

Lithium Ion Diffusion Behavior in Laser-Deposited TiO₂ Films

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Lithium ion diffusion processes in pulsed laser-deposited TiO₂ film electrodes are investigated by electrochemical and isothermal transient ionic current (ITIC) methods. Cyclic voltammogram and potential step measurements are used to examine the processes of insertion of Li ions into the TiO₂ electrode. Two diffusion processes of Li ion, driven by the concentration gradient and by an applied field, are demonstrated by ITIC analysis. The diffusion constants are dependent on the measuring method and the diffusion mechanism. These results clarify the diffusion behavior of Li ion in anatase TiO₂ film and prove that pulsed laser deposition is a promising method for producing TiO₂ film electrodes.

1. Introduction

Titanium oxide is an important electrode material for extensive applications in solar cells,¹ electrochromics,² and lithium batteries.³ Because the Li insertion capability of the anatase phase of TiO₂ far exceeds that of other TiO₂ polycrystalline phases (rutile and brookite), the fabrication and characterization of anatase TiO₂ thin films have attracted the attention of many researchers.^{4–9} TiO₂ films have been prepared by different kinds of deposition techniques, such as aerosol pyrolysis,⁶ anodic oxidation,⁷ chemical vapor deposition,⁴ sol–gel deposition,⁸ sputtering,⁹ spread,¹⁰ pulsed laser deposition,^{11,12} and so on. Among these techniques, pulsed laser deposition is a powerful and versatile technique for the fabrication of thin film that has experienced an explosive growth in recent 10 years.¹³ This technique has been successfully used to grow LiMn₂O₄, LiCoO₂, Nb₂O₅, V₂O₅, Ta₂O₅, ZnO, and tin-based composite oxide (TCO) thin-film electrodes with high-quality electrochemical properties.^{14–19} Dai et al. prepared TiO₂ thin film on glass substrates by 1064 nm laser evaporation of Ti and TiO₂ targets, and reported the composition and morphology of deposited thin film.²⁰ Garpon²¹ and Durand et al.²² deposited TiO₂ film by excimer laser ablation of the TiO₂ target, and measured the optical properties of the TiO₂ film. In our laboratory, the pulsed laser deposition method has also been employed to investigate the electrical and dielectric properties of TiO₂ thin film¹¹ and the electrochromic behavior of lithium insertion in the anatase TiO₂ film electrode.¹² To our knowledge, there is no report on studies of Li ion diffusion in laser-deposited TiO₂ film.

It is known that the diffusion constant of Li ion is one of the important parameters for understanding the basic physical and chemical processes of Li ion diffusion in TiO₂ film.²³ Many electrochemical measurements, such as potentiostatic, galvanostatic, potentiometric, and steady-state AC method,^{24–26} could provide some information on Li ion diffusion in TiO₂ film. Usually, Fickian's law is used to describe Li ion diffusion with the boundary conditions of potential or the current at the metal oxide/electrolyte interface. In this procedure, the active electrode area is one of the key parameters for calculating the chemical diffusion constant, but it is rather difficult to get an accurate measurement. This problem will become a fatal drawback to such a study for the intrinsic material properties, as pointed out

by Lindström et al.^{4,5} In their works, chemical diffusion constants were obtained by taking into account the inner area of the electrode, and showed larger difference for the nanoporous film and CVD film electrodes because of an obvious consequence of the larger difference in the active electrode area. To avoid this problem, we introduce the isothermal transient ionic current (ITIC) method in which the transient current of the metal oxides inserted Li ions with an ion blocking electrode is caused by mobile ions in the case of a constant applied field and is examined at a constant temperature. Although this method has been rarely used for determining ion diffusion, it proved to be a useful tool in the investigation of ion transport in metal oxides, and the ion mobility estimated by this method is dependent on parameters such as metal oxides thickness, applied field, and time of ion migration through the metal oxides.^{27–30} These parameters are easily examined and can give a relatively accurate calculation of the diffusion constant. Thus, ITIC measurement coupled with the electrochemical measurements might provide further important information about ion diffusion behavior.

