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Thermodynamics and Lithium Intercalation in CeO_2-TiO_2 Thin Film

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The kinetics and the thermodynamics of electrochemical intercalation of lithium into CeO_2-TiO_2 films prepared by the sol-gel process were studied by galvanostatic intermittent titration technique (GITT) as function of the depth of lithium intercalation. The open-circuit-potential versus x in $Li_x(CeO_2\text{-}TiO_2)$ curve consists of two straight lines with different slopes, one in the range of $0.03 \leq x \leq 0.09$ and the other of $0.09 < x \leq 0.15$. The standard Gibbs energy for lithium intercalation ΔG_1^0 was 6 kJ/mol for $x = 0.09$ in $Li_x(CeO_2\text{-}TiO_2)$ at room temperature. The chemical diffusion coefficient value, D_{Li^+}, of lithium intercalation into thin film oxide was $2.14 \cdot 10^{-11}$ cm^2/s at $x = 0.15$, and the value of the component diffusion coefficient $D_{Li^+,k}$ was about one order of magnitude lower than the coefficient of chemical diffusion.

Keywords Cerium-titanium oxide; kinetics; sol-gel process; thermodynamics

Introduction

The performance of electrochromic devices strongly depends upon the choice of the counter electrode. Two kinds of counter electrodes in smart windows are well known. One is an electrochromic layer complementary to the selected primary electrochromic material as, for example, the combination of WO_3 with NiO_xH_y, and the other is an optically passive counter electrode, which remains colorless in the insertion/extraction process [1,2].

The role of counter electrode films in an electrochromic device is to provide the balance of the charge, which is exchanged during the coloring/bleaching process. Therefore their ion storage capacity and cycling stability must be compared to those of the active coloring film aiming to compensate the Li^+ insertion/extraction reactions occurring at the active electrochromic film [3]. Also, it is generally accepted that Li^+ diffusion into the electrode is the limiting step, therefore determining the kinetics of the insertion reaction.

One of the different candidates for counter electrode, which exhibit a good reversibility for lithium insertion, is CeO_2 film. This film is colorless in both oxidized and reduced states but its reaction kinetics is too slow for devices. To overcome this

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slow reaction kinetics in CeO_2 films, Baudry et al. [4] suggested the replacement of some Ce atoms by an element of lower ionic radius, as Ti. Parallel, several other attempts have been performed to improve the reaction kinetics by mixing the ceria with different components, such as Zr, V, Sn, Mo and Si [5–12]. However until now the best results have been obtained with CeO_2-TiO_2, which is applied in small electrochromic devices [13].

The rapid diffusion of atoms in mixed conducting materials is of theoretical interest, as well as practical importance in battery electrode materials, electrochromic display devices, coulometers, etc. The use of electrochemical methods to measure chemical diffusion coefficient in mixed conducting electrodes, when combined with the detailed thermodynamic data derived from equilibrium cell measurements, has considerably simplified the acquisition and interpretation of the kinetics and thermodynamics of the electrochemical insertion of lithium into the film [14].

Since the electrochemical intercalation of lithium is, in general, limited by the lithium ion diffusion in the oxide electrode, the attention of the previous work [15] was focused on the determination of the chemical diffusion coefficient in the electrode material. The interaction between intercalated ions and oxide lattice or between intercalated ions may greatly influence the lithium ion diffusion through the oxide lattice [16].

The primary observation concerning the kinetics of lithium incorporation into the CeO_2-TiO_2 thin film is that, both diffusion and interface kinetics are important. The following considerations are relevant. Firstly, the thermodynamic and kinetic properties of CeO_2-TiO_2 thin film are very dependent on the crystalline degree of the films [17]. The structure of CeO_2-TiO_2 host materials plays an important role in the thermodynamic and kinetics of lithium intercalation into the oxide.

In the present paper, the kinetics and thermodynamics of electrochemical intercalation of lithium into CeO_2-TiO_2 film were studied.

Experimental

Preparation of the Sol

The preparation of stable cerium-titanium solution was obtained using a sonocatalytic process [6]. The starting solution to produce CeO_2-TiO_2 films with molar ratio of Ce/Ti of 0.5 was prepared by dissolving ammonium hexanitratocerate ($Ce(NH_4)_2(NO_3)_6$) powder (1.028 g, 1.9 mmol) and titanium isopropoxide ($Ti(O^iPr)_4$; 1.105 ml, 3.9 mmol) in isopropanol (15 ml) in a small (30 ml) Becker vessel. The solution mixture was submitted for $\sim$5 min to the action of 95 W ultrasonic irradiation from a Sonicator W385 Heat System-Ultrasonic, Inc, at 20 kHz equipped with a 13 mm disruptor horn resulting in a transparent and dark red solution. This solution was left aging in a closed glass vessel for about 72 h at room temperature until the color changed from deep red to transparent pale yellow. It was stable for several weeks when kept in a closed glass vessel in the fridge. It is true that the sonocatalytic process accelerates the chemical reaction of ammonium cerium (IV) nitrate and titanium isopropoxide with resulting in a solution similar obtained by Macedo [18].

