

Li⁺ ion diffusion in Li₄Ti₅O₁₂ thin film electrode prepared by PVP sol–gel method

Young Ho Rho^{a,b} and Kiyoshi Kanamura^{a,b,*}

^a Department of Applied Chemistry, Graduate School of Engineering, Tokyo Metropolitan University, 1-1 Minami-Ohsawa, Hachioji, Tokyo 192-0397, Japan

^b CREST, Japan Science and Technology Corporation, 4-1-8, Honcho Kawaguchi, 332-0012 Saitama, Tokyo, Japan

Received 15 October 2003; received in revised form 28 January 2004; accepted 15 February 2004

Abstract

Li₄Ti₅O₁₂ thin films for rechargeable lithium batteries were prepared by a sol–gel method with poly(vinylpyrrolidone). Interfacial properties of lithium insertion into Li₄Ti₅O₁₂ thin film were examined by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and potentiostatic intermittent titration technique (PITT). Redox peaks in CV were very sharp even at a fast scan rate of 50 mV s⁻¹, indicating that Li₄Ti₅O₁₂ thin film had a fast electrochemical response, and that an apparent chemical diffusion coefficient of Li⁺ ion was estimated to be 6.8 × 10⁻¹¹ cm² s⁻¹ from a dependence of peak current on sweep rates. From EIS, it can be seen that Li⁺ ions become more mobile at 1.55 V vs. Li/Li⁺, corresponding to a two-phase region, and the chemical diffusion coefficients of Li⁺ ion ranged from 10⁻¹⁰ to 10⁻¹² cm² s⁻¹ at various potentials. The chemical diffusion coefficients of Li⁺ ion in Li₄Ti₅O₁₂ were also estimated from PITT. They were in a range of 10⁻¹¹–10⁻¹² cm² s⁻¹.

© 2004 Elsevier Inc. All rights reserved.

Keywords: Diffusion coefficient; Sol–gel method; Li₄Ti₅O₁₂; Thin film; EIS; PITT

1. Introduction

Many research groups have investigated on all solid-state and/or micro-scaled rechargeable lithium batteries [1–6]. The micro-scale batteries will be realized in all solid-state type, and utilized in various application fields related to micro-systems, such as micro-sensor, micro-mechanics, micro-electronics, and so on. In order to develop micro-scale lithium ion batteries with a high-energy density, a fabrication technique for micro-scale anodes, cathodes, and electrolytes should be needed.

Li₄Ti₅O₁₂ has been investigated as a powerful anode material for all solid-state rechargeable lithium batteries, because of its very flat discharge and charge curves and high cycleability [7–11]. In general, Li₄Ti₅O₁₂ has been synthesized by heating a mixture of Ti and Li sources at 800°C for 24 h under air atmosphere. It

exhibits a working voltage of 1.55 V vs. Li/Li⁺ and its theoretical discharge capacity is 167 mA h g⁻¹.

By the way, some researchers have proposed several methods for preparing thin film electrodes in a micro-scale order, such as chemical vapor deposition, sputtering process, pulsed laser deposition, etc. [12–15]. When using these methods, good thin films have been prepared. However, a difficulty in controlling stoichiometry of thin films sometimes happens in these preparation processes.

The sol–gel method is well known as one of promising thin film preparation methods [6–8,16–20]. This method has some advantages, such as low fabrication cost, relatively easy stoichiometry control, and high deposition rate. The method, of course, is also well known as a low-temperature synthesis method for various ceramics.

We have investigated on preparation of thin film electrodes and electrolytes for rechargeable lithium batteries by using sol–gel method [6–8,18–19]. Crack-free thin films of Li₄Ti₅O₁₂, LiCoO₂ and LiMn₂O₄ on Au substrate were successfully obtained by adding poly(vinylpyrrolidone) (PVP) to reacting solutions. PVP was very effective to prepare a relatively thick

*Corresponding author. Department of Applied Chemistry, Graduate School of Engineering, Tokyo Metropolitan University, 1-1 Minami-Ohsawa, Hachioji, Tokyo 192-0397, Japan. Fax: +81-426-77-2828.

E-mail address: kanamura-kiyoshi@c.metro-u.ac.jp (K. Kanamura).

film. Actually, our preliminary reports showed a smooth surface morphology and excellent electrochemical properties of $\text{Li}_4\text{Ti}_5\text{O}_{12}$, LiCoO_2 and LiMn_2O_4 thin film electrodes [7,8,18,19].

