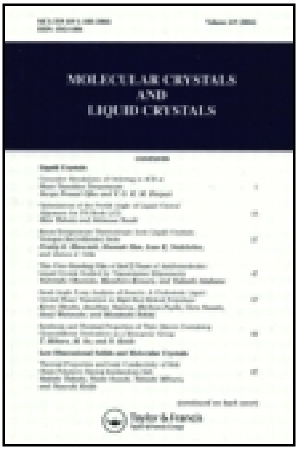

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LITHIUM INTERCALATION IN CeO_2-TiO_2 THIN FILM

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CeO_2-TiO_2 sol-gel thin coatings are known as transparent Li-ion storage electrode for electrochromic devices (ECD). As the charge capacity of the CeO_2-TiO_2 coatings is a limiting factor to get a high coloration intensity of such devices, the knowledge of transport kinetics parameters is of great importance to understand the behavior of this film during lithium insertion/extraction process. Aiming to understand better the lithium insertion behavior into CeO_2-TiO_2 film, a Galvanostatic Intermittent Titration Technique (GITT) and Electrochemical Impedance Spectroscopy (EIS) were performed. The results obtained showed that the chemical diffusion coefficient D_{Li} increases with increasing of the lithium concentration (x). The values approaching were $1.66 \times 10^{-13}\,cm^2s^{-1}$ at $x = 0.03$ and $2.14 \times 10^{-11}\,cm^2s^{-1}$ at $x = 0.153$. It was also observed from the Nyquist plot for the cerium-titanium electrode a Warburg-like dependence that can be associated to the semi-infinite diffusion through the oxide film.

Keywords: counter-electrode; electrochromic devices; thin films

INTRODUCTION

Electrochromic devices (ECD) are characterized by their ability to modulate the incident radiation from the visible to near infrared range of the electromagnetic spectrum of the solar light. In these systems, when a small current flows through the cell, the ions stored in electrolyte and counter electrode diffuse to the electrochromic layer and change its transmittance over a this wide spectral range and consequently modifies the overall optical transmission of the devices [1]. As described in many papers the

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typical ECD has a five-layer structure composed by: GS/TC/EC/IC/IS/TC/GS, where GS is a glass substrate, TC is a transparent conductor, usually ITO (indium tin oxide) or FTO (fluorine tin oxide), EC is an electrochromic coating such as WO_3 [2] or Nb_2O_5 [3], IC is an ionic conductor (solid or liquid electrolyte), in our case polymeric films based on natural polymers like starch [4] or cellulose, and IS is an ion storage coating such as CeO_2-TiO_2 [5–7], CeO_2-ZrO_2 [8,9] or CeO_2-SnO_2 [10].

A number of ceria based thin films have been reported. Among these works Varsano *et al.* [11], Pawlicka and Avellaneda [7,9] can be cited. All of these papers describe the different techniques of preparation and characterization of pure or modified CeO_2 thin films as well its possible utilization in ECD as transparent ion storage coating. However among these reports it is clear that the best results for this ECD purpose was achieved with sol-gel CeO_2-TiO_2 mixed structure proposed firstly by Baudry *et al.* [5]. The precursors used for preparation of sol were $Ce(NH_4)_2(NO_3)_6$ salt and titanium isopropoxide ($Ti(OPr^i)_4$). Later method was improved by application of ultrasonic irradiation during the sol synthesis [7]. The resulting ceria-titania films showed good optical and electrochemical properties with a charge density of 16 mC/cm^2. As it was demonstrated above there are some publications about preparation and characterization of thin ceria films for ECD, however there are not reports about kinetic behavior of this kind of films. Aiming to understand better the lithium intercalation process into the CeO_2-TiO_2 films we performed Galvanostatic Intermittent Titration Technique (GITT) and Electrochemical Impedance Spectroscopy (EIS) measurements and determined chemical diffusion coefficient of lithium.

EXPERIMENTAL

The starting solution to produce cerium-titanium based sol was prepared as reported in a previous work [7] where ammonium hexanitratocerate ($Ce(NH_4)_2(NO_3)_6$) powder, titanium isopropoxide ($Ti(OPr^i)_4$) and isopropanol were submitted to the ultrasonic irradiation. The coatings were deposited by dip-coating technique with withdrawing rate of 10 cm/min and submitted to the final heat-treatment at 450°C for 15 min in air atmosphere.