Preparation of the Films

The films were deposited by the *dip-coating* method on ITO coated glass substrate (Delta Technologies 14 $\Omega/\square$) previously cleaned and rinsed with bidestilled water and ethanol and then dried at room temperature. The substrates were immersed into the solution in ambient atmosphere (RH $<$ 60%) and withdrawn at the rate of 10 cm/min. The samples were subsequently dried in air at room temperature. The uniform films were then densified at 80°C for 15 min and kept at the final temperature at 450°C for 15 min.

Measurement Technique

The galvanostatic intermittent titration experiments were performed with an Autolab 30 computer-controlled potentiostat galvanostat. A conventional three-electrode cell was used, the counter-electrode was a platinum foil of 1 cm^2 of area and the quasi reference electrode was a silver wire. The electrolyte was a 1.0 M solution of $LiClO_4$ dissolved in propylene carbonate (PC) and the cell was previously purged with dry N_2 gas.

Results and Discussion

To obtain the chemical diffusion coefficient (D) of Li^+ in CeO_2-TiO_2 film, the galvanostatic intermittent 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 equations for the galvanostatic intermittent titration technique (GITT) have been developed by Weppner and Huggins [19]. The kinetics transport in solid was obtained by combining both transient and steady state measurements.

The method starts with a sample of know stoichiometric composition, and with the cell at thermodynamic equilibrium. In this case, the concentrations of all species are homogeneous throughout the electrode, corresponding to the cell voltage, E_o. The application of a constant current, I_o, to the cell for a time span, 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 the time. After a time interval, Δt, the current flux is interrupted and the composition within the CeO_2-TiO_2 film tends to become again homogeneous, by diffusion of the mobile species.

During this process, the surface composition of the films changes and the cell voltage shifts 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. Basically, with this method, a short time cathodic galvanostatic pulse is passed through the electrochemical cell. During the application of a constant current, the oxide electrode potential was recorded as a function of time.

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

$$x = \frac{ItM_B}{Z_A m_B F}, \tag{1}$$

where I, t, M_B, Z_A, m_B, and F are, respectively, the constant current pulse, duration of pulse, metal oxide molar mass, valence of Li^+, metal oxide mass and Faraday's constant.

If the condition $t \ll l^2/D$ if fulfilled, where l is the film thickness the potential can be expressed as:

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

where V, A and dE_e/dx are, respectively, the molar volume and surface area of the sample. The slope of the coulometric titration curve was determined by plotting the open circuit voltages against the change of stoichiometry. The present analysis considered that the molar volume of the metal oxide film did not change significantly in the range of x values investigated.

The diffusion coefficient was calculated from Equation (2) as

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

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

The data for several runs are shown in Figure 1, where different starting voltages represent different stoichiometries of Li_x in CeO_2-TiO_2 films. The order in which the points were taken indicates that the measurements were in fact taken at equilibrium, where the concentrations of all species are uniform. As it can be seen, the amount inserted into CeO_2-TiO_2 film was 0.15 at $E = 0.86\,V$. Also the results plotted in Figure 1 show that the open circuit potential (OCP)-x curve consists mainly of two straight lines with different slopes with intersection at $E = 0.79\,V$ for $x = 0.09$ in the $Li_x(CeO_2$-$TiO_2)$ film. The relationships between the OCP and the x-value for $Li_x(CeO_2$-$TiO_2)$ film are represented by

$$E = -0.55 - 2.61x \quad \text{for } x \leq 0.09, \tag{4}$$

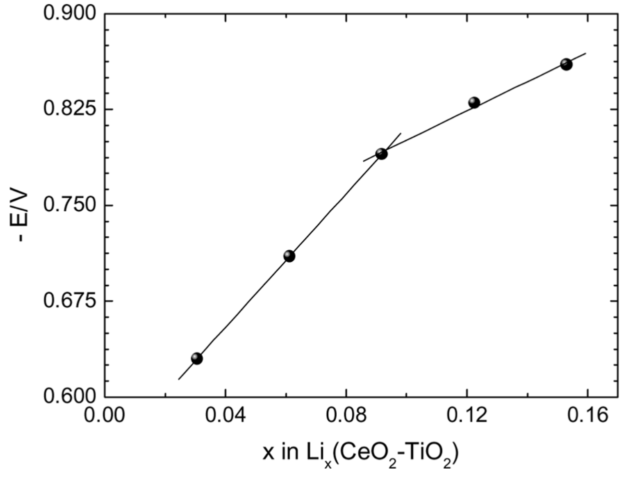

Figure 1. The steady-state voltages of the galvanic cell as a function of the stoichiometric x for $Li_x(CeO_2$-$TiO_2)$ film.

$$E = -0.69 - 1.14x \quad \text{for } x > 0.09, \tag{5}$$

These results suggest that the intercalated lithium atoms occupy more than one kind of crystallographic site and single phase of $Li_x(CeO_2\text{-}TiO_2)$ films [20], which in our case are constituted by cerianite structure of CeO_2 in TiO_2 amorphous phase [6].