For an application of active electrode materials prepared by the sol-gel method to all solid-state rechargeable lithium batteries, transport kinetics of Li^+ ion in active electrode materials must be evaluated. In general, chemical diffusion coefficient, \tilde{D} , is usually used to describe a compositional relaxation of insertion electrode. So far, some kinds of methods have been applied to a calculation of chemical diffusion coefficients of Li^+ ion in solid electrodes [21–24]. For example, galvanostatic intermittent titration technique (GITT) [21], potentiostatic intermittent titration technique (PITT) [13,22], electrochemical impedance spectroscopy (EIS) [23], and cyclic voltammogram (CV) [24] have been used.

In this study, sol-gel method with PVP was utilized to prepare $\text{Li}_4\text{Ti}_5\text{O}_{12}$ thin film as anode for rechargeable lithium batteries, and three types of methods (CV, EIS, and PITT) were used for studying an electrochemical response of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and the chemical diffusion coefficient of Li^+ ion in $\text{Li}_4\text{Ti}_5\text{O}_{12}$.

2. Experimental

$\text{Li}_4\text{Ti}_5\text{O}_{12}$ thin film was prepared on Au substrate by using PVP sol-gel method in our previous reports [7,8]. The film thickness was $0.4\ \mu\text{m}$ and the effective electrode area was $0.785\ \text{cm}^2$. A three-electrode electrochemical cell was employed for electrochemical measurements. Lithium metal foil and wire were used for reference and counter electrodes. An electrolyte was a mixed solvent of ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 in volume) containing $1\ \text{mol dm}^{-3}\ \text{LiClO}_4$ (1 M $\text{LiClO}_4/\text{EC} + \text{DEC}$).

Galvanostatic intermittent discharge-charge experiments were conducted under constant current conditions (C/50) by using automatic discharge and charge equipment (HJR-110mSM6, HOKUTO DENKO Co.). Cut-off voltages were 1.2 and 3.0 V vs. Li/Li^+ for discharge and charge processes, respectively.

EIS was carried out in the frequency range from 50 kHz to 10 mHz by using 5080 frequency response analyzer (NF electronic instruments) combined with an automatic polarization system (HZ-3000, HOKUTO DENKO Co.). CV and potentiostatic current transient experiment were also performed and recorded by using automatic polarization equipment (HZ-3000, HOKUTO DENKO Co.). A scan rate of CV was $10\ \text{mV min}^{-1}$ in a range of 1.2–3.0 V vs. Li/Li^+ .

All electrochemical experiments were conducted in an argon-filled glove box at room temperature.

3. Result and discussion

Fig. 1 shows the voltage profile vs. x in $\text{Li}_{4/3+x}\text{Ti}_5/3\text{O}_4$. The flat region in the discharge curve was observed at 1.55 V vs. Li/Li^+ , corresponding to a coexistence of two phases. From this figure, a differential factor (dE/dx) was obtained and tabulated in Table 1, which was required to calculate chemical diffusion coefficients using EIS method.

Fig. 2 shows the differential intercalation capacity, C_{int} obtained by EIS, PITT, and CV. The intercalation capacity can be obtained from each equation, $C_{\text{int}} = Q_{\text{t}}(dx/dE)$, (Q_{t} is the overall intercalation charge for a charge process) for GITT and PITT, $C_{\text{int}} = Iv^{-1}$ (v is the scan rate) for CV, and $C_{\text{int}} = -(1/\omega Z''_{\omega \rightarrow 0})$ for EIS, respectively. From this figure, sharp peaks were observed at 1.55 V vs. Li/Li^+ . A shift of the peak voltage was observed, reflecting to a deviation from equilibrium conditions during the measurements. The EIS spectra were measured after maintaining an electrode voltage corresponding to different intercalation levels for a long time (4 h). Therefore, the results

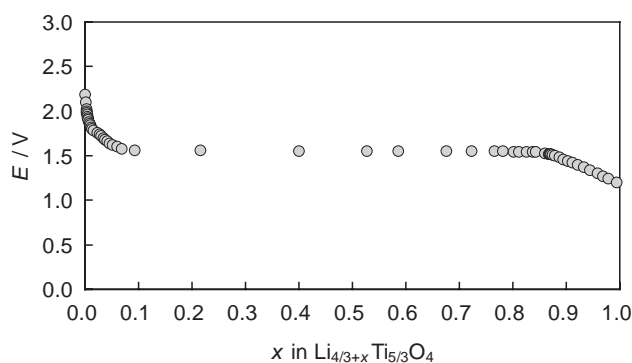


Fig. 1. Coulombic titration curve of $\text{Li}_{4/3+x}\text{Ti}_5/3\text{O}_4$ thin film electrode prepared by using sol-gel coating method with PVP at C/50 in 1 M $\text{LiClO}_4/\text{EC} + \text{DEC}$.