The GITT measures were performed with an EG&G PAR 273 computer-controlled potentiostat/galvanostat, controlled by 270 Electrochemical Analysis software. A conventional three-electrode cell was used, where counter electrode was a platinum foil of 1 cm^2 area and the quasi-reference electrode was a silver wire. The electrolyte was a 1 M solution of $LiClO_4$ dissolved in propylene carbonate. The EIS measurements were performed with Autolab equipment with FRA2 module, the frequency response between 200 kHz to 1 mHz were obtained with 5 mV rms amplitude perturbation.

RESULTS AND DISCUSSION

To obtain the chemical diffusion coefficient (D) of Li^+ in CeO_2-TiO_2 film, the galvanostatic titration technique was performed by the injection of known quantities of cathodic charge through the electrochemical cell, and allowing the cell to re-equilibrate in open circuit operation. The mathematical model for the GITT have been developed by Weppner and Huggins [12], which combined both transient and steady-state measurements to obtain kinetics properties of ion transport in solids. The method starts with a sample of known stoichiometric composition and with the cell in thermodynamic equilibrium. In this case, the concentration of all species is homogeneous throughout the electrode, corresponding to the cell voltage E_o. The application of a constant current I_o to the cell at time t_o by a galvanostat, according to the Fick's law, produces a constant concentration gradient $\partial c_i / \partial x$ within the CeO_2-TiO_2 at the phase boundary with the electrolyte $(x = 0)$. In order to maintain this constant concentration gradient, the applied cell voltage increases (or decreases, depending on the direction of the current) with time. After a time interval Δt, the current flux is interrupted and the composition within the CeO_2-TiO_2 film tends to again become homogenous by diffusion of mobile species. During this process the surface composition of the films and the cell voltage drifts to a new steady-state value E_e, corresponding to a new activity of Li^+ in the film as a result of the change of the stoichiometry (x) caused by the coulometric titration.

The change of stoichiometry (x) was calculated from Faraday's law expressed as:

$$x = (ItM_B) \, / \, (Z_A m_B F) \tag{1}$$

Where I, t, M_B, Z_A, m_B, and F are, respectively, the constant current pulse, duration of pulse, molecular weight of the electrode, valence of Li^+, the mass of the oxide, and the Faraday's constant. The potential can be expressed as:

$$E(t) = (2VI \, / \, FAZ_A) I (dE_e \, / \, dx) (t \, / \, \pi D)^{1/2} \tag{2}$$

where V, A, dE_e/dx are, respectively, the molar volume, surface area, and slope of the coulometric titration curve determined by plotting the open circuit voltages versus the change of stoichiometry. We consider that the molar volume of the oxide film did not change significantly in the range of x values investigated.

The diffusion coefficient may be calculated from Eq. (2) in the following form:

$$D = 4/\pi(V/AFZ_A)^2[I(dE_e/dx)/(dE/dt^{1/2})]^2 \tag{3}$$

where $dE/dt^{1/2}$ represents the slope of the total change of cell voltage during the application of the current pulse.

Figure 1 shows a typical voltage-time dependence for the case of the galvanostatic titration of CeO_2-TiO_2 film, with a current density of 0.25 mA/cm^2, applied for 120 s at room temperature. The voltage is also plotted in a Figure 1b as a function of the square root of time for the same measurement. In the initial period, between 0 and 2 s, the variation of the transient voltage is non linear. Nevertheless, E was found to vary linearly in the subsequent period from 1 to 58 s in the current pulse experiments in agreement with the theoretical considerations (Eq. (2)).

A sequence of selected galvanostatic titrations of CeO_2-TiO_2 films distributed over the entire range of the kinetic behavior of the electrodes is depicted in Figure 2. The higher potential variation is observed comparing the second with the fourth diagram where the stoichiometric factor (x) changes from 0.06 to 0.12.

