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Lithium Diffusion into Nb_2O_5 and Nb_2O_5:Li^+ Thin Films Prepared by Sol Gel Method

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Aiming to study the solid-state diffusion of lithium into pure and lithium doped niobium pentoxide (Nb_2O_5) thin sol-gel films were investigated by galvanostatic intermittent titration technique (GITT) and electrochemical impedance spectroscopy (EIS). The obtained values of the diffusion coefficient were 2.5×10^{-11} at $x = 0.83$ and 7.4×10^{-13} at $x = 1.65$ for pure and doped Nb_2O_5 films respectively. The impedance results of both kinds of films adjusted by equivalent circuits showed very good agreement between experimental and theoretical data.

Keywords: electrochromism; lithium intercalation; Nb_2O_5; sol-gel

INTRODUCTION

Niobium pentoxide is a promising material to be applied in electrochromic devices and as a counter-electrode thin film [1]. The first attempt to produce sol-gel Nb_2O_5 for electrochemical purpose was reported by Lee *et al*. [2] who spin-coated an ITO glass electrode with a mixture of $NbCl_5$ dissolved in ethanol. However the durability of these films subjected to voltammetric measurements, was only a few cycles. Later Ohtani *et al*. [3] prepared a sol of NbO_x by partial hydrolysis of niobium ethoxide ($Nb(OEt)_5$) with concentrated hydrochloric acid (HCl). The intercalation process of protons was studied in an acidic aqueous solution and the coloration efficiency was found to decrease in function of the number of cycles from about 38 cm^2/C to 8.7 cm^2/C, explained by authors as a probable corrosion of the layer in the acidic solution.

At the same time an Nb_2O_5 sol was prepared by an alkoxide route in Aegerter's laboratory [4] where niobium pentabutoxide ($Nb(OBu^n)_5$)

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was synthesized by dissolving $NbCl_5$ in butanol and then subjected to the reaction with sodium butoxide ($Na(OBu^n)$ under reflux. The resulting sol was stabilized with glacial acetic acid and used to obtain thin solid films by dip-coating method. These films subjected to the thermal treatment at 560°C were crystalline and after Li^+ intercalation during electrochemical measurements they showed a deep blue color with a variation in the transmittance from 70% to 25% at 550 nm. Later, a novel and simpler synthesis of a niobia sol-gel precursor was prepared using a sonocatalytic process by Pawlicka *et al*. [5,6]. The films presented reversible and fast insertion/extraction kinetics of Li ions with a coloration efficiency of 22 cm^2/C at 600 nm. Continuing these studies the authors prepared and characterized Nb_2O_5 thin films doped with a small amount of $LiCF_3SO_3$ which, as it was observed, improved the kinetics processes of these niobia films [7].

Ozer *et al*. [8,9] also prepared Nb_2O_5 coatings by hydrolysis and polymerization of niobium ethoxide solution in ethanol with addition of acetic acid. The coatings were amorphous when thermally treated up to 450°C, and above this temperature a formation of small crystallites was observed. In this study amorphous spin-coated films after Li^+ insertion showed a transmittance change from transparent to brown of about 40% in the visible range. Orel *et al*. [10] also obtained Nb_2O_5 and Nb_2O_5:Li films with excellent electrochromic properties.

An intensive study of the properties of pure Nb_2O_5 and doped Nb_2O_5:X (X = Sn, Zr, Li, Ti, Mo) layers, prepared by the sonocatalytic method as a function of the sintering temperature, the doping material and its concentration was preformed by Schmitt *et al*. [11,12]. They observed that the Nb_2O_5 layers doped with Li, Ti and Mo showed two interesting effects: deeper coloring properties and the possibility of obtaining a gray color in the intercalated state.

Aiming to better understand the Li^+ kinetic behavior during its electro-intercalation process in the cathodic Nb_2O_5 and Nb_2O_5:Li^+ thin films, galvanostatic intermittent titration technique (GITT) and electrochemical impedance spectroscopy (EIS) measurements were taken. The results of this investigation presented in this paper permitted the determination of the chemical diffusion coefficients as well as equivalent circuit approach.