In this paper, the cyclic voltammogram and potential step measurements as well as the ITIC method were employed for the investigation of Li ion diffusion processes in anatase TiO₂ film prepared by pulsed laser deposition. The aim of this work was to clarify Li ion diffusion behavior in anatase TiO₂ film, and elucidate the characteristics of TiO₂ film fabricated by pulsed laser deposition as an electrode film. Our results show that ITIC is an effective method to measure the Li ion diffusion constant in TiO₂ film.

2. Experimental Section

The apparatus for the TiO₂ film fabricated by pulsed laser deposition has been described previously.¹¹ The experimental conditions for the TiO₂ thin film deposition are described briefly as follows: A 355 nm beam is provided by the third harmonic frequency of a Q-switched Nd:YAG laser (Spectra Physics GCR-150) and is focused onto a rotating metallic Ti target with an angle 30° to the target surface normal. The pulsed laser repetition rate is 10 Hz, with a pulse width of 6 ns, and the laser fluence is ~3 J/cm². A stainless steel deposition chamber is evacuated by a turbomolecular pump to a base pressure of 1 × 10^{−3} Pa. The depositions are generally carried out with a continuous flow of the O₃/O₂ gas mixture. Ozone is prepared from O₂ by Tesla coil discharge as a conventional discharge

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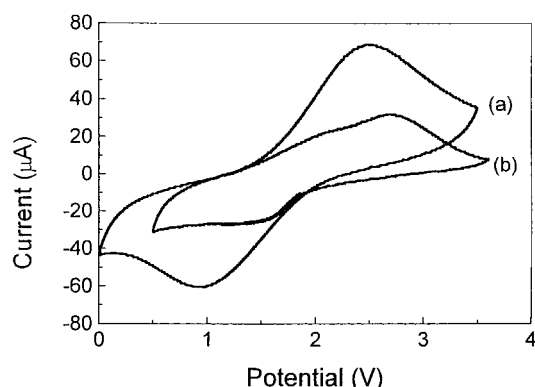


Figure 1. Cyclic voltammogram of TiO₂ film deposited in ambient pressure of (a) 20 Pa and (b) 5 Pa at a scan rate of 20 mV/s.

ozonizer. The ambient gas of the O₃/O₂ mixture is introduced via a glass tube, and its pressure can be adjusted by a needle valve. A typical ambient gas pressure is maintained during the deposition process. The titanium oxide thin films are deposited onto the indium–tin oxide (ITO)-coated glass (10 Ω/□). The heated substrate with a temperature of ~350 °C is placed at a distance of 25 mm from the target. The deposition time is fixed at 15 min. The film thickness of ~180 nm is measured by profilometry (Tencor Alpha Step-200). The composition and structure analysis of deposited TiO₂ film have been described in the previous studies,^{11,12} and X-ray diffraction (XRD) measurement shows that the deposited film is anatase TiO₂.

The electrochemical cells are assembled by using a conventional three-electrode cell, which consists of deposited TiO₂ film and two sheets of high-purity lithium metal foils as working electrode, counter-electrode, and reference electrode, respectively. The electrolyte consists of 1 M LiPF₆ in a nonaqueous solution of ethylene carbonate (EC) and dimethyl carbonate (DMC), with a volume ratio of 1:1 (Merck). Cycle voltammogram and potential step measurements are performed with CHI 660a electrochemical working station (CHI Instruments, TN).

After the insertion of Li ion into TiO₂ film electrode, the sample Li_xTiO₂ film electrode is taken out from the electrochemical cell. To carry out the isothermal transient ionic current measurements, the Al gate electrodes, with an area of ~6.4 × 10⁻³ cm² as an ion-blocking electrode are prepared on the top of the TiO₂ and Li_xTiO₂ surfaces by thermal evaporation. The ITIC measurements are performed at room temperature using the potential step function in the CHI 660a electrochemical working station.

