Intercalation of lithium in r.f.-sputtered niobium oxide film as electrode material for lithium-ion batteries

Naoaki Kumagai, Yasushi Tateshita, Yuichi Takatsuka, Mamoru Baba, Toshio Ikeda, Kazuo Tanno

Faculty of Engineering, Iwate University, Ueda 4-3-5, Morioka 020, Japan

Abstract

Niobium oxide films have been prepared by r.f. sputtering using an argon sputter gas and a Nb_2O_5 target; the oxide films have been characterized by scanning electron microscopy, X-ray diffraction method and electrochemical techniques. The oxide film heat-treated at 500 to 700 °C in argon atmosphere is a monoclinic Nb_2O_5 highly oriented along the c-axis perpendicular to the substrate. The oxide film undergoes a reversible lithium intercalation and de-intercalation process. The kinetics of the intercalation process of lithium into the highly oriented Nb_2O_5 film was studied using an a.c. impedance method. Furthermore, a rocking-chair-type V_2O_5 film/$Li_2Nb_2O_5$ film cell could be charge/discharged over 50 times at a current of 10 μA at 25 °C.

Keywords: Lithium intercalation; Niobium oxide; Lithium-ion batteries

1. Introduction

In recent years considerable attention has been devoted to the investigation of the lithium-free rocking-chair batteries, such as $Li_xC/Li_{1-x}CoO_2$ couples. We have previously reported the electrochemical, structural and kinetic characteristics of Nb_2O_5 electrode with lithium intercalation into the crystal lattice [1–4]. In the present work, the electrochemical characteristics of Nb_2O_5 thin film prepared by r.f. sputtering have been examined by galvanostatic and a.c. impedance methods. Furthermore, the lithium-free rocking-chair battery consisting of $Li_xNb_2O_5$ film and V_2O_5 film as the negative and positive electrodes has been constructed and the charge/discharge cycling behaviour has been examined.

2. Experimental

Thin films of Nb oxide were deposited on the SUS 303 stainless-steel substrates (thickness 0.05 mm) and the p-type Si(100) substrate using r.f. (13.56 MHz)-sputtering method in an argon atmosphere (ANELVA, SPF-210B). The r.f. power was 100 W and the argon pressure was 80 mtorr. A pressed and sintered 99.2%

Nb_2O_5 target was used as the source of evaporation. The oxide films were heat-treated in the temperature range from 400 to 1000 °C in argon atmosphere for 1 h. The surface area of the Nb oxide layer was 1.0 cm². The thickness of the Nb oxide film was measured by observing interference fringes using a multiple-beam interferrometer (Mizojiri, type II). The weight of the Nb oxide layer was calculated using the density of Nb_2O_5 (4.94 g/cm³).

The characterization of the oxide films was carried out by means of scanning electron microscopy (SEM) (Hitachi S-450) and X-ray diffractometry (XRD) (Rigaku Denki Geiger flex 20B, Cu $K\alpha$). In order to investigate the electrochemical properties, an electrochemical cell was constructed by coupling the oxide film with an Li counter electrode and an Li reference electrode in a 1 M $LiClO_4$/propylene carbonate (PC) electrolyte, containing a small amount of water (less than 20 mg/dm³). A glass beaker-type cell was used as electrochemical cell. All the measurements were carried out in a dry box filled with argon. A.c. impedance measurements were performed by using NF Electronic Instrument 5720B frequency response analyzer, Tohogiken potentiostat 2000 and HP 9000-200 microcomputer. A 5 mV r.m.s. perturbation was supplied in the frequency range from 10^5 to 10^{-3} Hz.