The data for several runs are shown in Figure 3a, the different starting voltage (from Fig. 2) represent different stoichiometries of Li_x in CeO_2-TiO_2 film. The order in which the points were taken indicates that the measures were in fact made at equilibrium, where the concentrations of

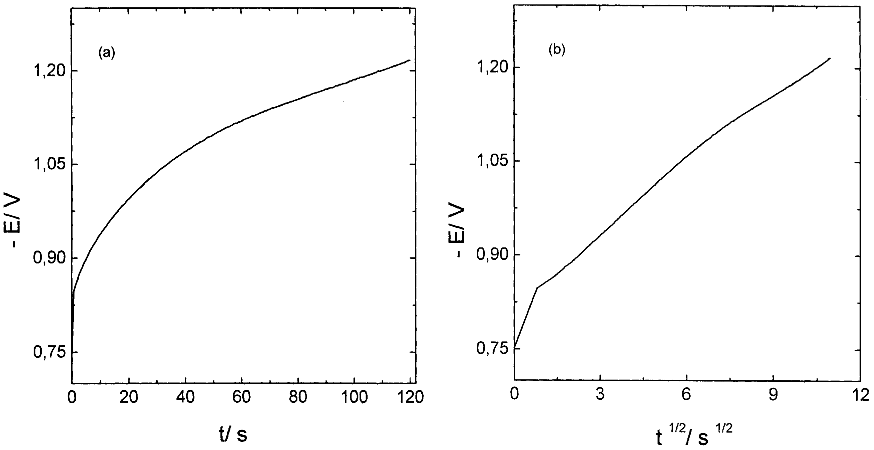

FIGURE 1 Transient voltage changes of the CeO_2-TiO_2 film as a function of t (a) and as a function of $t^{1/2}$ (b) for polarization with 0.25 mA/cm^2.

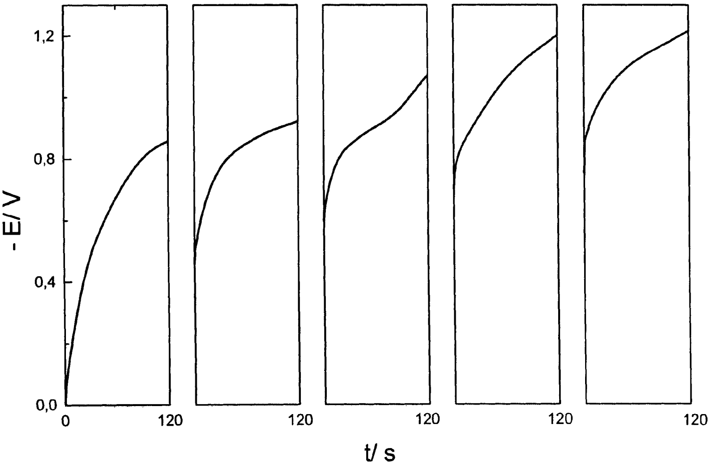

FIGURE 2 Transient voltage of CeO_2-TiO_2 as a function of time for several initial steady-state voltages, during successive polarization with 50 $\mu A/cm^2$.

all species are uniform and increase with increasing of applied potential. At potential of 0.63 V only a very small amount of lithium could be inserted into the electrode ($x = 0.03$), however for the potential 0.86 V a higher amount of lithium was inserted ($x = 0.15$).

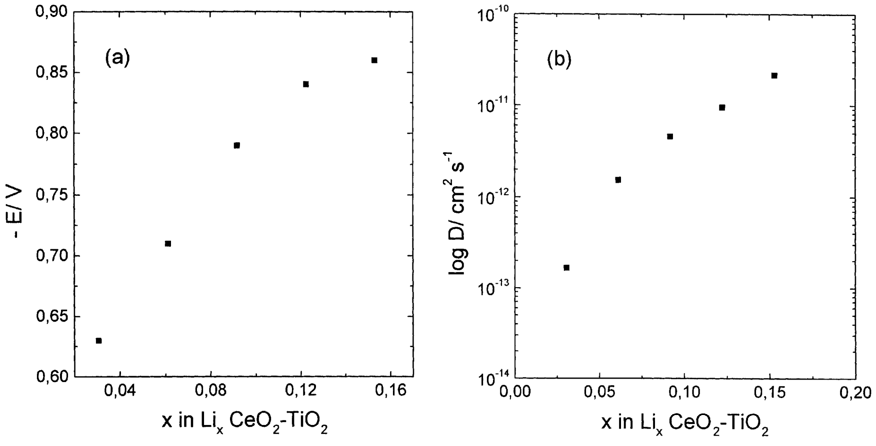

FIGURE 3 The steady-state voltages of the galvanic cell (a) and variation of the chemical diffusion coefficient as a function of the stoichiometry x for CeO_2-TiO_2 film (b).

