Investigation of lithium transport through an electrodeposited vanadium pentoxide film electrode

Jong-Won Lee, Su-Il Pyun[*]

Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology,
373-1 Guseong-Dong, Yuseong-Gu, Daejeon 305-701, Republic of Korea

Abstract

Lithium intercalation into vanadium pentoxide film electrodes prepared by electrodeposition methods has been investigated in a 1 M solution of $LiClO_4$ in propylene carbonate (PC) by employing potentiostatic current transient technique. From the analysis of the current transient experimentally measured, it is proposed that lithium transport through the electrodeposited vanadium pentoxide film electrode is exclusively controlled by the cell impedance. The theoretical current–time relation has been analytically obtained from the solution to the diffusion equation under the assumption of the cell impedance-controlled constraint at the electrolyte/electrode interface. On the basis of the theoretical current transient, the current transient experimentally measured has been analysed to estimate the kinetic parameters governing lithium intercalation such as the cell impedance and the chemical diffusivity of lithium. In particular, the chemical diffusivity of lithium was determined to be 2.1×10^{-13} to 2.1×10^{-10} cm^2 s^{-1}, and was found to be in good accordance with that obtained from electrochemical impedance spectroscopy.
© 2003 Elsevier Science B.V. All rights reserved.

Keywords: Vanadium pentoxide film electrode; Electrodeposition; Potentiostatic current transient technique; Cell impedance-controlled lithium transport; Chemical diffusivity of lithium

1. Introduction

Ever since vanadium pentoxide (V_2O_5) was realised as intercalation electrode for use in rechargeable lithium batteries and electrochromic devices, such various techniques for deposition of V_2O_5 thin films as RF-sputtering [1], thermal evaporation [2], ozone oxidation [3], electrodeposition [4] and sol–gel methods [5] have been extensively studied. Among these, the electrodeposition from the aqueous $VOSO_4$ solution has been known to be an effective technique to prepare poorly crystallised V_2O_5 film electrode in the hydrated form [6].

Potentiostatic current transient technique has been widely employed to specify the kinetics of lithium transport through transition metal oxides. In most studies on lithium intercalation, the current transient has been analysed to determine the chemical diffusivity of lithium ion by assuming that diffusion of lithium is the rate-controlling step of the lithium intercalation process [7–10]. However, it has frequently been observed [7,11,12] that the chemical diffusivities of lithium obtained from the potentiostatic current transient technique differ in value by several orders of magnitude from those determined by other electrochemical techniques such as galvanostatic intermittent titration technique (GITT) and electrochemical impedance spectroscopy (EIS).

In a series of publications on the current transient from our laboratory [13–17], it has been suggested that lithium transport through the transition metal oxides is not governed by diffusion of lithium but by the cell impedance. Under this constraint, the current is given by the quotient of the potential difference between the electrode potential and the applied potential divided by the cell impedance. In view of these circumstances, the analysis of the current transient based upon the cell impedance-controlled lithium transport is necessary to be extended to the quantitative evaluation of the kinetic properties of the intercalation electrode.

In the present work, lithium transport through the V_2O_5 film electrode prepared by the electrodeposition technique was examined on the basis of the cell impedance-controlled concept. For this purpose, the current transient was first measured on the film electrode at various initial potentials. According to the theoretical equation for the current transient derived under the cell impedance-controlled constraint, kinetic quantities such as the cell impedance and the

chemical diffusivity of lithium were then estimated. Finally, the value of the chemical diffusivity of lithium was compared with that value determined from the EIS.

2. Experimental

A V_2O_5 film specimen was potentiostatically deposited on Pt current collector at 1.0 V with respect to a saturated calomel electrode for 5.4×10^3 s in 0.1 M $VOSO_4$ solution. The Pt was previously sputtered to a thickness of 0.2 μm onto one side of an Al_2O_3 substrate (Japan Fine Ceramic). The $VOSO_4$ solution involved in this work was deaerated for 24 h by bubbling with purified Ar gas before the electrodeposition of V_2O_5 film, and its pH value was adjusted to 1.8 by the addition of 10 wt.% H_2SO_4 solution.

