LITHIUM DIFFUSION IN WO_3 DOPED AND UNDOPED THIN FILMS

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Abstract

The electrochromic behavior of tungsten oxide thin films doped with Li, Nb, Zr Ta and Ti was investigated. The addition of lithium, niobium, zirconium, tantalum and titanium to the precursor solutions leads to films with different electrochemical performance. 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. The kinetics and thermodynamics of electrochemical intercalation of WO_3 doped and undoped and films were investigated. The standard Gibbs energy for lithium intercalation was calculated

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. The rapid diffusion of atoms in mixed conducting materials is of the theoretical interest, as well as practical importance in battery electrode material, electrochromic display devices [1].
The primary observation concerning the kinetics of lithium incorporation into the WO_3 thin films is that both diffusion and interface kinetics are important. The following considerations are relevant. Firstly, the thermodynamic and kinetics properties of WO_3 thin films are very dependent on the method preparation, and in particular are dependent on the degree of crystallinity of the films [2]. In the present work, the kinetics and thermodynamics of electrochemical intercalation of lithium into WO_3 doped and undoped thin films were studied.

Experimental

Sol was prepared according to previous paper [3]. The final solution was doped with, Li, Nb, Zr, Ta and Ti. The films were deposited by the dip-coating at a speed of 12 cm/min and then heat treated at 240^{o}C for 1h. Electrochemical measurements were performed using 1M $LiClO_4$ dissolved in propylene carbonate (PC) as electrolyte.

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Results

To obtain the chemical diffusion coefficient (D) of Li^+ in WO_3 doped and undoped thin films, the galvanostatic intermittent titration technique (GITT) was performed. The mathematical model for GITT have been developed by Weppner and Huggins [4].
The standard free energy of lithium intercalation, ΔG_1^0 in Li_xWO_3 doped and undoped films were calculated from the following equation.

$$\Delta G_1^0 = -F \int_0^x E(x)dx$$

The determined chemical diffusion coefficient D_{Li^+} of lithium ion in the WO_3 doped and undoped films are plotted in Figures 1a. At room temperature the D_{Li^+} reached the values of $1.7x10^{-9}$ cm^2/s at x=0.09, $5.6x10^{-10}$ cm^2/s at x=0.37, $1.77x10^{-10}$ cm^2/s at x=0.29, $9x10^{-11}$ cm^2/s at x=0.36, $3.1x10^{-10}$ cm^2/s at x=0.29 and $2.4x10^{-10}$ cm^2/s at x=0.29, for WO_3, WO_3:Li, WO_3:Nb, WO_3:Zr, WO_3:Ta, and WO_3:Ti thin films, respectively.
The ΔG_1^0 values obtained as a function of the depth of lithium intercalation, x, are given in Figures 1b. As it can be seen, the ΔG_1^0 values increase with the increase in the x-value, being 5 kJ mol^{-1} at x=0.09, 26 kJ mol^{-1} at x=0.37, 27.2 kJ mol^{-1} at x=0.29, 34.4 kJ mol^{-1} at x=0.36, 26.9 kJ mol^{-1} at x=0.29 and 25 kJ mol^{-1} at x=0.29, for WO_3, WO_3:Li, WO_3:Nb, WO_3:Zr, WO_3:Ta, and WO_3:Ti thin films, respectively. The intercalation free energy mainly reflects the site energy of lithium atoms intercalated into the structures.

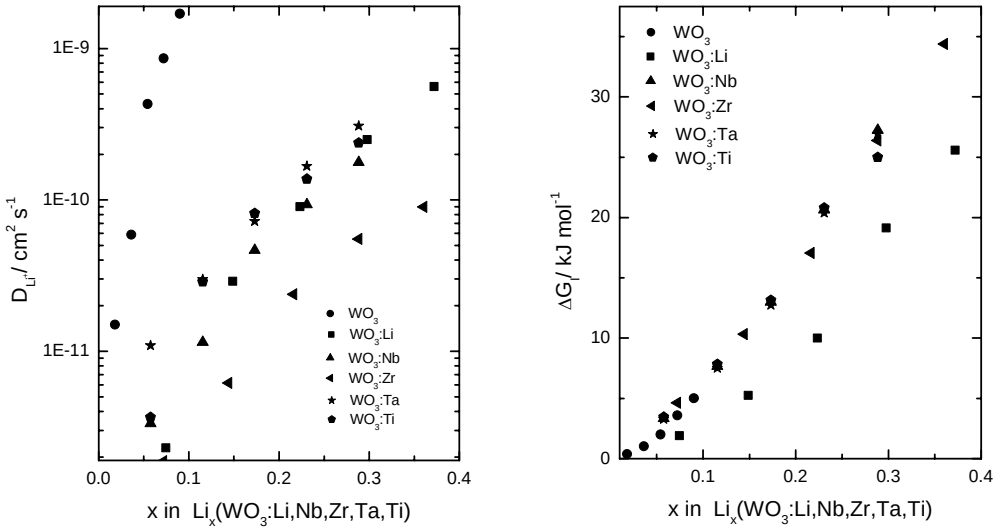

Fig. 1 *Chemical diffusion coefficient D (left) and standard Gibbs energy (right) as a function of lithium content for WO_3 doped and undoped thin films.*

Conclusions

Lithium chemical diffusion coefficient and standard Gibbs energy in WO_3 doped and undoped films was estimated by galvanostatic intermittent titration technique (GITT) as

functions of the depth of lithium intercalation. A high level of lithium insertion correspond to the WO_3:Li film with a value of $5.6x10^{-11}$ cm^2/s and 26 kJ mol^{-1} at x=0.37.

Acknowledgments

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