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# Electrochemical lithium intercalation reaction of anodic vanadium oxide film

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## Abstract

The electrochemical lithium intercalation reaction of anodic vanadium oxide films in 1 M LiClO<sub>4</sub> propylene carbonate solution has been investigated by the galvanostatic intermittent titration technique (GITT) and electrochemical impedance spectroscopy (EIS) as a function of electrode potential. Measured impedance spectra were analysed using the complex non-linear least-squares (CNLS) fitting method. The impedance spectra measured in the potential range from 3.6 to 2.6 V<sub>Li/Li+</sub> showed that the electrochemical intercalation reaction of lithium ions into the anodic vanadium oxide film consists of three consecutive steps of charge transfer at the electrolyte–oxide film interface, lithium ion incorporation into the oxide film and diffusion through the oxide film. The charge transfer reaction at the electrolyte–anodic vanadium oxide film interface is mainly affected by the valence change of vanadium ions in the anodic vanadium oxide film. In the electrode potential range from 3.0 to 3.6 V<sub>Li/Li+</sub>, i.e., lower lithium content ( $\delta=0-1$ ) of the oxide film, intercalated lithium ions are highly accumulated in the near-surface region of the anodic vanadium oxide film. The component diffusivity of lithium in the oxide film was determined to be 10<sup>-12</sup>–10<sup>-14</sup> cm<sup>2</sup> s<sup>-1</sup> in the lithium content range investigated, owing to the increased interaction between intercalated lithium ions.

**Keywords:** Electrochemical intercalation reaction; Vanadium oxide film

## 1. Introduction

Electrochemical lithium intercalation into and deintercalation from lithium vanadium oxide have been studied by many researchers [1–3], because of the interest in their applications to the cathode material for high energy density storage batteries and electrochromic display devices.

Since electrochemical intercalation and deintercalation are in general limited by the rate of diffusion of the ion in the oxide electrode, the attention of previous works [4,5] has been focused on the determination of diffusivity in the electrode material. In contrast, the mechanism by which lithium ions cross the electrolyte–electrode interface has received little attention. Knowledge of the kinetic parameters of electrochemical intercalation and study of their variation

with lithium content must give a better understanding of lithium intercalation into vanadium oxide.

The analysis of current or potential transients and a.c. impedance spectra obtained from a pressed powder disk usually used as the test specimen is very complicated because of the ambiguity of the specimen geometry. In order to circumvent this problem, in this work, an anodic oxide film was used as the test specimen.

This work is concerned with the interfacial reaction at and lithium transport through the anodic vanadium oxide film as a function of lithium content. Electrochemical impedance spectra were measured at various electrode potentials from anodic vanadium oxide film in 1 M LiClO<sub>4</sub> (lithium perchlorate) propylene carbonate solution and analysed using the complex non-linear least-squares (CNLS) fitting method [6]. The chemical and component diffusivities of lithium in the anodic oxide film were determined as a function of electrode potential by the galvanostatic intermittent titration technique (GITT) [7].

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## 2. Experimental details

### 2.1. Specimen preparation

The anodic vanadium oxide film used as the working electrode was prepared from vanadium foil of 99.7% purity. The foil specimen was mechanically polished with #1200 and #1500 emery paper and 0.05  $\mu\text{m}$  alumina powder and finally electropolished at a potential of 16 V for 5–7 min in a mixture of 25% sulphuric acid and 75% ethyl alcohol solution at room temperature.

Anodic vanadium oxide films were prepared galvanostatically at a constant current density of 500  $\mu\text{A cm}^{-2}$  at room temperature until the formation potentials of 30, 40 and 50 V were reached, then held at the respective formation potentials for 5 min. The electrolyte used was 0.5 M  $\text{H}_2\text{O}$  glacial acetic acid solution saturated with  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ . A platinum strip was used as the counterelectrode. The prepared oxide films were then sufficiently dried at room temperature in vacuum for 1–2 days in order to eliminate water and acetic acid molecules remaining in the films. Annealing of fresh specimens was performed at 400  $^\circ\text{C}$  for 15 min under a purified argon atmosphere.

### 2.2. Characterization of specimens

In order to identify the V–O bond in the fresh anodic vanadium oxide films, Fourier transform IR (FTIR) absorption spectra were measured in the wavenumber range from 1200 to 400  $\text{cm}^{-1}$  with a resolution of 4  $\text{cm}^{-1}$ . The FTIR spectra of anodic vanadium oxide films were obtained by the attenuated total reflectance (ATR) method. A ZnSe single crystal was used as the ATR crystal. From a comparison with the FTIR spectrum of crystalline  $\text{V}_2\text{O}_5$  powder, the fresh anodic vanadium oxide film proved to have an amorphous structure.