3. Results and discussion

3.1. The structure of the Nb oxide film prepared by r.f. sputtering

The SEM photographs of the Nb oxide films on the Si substrate heat-treated at various temperatures in argon atmosphere are shown in Fig. 1. As can be seen from the Figure, the Nb oxide crystals grow along the direction perpendicular to the substrate in the temperature range from 500 to 700 °C and the surface of the oxide film is considerably flat at a higher temperature of 600 to 700 °C. The XRD patterns of the Nb oxide films prepared on the Si substrate by r.f. sputtering are given in Fig. 2. The oxide films as deposited and heat-treated at 400 to 500 °C in argon atmosphere were amorphous without any significant peaks of Nb_2O_5. The crystalline Nb_2O_5 phase appeared with the heat treatment of 600 to 700 °C. However, these X-ray patterns showed a large deviation from the standard pattern of polycrystalline Nb_2O_5 having a monoclinic system or T-type modification [1], but (001) diffraction peaks of the T-type Nb_2O_5 were observed. This shows that the Nb_2O_5 crystals were strongly oriented along the c-axis perpendicular to the Si substrate. This X-ray result is consistent with the SEM observation. Similar X-ray patterns were observed in the case of the Nb oxide film on the stainless-steel substrate heat-treated at 400–600 °C, but at a higher temperature of 900 °C the diffraction peaks of Ni_2O_3 appeared at $2\theta = 45°$ and 51°, while the (001) peaks of Nb_2O_5 almost disappeared around 900 °C. This shows that the reaction between the Nb_2O_5 film and the stainless-steel substrate occurred at 900 °C, leading to the formation of Ni_2O_3.
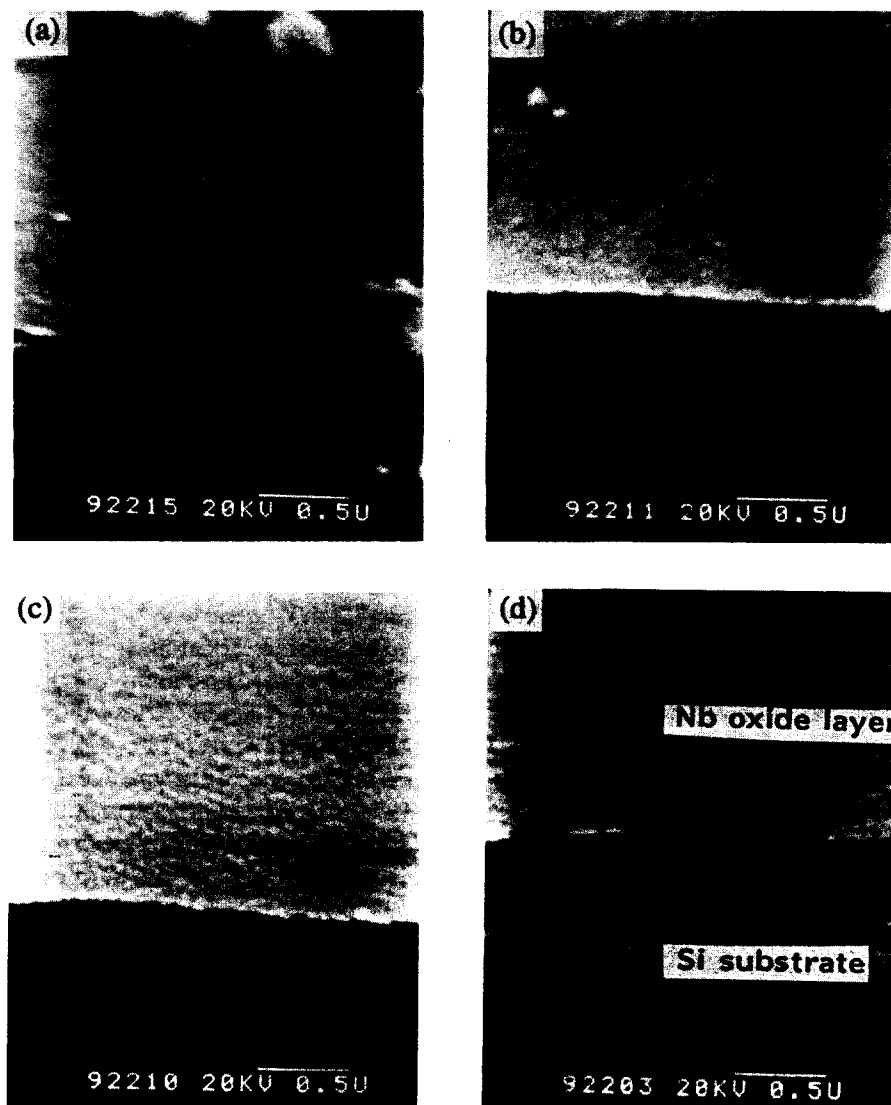