Table 1
Values of a differential factor (dE/dx) obtained from Fig. 1

Voltage (V)	(dE/dx)
1.20	3.78
1.30	2.76
1.35	3.26
1.41	2.20
1.44	2.93
1.47	3.08
1.50	3.03
1.51	2.66
1.60	2.53
1.65	7.38
1.70	6.52
1.75	5.86
1.85	18.91
1.95	27.61

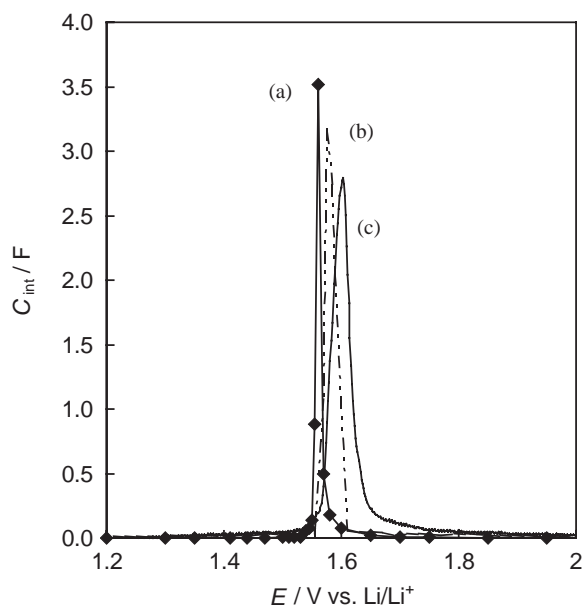


Fig. 2. Differential intercalation capacities (C_{int}) obtained by (a) EIS, $C_{\text{int}} = -1/\omega Z''_{\omega \rightarrow 0}$; (b) PITT, $C_{\text{int}} = \Delta Q/\Delta E$; and (c) CV, $C_{\text{int}} = Itv^{-1}$.

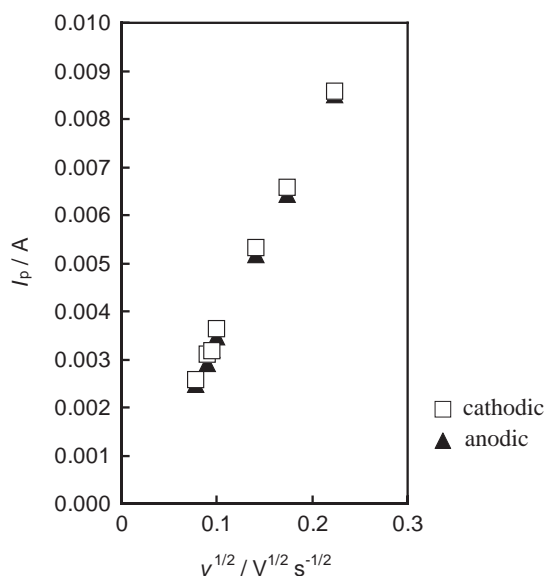


Fig. 3. Relationship of the peak current to $v^{1/2}$ for fast scans of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ thin film electrode from CV.

from EIS were obtained under more equilibrium conditions compared with other methods (PITT and CV).

The kinetic response was firstly examined from the dependence of peak current in CV on the scan rate. A linear relationship was observed up to 5 mV s^{-1} , but it deviates at scan rates greater than 5 mV s^{-1} . This deviation indicates that the process is limited by a semi-infinite diffusion of Li^+ ion into the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ solid matrix. Fig. 3 shows a linear relationship between both anodic and cathodic peak currents and square root