3. Results and Discussion

3.1. Electrochemical Behavior. 3.1.1. Cyclic Voltammetry.

Cyclic voltammetry was used to examine the behavior for the Li ion intercalation into TiO₂ electrode. Figure 1 shows cyclic voltammogram curves of two TiO₂ film electrodes fabricated by pulsed laser deposition under the ambient gas pressures of 20 and 5 Pa, respectively. From the curves (a) and (b) in Figure 1, it can be seen that a couple of oxidation–reduction peaks appear when the electrode potential scans from 0 to 3.5 V (versus Li/Li⁺) at a scan rate of 20 mV/s, corresponding to the insertion and the extraction processes of Li ion for TiO₂ film, respectively. Compared with curve (b), curve (a) exhibits well-distinguished oxidation–reduction peaks and the oxidation–reduction current is much larger. This result suggests that the shape of the cyclic voltammogram of TiO₂ film is dependent on the deposition condition, such as the TiO₂ film deposited at an ambient pressure of 20 Pa exhibits good behavior of the

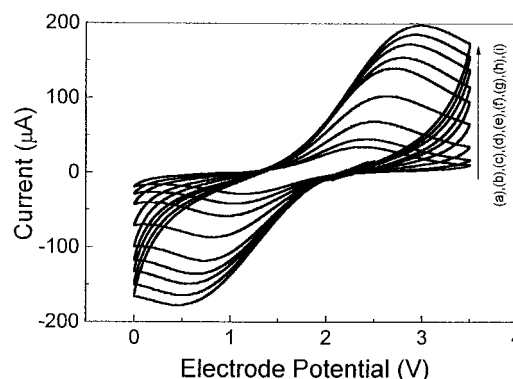


Figure 2. Cyclic voltammogram of TiO₂ film electrode at various scan velocities: (a) 5; (b) 10; (c) 20; (d) 40; (e) 60; (f) 80; (g) 100; (h) 120; and (i) 140 mV/s.

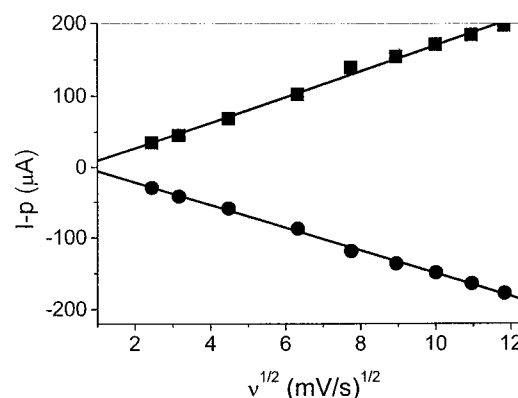
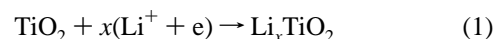


Figure 3. The relationship between $I-p$ for the insertion and extraction peaks and $v^{1/2}$: (■) anodic; (●) cathodic.

cyclic voltammogram. Our preliminary experiments showed that the substrate temperature of 350 °C for film deposition, with a laser fluence of 3 J/cm², is appropriate for the fabrication of anatase phase TiO₂ film. Thus, the typical pressure of 20 Pa is one of optimal conditions of pulsed laser deposition for the preparation of anatase TiO₂ film with a superior electrochemical property.

To further examine the features of the cyclic voltammogram for TiO₂ film deposited at 20 Pa, we measured the cyclic voltammograms of the Li/TiO₂ cell at various scan rates. As shown in Figure 2, the peak currents and potentials, as well as peak splits, for the oxidation–reduction processes are dependent on the scan rate. Such cycle voltammogram curves are the characteristic feature for an irreversible electrochemical reaction. For curves (a), (b), and (c) in Figure 2, integration of the total voltammetric charge between 0 and 3.5 V gives 570 Cg⁻¹ of cathodic charge and 562 Cg⁻¹ of anodic charge. The electrochemical process for the intercalation of Li ion into TiO₂ can be expressed by



the insertion coefficients x are estimated to be 0.48 and 0.47 for the cathodic and anodic processes, respectively, and the charge reversibility is ~98%. These results are close to the values obtained in previous reports.^{4,31}