Fig. 1. Scanning electron microscopy photographs of Nb oxide films on Si substrate heat-treated at various temperatures for 1 h in argon: (a) 400 °C; (b) 500 °C; (c) 600 °C, and (d) 700 °C.
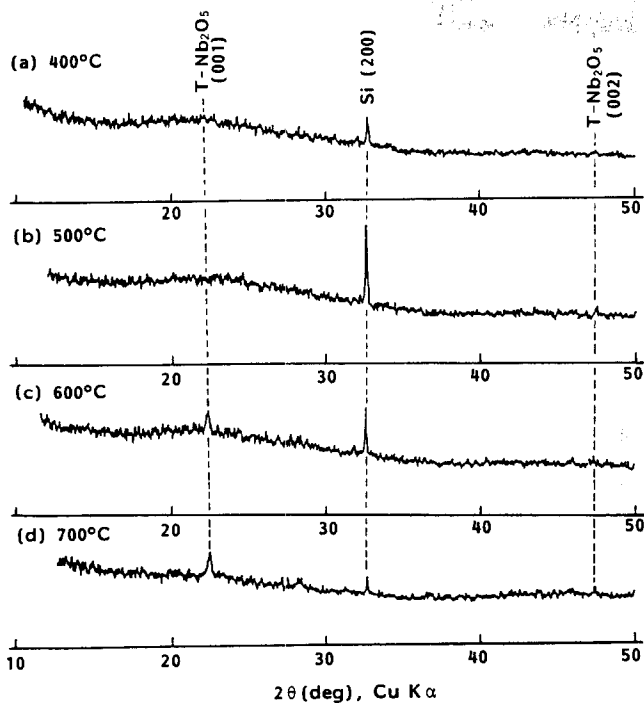
Fig. 2. X-ray diffraction patterns of Nb oxide films on Si substrate heat-treated at various temperatures for 1 h in argon.

3.2. Electrochemical behavior of r.f. sputtered niobium oxide film

Fig. 3 shows the charge/discharge cyclic curves of the Nb_2O_5 films obtained by r.f. sputtering on the stainless-steel substrate, measured at a current density of 10 $\mu A/cm^2$ in 1 M $LiClO_4/PC$ at 25 °C. As seen in

the Figure, the oxide film as deposited showed the initial discharge capacity of about 200 mAh/g oxide corresponding to 2 Li/mol of the oxide, however the capacity significantly decreased with increasing cycling number up to 30th. On the other hand, the oxide film heat-treated at 500 °C for 1 h in argon atmosphere gave almost constant discharge capacity of about 150 mAh/g oxide during 30 cyclings. This electrochemical behavior was in an agreement with that of a T-type Nb_2O_5 powder pressed electrode [1]. When the heat-treatment temperature of the oxide film was raised up to 900–1000 °C, the discharge capacity at 5–10th cyclings highly decreased to 20 mAh/g. This is due to the loss of the Nb oxide layer by the reaction with the stainless-steel substrate. Thus it is found that the oxide film heat-treated at 500 °C shows the most excellent charge/discharge cyclic behavior.