The freshly deposited film was thoroughly rinsed with distilled water and then dried under vacuum at 100 °C for 1 h. From the X-ray diffraction analysis, it was recognised that the dried film adopts the poorly crystallised structure exhibiting the layered character with the interlayer distance of ca. 1.07 nm in the hydrated form. The dried film was found to be deposited to the thickness of ca. 0.4 μm by scanning electron microscopy.

A three-electrode electrochemical cell was employed for the electrochemical experiments. Both the reference and counter electrodes were constructed from lithium foil (Foote Mineral, USA, purity 99.9%) and a 1 M solution of lithium perchlorate ($LiClO_4$) in propylene carbonate (PC) was used as the electrolyte. The area of the film electrode exposed to the electrolyte amounted to 1 cm^2.

Galvanostatic intermittent titration technique was employed by using Solartron 1287 electrochemical interface (ECI). Applying a constant current density of 20 μA cm^{-2} to the cell during 250 s upon discharging, the resulting cell potential transients were recorded. The deviation from the ideal stoichiometry of $Li_\delta V_2O_5$, δ, was calculated from the mass of the oxide and the electrical charge that was transferred upon discharging. In order to obtain uniform distribution of lithium over the electrode after interruption of the constant current, it requires about 1 h to reach equilibrium. After that, the open circuit potential was recorded just as an electrode potential.

The potentiostatic current transient and the ac-impedance spectra were measured on the film electrode by using Solartron 1287 ECI combined with Solartron 1255 frequency response analyser (FRA). First, the film electrode was polarised at 3.6 V_{Li/Li^+} for 1×10^3 s to obtain a low steady-state current. Then, the potential was dropped successively to 2.0 V_{Li/Li^+} by the potential step of 0.1 V for 1×10^3 s, and from the moment of each potential drop on, the resulting cathodic current was measured with time during lithium intercalation. After a low steady-state current was attained, the ac-impedance spectra were finally measured by applying an ac-amplitude of 5 mV_{rms} over the frequency range from 50 mHz to 100 kHz. All the

electrochemical experiments were performed at 25 °C in a glove box (MECAPLEX GB94, Switzerland) filled with purified Ar gas.

3. Results and discussion

Fig. 1 shows the electrode potentials obtained from the galvanostatic intermittent discharge curve of the electrodeposited $Li_\delta V_2O_5$ film electrode in a 1 M $LiClO_4$–PC solution as a function of the lithium content. As the lithium content increases, the electrode potential decreases monotonously from 3.6 to 2.0 V_{Li/Li^+} without any potential plateau regions. This indicates that the single phase is maintained over the whole composition range under investigation, i.e. the phase transition does not occur during lithium intercalation [18]. It is also noted that the electrode potential versus lithium content curve can be approximately linearised if the respective potential interval within about 0.1 V is considered over the whole composition range.

Fig. 2a presents on a logarithmic scale the cathodic current transients measured successively at the potential drops of 3.4–3.3 V_{Li/Li^+} and 3.3–3.2 V_{Li/Li^+}. Both the current transients never follow the Cottrell behaviour [19], viz. there is no linear relationship between logarithmic current and logarithmic time with a slope of -0.5 in the early stage. Instead, the logarithmic current transients show a linear relationship between logarithmic current and logarithmic time with a slope between -0.5 and 0, followed by an exponential decay with time. To demonstrate clearly this non-Cottrell behaviour, the plot of (current × time$^{1/2}$) against logarithmic time is given in Fig. 2b. It exhibits the upward convex shape with a local maximum even in
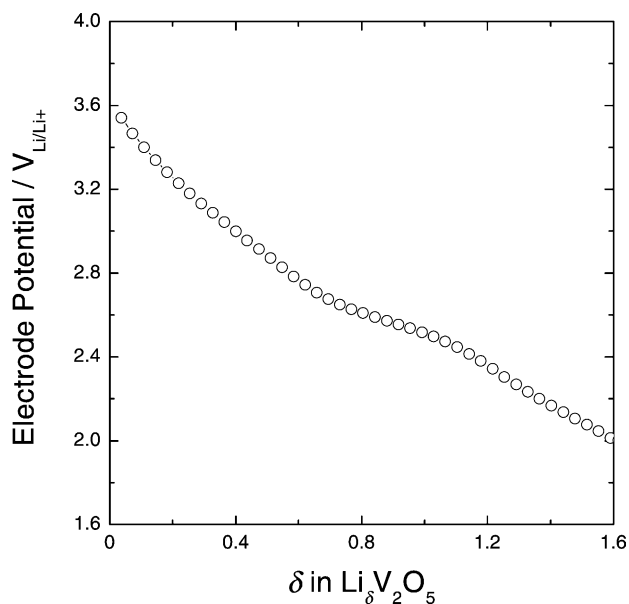