In order to identify the crystallinity of the anodic vanadium oxide film, X-ray diffraction (XRD) patterns before and after annealing of the film were measured in the scanning angle range from 10 $^\circ$  to 50 $^\circ$  ( $2\theta$ ). From an inspection of the obtained XRD patterns, the crystallinity of the fresh anodic oxide film was found to be increased after annealing of the film.

The FTIR spectra and XRD patterns were obtained using a Nicolet 520P FTIR spectrophotometer and an automated Rigaku X-ray diffractometer respectively.

### 2.3. Electrochemical measurements

Cyclic voltammograms were obtained at a scan rate of 10  $\text{mV s}^{-1}$  in the potential ranges from 0.5 to 4.0  $\text{V}_{\text{Li}/\text{Li}^+}$  and from 2.0 to 4.0  $\text{V}_{\text{Li}/\text{Li}^+}$  for the fresh anodic

oxide film specimen and the annealed oxide film specimen respectively.

The lithium contents of the anodic vanadium oxide films were modified by the application of a constant cathodic current pulse to an electrochemical cell, accompanied by potential transient measurements. Pure lithium metal foil (Foote Mineral Co., USA, purity 99.9%) was used as the reference electrode and the counterelectrode; 1 M  $\text{LiClO}_4$  propylene carbonate solution was used as the electrolyte.

When an equilibrium potential was attained, electrochemical impedance measurements were made by applying an a.c. amplitude of 5  $\text{mV}_{\text{rms}}$  on the equilibrium electrode potentials of 2.6–3.6  $\text{V}_{\text{Li}/\text{Li}^+}$  over the frequency range from 10 mHz to 100 kHz. For impedance measurements a Solartron 1255 frequency response analyser (FRA) was used in conjunction with a Solartron 1286 electrochemical interface (ECI) under the remote control of an IBM-compatible personal computer. All the electrochemical experiments were carried out in an argon-filled glove-box (VAC HE493).

## 3. Results and discussion

Fig. 1 shows the cyclic voltammograms obtained from the fresh and annealed oxide films in 1 M  $\text{LiClO}_4$  propylene carbonate solution. For comparison the cyclic voltammogram for the vanadium substrate is also presented, revealing that no notable oxidation–reduction reaction occurs at the electrolyte solution–pure va-

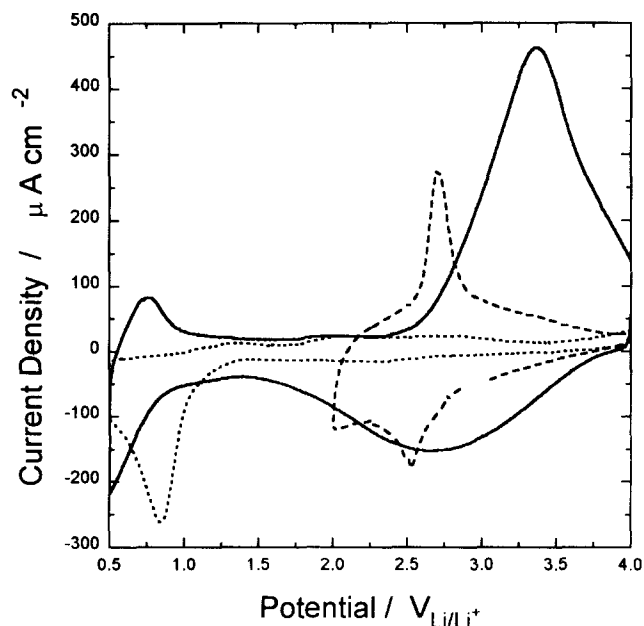


Fig. 1. Cyclic voltammograms obtained at a scan rate of 10  $\text{mV s}^{-1}$  in potential ranges from 0.5 to 4.0  $\text{V}_{\text{Li}/\text{Li}^+}$  and from 2.0 to 4.0  $\text{V}_{\text{Li}/\text{Li}^+}$  for fresh anodic oxide film and annealed oxide film specimens respectively: —, fresh anodic film; ---, annealed anodic oxide film; ·····, vanadium substrate.

nadium metal interface in the potential range from 1.5 to 4.0  $V_{Li/Li+}$ .

The broad current peak in the cyclic voltammogram indicates the statistical distribution of intercalation sites in the anodic vanadium oxide available for the lithium ion. The appearance of a broader current peak for the fresh specimen as compared with the annealed specimen reveals a more amorphous character of the fresh oxide film.