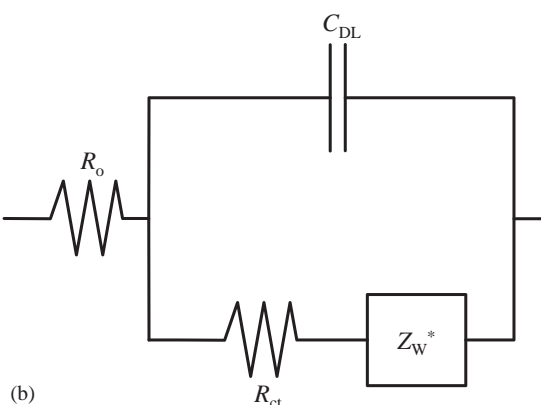
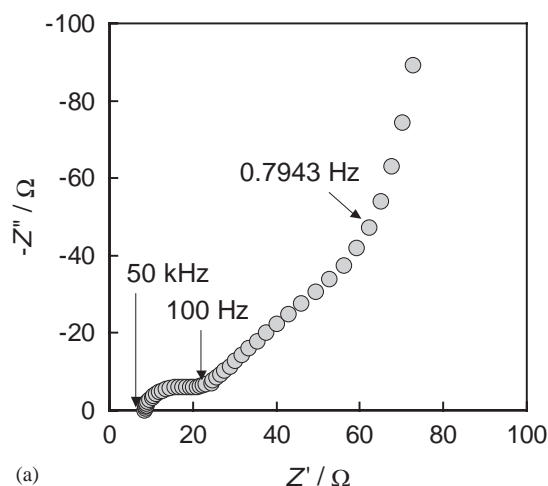


Fig. 4. (a) Cole–Cole plot for the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ film electrode at $1.59 \text{ V vs. Li/Li}^+$; and (b) the Randles equivalent circuit for the ac responses.

of scan rates. Assuming that the film is regarded as a compact uniform layer, the diffusion coefficient of Li^+ ion in the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ thin film was estimated to be $6.8 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$ from a preliminary calculation.

At an open circuit potential, a chemical diffusion coefficient was also estimated by using an EIS. Fig. 4 shows the Cole–Cole plot for the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ thin film electrode. For calculating diffusion coefficients from the impedance result, Z_W^* is frequently used as a complex impedance arising from diffusion of electroactive species, which is known as Warburg impedance. The following expression for Z_W^* was derived by solving Fick's law with appropriate initial and boundary conditions [23].

$$Z_W^* = A\omega^{-1/2} - jA\omega^{-1/2}, \quad (1)$$

where ω is the radial frequency, $j = \sqrt{-1}$, and A is a constant which contains a concentration-independent chemical diffusion coefficient, \tilde{D} , of electroactive species in solid matrix

$$A = \frac{V_M(dE/dx)}{\sqrt{2zF\tilde{D}^{1/2}a}}, \quad (2)$$

where V_M is the molar volume of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ($45.73 \text{ cm}^3 \text{ mol}^{-1}$), dE/dx is the slope of the electrode potential curve vs. x in Fig. 1, z is the charge transfer number for lithium intercalation reaction, which is equal to 1, the constant a is the electroactive surface area of the electrode (0.785 cm^2), and F is the Faraday constant.

At 1.59 V vs. Li/Li^+ , a semi-circle and a straight line were observed in the high- and intermediate-frequency regions ($50 \text{ kHz} - 0.7943 \text{ Hz}$), and a vertical line in the low-frequency region ($0.7943 \text{ Hz} - 10 \text{ mHz}$). The diameter of semi-circle appeared at higher-frequency region corresponding to a charge transfer resistance, which is estimated to be 14Ω . As mentioned above, chemical diffusion coefficients can be obtained by using the region of the straight line corresponding to Warburg impedance due to a semi-infinite diffusion.

Fig. 5 shows the relationship between impedances and frequencies at each potential. From this figure, it is clear that both real and imaginary parts of impedance are proportional to $\omega^{-1/2}$, and parallel with each other. The pre-exponential factor, A can be obtained from the slope of the plot, and the values changed with electrode potential. Fig. 6 shows the relationship between the obtained slope, A , and electrode potential. The slope, A , is in unit of $\Omega \text{ s}^{-1/2}$ and inversely proportional to the chemical diffusion coefficient, \tilde{D} . Thus, A can be considered as a resistance barrier for Li^+ ion diffusion. The small A value at around 1.55 V vs. Li/Li^+ indicates that Li^+ ions move fast in the solid matrix of the electrode. At a coexistence of two phases, the chemical diffusion coefficient cannot be calculated, because of $dE/dx \approx 0$. However, the obtained A value indicates that the diffusion of Li^+ ion is very fast at 1.55 V vs. Li/Li^+ at a coexistence region of two phases.

Fig. 7 shows the chemical diffusion coefficients obtained from Eq. (2). \tilde{D} is ranging from 10^{-10} to $10^{-12} \text{ cm}^2 \text{ s}^{-1}$ at various potentials except to around 1.55 V vs. Li/Li^+ corresponding to the coexistence region of two phases.