Fig. 1. The electrode potential obtained from the electrodeposited $Li_\delta V_2O_5$ film electrode in a 1 M $LiClO_4$–PC solution as a function of lithium content δ during lithium intercalation.
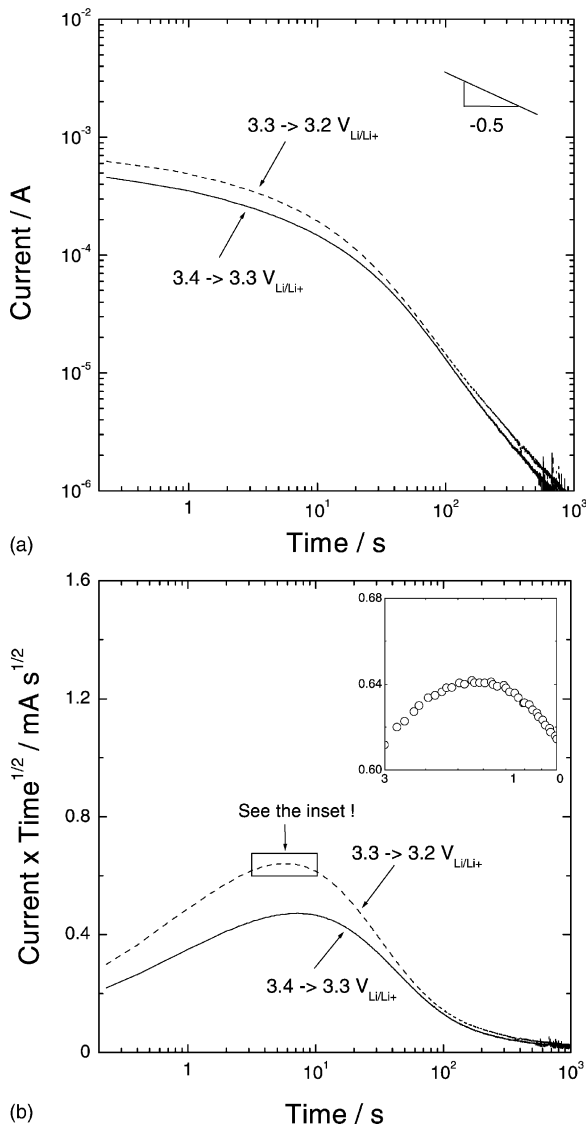
Fig. 2. (a) The cathodic current transients on a logarithmic scale measured on the electrodeposited $Li_\delta V_2 O_5$ film electrode in a 1 M $LiClO_4$–PC solution at the potential drops of 3.4–3.3 $V_{Li/Li+}$ and 3.3–3.2 $V_{Li/Li+}$ successively, and (b) the plots of (current × time$^{1/2}$) against logarithmic time reproduced from (a).

the flattest region (see the inset) rather than the plateau which is expected to appear in the case of the diffusion-controlled lithium transport [9,10].

Moreover, it was observed that the initial current in the current transient is linearly proportional to the potential drop, i.e. the initial current–potential relation holds Ohm's law. In our previous works [13–17], both the non-Cottrell behaviour of the current transient and the Ohmic relationship between initial current and potential step are responsible for the cell impedance-controlled lithium transport. Therefore, in the present work, it seems to be reasonable to say that lithium transport through the electrodeposited $Li_\delta V_2 O_5$ film electrode is also governed by the cell impedance. It should be stressed that the linear relationship between initial current and potential step was found to

extend over the large potential step of about 1.5 V in this work. This fact allows us to distinguish the cell impedance-controlled intercalation process from the process under the influence of the charge transfer kinetics governed by the Butler–Volmer reaction rate [20].