In the annealed oxide film specimen, on the other hand, sharp reduction and oxidation current peaks were encountered at the potentials of 2.5 and 2.6  $V_{Li/Li+}$  respectively. West et al. [3] have suggested that lithium intercalation into the square pyramidal interstitial site in vanadium oxide gives rise to the reduction current peak around the potential of 2.6  $V_{Li/Li+}$ . The reduction and oxidation current peaks at the potentials of 2.5 and 2.6  $V_{Li/Li+}$  are probably due to the intercalation and deintercalation of lithium into and from this interstitial site respectively.

In the FTIR absorption spectra of the fresh anodic oxide film the absorption peak ( $V=O$  bond) near  $1000\text{ cm}^{-1}$  moves towards lower wavenumber as the electrode potential decreases, i.e. the lithium content of the oxide film increases. The shift of the absorption peak indicates that the  $V-O$  distance is increased with increasing lithium content of the oxide film.

Fig. 2(a) shows typical Nyquist plots obtained from the fresh anodic oxide film at various electrode potentials in 1 M  $LiClO_4$  propylene carbonate solution. The impedance spectra of the fresh specimen consist of two overlapping arcs in the higher frequency range from 1 Hz to 100 kHz and a line inclined at approximately  $45^\circ$  to the real axis in the lower frequency range from 10 mHz to 1 Hz.

The two arcs in the higher frequency range are due to the reaction at the electrolyte–electrode interface and the inclined line in the lower frequency range is attributed to the Warburg impedance associated with lithium diffusion through the oxide film. The impedance spectra suggest that the electrochemical intercalation reaction of lithium into anodic vanadium oxide film exposed to 1 M  $LiClO_4$  propylene carbonate solution consists of three consecutive steps of charge transfer at the electrolyte–anodic vanadium oxide film interface, absorption into the oxide film and diffusion through the oxide film.

From the appearance of the Nyquist plots an equivalent circuit is proposed for electrochemical lithium intercalation into anodic vanadium oxide film as shown in Fig. 2(b).  $R_{ct}$  is the resistance associated with charge transfer at the electrolyte–anodic vanadium oxide film interface,  $C_{dl}$  is the double-layer capacitance due to the accumulation of charged species in the electrolyte at the interface,  $C_{ad}$  is the capacitance arising from the adsorption of lithium in the near-surface region of

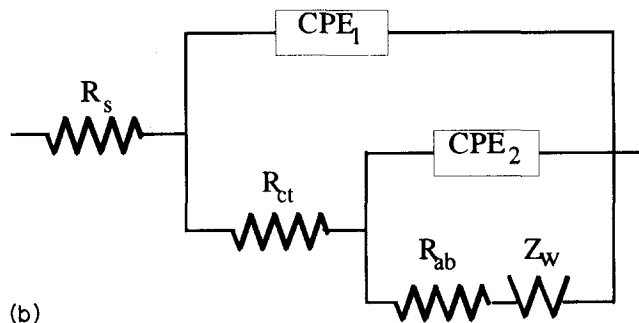
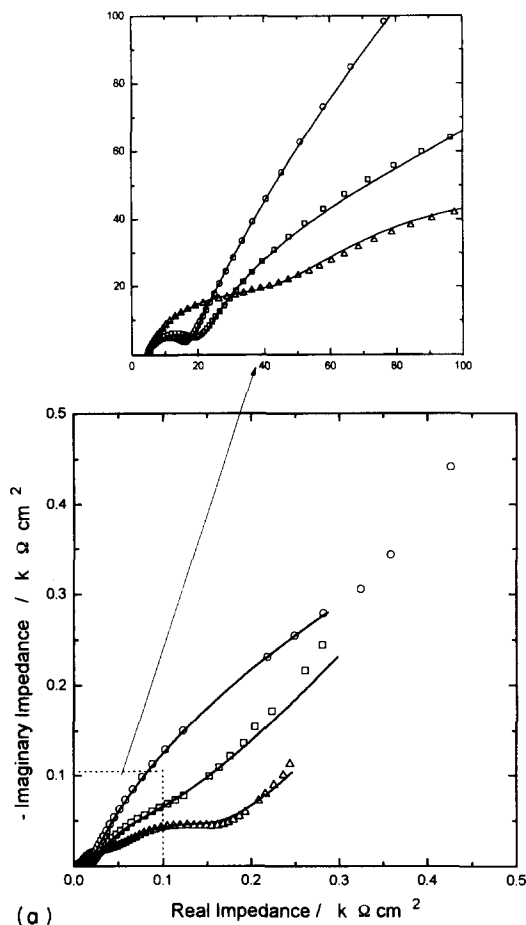


