electrode) in electrochromic devices was studied by electrochemical (cyclic voltammetry and chronoamperometry) and optical measurements. The reversibility of the insertion/extraction process and the stability of the films as a function of the cycles number was performed.

Keywords: thin films; counter-electrode; electrochromic devices

INTRODUCTION

The counter electrode like working electrode and electrolyte is a very important part of the electrochromic device [1]. Different thin films containing CeO_2 remains transparent under cyclic voltammetry conditions, contrary to Nb_2O_5 [2] or WO_3 [3] which change their optical transmission from transparent to deep blue, have been reported [4]. Within these different materials the most

widely studied are CeO_2-TiO_2 and CeO_2-SnO_2 both prepared by the sol-gel process [1,5] or sputtering [6]. These films combine optical transparency in electrochemical conditions with ability to insert/extract large charge densities. These coatings show also a good compatibility with WO_3 films when applied in electrochromic devices [7,8]. Very few study report about thin films of CeO_2-ZrO_2. Baudry *et al.* [9] several years ago mentioned that this film, prepared by the sol-gel process, can be another candidate for counter electrode. Luo *et al.* [10] have reported in recent work the first results concerning cerium-zirconium sols prepared by three different routes always starting from ethanol solution of $Ce(NO_3)_3 \cdot 6H_2O$ and $ZrOCl_2 \cdot 9H_2O$. These films with ~50% molar ratio of CeO_2, after thermal densification at 500° C presented cubic structure similar to the CeO_2-TiO_2 films [11] and permanent transparent during Li^+ ions insertion/extraction process in the range from 200 to 2500 nm. Veszelei *et al.* [12] characterized thin films of mixed oxides of CeO_2-ZrO_2 obtained by magnetron sputtering. These films showed good transparency with inserted/extracted charge density of 13.4 $mC/cm^2\mu m$ (0.5 μm thick film) after 200 voltammetric cycles. These results prove that the cerium-zirconium mixed films are very promising alternative to be used in electrochromic smart windows, due to their good electro-optical performance [1,9,10]. These films remains colorless in the insertion/extraction process and can be prepared by different process. Moreover the sol-gel process with dip coating technique, a common method of film deposition in this field, seems to be more interesting. This method allows for easy fabrication of large area coatings at a low cost and offers advantages in controlling the microstructure of the film, an asset for eventual technological application.

In this work we report on the preparation and characterization of CeO_2-ZrO_2 films dip coated on ITO Asahi-Glass from a sol easy to prepare. Xerogels of CeO_2-ZrO_2 have been characterized by differential thermal analysis (DTA/TG) and X-ray diffraction and the coatings by electrochemical and optical techniques.

EXPERIMENTAL

The preparation of dark red and stable cerium-zirconium solution was realizedd using a sonocatalytic process similar to of CeO_2-TiO_2 [10,13]. The starting solution to produce CeO_2-ZrO_2 films with molar ratio Ce/Zr=0.73 was prepared by dissolving ammonium hexanitratocerate ($Ce(NH_4)_2(NO_3)_6$) powder (1.028 g, 1.9 mmol) and titanium isopropoxide ($Zr(OPr^i)_4$) (1.177 ml, 2.6 mmol) in isopropanol (15 ml) in a small (30ml) Becker recipient. The solution mixture was submitted for a few minutes (~5min) to the action of 95 W ultrasonic irradiation from a Sonicator ® W385 Heat System-Ultrasonic, Inc. at 20 kHz equipped with a 1/2" Disruptor Horn resulting in a transparent and dark red solution. This solution was left to aging in closed glass recipient for about 72 hours at room temperature until to change the color from deep red to transparent pale yellow. It was stable for some months when kept in a closed glass recipient in the fridge.