According to the cell impedance-controlled model, the current is determined by the quotient of the potential difference between the electrode potential E_{eq} and the applied potential E_{app} divided by the cell impedance R_{cell}. Here, R_{cell} means the total internal cell resistance, major sources of which may be the bulk electrolyte, electrolyte/electrode interface and bulk electrode. Under the circumstance, it is very instructive to obtain the theoretical current–time behaviour for the cell impedance-controlled lithium transport.

The following assumptions apply when we derive the theoretical equation for the current transient under the cell impedance-controlled constraint: (i) the electrode potential depends in a linear manner on the lithium content; (ii) the phase transformation does not occur during lithium intercalation. These are the reasonable assumptions, at least for the electrodeposited $Li_\delta V_2 O_5$ film electrode under study, as verified from the electrode potential versus lithium content curve in Fig. 1; (iii) the double-layer charging current is neglected; (iv) the cell impedance R_{cell} and the chemical diffusivity of lithium $\tilde{D}_{Li}$ remain constant during lithium intercalation. If we consider lithium intercalation in a sufficiently early time when the lithium content does not change abruptly, then the last assumption (iv) becomes valid.

The calculation of the current limited by the cell impedance involves the solution of the Fick's diffusion equation for plane under the following initial condition (I.C.) and boundary condition (B.C.)

$$\text{I.C.} : c = c^0 \quad \text{for} \quad 0 \le x \le L \quad \text{at} \quad t = 0 \tag{1}$$

$$\text{B.C.} : I(t) = -F\tilde{D}_{Li}A_{ea}\left(\frac{\partial c}{\partial x}\right)_{x=0} = \frac{E_{app} - E_{eq}(t)}{R_{cell}}$$
$$= \frac{V_m}{R_{cell}}\left(\frac{dE}{d\delta}\right)[c_{app} - c(t)] \quad \text{for} \quad x = 0 \quad \text{at} \quad t \ge 0 \tag{2}$$

where c and c^0 are the local and the initial concentration of lithium, c_{app} the lithium concentration corresponding to E_{app}, t the lithium intercalation/deintercalation time, x the distance from the electrolyte/electrode interface, L the electrode thickness, A_{ea} the electrochemical active area, V_m the molar volume of the electrode, $(dE/d\delta)$ the slope of the electrode potential versus lithium content curve in Fig. 1 at a given lithium content and F represents the Faraday constant. Eq. (2) indicates the cell impedance-controlled constraint at the electrolyte/electrode interface under the assumption of the linear relationship between the electrode potential and the lithium content.

The application of the Laplace transform to the diffusion equation in consideration of the semi-infinite diffusion

condition combined with Eqs. (1) and (2) yields the following current–time relation,

$$I(t) = \left[\frac{E_{app} - E_{eq}(0)}{R_{cell}}\right] \exp\left[\left(\frac{H}{R_{cell}}\right)^2 t\right] \mathrm{erfc}\left[\left(\frac{H}{R_{cell}}\right)t^{1/2}\right]$$

$$\text{for} \quad t \ll \frac{L^2}{\tilde{D}_{Li}} \tag{3}$$

where $H = (V_m/F\tilde{D}_{Li}^{1/2}A_{ea})(dE/d\delta)$. The current–time relations similar to Eq. (3) were proposed in the previous studies on the diffusion coupled with surface evaporation [21] and

on the insertion reaction into the electrode in series with an uncompensated resistance [20,22], in which the detailed derivations were described.