EXPERIMENTAL

Preparation of the Sol

The starting solution to produce Nb_2O_5 films was prepared by dissolving $NbCl_5$ powder (1.3 g, 0.005 mol) in butanol (15 mL, 0.16 mol) and

acetic acid (3 mL, 0.05 mol). Then the solution mixture was subjected, for about 5 min, to the action of a 95 W, 20 kHz ultrasonic irradiation from a sonicator (Branson Digital Sonifier 450) resulting in a transparent and viscous solution [7]. In order to produce Nb_2O_5:Li^+ sol the final solution was doped with 10% mol of $LiCF_3SO_3$ salt.

Preparation of the Films

The films were deposited by dip-coating method onto ITO coated glass substrates (Delta Technologies 8Ω/□). The ITO glass was immersed into the solution at room temperature with humidity less than 50%. Next the substrate was withdrawn at rate of 10 cm/min, dried at room temperature for 5 min and then sintered at 400°C for 5 min. The process was repeated to obtain 3 layer films. The final thermal treatment was performed at 560°C in air atmosphere for 10 min. The resulting coatings were transparent and homogeneous without any visual cracking. For these preparation conditions the mean thickness was about 450 nm.

Measurement Techniques

Impedance spectroscopy technique measurements were performed with Autolab equipment with FRA2 module. The frequency response between 50 kHz to 1 mHz was obtained with 10 mV rms amplitude perturbation. The galvanostatic intermittent titration technique was performed with an EG&G PAR 273 potentiostat/galvanostat, controlled by 270 Electrochemical Analysis software. A conventional three-electrode cell was used, where a platinum foil was the counter-electrode and a silver wire was the quasi-reference electrode. The electrolyte was 0.1 M solution of $LiClO_4$ dissolved in propylene carbonate (PC) and the cell was previously purged with dry N_2 gas.

Method Applied

To obtain the chemical diffusion coefficient (D) of Li^+ in Nb_2O_5 and Nb_2O_5:Li^+ films, the galvanostatic intermittent titration technique was performed by the injection of known quantities of cathodic charge through the electrochemical cell, and allowing it to reequilibrate in open circuit operation. The mathematical model for the GITT was developed by Weppner and Huggins [13], who combined both transient and steady-state measurements to obtain kinetic properties of transport in solids.

The method starts with a sample of known stoichiometry composition and 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 Fick's law, produces a constant concentration gradient $\partial c_i/\partial x$ in the solid, in our case Nb_2O_5 and Nb_2O_5:Li^+ 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 in the pure and Li doped Nb_2O_5 films tends again to become homogenous by diffusion of mobile species. During this process the surface composition of the films and the cell voltage shift 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 and the oxide electrode potential in our experiment was recorded as a function of time.

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

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

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. Also if the following condition, $t << L^2/D$ is fulfilled, where L is the film thickness (in our case $L = 4.5 \times 10^{-5}$ cm and $D_{Li} = 10^{-13}$, $L^2/D = 4500$ s for $t = 120$ s), the potential can be expressed by:

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

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

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

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

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

RESULTS AND DISCUSSION

Figure 1a shows typical voltage-time dependence for the case of galvanostatically titration of lithium into pure and doped Nb_2O_5 films, with a current density of 50 $\mu A/cm^2$, applied for 120 s at room temperature. The voltage was plotted as a function of the square root of time for the same measurements (Fig. 1b). In this figure it can be observed that in the initial period, between 0 and 14 s, the variation of the transient

