Thermodynamic study of WO$_3$ and WO$_3$:Li$^+$ thin films

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Abstract

There is a considerable interest in the research and development of materials and devices that can be used for optical switching of large-scale glazings. Several potential switching technologies are available for glazings, including those based on electrochromic, thermochromic and photochromic phenomena. One of the most promising technologies for optical switching devices is the electrochromism (EC). In order to improve the electrochromic properties of tungsten oxide we have investigated the effect of lithium insertion on the electrochromic behavior of oxide films prepared by the sol–gel process.

The kinetics and thermodynamics of electrochemical intercalation of lithium into Li$_x$WO$_3$ and Li$_x$(WO$_3$:Li) films prepared by the sol–gel process were investigated. The standard Gibbs energy for lithium intercalation was calculated. The chemical diffusion coefficients, $D$, of lithium intercalation into oxide were measured by galvanostatic intermittent titration technique (GITT) as functions of the depth of lithium intercalation.

Keywords: Electrochromism; Thermodynamic; Kinetics; Sol–gel process

1. Introduction

Certain materials, referred as electrochromic materials, are known to change their optical properties in response to the application of an electric current or an electric potential. This property has been used to produce electrochromic devices, which can be controlled to transmit optical energy selectively. The reaction may be written as

$$\text{WO}_3 \text{(colorless)} + yM^+ + ye^- \leftrightarrow M_y\text{WO}_3 \text{(colored)}$$

where for each atom injected an electron enters the conduction band of the host oxide and a deep blue coloration develops. At the same time, the electronic conductivity of the oxide rapidly increases [1–3].

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. Using electrochemical methods to measure chemical diffusion coefficients in mixed conducting electrodes, which, combined with the detailed thermodynamic data derived from equilibrium cell measurement, has considerably simplified the acquisition and interpretation of the kinetics and thermodynamics of the electrochemical insertion of lithium into WO$_3$ thin films [4].

Since the electrochemical intercalation of lithium is, in general, limited by the lithium ion diffusion in the oxide electrode, the attention of a previous research [5] 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 [6].

The primary observation concerning the kinetics of lithium incorporation into WO$_3$ thin films is that both diffusion and interface kinetics are important. The following considerations are relevant. Firstly, the thermodynamic and kinetic properties of WO$_3$ thin films are very dependent on the method preparation, and in particular are dependent on the crystallinity degree of the films [7]. The structure of WO$_3$ host material plays an important role to the thermodynamics and kinetics of lithium intercalation into the oxide.

The present paper deals with the kinetics and thermodynamics of electrochemical intercalation of lithium into WO$_3$ and WO$_3$:Li$^+$ thin films.
2. Experimental

2.1. Preparation of the sol

The route proposed by Cronin et al. [8] was followed for the preparation of WO₃ sol. Metallic tungsten reacts with hydrogen peroxide (30%, v/v) and acetic acid between 0 and 12°C for 24 h. After that, this product is filtered and then evaporated to dryness, resulting in a transition metal-peroxy acid product (yellow powder), which reacts at room temperature with ethanol to form a transition metal-peroxy ester derivative. LiCF₃SO₃ is added to the final solution in order to achieve a doping level of 5 mol% in the final product [9].

2.2. Preparation of the films

The films were deposited by the dip-coating method on ITO coated glass substrates (Asahi Glass 14 Ω□) previously cleaned and rinsed with bidistilled water and ethanol and then dried at room temperature. The substrates were immersed into the solution in ambient atmosphere (RH < 60%) and withdrawn at a rate of 10 cm/min. Subsequently, the samples were dried in air at room temperature and then heat-treated at 240°C for 1 h. The resulting coating with a thickness of 250 nm was transparent and homogeneous without any visual cracking.

2.3. Measurement technique

The galvanostatic intermittent titration experiments were performed with an EG&G PAR 273 computer-controlled potentiostat galvanostat, driven by 270 Electrochemical Analysis software. A conventional three-electrode cell was used; the counter-electrode was a platinum foil of 1 cm² of area and the quasi reference electrode was a silver wire. The electrolyte was 1.0 M solution of LiClO₄ dissolved in propylene carbonate (PC) and the cell was previously purged with dry N₂ gas.

3. Results and discussion

To obtain the chemical diffusion coefficient (D) of Li⁺ in WO₃ and WO₃:Li⁺ films, 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 mathematical model for the galvanostatic intermittent titration technique (GITT) have been developed by Weppner and Huggins [10], which combined both transient and steady-state measurements to obtain kinetic properties of transport on solids.

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

\[ x = \frac{ItM_B}{Z_Am_BF} \]  

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⁺, the metal oxide mass, and the Faraday’s constant:

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

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 present analysis it was considerate 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 Eq. (3) in the following form:

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

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

The data for several runs are shown in Fig. 1a and b and the different starting voltages represent different stoichiometries of Liₓ in WO₃ and WO₃:Li films. The order in which the points were taken is indicated, showing that the measurements were, in

![Fig. 1. Steady-state voltages of the galvanic cell as a function of the stoichiometric coefficient x, for pure WO₃ (a) and WO₃:Li (b) films.](image-url)
fact, taken at equilibrium, where the concentrations of all species are uniform. As it can be seen, the amount inserted into WO_3 film was 0.09, however a higher quantity of lithium was inserted into WO_3:Li film (x = 0.37). It can be explained by the fact that lithium, already present in the WO_3 structure as a dopant, causes a more favorable lattice arrangement, i.e., a more opened lattice, favoring the lithium insertion through the lattice.