The coatings were deposited by dipping ITO coated glass substrates (Asahi-Glass, 14Ω/□) previously cleaned and rinsed with bidistilled water, ethanol and then dried at room temperature, into the solution in ambient atmosphere (RH<60%) and withdrawing it at a rate of 20 cm/min. The samples were subsequently dried in air at room temperature for 15 minutes. The uniform gel films were then densified at 80°C for 15 min. and kept the final temperature in oxygen atmosphere at 450°C for 15 min. The resulting coatings with a thickness of about 100nm for 1 dip were transparent and homogeneous without any visual cracking.

Differential Scanning Calorymetry (DSC) and Thermal Gravimetry (TG) were performed on xerogel sample with Shimadzu DSC-50 and TGA-50. All analysis were executed in air atmosphere at a heating rate of 10°C/min.

X-ray diffraction measurements have been performed on sample of xerogel obtained from the same sols and heat treated up to 600°C for 15 min with a Simens D instrument with the CuK_α radiation.

The electrochemical measurements were realized using a Solartron 1286 analyzer and a conventional three electrode cell. The counter electrode was a platinum foil of 1cm^2 area and the quasi-reference electrode was a silver wire. The electrolyte was a 0.1M solution of $LiClO_4$ dissolved in propylene carbonate (PC). The cell was previously purged with dry N_2 gas.

The thickness of the films was measured with a Taylor-Hobson Talystep and optical spectra in the UV-Vis range were recorded *in situ* with a 5G model Varian spectrophotometer.

RESULTS AND DISCUSSION

Figure 1 shows X-ray diffraction patterns of xerogel obtained with the same sol used for the coatings and heat treated at different temperatures between room temperature and 600°C during 15 min. following the same densification procedure. The heat treatment of the samples change the precipitate structure. Up to 100°C the crystalline structure is due to the cerium xerogel component and with the increasing temperature (235°C) the structure change to the crystalline phase of CeO_2 (cerianite) with the peaks of the following Miller indexes (111), (200) and (220), that correspond to the d = 0.303; 0.262 and 0.186 nm. The absence of ZrO_2 crystalline peaks suggest that the crystalline CeO_2 phase is dispersed in the amorphous phase of ZrO_2 similar to the CeO_2-TiO_2 xerogels [13,14].

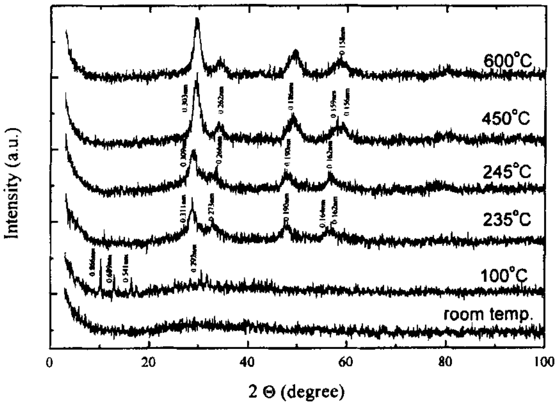

FIGURE 1 X-ray diffraction of CeO_2-ZrO_2 xerogels heat treated from 100 to 600°C showing the transition of the Ce salt phase to CeO_2 phase.

This structural change of cerium zirconium xerogel was also followed by DTA and TG (Figure 2). A large endothermic peak was clearly visible in the DTA curve. Since this peak was accompanied by a weight loss (~20%) around 90 - 130°C it can correspond to the cerium salt decomposition giving NH_3, water as volatile products and/or to organic residues elimination. The latter ones can originate from i-propylate hydrolysis and from the solvent molecules trapped within the matrix in the course of the xerogel formation. A sharp exothermic peak followed by an endothermic peak (235 and 245°C) with very accentuated weight loss (~50%) in part can correspond to the crystallization process of CeO_2 and the final cerium salt decomposition respectively. It should be stated here that a very similar exotherm/endotherm set of peaks is present in CeO_2–TiO_2 and CeO_2-TiO_2-ZrO_2 xerogels [13,15]. This conclusion is corroborated by X-ray diffraction studies which show the appearance of cerianite phase at the same temperature (vide supra).