In this work, Eq. (3) was used to extract the kinetic parameters characterising lithium intercalation under the cell impedance-controlled constraint, i.e. R_{cell} and $\tilde{D}_{Li}$, from the current transient experimentally measured on the electrode-posited $Li_\delta V_2O_5$ film electrode. Fig. 3a compares the experimental current transients shown in Fig. 2a (open symbols) with those current transients theoretically calculated from Eq. (3) (dotted lines) by taking $[E_{app} - E_{eq}(0)] = 0.1$ V. As
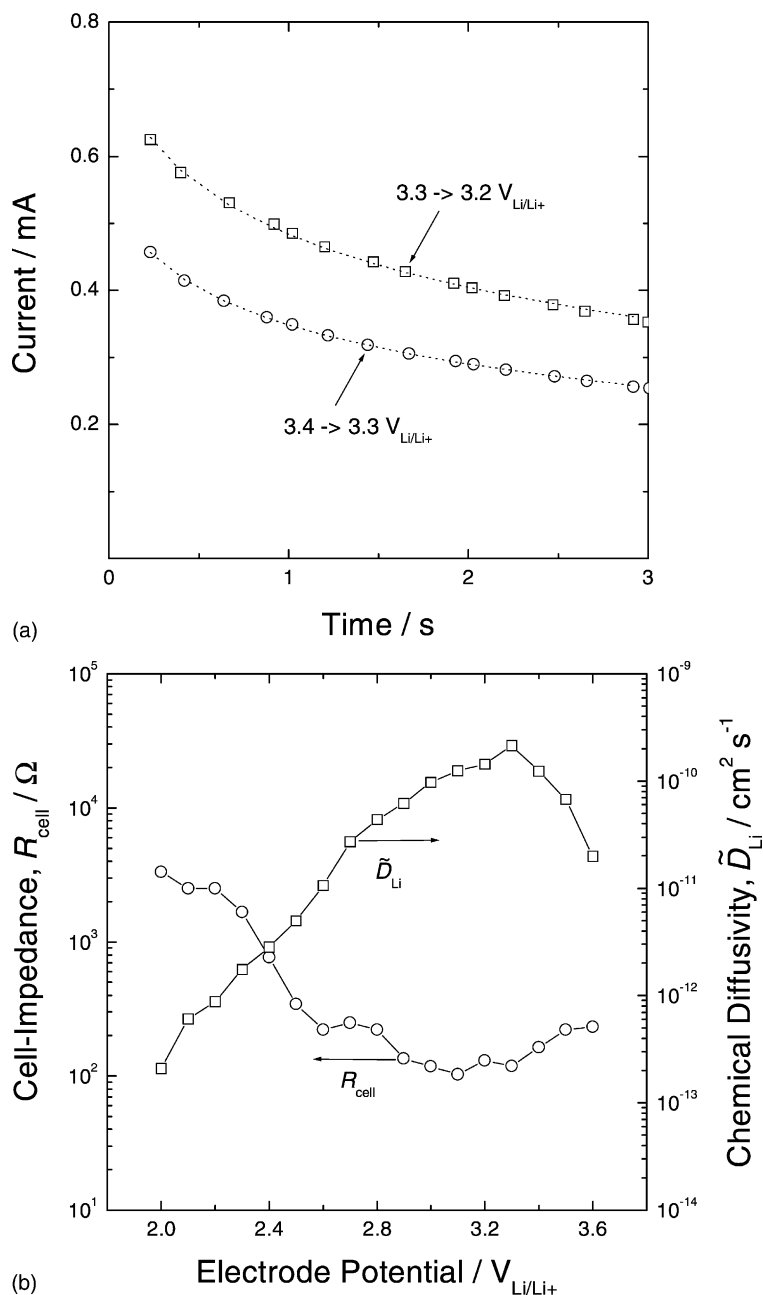

Fig. 3. (a) The cathodic current transients experimentally measured (open symbols) and theoretically calculated from Eq. (3) (dotted lines) at the potential drops of 3.4–3.3 V_{Li/Li^+} and 3.3–3.2 V_{Li/Li^+}, and (b) the plots of the cell impedance R_{cell} and the chemical diffusivity of lithium $\tilde{D}_{Li}$ on a logarithmic scale against the electrode potential obtained from the cathodic current transients.

shown in Fig. 3a, the current transients experimentally measured at the potential drops of 3.4–3.3 V_{Li/Li^+} and 3.3–3.2 V_{Li/Li^+} can be fitted quite well to Eq. (3) with the parameters of $R_{cell} = 163.9\,\Omega$ and $H = 98.5$ and of $R_{cell} = 119.0\,\Omega$ and $H = 68.7$, respectively. Here, the time (3 s) to which the experimental current transient was fitted to Eq. (3) was selected to be short enough to ensure the semi-infinite diffusion condition and other assumptions ((i) and (iv)) used in the derivation of Eq. (3).