Fig. 2. (a) Typical Nyquist plots obtained from fresh anodic vanadium oxide film in 1 M  $LiClO_4$  propylene carbonate solution at various electrode potentials:  $\circ$ , 3394  $mV_{Li/Li+}$ ;  $\square$ , 3154  $mV_{Li/Li+}$ ;  $\Delta$ , 2880  $mV_{Li/Li+}$ . The thickness of the oxide film specimen was 145 nm. Solid lines represent the simulated curves calculated by using optimum fit parameters based upon the equivalent circuit shown in (b). (b) Equivalent circuit used for analysis of electrochemical lithium intercalation reaction into anodic vanadium oxide film in 1 M  $LiClO_4$  propylene carbonate solution.  $CPE_i: A_i(j\omega)^{n_i}$ , where  $A_i = R_i^{n_i-1}C_i^{n_i-1}$ , with  $0.5 < n_i < 1$ ,  $R_i = R_{ct}$  or  $R_{ab}$  and  $C_i = C_{dl}$  or  $C_{ad}$ .

the oxide film,  $R_{ab}$  is the resistance associated with the absorption reaction of adsorbed lithium into the oxide film and  $Z_w$  is the finite length Warburg impedance for the diffusion of lithium through the oxide film.

By virtue of the very low solubility of lithium in vanadium, it is reasonable to assume that the interface

between the anodic oxide film and the metal substrate is impermeable to lithium ions. The Warburg impedance ( $Z_w$ ) representing the diffusion of lithium through the oxide film under the impermeable boundary condition can be expressed as

$$Z_w = \frac{V_m \tau_D}{SF} \left( \frac{\partial E}{\partial \delta} \right)_{x=0} \frac{\coth[(j\omega\tau_D)^{1/2}]}{(j\omega\tau_D)^{1/2}} \quad (1)$$

where  $\tau_D = l^2/\tilde{D}_{Li^+}$ ,  $E$  is the electrode potential,  $\delta$  is the deviation from the ideal stoichiometry,  $l$  is the thickness of the oxide film,  $S$  is the surface area of the oxide film,  $F$  is the Faraday constant,  $V_m$  is the molar volume of the anodic vanadium oxide film ( $60.225 \text{ cm}^3 \text{ mol}^{-1}$ ),  $\omega$  is the angular frequency and  $\tilde{D}_{Li^+}$  is the chemical diffusivity of lithium in the oxide film. The chemical diffusivity  $\tilde{D}_{Li^+}$  could not be determined from the CNLS fitting of impedance spectra to Eq. (1), since low frequency impedance data are lacking.

$R_{ct}$ ,  $C_{ad}$  and  $R_{ab}$  were determined as functions of electrode potential by using the CNLS fitting method first written by Macdonald and Garber [6] and Macdonald [8] and subsequently modified in our laboratory [9]. The results are presented in Figs. 3–5.

In Fig. 3 it is seen that  $R_{ct}$  of the fresh anodic vanadium oxide film remains nearly constant in the electrode potential range from 3.0 to 3.6  $V_{Li/Li^+}$ . This independence of charge transfer resistance on electrode potential indicates that the heterogeneous interfacial charge transfer process is mainly controlled not by electron transfer from the vanadium metal substrate to the electrode but by lithium ion transfer at the

electrolyte–electrode interface in this electrode potential range from 3.0 to 3.6  $V_{Li/Li^+}$ . This result is in good agreement with that of Farcy et al. [10] for crystalline  $Li_8V_2O_5$  bronze ( $\delta=0-1$ ).

$R_{ct}$  increases abruptly at potentials lower than 3.0  $V_{Li/Li^+}$ . This abrupt change in charge transfer reaction with electrode potential is probably associated with a valence change of the vanadium ion within vanadium oxide. It is reported [11] that an electron incorporated into vanadium oxide during lithium intercalation reduces  $V^{5+}$  to  $V^{4+}$  in the vanadium oxide. On further intercalation of lithium the reduction of  $V^{4+}$  to  $V^{3+}$  occurs. This successive valence change of the vanadium atom presumably impedes the charge transfer reaction at the electrolyte–oxide film interface in the electrode potential range corresponding to the higher lithium ion content.