Thus, the endotherm peak must originate from the decomposition of the cerium oxide precursor rather than from the zirconium one. The final decomposition of the cerium salt involves predominantly nitrogen oxides elimination.

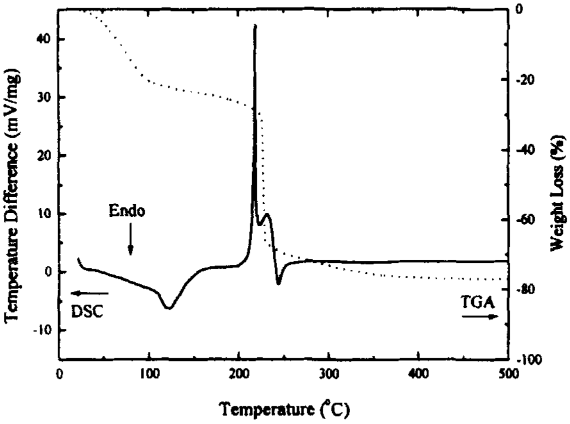

FIGURE 2 DTA/TG of cerium-zirconium xerogel (10°C/min, air atmosphere).

The typical cyclic voltammograms (Figure 3) were registered for the 100th and 500th cycle between -1.8 and +2.0V vs Ag at a scan rate of 50 mV/s. This figure shows the cathodic wave maximum at -1.1V that correspond to the insertion of Li^+ ions and the anodic wave due to the Li^+ extraction at -0.1V. The insertion/extraction process does not change the color of the film which remains transparent. The anodic and cathodic charge density (in mC/cm^2) were measured from the integration of the cyclic voltammograms and current response and presented as a function of the number of the cycles (Figure 4). The exchanged charge increase from 3.3 mC/cm^2 (±3%) to 4.0 mC/cm^2 for the first 400 cycles and then stabilize up to 500 voltammetric cycles. The chronoamperometric measurements for insertion and extraction process (15 s at -1.8 V and 15 s at 2.0V) show the higher charge densities on the beginning when compared with values obtained from integration of cyclic voltammograms. The initial value increase from 5.4 mC/cm^2 to 6.7 mC/cm^2 for cycle 100 and then decrease to 4.5 mC/cm^2 for the cycle 500. This last value remains without more significantly changes up to cycle 1000 (Figure 4). During the consecutive voltammograms cycles the insertion/extraction peaks remains the same position -1.1V and -0.1V respectively (Figure 3).

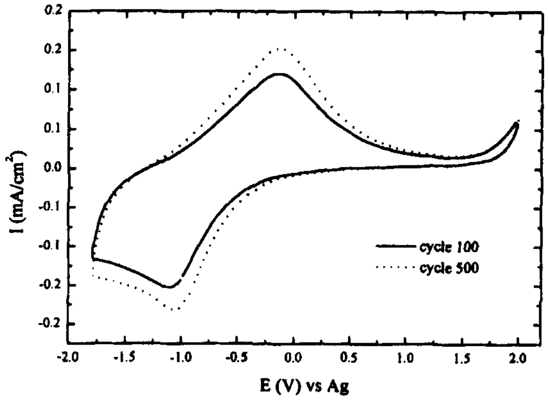

FIGURE 3 Typical cyclic voltammetry of a CeO_2-ZrO_5 one layer film deposited on Asahi ITO coated glass heat treated at 450°C/15min. Electrolyte (0.1M) $LiClO_4$/PC, rate 50mV/s.

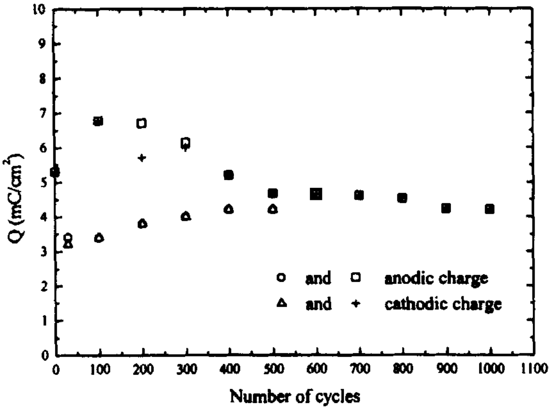

FIGURE 4 Charge densities as a function of number of voltammetric (○,△) and chronoamperometric (□,+) cycles. The triangle and square symbols represent insertion and the other extraction process.