The sputtered Nb_2O_5 film heat-treated at 500 °C in argon was at first electrochemically lithiated up to $x=2$ in $Li_xNb_2O_5$, and then the $Li_2Nb_2O_5$ film was used as a negative electrode for the rocking-chair $V_2O_5/Li_2Nb_2O_5$ cell. The V_2O_5 film electrode was prepared by r.f. sputtering on the stainless-steel substrate under the same condition as Nb_2O_5. Fig. 4 shows the charge/discharge cyclic curves of V_2O_5 film/$Li_2Nb_2O_5$ film cell containing 1 M $LiClO_4/PC$ at a current of 10 μA at 25 °C. As seen in the Figure, the charge/discharge cyclings were possible over 50 times at a voltage of 2.5–1.0 V.

The a.c. impedance spectra of $Li_xNb_2O_5$ films having (001) orientation were measured at various x-values in 1 M $LiClO_4/PC$ at 25 °C. Fig. 5(a) shows a typical
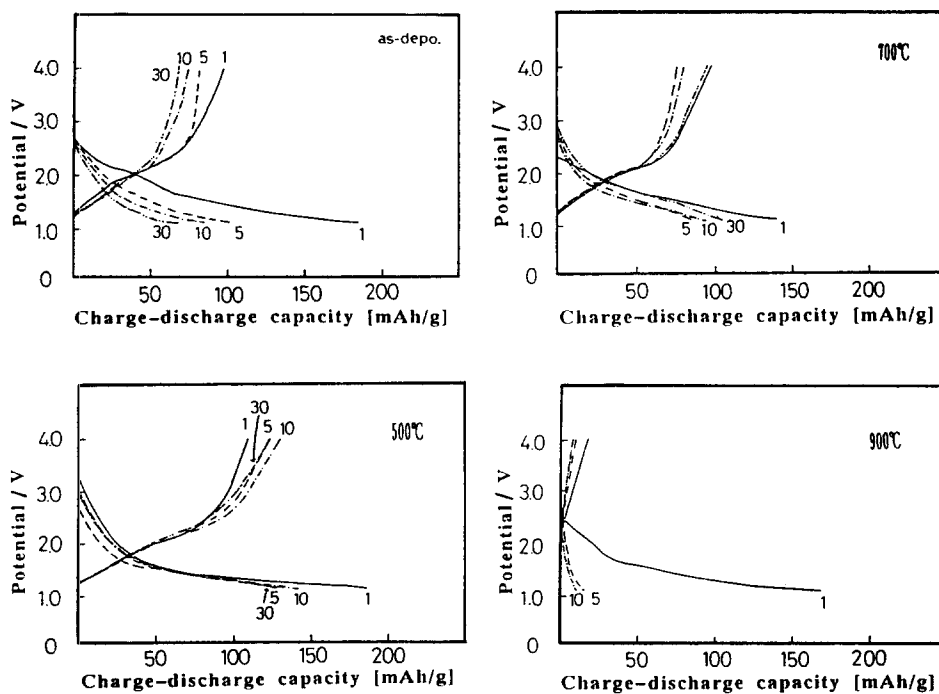