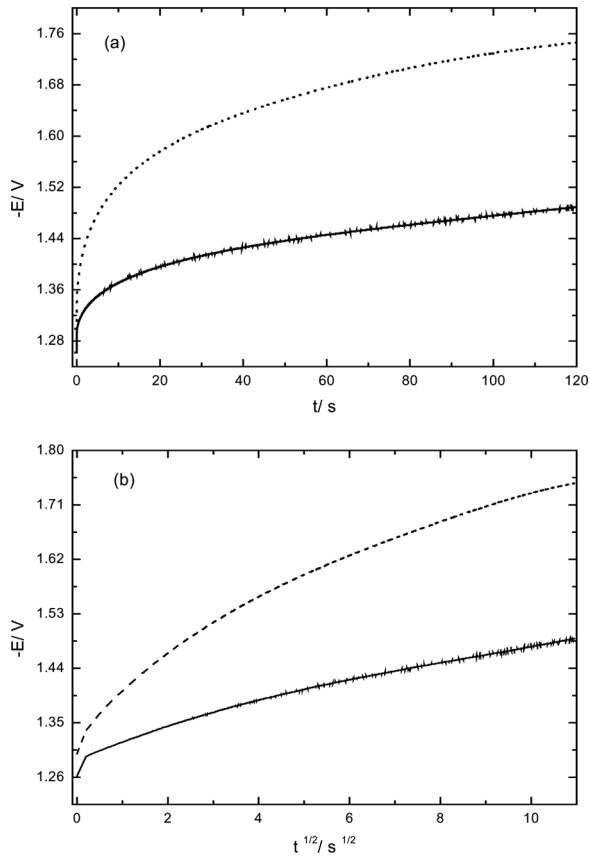

FIGURE 1 Transient voltage changes of the galvanic cell as a function of both time (a) and square root (b) for pure (—) and lithiated Nb_2O_5 (- - -) films after applying a current of 50 $\mu A/cm^2$.

voltage is non-linear (more pronounced for Nb_2O_5:Li^+ film). However, E was found to vary linearly in the subsequent period from 16 to 100 s in the constant current pulse experiments in agreement with theoretical considerations (Eq. (2)). Also, as it can be observed, the values obtained for doped film are higher than those for pure one, which can be attributed to the presence of lithium in the doped film composition.

The data of several runs are shown in Figure 2, where the different starting voltage represents different stoichiometries of Li_x inserted in pure and doped Nb_2O_5 films. As the obtained results represented by points in Figure 2 show a good order, it can be considered that the measurements were in fact taken in equilibrium, where the concentrations of all species are uniform. This figure also shows that the maximum lithium amount inserted into Nb_2O_5 film was 0.8. Such amount was lower than in Nb_2O_5:Li^+ film, where it was found 1.65. Comparing the results of both samples and at the same potential of 1.35 V it can be stated that the amount of inserted lithium in doped film is 0.2 larger than in the undoped one. Again this difference can be explained by the fact that lithium is already present in the doped Nb_2O_5 film structure as a dopant, probably causing a more favorable lattice arrangement, i.e. a more opened lattice, which favors its insertion through the lattice [10].

The chemical diffusion coefficient (D) is an important measurement of the lithium ion dynamics in electrode intercalation. According to

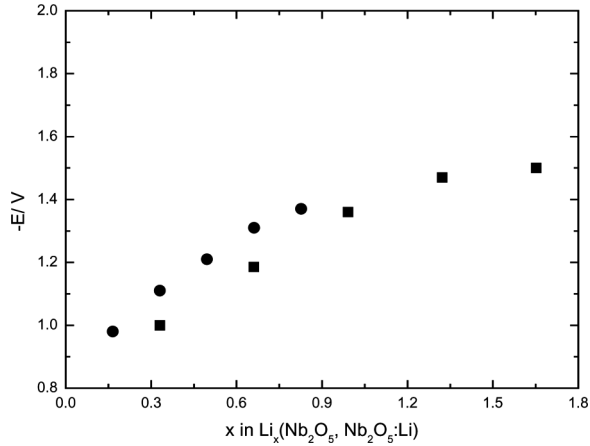

FIGURE 2 The steady-state voltages of the galvanic cell as a function of stoichiometry (x) for pure (●) and lithiated Nb_2O_5 (■) films.

Eq. (3) the value of D can be determined from the slope $dE/dt^{1/2}$ and the factor dE/dx, which is assumed to be constant during each small current pulse. These two quantities are not affected by the voltage drop in the bulk electrolyte between the sample and the reference electrode when using the GITT method.