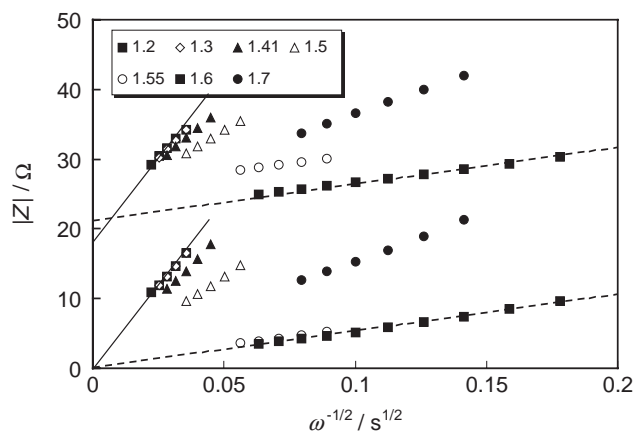


Fig. 5. Real and imaginary parts of the complex impedance vs. $\omega^{-1/2}$ at various potentials.

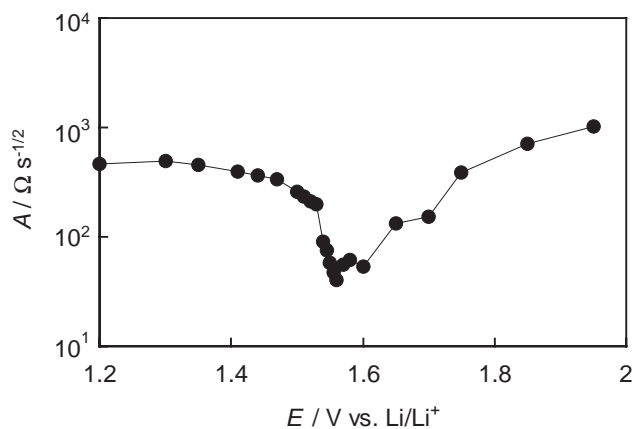


Fig. 6. Variation of pre-exponential factor, A , of Warburg impedance as a function of electrode potential for $\text{Li}_4\text{Ti}_5\text{O}_{12}$.

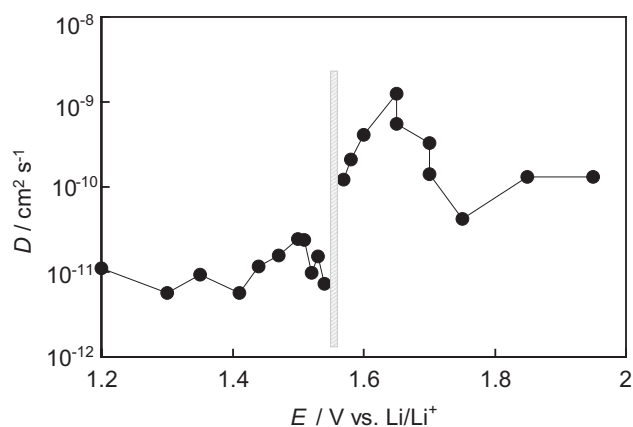


Fig. 7. Chemical diffusion coefficients of Li^+ ion in the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ film as a function of electrode potential (EIS).

The chemical diffusion coefficients were also estimated by using the PITT. This technique has an advantage that reactions such as nucleation of new phases can be avoided if the electrode potential is controlled within stable ranges of single phase.

The Li^+ ion diffusion for the PITT experiment can be modeled as one-dimensional transport based on Fick's second law

$$\frac{\partial C_{\text{Li}}}{\partial x} = \tilde{D} \frac{\partial^2 C_{\text{Li}}}{\partial x^2}, \quad (3)$$

where x is the distance into the solid film from the electrolyte/electrode interface and C_{Li} is the Li concentration at x and time t , and \tilde{D} is the chemical diffusion coefficient. The initial and boundary conditions for diffusion into a finite sheet of thickness, L , with a constant surface concentration, C_s , are

$$C_{\text{Li}} = C_0 \text{ at } 0 \leq x \leq L \text{ and } t = 0, \quad (4)$$

$$C_{\text{Li}} = C_s \text{ at } x = 0 \text{ and } t > 0, \quad (5)$$

$$\frac{\partial C}{\partial x} = 0 \text{ at } x = L \text{ and } t \geq 0. \quad (6)$$