In Fig. 4 the values of the adsorption capacitance  $C_{ad}$  are about one to two orders of magnitude larger than those of the double-layer capacitance  $C_{dl}$ . From the maximum value ( $2.75 \text{ mF cm}^{-2}$ ) of the adsorption capacitance and the following equation the value of the maximum coverage of lithium ions on the “Langmuir” surface of anodic vanadium oxide is determined to be  $2.82 \text{ C cm}^{-2}$ :

$$\theta = \frac{4RTC_{ad}}{F} \quad (2)$$

where  $\theta$  is the adsorption coverage,  $F$  is the Faraday constant,  $R$  is the gas constant and  $T$  is the absolute temperature. This value is approximately 2.5 times larger than the value of  $1.025 \times 10^{-4} \text{ C cm}^{-2}$  calculated for a monolayer of lithium ions adsorbed on the orthorhombic  $V_2O_5$  surface ( $a=11.510 \text{ \AA}$ ,  $b=3.563 \text{ \AA}$ ,

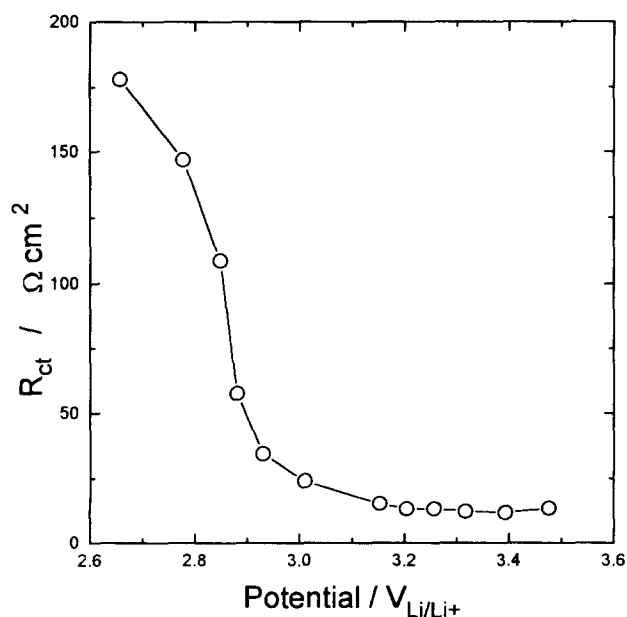


Fig. 3. Potential dependence of charge transfer resistance  $R_{ct}$  associated with lithium intercalation reaction into fresh anodic vanadium oxide film in 1 M  $LiClO_4$  propylene carbonate solution.

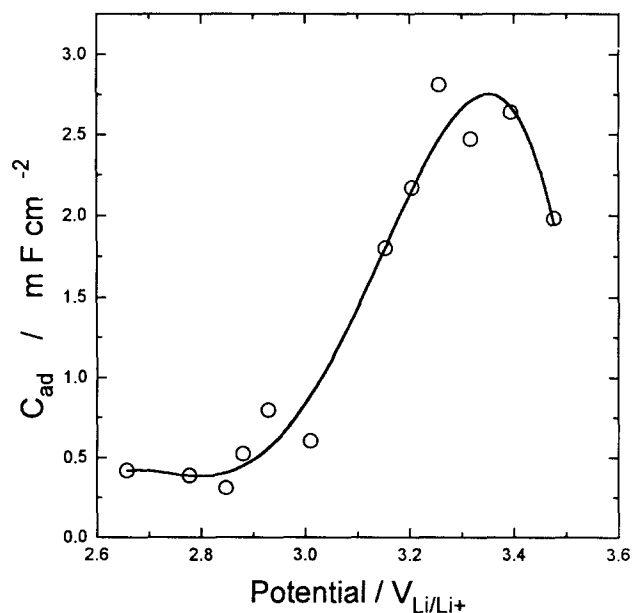


Fig. 4. Potential dependence of adsorption capacitance  $C_{ad}$  associated with lithium intercalation reaction into anodic vanadium oxide film in 1 M  $LiClO_4$  propylene carbonate solution.

$c = 4.369 \text{ \AA}$ ), assuming that one lithium ion is adsorbed per  $\text{V}_2\text{O}_5$  molecular unit. This means that a layer of high lithium ion content exists in the near-surface region of the oxide film and that lithium ions are adsorbed in a quasi-two-dimensional manner in the near-surface region of the oxide as suggested by Conway [12].

The gradual decrease in adsorption capacitance with decreasing electrode potential from 3.3 to 2.6  $\text{V}_{\text{Li}/\text{Li}^+}$  can be attributed to the fewer sites available for adsorption of lithium ions on the surface of the anodic vanadium oxide. The concentration of lithium ions adsorbed on the surface of the oxide film reaches a maximum at electrode potentials lower than 3.0  $\text{V}_{\text{Li}/\text{Li}^+}$ , thus leading to the independence of  $C_{\text{ad}}$  on the electrode potential.