The dependence of the chemical diffusion coefficient on lithium in both pure and lithium-doped Nb_2O_5 films as a function of the lithium intercalation content (x) is depicted in Figure 3. According to Levi *et al*. [14] and Molenda *et al*. [15], the chemical diffusion could either increase or decrease with the increasing content of intercalated species, depending on the nature of long range interactions between these species. Similar results were obtained in these studies, where the values of D increase with the increase in lithium concentrations, approaching the values of $2.5 \times 10^{-11}\,cm^2/s$ at $x = 0.83$ and $7.4 \times 10^{-13}\,cm^2/s$ at $x = 1.65$ for Nb_2O_5 and Nb_2O_5:Li^+, respectively. As it can be also observed from this figure, the chemical diffusion coefficient of doped niobia film is smaller than that of pure one, probably due to the presence of lithium in the structure of the doped film.

In order to obtain information on the dynamics of guest ions and correlate this information with the general electrochemical features of the host, electrochemical impedance spectroscopy was used. An example is given in Figures 4a and 4b, which shows the impedance responses of both pure and lithium doped Nb_2O_5 materials at three different *dc* potentials: $-1.3\,V$, $-1.5\,V$ and $-1.7\,V$, regions where

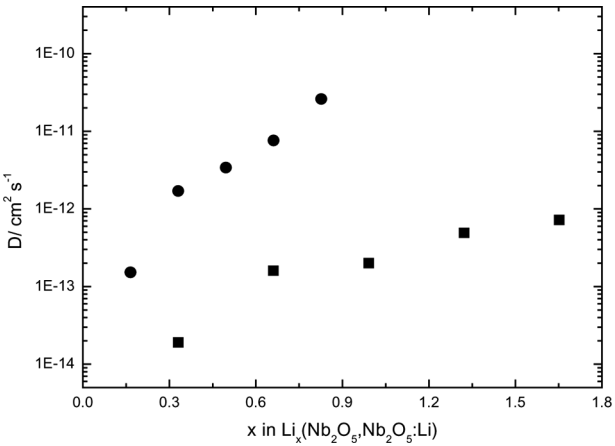

FIGURE 3 Variation of the chemical diffusion coefficient as a function of stoichiometry (x) for pure (●) and lithiated Nb_2O_5 (■) films.

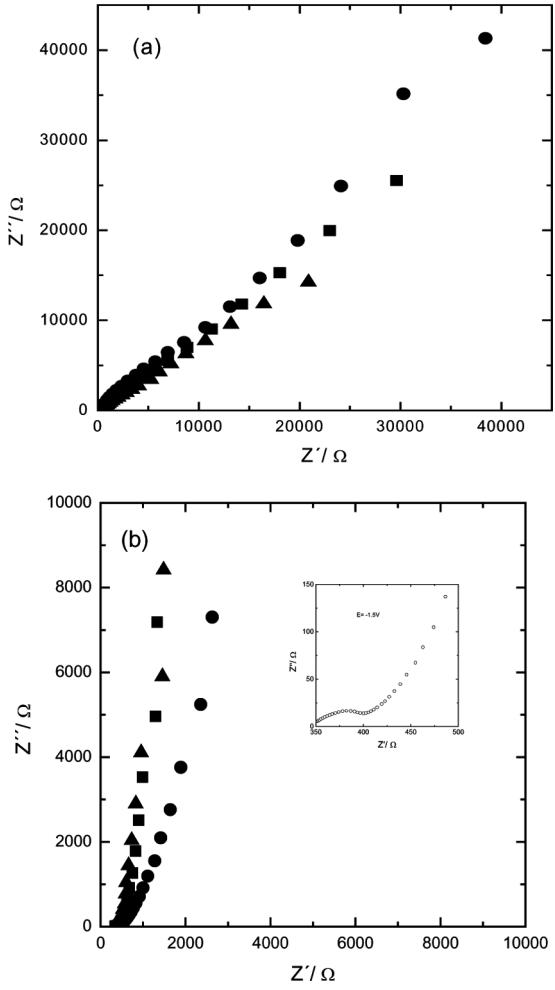

FIGURE 4 Nyqvist diagram for pure (a) and lithiated Nb_2O_5 (b) at different potentials: −1.3 V (●), −1.5 V (■) and −1.7 V (▲). The inset represents the high frequency region of the spectrum.

the films become colored. Figure 4a displays the impedance data for the pure niobia film and shows part of a depressed semicircle at frequencies higher than some kHz. At low and intermediate frequencies a straight line is observed. For the Nb_2O_5:Li^+ film (Fig. 4b) it is also possible to observe a semicircle at high frequency (insert in Fig. 4b), which passes trough a straight line with a constant phase angle (CPA).