Fig. 3. Charge/discharge cyclic curves of Nb oxide films on the stainless-steel substrate heat-treated at various temperatures in argon.
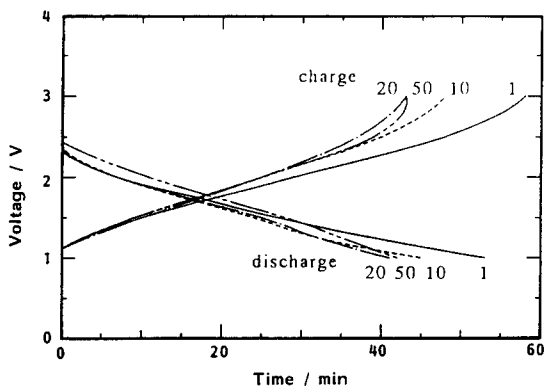
Fig. 4. Charge/discharge cyclic characteristics of $V_2O_5/Li_2Nb_2O_5$ cell containing 1 M $LiClO_4$/PC at a current of 10 μA at 25 °C. The Nb_2O_5 film (thickness 4000 Å) heat-treated at 500 °C for 1 h in argon and the V_2O_5 film (3000 Å) heat-treated at 500 °C for 1 h in air were used as the negative and positive electrodes.
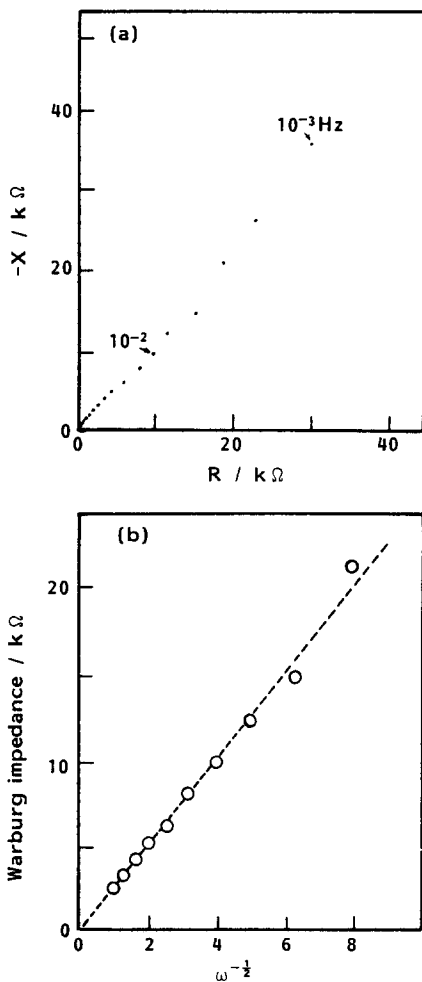

Fig. 6. Open-circuit and closed-circuit potentials as a function of x in $Li_xNb_2O_5$ in 1 M $LiClO_4$/PC at 25 °C. The open-circuit potential was measured after standing about 60 h after discharge at 10 μA/cm².

Fig. 5. Typical impedance diagram for (a) $Li_{1.0}Nb_2O_5$ film and (b) plot of Warburg impedance $|Z_w|$ against $\omega^{-1/2}$. The Nb_2O_5 film (thickness 3000 Å) on the stainless-steel substrate was heat-treated at 700 °C for 1 h in argon.

Fig. 7. Chemical ($\tilde{D}$) and component (D_{Li}) diffusion coefficient of lithium for $Li_xNb_2O_5$ film at 25 °C.
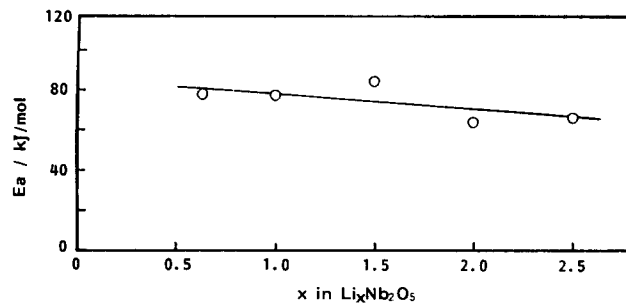
Fig. 8. Activation enthalpies for lithium diffusion in $Li_xNb_2O_5$.