As shown in Fig. 5, as the electrode potential decreases, the absorption resistance decreases up to 3.0  $\text{V}_{\text{Li}/\text{Li}^+}$  and then increases. Since the Fermi level of n-type vanadium oxide ( $\text{V}_2\text{O}_5$ ) is known to be very low [13], the contact of the oxide with electrolyte solution gives rise to a high electron density in the near-surface region of the oxide. The decrease in absorption resistance in the higher electrode potential range indicates that lithium absorption into the oxide film is progressively facilitated by the increased concentration of electrons in the near-surface region of the anodic vanadium oxide film with decreasing electrode potential.

The increase in absorption resistance in the electrode potential range lower than 3.0  $\text{V}_{\text{Li}/\text{Li}^+}$  is no doubt caused by the decrease in the number of empty sites available for absorption of lithium ions into the oxide film.

The chemical diffusivity was calculated as a function of electrode potential from potential transient curves

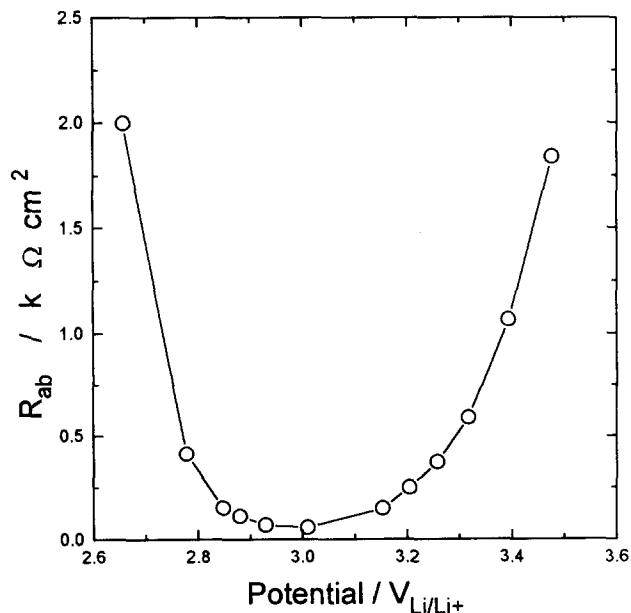


Fig. 5. Potential dependence of absorption resistance  $R_{\text{ab}}$  associated with lithium intercalation reaction into anodic vanadium oxide film in 1 M  $\text{LiClO}_4$  propylene carbonate solution.

and the coulometric titration curve measured during the application of a cathodic current pulse by using the following equation previously suggested by Weppner and Huggins [7]:

$$\tilde{D}_{\text{Li}^+} = \frac{4}{\pi} \left( \frac{V_m}{SF} \right)^2 \left( \frac{I_o dE/d\delta}{dE/dt^{1/2}} \right)^2 \quad (3)$$

where  $I_o$  is the value of constant current applied to the specimen.

Typical potential transient curves are presented in Fig. 6(a). The potential transients show an instantaneous  $IR$  drop followed by a gradual potential decay due to the diffusion of lithium through the oxide film. The larger instantaneous  $IR$  drop at lower electrode potential, i.e. higher lithium content of the oxide film, is responsible for the decreased electronic conductivity of the oxide film. Fig. 6(b) shows the coulometric titration curve obtained from the anodic vanadium oxide film in 1 M  $\text{LiClO}_4$  propylene carbonate solution. The fresh anodic vanadium oxide film was assumed to have a stoichiometry of  $\text{V}_2\text{O}_5$  [14].

From the coulometric titration curve in Fig. 6(b) and the potential transient curves in Fig. 6(a) the chemical diffusivity of lithium in the anodic vanadium oxide film was determined to be of the order of  $10^{-11}$ – $10^{-13} \text{ cm}^2 \text{ s}^{-1}$  in magnitude. This value is one order of magnitude lower than that for a powder specimen reported in previous works [5,10]. The low value is probably attributable to the stronger residual compressive stress in the vanadium oxide film as compared with the powder specimen [15].

Considering the thermodynamic enhancement factor obtained from the coulometric titration curve, the component diffusivity of lithium in the anodic vanadium oxide film is calculated from

$$D_{\text{Li}^+,k} = - \frac{RT}{\delta F} \frac{\partial \delta}{\partial E} \tilde{D}_{\text{Li}^+} \quad (4)$$