The values of R_{cell} and $\tilde{D}_{Li}$ obtained from the current transient according to Eq. (3) are plotted on a logarithmic scale against the electrode potential in Fig. 3b. As the electrode potential decreases from 3.6 to 2.0 V_{Li/Li^+}, R_{cell} decreases slightly to 103 Ω, then remains nearly constant, and finally increases drastically to 3330 Ω. On the other hand, $\tilde{D}_{Li}$ increases from 2.0×10^{-11} to $2.1 \times 10^{-10}\,cm^2\,s^{-1}$ and then decreases exponentially to $2.1 \times 10^{-13}\,cm^2\,s^{-1}$ with the lowering of the electrode potential. These tendencies for R_{cell} and $\tilde{D}_{Li}$ to vary with the electrode potential (or lithium content) are in good agreement with those for the internal cell resistance and $\tilde{D}_{Li}$, respectively, reported by Guyomard and co-workers employing GITT [6].

It is worthwhile to emphasise that the determination of R_{cell} is much more convenient from Eq. (3) than from the plot of initial current versus potential step employed mainly in the previous works [13–17], since the extrapolation of Eq. (3) to $t = 0$ gives directly the precise value of R_{cell} at a given electrode potential. Furthermore, this method has proven to be valuable, especially when it is difficult to obtain experimentally the plot of initial current versus potential step at a very early time either due to the interference with the double-layer charging current or due to the limitation of the data acquisition device.

Now, it is necessary to check whether or not $\tilde{D}_{Li}$ determined from the current transient under the cell impedance-controlled constraint has a reliable value. In this respect, the ac-impedance spectra were measured on the electrodeposited $Li_\delta V_2O_5$ film electrode in a 1 M $LiClO_4$–PC solution as a function of the electrode potential, and subsequently analysed to estimate $\tilde{D}_{Li}$.

Fig. 4a illustrates the Nyquist plots of the ac-impedance spectra measured at the electrode potentials of 3.3 and 3.4 V_{Li/Li^+}. For the clear distinction between two series of ac-impedance data at 3.3 and 3.4 V_{Li/Li^+}, we imagine Fig. 4a so that the ac-impedance data at 3.3 V_{Li/Li^+} were simply parallel shifted by 30 Ω in the negative direction of the imaginary axis. The ac-impedance spectra are composed of a depressed arc in the high frequency range and a straight line inclined at a constant angle of 45° to the real axis (Warburg region) in the low frequency range. It has been generally accepted [5] that the high frequency arc is due to the absorption/desorption of lithium (or charge-transfer reaction) at the electrolyte/electrode interface. The Warburg impedance is associated with a semi-infinite diffusion of lithium in the electrode [23].
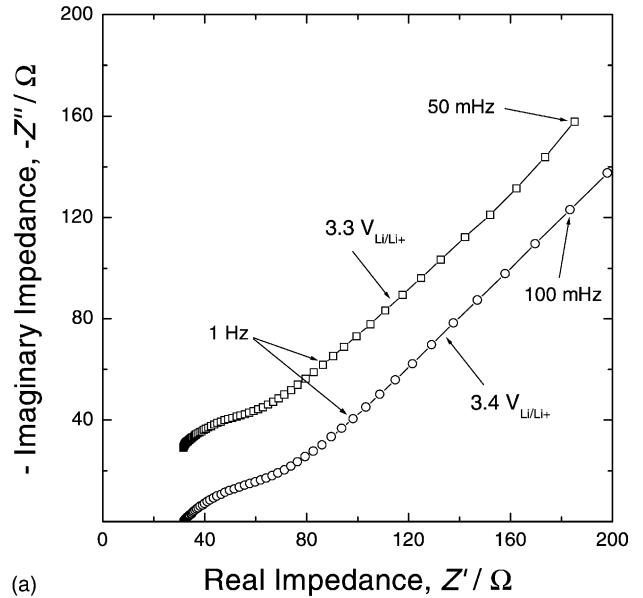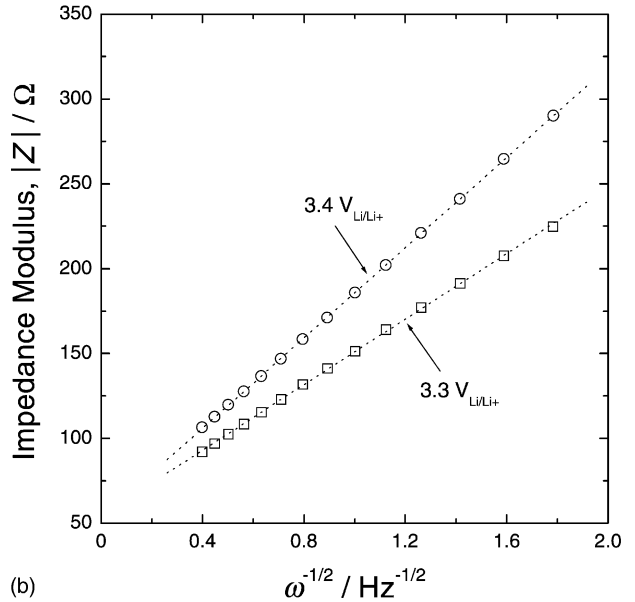
Fig. 4. (a) The Nyquist representations of the ac-impedance spectra measured on the electrodeposited $Li_\delta V_2O_5$ film electrode in a 1 M $LiClO_4$–PC solution at the electrode potentials of 3.3 and 3.4 V_{Li/Li^+}. For the clear distinction between two series of ac-impedance data, (a) was so constructed that the ac-impedance data at 3.3 V_{Li/Li^+} were simply parallel shifted by 30 Ω in the negative direction of imaginary axis. (b) The plots of the impedance modulus |Z| vs. $\omega^{-1/2}$ for the Warburg region in the ac-impedance spectra of (a).