Based on the cyclic voltammogram data presented in Figure 2, the peak currents ($I-p$) can be plotted as a function of the scan rate v for the cathodic and anodic processes. As shown in Figure 3, the peak currents $I-p$ show a linear dependence on the square root of the scan rate for both the insertion and

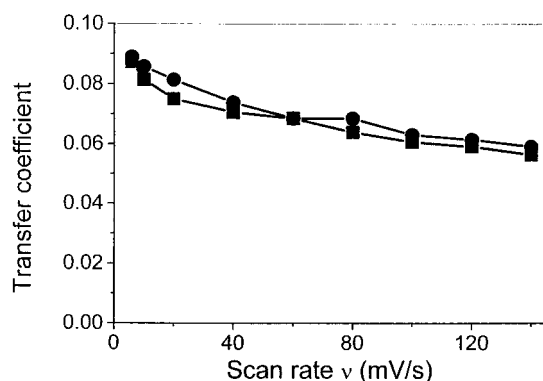


Figure 4. Transfer coefficient for various scan velocities: (■) cathodic; (●) anodic.

extraction processes. Because the ionic diffusion in the liquid electrolyte LiPF₆-EC+DMC (1 M) is high, the limiting step may be the diffusion of Li ions into TiO₂ thin film. It is reasonable to assume that the rate-determining process in the insertion and extraction is the diffusion of Li ion into a homogeneous semi-infinite material. An irreversible electrochemical reaction can be determined by following equations:³²

$$\alpha = 1.857RT/n_a F |E_p - E_{p/2}| \quad (2)$$

$$I-p = 0.4958nFAC(\alpha n_a F D_0 \nu / RT)^{1/2} \quad (3)$$

where α is the charge-transfer coefficient of electrode reaction, A is the area of electrode that is provided to be identical to the macroscopic area (0.8 cm²), F is the Faraday constant, D_0 is the diffusion constant of the Li ion, C is the obtained maximum concentration of Ti³⁺ in the lattice (i.e., 24×10^{-3} mol/cm³ for $x = 0.5$ as suggested by Kavan et al.³³), n is the electron number involved in the overall electrode process, and n_a is the number of electrons involved in the rate-determining step (n and n_a are assumed to be unity). According to eq 1, the charge-transfer coefficient (α) of the electrode reaction at different scan rates can be obtained by using the difference between the peak potential, E_p , and the half-peak potential, $E_{p/2}$, from Figure 2. As shown in Figure 4, the charge-transfer coefficient is close to 0.07 ± 0.01 for both insertion and extraction.

Additionally, the slope of the straight lines obtained from the plot of $I-p$ versus $\nu^{1/2}$ in Figure 3 are estimated to be 17.8 and $16.0 \mu\text{A}/(\text{mV/s})^{1/2}$ for insertion and extraction processes, respectively, and their diffusion constants D_0 of Li ion are calculated to be 1.12×10^{-13} and 1.39×10^{-13} cm²/s, respectively, using eq 2. It should be pointed out that the C value would decrease during the extraction process for the deintercalation case, so our assumption on the constant C value would cause an overestimate of the diffusion coefficient.

3.1.2. Potential Step. A chemical diffusion coefficient for Li insertion in the TiO₂ film electrode can be estimated by a potential step measurement. Figure 5 shows the current variation with $t^{-1/2}$ during the potential step from 3.5 to 1.5, 1.2, 0.9, 0.6, 0.3, and 0 V. It can be seen that a linear variation is obtained, and the slope k of the straight lines are estimated to be 0.46, 0.83, 1.06, 1.32, 1.71, and 2.07 mA s^{1/2}, respectively. If we still make the same hypothesis as we already presented, the diffusion coefficient D_0 of lithium in the TiO₂ electrode in describing a chronoamperometric response is obtained by using the following equation for an irreversible electrochemical reaction at a planar electrode:³²