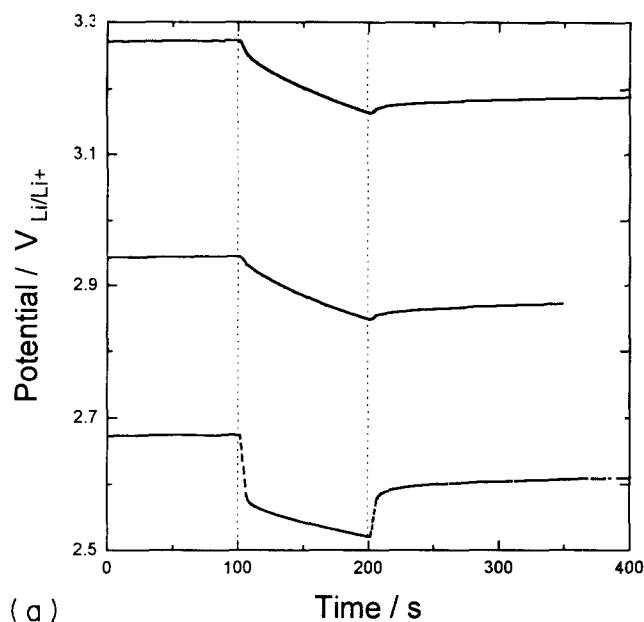
where

$$- \frac{RT}{\delta F} \frac{\partial \delta}{\partial E}$$

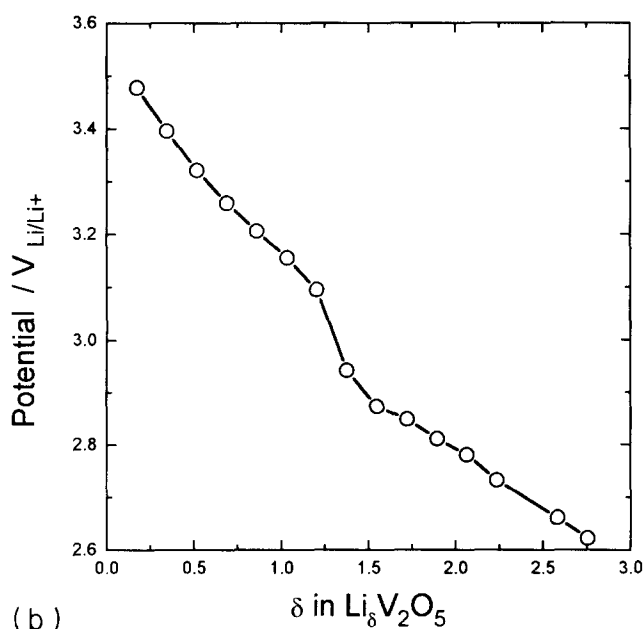
is the inverse of the thermodynamic enhancement factor.

The determined chemical ( $\tilde{D}_{\text{Li}^+}$ ) and component ( $D_{\text{Li}^+,k}$ ) diffusivities of lithium ions in the oxide film are plotted in Figs. 7(a) and 7(b) as functions of electrode potential and lithium content of the oxide film respectively. The component diffusivity  $D_{\text{Li}^+,k}$  of lithium ions in the oxide film decreases from  $10^{-12}$  to  $10^{-14} \text{ cm}^2 \text{ s}^{-1}$  as the lithium content of the oxide film increases from  $\delta = 0$  to 2.

The component diffusivity  $D_{\text{Li}^+,k}$  is a measure of the random motion of lithium ions in the absence of a concentration gradient and is expected to be largely affected by two factors. The first is the number of



(a)

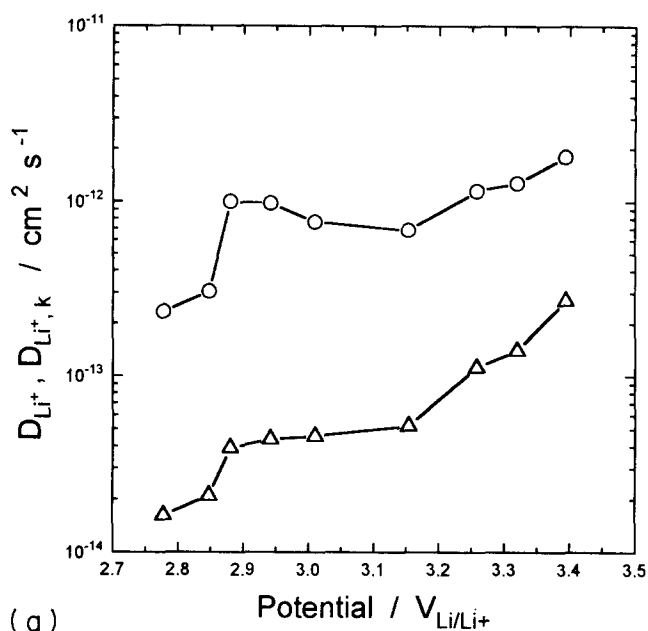


(b)