$\tilde{D}_{Li}$ was obtained from the slope of |Z| versus $\omega^{-1/2}$ plot (Fig. 4b) in the Warburg region according to the following equation previously suggested by Ho et al. [23],

$$|Z| = \frac{V_m}{F\tilde{D}_{Li}^{1/2} A_{ea}}\left(\frac{dE}{d\delta}\right)\omega^{-1/2} \quad \text{for} \quad \omega \gg \frac{\tilde{D}_{Li}}{L^2} \qquad (4)$$

where |Z| is the modulus of the impedance Z and ω is the angular frequency. It was impossible to determine $\tilde{D}_{Li}$ at the
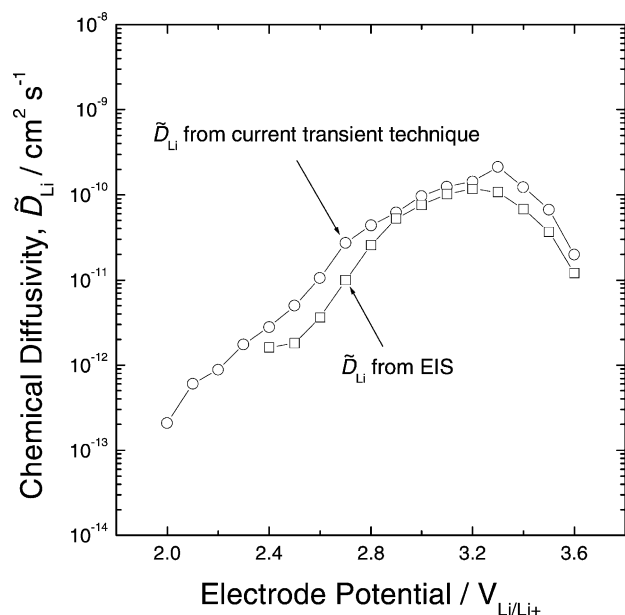
Fig. 5. The plots of the chemical diffusivities of lithium $\tilde{D}_{Li}$ on a logarithmic scale determined from the potentiostatic current transient technique with Eq. (3) and from the EIS with Eq. (4) as a function of the electrode potential.

electrode potentials below $2.4 \, V_{Li/Li^+}$, because the magnitude of the high frequency arc is so large that the Warburg impedance cannot be clearly distinguishable. Fig. 5 envisages the plot of $\tilde{D}_{Li}$ on a logarithmic scale against the electrode potential along with the plot of $\tilde{D}_{Li}$ in Fig. 3b estimated from the current transients. It is seen from Fig. 5 that the value of $\tilde{D}_{Li}$ determined by the EIS is surprisingly very close to the value determined by the potentiostatic current transient technique. From the results, it is recognised that the potentiostatic current transient technique can be successfully utilised to extract the reliable value of $\tilde{D}_{Li}$ even in case that the lithium transport proceeds by the cell impedance-controlled process.