The standard free energy of lithium intercalation, ΔG_1^0 in $Li_x(CeO_2\text{-}TiO_2)$ films was calculated from the following equations:

$$\mu_{Li} - \mu_{Li}^o = RT\ Ln\ a_{Li} = -FE(x), \tag{6}$$

$$\Delta G_1^o = -F \int_0^x E(x)dx, \tag{7}$$

where E(x) is the open circuit potential at the respective x value and μ_{Li}, μ_{Li}^o and a_{Li} are the lithium chemical potential, the chemical potential for pure lithium and the activity of lithium, respectively [21].

The ΔG_1^0 values obtained as a function of the depth of lithium intercalation x for $Li_x(CeO_2\text{-}TiO_2)$ film are given in Figure 2. As it can be observed, the ΔG_1^0 values increase with the increase in the x-value, from 1.77 kJ/mol at $x = 0.03$ to 11.48 kJ/mol at $x = 0.15$. The intercalation free energy mainly reflects the site energy of lithium atoms, intercalated into the structures. Therefore the site energy of the intercalated lithium atoms, namely the bond strength of the intercalated lithium atoms with the host structures increases with addition of TiO_2 into the CeO_2 structure.

The X-ray diffraction patterns of xerogel (not showed here) obtained with the same sol used for the coating and heat treatment at 450°C during 15 min following the same densification protocol. The structure of the films presents a crystalline phase of CeO_2 (cerianite). The absence of TiO_2 crystalline peaks confirm that the crystalline CeO_2 phase is dispersed in the amorphous phase of TiO_2 [6].

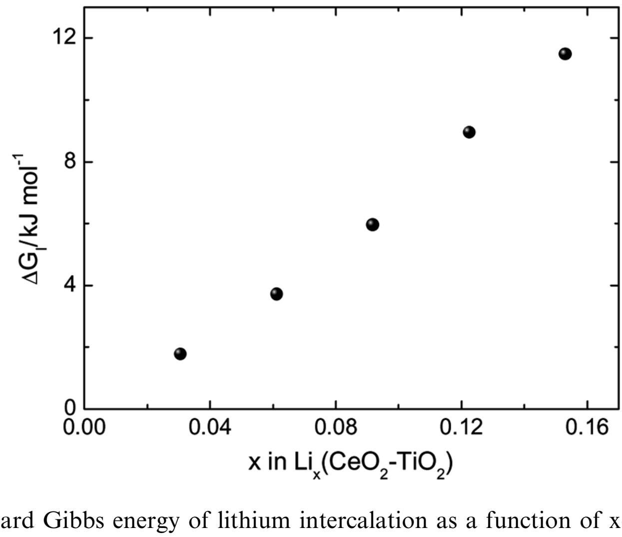

Figure 2. Standard Gibbs energy of lithium intercalation as a function of x-value $Li_x(CeO_2\text{-}TiO_2)$ film.

The chemical diffusion coefficient (D) is an important measurement of the lithium ion dynamics in electrode intercalation. According to Weppner and Huggins model, the value of D can be determined from the $dE/dt^{1/2}$ slope and the dE/dx factor, which is assumed to be constant during each small current pulse. Also the voltage drop in the bulk electrolyte between the sample and reference electrode does not affect these two quantities. Therefore, the ohmic effects on the electrolyte and interface are totally eliminated when using the GITT method.

The diffusivity or component diffusion coefficient $D_{Li^+,k}$ is a measurement of the random motion of a species in the absence of a concentration gradient. It is related to D_{Li^+} by expressions [22]

$$D_{Li^+} = D_{Li^+,k} d(\ln\ a_{Li})/d(\ln\ C_{Li}), \tag{8}$$

$$D_{Li^+} = D_{Li^+,k}(F/RT)x(dE/dx), \tag{9}$$

where $d(\ln\ a_{Li})/d(\ln\ C_{Li})$ is the thermodynamic enhancement factor W calculated from dE/dx and R is the gas constant.

The influence of the thermodynamic enhancement factor W on diffusion in a mixed ionic/electronic conductor has been interpreted as being due to the influence of an internal electric field generated by the flux of mobile electronic species accelerating the slower ions [16].