Fig. 1a and b shows that the open circuit potential (OCP) increases linearly with an increase in the x-value in Li_xWO_3 or Li_x(WO_3:Li). The OCP–x curves mainly consist of two straight lines with different slopes. The relationships between the OCP(E) and the x-value for WO_3 film are represented by

$$E = -0.13 - 9.41x, \text{ for } x \leq 0.054$$  \hspace{1cm} (5)

$$E = -0.28 - 6.6x, \text{ for } x > 0.054$$  \hspace{1cm} (6)

and for WO_3:Li film they are represented by

$$E = -0.17 - 2.68x, \text{ for } x \leq 0.22$$  \hspace{1cm} (7)

$$E = -0.48 - 1.26x, \text{ for } x > 0.22.$$  \hspace{1cm} (8)

These results suggest that the intercalated lithium atoms occupy more than one kind of crystallographic site and single

$$\mu_{Li} - \mu_{Li}^0 = RT \ln a_{Li} = -FE(x)$$  \hspace{1cm} (9)

$$\Delta G_1^0 = -F \int_0^x E(x) \, dx$$  \hspace{1cm} (10)

where E(x) is the open circuit potential at the respective x-value and $\mu_{Li}$, $\mu_{Li}^0$ and $a_{Li}$ are the lithium chemical potential, the chemical potential for pure lithium and the activity of lithium, respectively [12].

The $\Delta G_1^0$ values obtained as a function of the depth of lithium intercalation, x, are given in Fig. 2a and b. As it can be seen, the $\Delta G_1^0$ values increase with the increase in the x-value, being 5 kJ mol$^{-1}$ at x = 0.09 in Li_xWO_3 and 25.6 kJ mol$^{-1}$ at x = 0.37 in Li_x(WO_3:Li). Comparing both films the effect of lithium leading the $\Delta G_1^0$ value is somewhat higher. 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 doping lithium in the WO_3 film structure [11].

The chemical diffusion coefficient (D) is an important measurement of the lithium ion dynamics in electrode intercalation. According to the model of Weppner and Huggins 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. Therefore, the ohmic effect on the electrolyte and the interface is totally eliminated when using the GITT method.

The diffusivity, or component diffusion coefficient is related to the component, $D_{Li^{+},k}$ of a species. It is a measurement of its random motion in the absence of a concentration gradient; it is related to $D_{Li^{+}}$ by the expression [13]:

$$D_{Li^{+}} = D_{Li^{+},k} \frac{d(ln a_{Li})}{d(ln C_{Li})}$$  \hspace{1cm} (11)

$$D_{Li^{+}} = D_{Li^{+},k} \left( \frac{F}{RT} \right) \frac{dE}{dx}$$  \hspace{1cm} (12)

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 the 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 [10].

According to Levi et al. and Molenda and Kubik [14,15], the chemical diffusion could either increase or decrease with the increasing content of intercalated species, depending on the nature of the long-range interactions between species. Similar results were obtained in these studies, where the $D$ values increase with the increase in the lithium concentrations the films.
The determined chemical diffusion coefficient $D_{Li^+}$ and component diffusion coefficient $D_{Li^+,k}$ of lithium ion in the WO$_3$ and WO$_3$:Li films are plotted in Fig. 3a and b. At room temperature the $D_{Li^+}$ in the amorphous WO$_3$ and WO$_3$:Li films reached the values of $1.7 \times 10^{-9}$ cm$^2$/s at $x = 0.09$ and $5.6 \times 10^{-10}$ cm$^2$/s at $x = 0.37$ for WO$_3$ and WO$_3$:Li films, respectively. The values of the component diffusion coefficient $D_{Li^+,k}$ were, in both films, about two orders of magnitude lower than those of chemical diffusion coefficient $D_{Li^+}$, approaching the values of $6.1 \times 10^{-11}$ cm$^2$/s at $x = 0.09$ and $1.7 \times 10^{-11}$ cm$^2$/s at $x = 0.37$ for WO$_3$ and WO$_3$:Li films, respectively.

The determined thermodynamic enhancement factor $W$ for WO$_3$ and WO$_3$:Li films is plotted against lithium content $x$ in Fig. 4a and b. As the lithium content $x$ increased from 0.018 to 0.09, the thermodynamic enhancement factor $W$ increased from 5.5 to 27.7 up to $x = 0.09$ for WO$_3$ thin film. On the other hand, as the lithium content $x$ increased from 0.07 to 0.37, the thermodynamic enhancement factor $W$ increased from 6.6 to 33.01 up to $x = 0.37$ for WO$_3$:Li film.

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 WO$_3$ and WO$_3$:Li films may be associated with the microcrystalline features of the sol–gel amorphous WO$_3$ films [11]. According to the results of a previous research [9], the presence of lithium in the WO$_3$ film produces a more open structure. The presence of lithium in the WO$_3$ films improves the electrochemical response of the films, exhibiting a higher charge density and higher mass variation during the insertion/extraction process.

4. Conclusions

Measurements of the equilibrium OCVs as a function of 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 amorphous WO$_3$ and WO$_3$:Li thin films reached the values of $1.7 \times 10^{-9}$ cm$^2$/s at $x = 0.09$ and $5.6 \times 10^{-10}$ cm$^2$/s at $x = 0.37$ for WO$_3$ and WO$_3$:Li films, respectively. The values of the component diffusion coefficient $D_{Li^+,k}$ were, in both films, about two orders of magnitude lower than those of chemical diffusion coefficient. The drastic rise in the component diffusion coefficient
can be explained by the increase in the electronic conductivity promoted by the lithium intercalation.

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