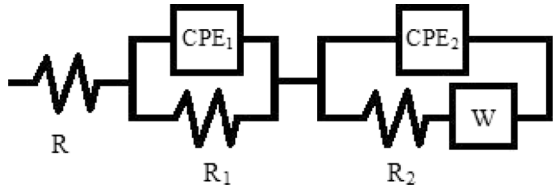

FIGURE 5 Equivalent circuit diagram of pure and lithium doped Nb_2O_5 films. The CPEs are constant phase elements and the Rs are resistances.

To analyze these impedance curves the equivalent circuits approach was used resulting in the diagram showed in Figure 5. This diagram can be applicable for both kinds of films and explained in terms of R being the ohmic resistance of the electrolyte and the ITO back contact [16], R_1 being related to charge transfer resistance and CPE_1 being a constant phase element related to the space charge capacitance at the film/electrolyte interface. R_2 corresponds to the charge transfer at the ITO/film interface and CPE_2 element is associated with the double-layer capacitance at this interface. The W elements correspond to a Warburg element responsible for the diffusional control of the system. On the other hand, the parallel combination of R_1 and CPE_1 represents the film/electrolyte interface and the parallel combination of R_2 and CPE_2 represents the ITO/film interface.

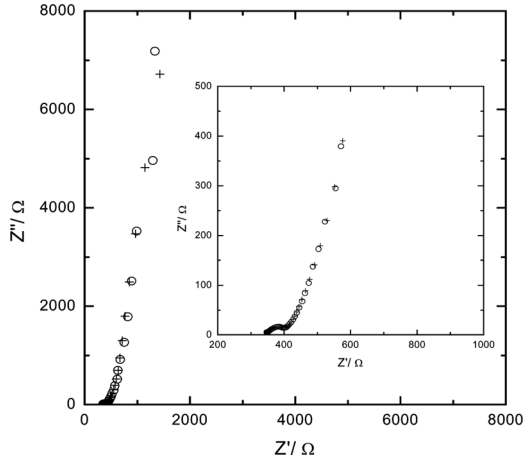

FIGURE 6 Nyqvist graph for lithiated Nb_2O_5 film at -1.5 V. Experimental (○) and theoretical (+) data obtained from the fitting of the circuit of Figure 5.

The impedance data for the films were fitted for the circuit showed in Figure 5 using Equivcrt software. Figure 6 shows typical examples of the good agreement that could be accomplished between both experimental and fitted data.

CONCLUSION

Galvanostatic intermittent titration technique was applied to study the lithium insertion kinetics in Nb_2O_5 doped and undoped films to obtain the chemical diffusion coefficient. From the results obtained it was stated that within each film, D increases as lithium content (x) increases yelding maximum values of $2.5 \times 10^{-11}\,cm^2/s$ at $x = 0.83$ and $7.4 \times 10^{-13}\,cm^2/s$ at $x = 1.65$ for Nb_2O_5, Nb_2O_5:Li^+, respectively. From the impedance measurements conductivity values were obtained as a function of frequency for low potential value ($-0.5\,V$), being 8×10^{-8} S/cm and 5.5×10^{-8} S/cm for Nb_2O_5 pure and Nb_2O_5:Li^+ films, respectively, at 31.6 kHz. The impedance results were also analysed by equivalent circuit approach, with very good agreement between the experimental and theoretical data. Concluding it was observed that the doped film promoted higher lithium quantities inserted when compared with undoped film, probably due to the more opened lattice. However, it seems that the presence of lithium in the structure of doped films decreases the chemical diffusion coefficient and conductivity values when compared with the undoped ones.

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