According to Levi *et al.* [23] and Molenda *et al.* [24], 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 the present study, where the values of D increase with the increase of lithium concentrations.

The determined chemical diffusion coefficient D_{Li^+} and component diffusion coefficient $D_{Li^+,k}$ of lithium ion in the CeO_2-TiO_2 film are plotted in Figure 3. At room temperature the D_{Li^+} in the $Li_x(CeO_2$-$TiO_2)$ film reaches the value of $2.14 \cdot 10^{-11}\,cm^2/s$ at $x = 0.15$. The value of the component diffusion coefficient

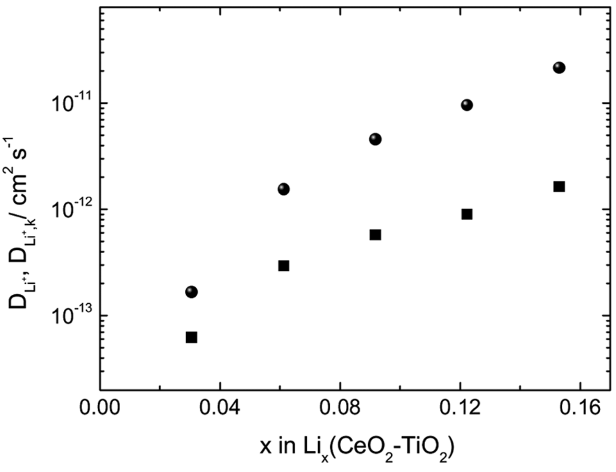

Figure 3. Chemical diffusion coefficient D_{Li^+} (●) and component diffusion coefficient $D_{Li^+,k}$ (■) as a function of lithium content in CeO_2-TiO_2 film.

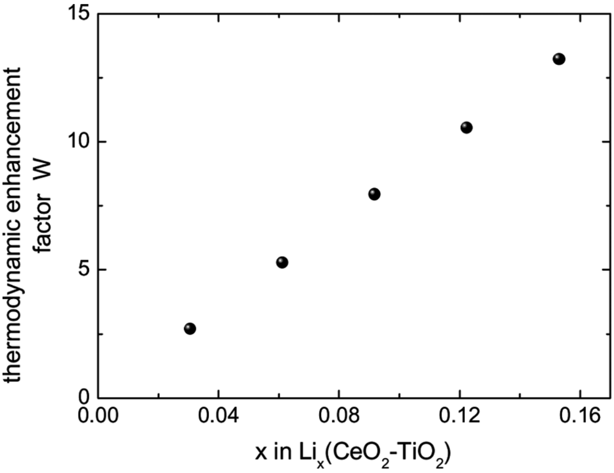

Figure 4. Thermodynamic enhancement factor W as a function of the lithium content in CeO_2-TiO_2 film.

$D_{Li^+,k}$ was found to be one order of magnitude lower than that of chemical diffusion coefficient D_{Li^+}, which approaches the value of $1.66 \cdot 10^{-12}\,cm^2/s$ at $x = 0.15$. Also a drastic rise of one order of magnitude can be observed in the range of $0.03 \leq x \leq 0.15$ of the component diffusion coefficient $D_{Li^+,k}$, which can account for the raised electronic conductivity caused by the lithium intercalation.

The determined thermodynamic enhancement factor W for $Li_x(CeO_2$-$TiO_2)$ film is plotted against lithium content x in Figure 4. As the lithium content x increased from 0.03 to 0.15, the thermodynamic enhancement factor W increased from 2.68 to 11.48.

The rise in the chemical diffusion coefficient D_{Li^+}, component diffusion coefficient $D_{Li^+,k}$ and thermodynamic enhancement factor W of lithium ions in the $Li_x(CeO_2$-$TiO_2)$ film may be associated with the microscrystalline features of the sol-gel crystalline CeO_2-TiO_2 films, where a cerianite structure of CeO_2 in TiO_2 amorphous phase [6] was found.

Conclusions

Measurements at the equilibrium of the OCP vs lithium content were used to determine chemical diffusion coefficient, component diffusion coefficient and standard Gibbs energy. The chemical diffusion coefficient D_{Li^+} of lithium ion in the $Li_x(CeO_2$-$TiO_2)$ film approached the value of $2.14 \cdot 10^{-11}\,cm^2/s$ at $x = 0.15$. The value of the component diffusion coefficient $D_{Li^+,k}$ was about one order of magnitude lower than that of chemical diffusion coefficient D_{Li^+}. The drastic rise in the component diffusion coefficient $D_{Li^+,k}$ was attributed to the raised electronic conductivity caused by the lithium intercalation. The standard Gibbs energy for lithium intercalation ΔG_1^0 was 6 kJ/mol for $x = 0.09$ in $Li_x(CeO_2$-$TiO_2)$ at room temperature.

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