The constant surface concentration can be achieved by potentiostatic conditions. Here, \tilde{D} is assumed to be constant over the concentration difference, $C_s - C_0$, induced by the potential step. This assumption can be realized by a small potential width in the PITT experiment. It is also assumed that Li enters the electrode only at the electrolyte/electrode interface ($x = 0$), and the phase boundary ($x = L$) is impermeable. A solution to this diffusion problem is

$$C_{\text{Li}}(x, t) = C_s - (C_s - C_0) \frac{4}{\pi} \sum_{n=0}^{\infty} \left[\frac{1}{2n+1} \sin\left(\frac{(2n+1)\pi x}{2L}\right) \exp\left(-\frac{(2n+1)^2 \pi^2 \tilde{D} t}{4L^2}\right) \right]. \quad (7)$$

The current–time transient current, $I(t)$, is related to the concentration gradient at the electrode/electrolyte interface

$$I(t) = -zFa\tilde{D} \left(\frac{\partial C}{\partial x} \right)_{x=0}, \quad (8)$$

$$I(t) = \frac{2zFa(C_s - C_0)\tilde{D}}{L} \sum_{n=0}^{\infty} \exp\left(-\frac{(2n+1)^2 \pi^2 \tilde{D} t}{4L^2}\right), \quad (9)$$

where z is charge transfer number of the electroactive species, which is equal to 1 for Li, F is the Faraday constant, a is the cross-sectional area common to both the electrolyte and the electrode. The change of stoichiometry, dx , in the course of the PITT measurement is directly related to the concentration difference ($C_s - C_0$) according to a following expression:

$$dx = V_M(C_s - C_0) = Q/zFn_B, \quad (10)$$

with

$$Q = \int_0^{\infty} I(t) dt, \quad (11)$$

where V_M is the molar volume of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ($45.73 \text{ cm}^3 \text{ mol}^{-1}$), Q is the total charge transferred during the PITT experiment, and n_B is the number of moles of the static component. Since $V_M n_B / S = L$, the current–time transient can be expressed in terms of charge, Q and the thickness of the electrodes, L by substituting Eq. (10) into Eq. (9) as follows:

$$I(t) = \frac{2Q\tilde{D}}{L^2} \sum_{n=0}^{\infty} \exp\left(-\frac{(2n+1)^2 \pi^2 \tilde{D} t}{4L^2}\right). \quad (12)$$

For a long time ($t \gg L^2 \tilde{D}$), a reasonable approximation can be made by taking only the first term of the series in equation [12]

$$I(t) = \frac{2Q\tilde{D}}{L^2} \exp\left(-\frac{\pi^2 \tilde{D} t}{4L^2}\right). \quad (13)$$

After each potential step, the charge, Q , can be determined by an integration current passed during the PITT experiment. The chemical diffusion coefficient, \tilde{D} ,

was calculated from the intercept at $t = 0$ and the slope of the linear region in the plot of $\ln I(t)$ vs. t , where

$$\tilde{D} = -\frac{d \ln(I) 4L^2}{dt \pi^2}. \quad (14)$$

Fig. 8 shows the current–time transient for a potential step of 20 mV (1.44–1.46 V Li/Li^+), and its semi-logarithmic plot. As shown in Fig. 8(b), a straight line was obtained for a long time region, and the $I-t$ curve was well fitted by a computational simulation of Eq. (12).

Fig. 9 shows the $I-t$ plot for a potential step of 10 mV (1.53–1.54 V Li/Li^+), and its semi-logarithmic plot. A straight line was also observed for a long time region, and the $I-t$ curve was well fitted by a computational simulation of Eq. (12), too.

The chemical diffusion coefficients obtained by PITT were plotted in Fig. 10. \tilde{D} was ranging from 10^{-11} to $10^{-12} \text{ cm}^2 \text{ s}^{-1}$ at various electrode potentials except for 1.55 V vs. Li/Li^+ corresponding to the coexistence region of two phases.