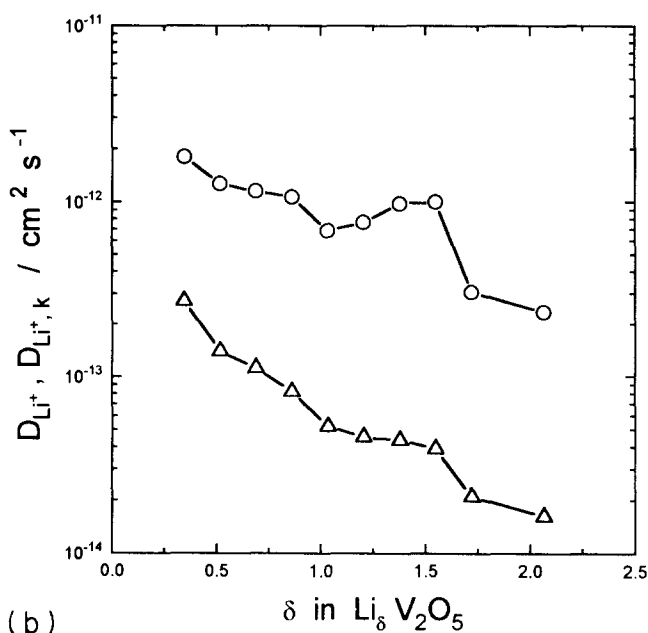
Fig. 6. (a) Typical potential transient curves measured during application of a cathodic current density of  $4 \mu\text{A cm}^{-2}$  to anodic vanadium oxide film in 1 M  $\text{LiClO}_4$  propylene carbonate solution for 100 s. (b) Coulometric titration curve obtained from anodic vanadium oxide film in 1 M  $\text{LiClO}_4$  propylene carbonate solution. A galvanostatic current pulse of  $1 \mu\text{A}$  for 100 s was applied to the oxide film specimen with an exposed area of  $0.25 \text{ cm}^2$  and a thickness of 145 nm

adjacent empty sites available for the jump of a lithium ion in the oxide lattice. The second is the structural rearrangement of the oxide lattice induced by the intercalated lithium.

The number of empty sites in the oxide film can be expressed as  $\delta_{\text{max}} - \delta$  and the component diffusivity is expected to decrease linearly with increasing lithium content of the vanadium oxide film. On the other hand,



(a)



(b)

Fig. 7. Chemical,  $\bar{D}_{\text{Li}^+}$  (O), and component,  $D_{\text{Li}^+,k}$  ( $\Delta$ ), diffusivities of lithium ions in anodic vanadium oxide film as functions of (a) electrode potential and (b) lithium content of oxide film.

the structural rearrangement of the vanadium oxide film by the intercalated lithium possibly gives rise to a deviation from the linear decrease in the component diffusivity with increasing lithium content.

$D_{\text{Li}^+,k}$  decreases linearly with increasing lithium content owing to the increased interaction between intercalated lithium ions in the range  $\delta=0-2$ , except around  $\delta=1.2$ . The change in slope around the lithium content  $\delta=1.2$  in Fig. 7(b) suggests that the anodic vanadium oxide lattice is rearranged to a structure more favourable for lithium transport when the lithium content exceeds  $\delta=1$ .

#### 4. Conclusions

Measurements of the electrochemical impedance spectra at various electrode potentials and the galvanostatic intermittent titration curve of anodic vanadium oxide film in 1 M LiClO<sub>4</sub> propylene carbonate solution led to the following conclusions.

(1) The impedance spectra showed that the electrochemical intercalation reaction of lithium into anodic vanadium oxide film exposed to 1 M LiClO<sub>4</sub> propylene carbonate solution consists of three consecutive steps of charge transfer at the electrolyte–anodic vanadium oxide film interface, absorption into the oxide film and diffusion through the oxide film.

(2) The charge transfer reaction at the electrolyte–anodic vanadium oxide film interface is mainly affected by the valence change of the vanadium ion of the oxide film. In the electrode potential range from 3.0 to 3.6 V<sub>Li/Li<sup>+</sup></sub>, i.e. lower lithium content ( $\delta=0-1$ ) of the oxide film, intercalated lithium ions are largely accumulated in the near-surface region of the oxide film.

(3) The component diffusivity of lithium ions in the anodic vanadium oxide film was found to decrease from about 10<sup>-12</sup> to 10<sup>-14</sup> cm<sup>2</sup> s<sup>-1</sup> at room temperature as the lithium content increases from  $\delta=0$  to 2 in Li <sub>$\delta$</sub> V<sub>2</sub>O<sub>5</sub>, owing to the increased interaction between intercalated lithium ions.

#### Acknowledgement

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