The dependence of the chemical diffusion coefficient of lithium in the CeO_2-TiO_2 film is depicted in Figure 3b as a function of the lithium intercalation content x. According to Levi *et al.* [13] and Molenda *et al.* [14], the chemical diffusion could either increase or decrease with the increasing content of intercalated species, depending on the nature of long-range interactions between species. Similar results were obtained in this studies, where the values of D increase with the increase of lithium concentrations, approaching the values to the $1.66 \times 10^{-13}\,\mathrm{cm^2s^{-1}}$ at $x = 0.03$ and $2.14 \times 10^{-11}\,\mathrm{cm^2s^{-1}}$ at $x = 0.153$.

In Figure 4 a typical Nyquist plot is reported for the CeO_2-TiO_2 film. From these measurements it is possible to extract information on the dynamics of guest ions and correlate this information with the general electrochemical features of the film. From the spectrum taken at $-0.5\,\mathrm{V}$ vs. Ag was evidenced a Warburg-like dependence (line inclined at 45°C in complex plane). This result can be associated to the process of the semi-infinite diffusion through the oxide films. Accumulation in the bulk is generally seen in the Nyquist plot as a steep vertical line, signifying a pure capacitive element in the equivalent circuit that represents the material active mass intercalation capacity [11]. The impedance spectra of the electrode is better visualized in Figure 4b (at higher frequencies), thus, the ac impedance response can be simply modeled by Randle's equivalent circuit [15] showed in Figure 4b (inside), where R_o is the uncompensated ohmic resistance of the electrode and electrolyte, C_{DL} is the double-layer capacitance of electrode-electrolyte interface, R_{ct} is the charge transfer resistance and de Z_w is the Warburg impedance due to the lithium diffusion.

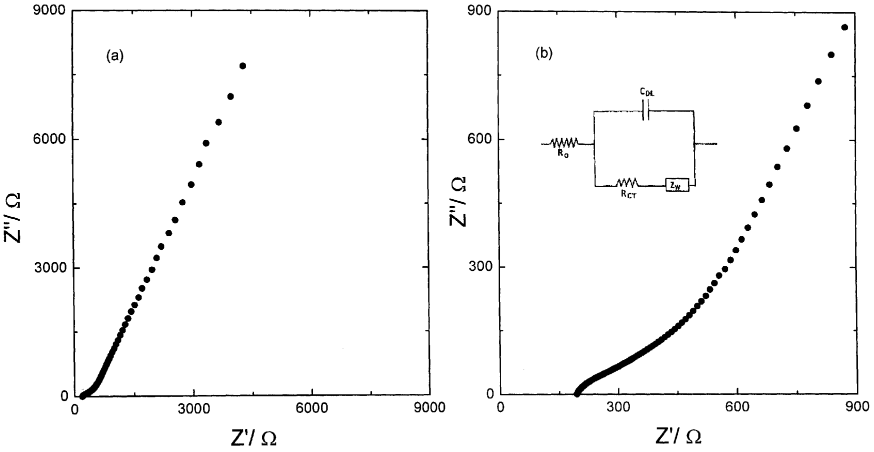

FIGURE 4 Impedance diagrams for CeO_2-TiO_2 film at $E = -0.5\,\mathrm{V}$.

CONCLUSION

In conclusion we have investigated the intercalation process in the CeO_2-TiO_2 film. The studies were realized on the framework of ionic intercalation kinetics to demonstrate the diffusion and ionic processes. Galvanostatic intermittent titration have been applied into CeO_2-TiO_2 film and showed that the chemical diffusion coefficient D_{Li} increases with increasing of the amount of lithium concentration (x). The values approaching were $1.66 \times 10^{-13}\,cm^2s^{-1}$ at $x = 0.03$ and $2.14 \times 10^{-11}\,cm^2s^{-1}$ at $x = 0.153$.

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