4. Conclusions

In the present work, lithium transport through the electrodeposited vanadium pentoxide film electrode has been examined in a 1 M solution of $LiClO_4$ in propylene carbonate by analysis of current transient. The results are summarised as follows:

1. From the non-Cottrell behaviour of the current transient and the linear relationship between initial current and potential step, it is suggested that lithium transport through the electrodeposited $Li_\delta V_2 O_5$ film electrode is crucially governed by the cell impedance.
2. According to the theoretical current transient derived analytically under the cell impedance-controlled constraint at the electrolyte/electrode interface, the cell

impedance and the chemical diffusivity of lithium were determined to be 103–$3330 \, \Omega$ and 2.1×10^{-13} to $2.1 \times 10^{-10} \, cm^2 \, s^{-1}$, respectively, depending on the electrode potential. Especially, the chemical diffusivity of lithium was satisfactorily consistent in value with that estimated from the electrochemical impedance spectroscopy.

References

[1] N. Kumagai, H. Kitamoto, M. Baba, S. Durand-Vidal, D. Devilliers, H. Groult, J. Appl. Electrochem. 28 (1998) 41.
[2] Z. Lu, M.D. Levi, G. Salitra, Y. Gofer, E. Levi, D. Aurbach, J. Electroanal. Chem. 491 (2000) 211.
[3] Y. Sato, T. Asada, H. Tokugawa, K. Kobayakawa, J. Power Sources 68 (1997) 674.
[4] Y. Sato, T. Nomura, H. Tanaka, K. Kobayakawa, J. Electrochem. Soc. 138 (1991) L37.
[5] S.-I. Pyun, J.-S. Bae, J. Power Sources 68 (1997) 669.
[6] E. Potiron, A. Le Gal La Salle, A. Verbaere, Y. Piffard, D. Guyomard, Electrochim. Acta 45 (1999) 197.
[7] H. Sato, D. Takahashi, T. Nishina, I. Uchida, J. Power Sources 68 (1997) 540.
[8] Y.-I. Jang, B.J. Neudecker, N.J. Dudney, Electrochem. Solid-State Lett. 4 (2001) A74.
[9] M.D. Levi, Z. Lu, D. Aurbach, Solid State Ionics 143 (2001) 309.
[10] F. Artuso, F. Bonino, F. Decker, A. Lourenco, E. Masetti, Electrochim. Acta 47 (2002) 2231.
[11] K.A. Striebel, C.Z. Deng, S.J. Wen, E.J. Cairns, J. Electrochem. Soc. 143 (1996) 1821.
[12] T. Uchida, Y. Morikawa, H. Ikuta, M. Wakihara, K. Suzuki, J. Electrochem. Soc. 143 (1996) 2606.
[13] H.-C. Shin, S.-I. Pyun, Electrochim. Acta 45 (1999) 489.
[14] H.-C. Shin, S.-I. Pyun, S.-W. Kim, M.-H. Lee, Electrochim. Acta 46 (2001) 897.
[15] M.-H. Lee, S.-I. Pyun, H.-C. Shin, Solid State Ionics 140 (2001) 35.
[16] S.-I. Pyun, S.-W. Kim, J. Power Sources 97-98 (2001) 371.
[17] H.-C. Shin, S.-I. Pyun, in: R.E. White, B.E. Conway, C.G. Vayenas (Eds.), Modern Aspects of Electrochemistry, vol. 36, Plenum Press, New York, 2002, pp. 255–301.
[18] M. Nabavi, C. Sanchez, F. Taulelle, J. Livage, A. de Guibert, Solid State Ionics 28-30 (1988) 1183.
[19] C.J. Wen, B.A. Boukamp, R.A. Huggins, W. Weppner, J. Electrochem. Soc. 126 (1979) 2258.
[20] C. Montella, J. Electroanal. Chem. 518 (2002) 61.
[21] J. Crank, The Mathematics of Diffusion, Oxford University Press, London, 1975, p. 35.
[22] I.D. Raistrick, R.A. Huggins, Solid State Ionics 7 (1982) 213.
[23] C. Ho, I.D. Raistrick, R.A. Huggins, J. Electrochem. Soc. 127 (1980) 343.