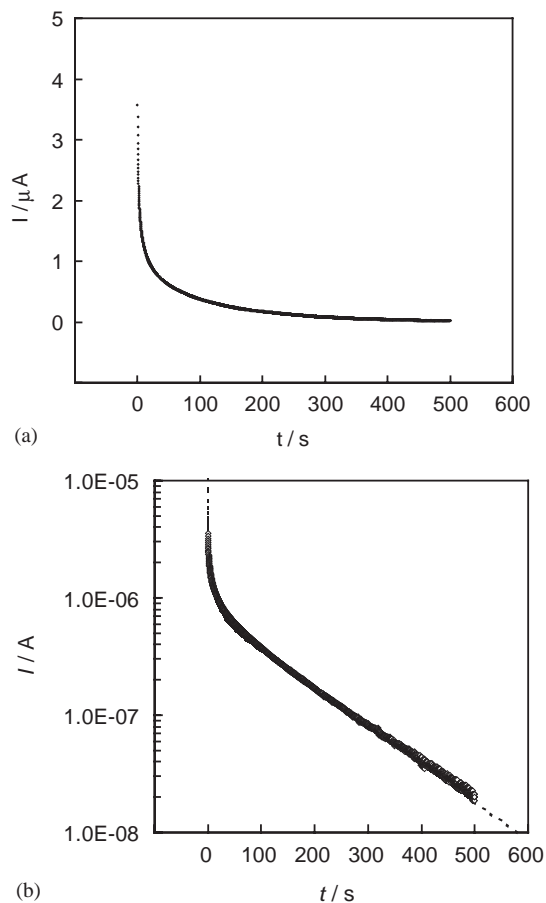


Fig. 8. Time dependence of the current in the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ film for a potential step of 1.44–1.46 V vs. Li/Li^+ : (a) I vs. t ; and (b) $\log I$ vs. t (\diamond : experimental, —: calculation).

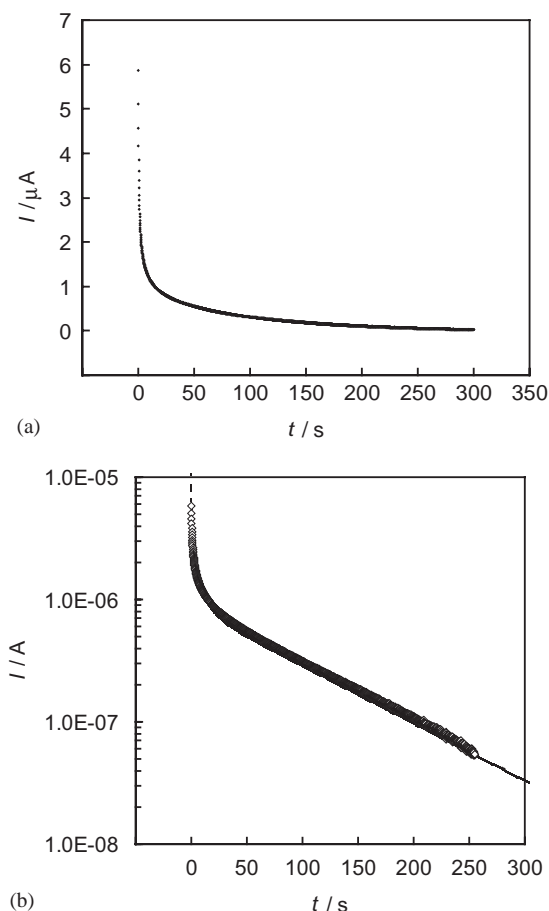


Fig. 9. Time dependence of the current in the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ film for a potential step of 1.53–1.54 V vs. Li/Li^+ : (a) I vs. t ; and (b) $\log I$ vs. t (\diamond : experimental, —: calculation).

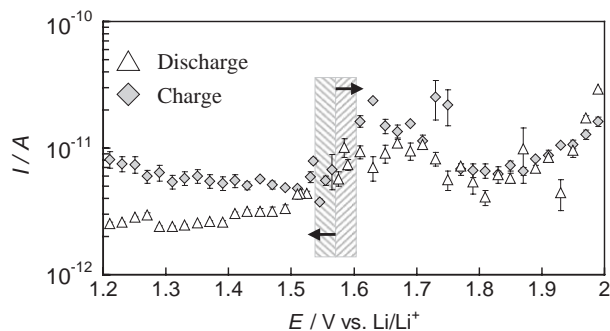


Fig. 10. Chemical diffusion coefficients as a function of electrode potential in the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ film during charging and discharging (PITT).