impedance spectrum for $Li_{1.0}Nb_2O_5$ film. The response mainly consists of a low frequency spike having a phase angle of about 45°. This reveals that the discharge
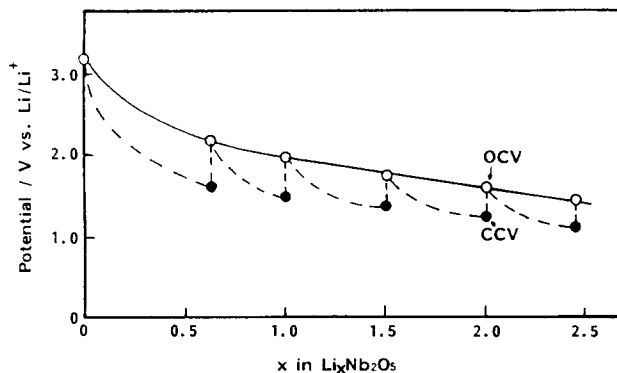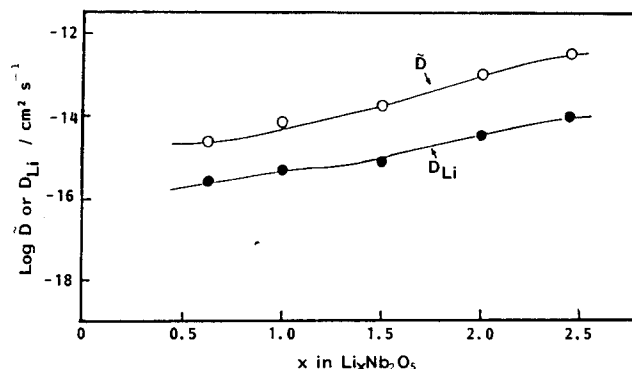
process is controlled by the lithium diffusion in the oxide lattice. The chemical diffusion coefficient of lithium, $\tilde{D}$, in the oxide was obtained from the following equation [5]:

$$Z_w = A_w \omega^{-1/2} \tag{1}$$

$$A_w = \frac{V_m(dE/dx)}{zFa\tilde{D}^{1/2}} \tag{2}$$

where Z_w is the Warburg impedance, ω is the angular frequency of the a.c. perturbation, V_m is the molar volume of Nb_2O_5 (53.8 cm³), dE/dx is the slope of the open-circuit potential/x-value in $Li_xNb_2O_5$ curve

(Fig. 6) and a is the electroactive surface area of the oxide electrode (1.0 cm^2). The Warburg prefactor, A_w, was obtained from the plot of the observed Warburg impedance $|Z_w|$ against $\omega^{-1/2}$ (Eq. (1)), as shown in Fig. 5(b). The chemical diffusion coefficient is related to the component diffusion coefficient for lithium, D_{Li}, by the following equation [6]:

$$\tilde{D} = D_{Li} \frac{d \ln a_{Li}}{d \ln C_{Li}} = -D_{Li} \frac{F}{RT} \times \frac{dE}{dx} \tag{3}$$

where $(d \ln a_{Li}/d \ln C_{Li})$ is the thermodynamic enhancement factor, and R is a gas constant.

The chemical diffusion coefficient $\tilde{D}$ and lithium component diffusion coefficient D_{Li} are shown in Fig. 7 as a function of the x-value in Li$_x$Nb$_2$O$_5$. As seen in the Figure, the $\tilde{D}$ values are found to be of the order of 10^{-13}–10^{-14} cm^2 s^{-1} at 25 °C. They tend to increase with increasing x-value, which was also observed in the case of T-type Nb$_2$O$_5$ powder pressed electrode [3,4]. The D_{Li} values were found to be of the order of 10^{-14}–10^{-15} cm^2 s^{-1} at 25 °C. Furthermore, from the Arrhenius plots of the component diffusion coefficients

for Li$_x$Nb$_2$O$_5$ ($x = 0.5$–2.5) films, the activation enthalpy of 70–90 kJ/mol was obtained (Fig. 8).

Acknowledgements

References

[1] N. Kugamai and K. Tanno, *Denki Kagaku, 50* (1982) 704.
[2] N. Kumagai, K. Tanno, T. Nakajima and N. Watanabe, *Electrochim. Acta, 28* (1983) 17.
[3] N. Kumagai, I. Ishiyama and K. Tanno, *J. Power Sources, 20* (1987) 193.
[4] N. Kumagai, K. Satodate and K. Tanno, *Denki Kagaku, 62* (1994) 56.
[5] C. Ho, I.D. Raistrick and R.A. Huggins, *J. Electrochem. Soc., 127* (1980) 343.
[6] W. Weppner and R.A. Huggins, *Annu. Rev. Mater. Sci., 8* (1978) 269.