Figure 5 shows the transmission spectra of one layer film of CeO_2-ZrO_2 that is almost transparent in the whole visible range. However, it can be observed that for longer time (60 s) of Li^+ insertion at −1.8 V (inserted figure) the transmission response of optical spectra measured at 550 nm change only in 0.5%. The extraction process at +2.0V during the same time return very fast (in ~4 s) to the initial, 72.5% transmission value. For the shorter times of the insertion process this change is smaller that when measured in the whole range from 350 to 800 nm the both curves have the same values. It can be concluded that the Li^+ insertion/extraction process remains the films in the transparent state.

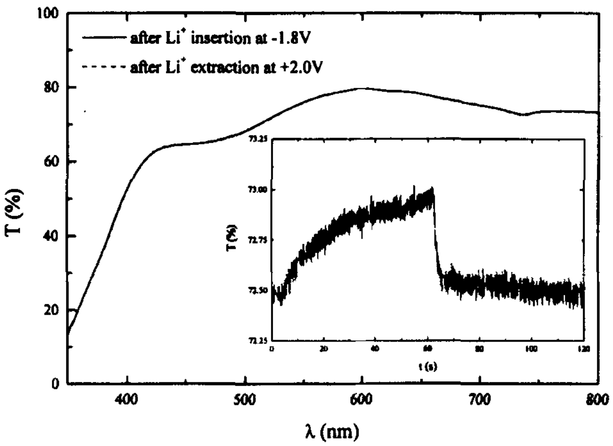

FIGURE 4 UV-Vis spectral variation after Li^+ insertion (——) and extraction (----) process and the change of transmission (at 550 nm) during 60/60 s insertion/extraction process (inserted figure) in one layered film of CeO_2-ZrO_2.

The use of sonocatalysis for the preparation of cerium-zirconium based sols leads to obtain homogeneous CeO_2-ZrO_2 films presenting excellent and reversible electrochemical properties similar to those obtained by Veszelei *et al.* [12] but with higher charge density. The Ce-Zr alkoxide precursor prepared under sonocatalysis is also easier and cheaper to prepare and allows to obtain sols which can be kept unaltered during some months. These parameters being of fundamental importance for an eventual industrial development.

CONCLUSION

The sonocatalytic method was used for the preparation of stable, cheap and easy to prepare cerium-zirconium sol based on $Ce(NH_4)_2(NO_3)_6$ and $Zr(OPr^i)_4$ precursors. CeO_2-ZrO_2 films obtained from this sol exhibit excellent electrochemical properties and are promising candidates for counter electrodes in electrochromic devices using either protonic or lithium electrolytes. CeO_2-ZrO_2 coatings calcined at different temperatures from 100 to 600°C change their structure from crystalline phase of already decomposed $Ce(NH_4)_2(NO_3)_6$ salt to crystalline phase of CeO_2. No crystalline phase of ZrO_2 was observed. The films present a reversible and fast insertion/extraction kinetics of Li^+ ions. The charge density inserted into one layer coating was 4 mC/cm^2 after 500 cycles and does not change until 1000 cycles. The optical measurements confirm that the insertion/extraction process does not change the color of the film, that is almost transparent in visible range of electromagnetic spectra. This property confirms their possible use in electrochromic devices as storage - counter electrode.

All these results are very similar to those already obtained by us for CeO_2-TiO_2, but with smaller charge density. These results confirm too, that the sonocatalytic route to prepare the sol-gel coatings is very simple, cheap and quick. This method gives the thin homogeneous coatings with good opto-elecrochemical responses.

Acknowledgment

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