4. Conclusion

Three types of techniques were carried out for an evaluation on diffusion coefficients of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ thin film, which were CV, EIS, and PITT. From the CV, it was found that the film had a fast electrochemical response and the apparent diffusion coefficient of

$10^{-11} \text{ cm}^2 \text{ s}^{-1}$. The EIS and PITT results showed that \bar{D} was changed in the range of 10^{-10} – 10^{-12} and 10^{-11} – $10^{-12} \text{ cm}^2 \text{ s}^{-1}$, respectively. Here, a slight difference between diffusion coefficients obtained from EIS and PITT was observed. In case of EIS, the results were obtained under more equilibrium conditions compared with other methods such as PITT and CV, but it is very difficult to obtain the exact value of a diffusion coefficient due to a strong dependence on the dE/dx value. On the other hand, more exact value can be obtained from PITT although a slight deviation from equilibrium conditions during the measurements was observed. Of course, it was impossible to evaluate the diffusion coefficient in the two-phase region (~ 1.55 V vs. Li/Li^+) from both techniques, where a transient behavior may be attributed to a phase boundary movement and/or a nucleation of new phase. Nonetheless, the pre-exponential factor, A , was obtained from EIS, which is considered as a resistance barrier for Li^+ ion diffusion, and showed that Li^+ ion was more mobile in $\text{Li}_4\text{Ti}_5\text{O}_{12}$ near 1.55 V vs. Li/Li^+ corresponding to the two-phase coexistence region.

References

- [1] J.B. Bates, N.J. Dudney, B. Neudecker, A. Ueda, C.D. Evans, *Solid State Ionics* 135 (2000) 33.
- [2] P. Birke, W.F. Chu, W. Weppner, *Solid State Ionics* 93 (1997) 1.
- [3] S.D. Jones, J.R. Akridge, *J. Power Sources* 54 (1995) 63.
- [4] J. Fu, *J. Mater. Sci.* 33 (1998) 1549.
- [5] Y. Inaguma, C. Liqun, M. Itoh, T. Nakamura, T. Uchida, H. Ikuta, M. Wakihara, *Solid State Commun.* 86 (1993) 689.
- [6] K. Kanamura, T. Mitsui, Y.H. Rho, T. Umegaki, *Key Eng. Mater.* 228–229 (2002) 285.
- [7] Y.H. Rho, K. Kanamura, T. Umegaki, *J. Electrochem. Soc.* 150 (2003) A107.
- [8] Y.H. Rho, K. Kanamura, T. Umegaki, *Chem. Lett.* 2001 (2001) 1322.
- [9] P.P. Prosini, R. Mancini, L. Petrucci, V. Contini, P. Villano, *Solid State Ionics* 144 (2001) 185.
- [10] K. Zaghib, M. Armand, M. Gauthier, *J. Electrochem. Soc.* 145 (1998) 3135.
- [11] T. Ohzuku, A. Ueda, N. Yamamoto, *J. Electrochem. Soc.* 142 (1995) 1431.
- [12] J.B. Bates, N.J. Dudney, B.J. Neudecker, F.X. Hart, H.P. Jun, S.A. Hackey, *J. Electrochem. Soc.* 147 (2000) 59.
- [13] J.M. McGraw, C.S. Bahn, P.A. Parilla, J.D. Perkins, D.W. Readey, D.S. Ginley, *Electrochim. Acta* 45 (1999) 187.
- [14] P. Fragnaud, R. Nagarajan, D.M. Schleich, D. Vujic, *J. Power Sources* 54 (1995) 362.
- [15] K.A. Striebel, C.Z. Deng, S.J. Wen, E.J. Cairns, *J. Electrochem. Soc.* 143 (1996) 1821.
- [16] M.K. Kim, H.T. Chung, Y.J. Park, J.G. Kim, J.T. Son, K.S. Park, H.G. Kim, *J. Power Sources* 99 (2001) 34.
- [17] K. Kushida, K. Kuriyama, *Solid State Commun.* 118 (2001) 615.
- [18] Y.H. Rho, K. Kanamura, *J. Electrochem. Soc.* 151 (2004) A106.
- [19] Y.H. Rho, K. Kanamura, M. Fujisaki, J. Hamagami, S. Suda, T. Umegaki, *Solid State Ionics* 151 (2002) 151.
- [20] C.J. Brinker, G.W. Scherer, *Sol–Gel Science*, Academic Press, Boston, 1990 (Chapter 13).

- [21] W. Weppner, R.A. Huggins, *J. Electrochem. Soc.* 124 (1977) 1569.
- [22] C.J. Wen, B.A. Boukamp, R.A. Huggins, W. Weppner, *J. Electrochem. Soc.* 126 (1979) 2258.
- [23] C. Ho, I.D. Raistrick, R.A. Huggins, *J. Electrochem. Soc.* 127 (1980) 343.
- [24] A.J. Bard, L.R. Faulkner, *Electrochemical Methods*, 2nd Edition, Wiley, NY, 1991 (Chapter 6).