$$D_0 = \pi k^2 (FAC_0)^{-2} \quad (4)$$

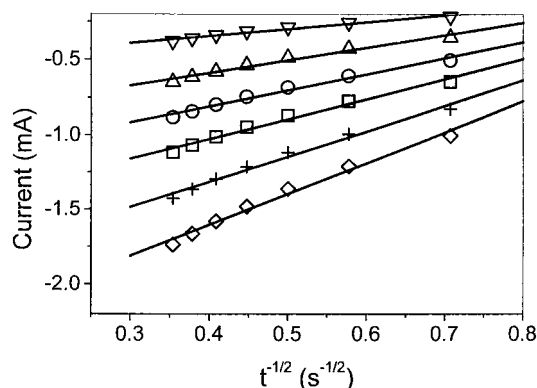


Figure 5. The current versus $t^{-1/2}$ for TiO₂ film electrode during the potential stepping (∇) 3.5 \rightarrow 1.5 V; (Δ) 3.5 \rightarrow 1.2 V; (\circ) 3.5 \rightarrow 0.9 V; (\square) 3.5 \rightarrow 0.6 V; (+) 3.5 \rightarrow 0.3 V; and (\diamond) 3.5 \rightarrow 0 V. The solid lines are the fit with a linear relationship.

where A and F are the same meaning as described in eq 3, C_0 is the surface concentration and is assumed to be constant at 24×10^{-3} mol/cm³, and k is the slope of the straight line obtained from the plot of the current versus $t^{-1/2}$ as already described. Using eq 4 and the k values already obtained, the corresponding D_0 values are estimated to be in the range $1.95 - 16.0 \times 10^{-13}$ cm²/s for the insertion of Li ion in TiO₂ electrode. Apparently, D_0 values estimated by potential steps are dependent on stepping potential, and the values are larger at more negative steps. Table 1 lists available data about chemical diffusion coefficient of Li insertion in TiO₂ electrode. It can be seen that D values obtained in this work fall in the range $10^{-11} \sim 10^{-13}$ cm²/s for the TiO₂ electrode fabricated by sputtering methods in previous reports.^{25,26} But these values are different from that of TiO₂ electrode prepared by CVD, nanoporous, and other methods.^{4-5,24} This difference implies that Li ion diffusion behavior in the TiO₂ electrode is dependent on the fabrication method, and there is a similar Li ion diffusion property in TiO₂ electrode for film electrode fabricated by using sputtering methods and pulsed laser deposition method.

3.2. Isothermal Transient Ionic Current. In the ITIC measurement, the charge carriers distributed uniformly in the film can be migrated when a constant field is applied across the film, and the ionic current is recorded at different times. Figure 6 shows the ionic currents of both TiO₂ and Li_xTiO₂ films as a function of time during potential stepping from 0 to 1 V, respectively. It can be seen that the observed current for the Li_xTiO₂ film is higher than that for the TiO₂ film, and the current change lasts several hundred seconds for the Li_xTiO₂, whereas the current for the TiO₂ after 100 s hardly varies. When the typical potential applies across the TiO₂ film in the case of ion-blocking, the current response is very complicated and may be attributed to the dipole orientation or the migration of stained protons in TiO₂.^{28,30} However, it should be reasonable to assume that the higher current and its evolution with longer time in the Li_xTiO₂ film are mainly caused by the migration of Li ions, and the effect of dipole orientation or the migration of stained protons on the observed current of the Li_xTiO₂ could be neglected.

In addition, the maximum current in the ITIC curve is observed at $\tau = 53$ s. It should be noted that the Li ions in the original Li_xTiO₂ films are located close to the vicinity of the surface by the Li ions insertion into TiO₂ films, and their distribution does not change as the potential is zero. When the potential steps from zero to a finite value, the Li ions migrate to the opposite contact. As pointed out by Mattsson et al.,³⁰ the current maximum time τ represents the time-of-flight for Li ions

TABLE 1: Comparison of Chemical Diffusion Constant for Li Ion in TiO₂

Preparation	Measurement	D (cm ² /s)	Ref
Commercially available Rf sputtering	A galvanostatic pulse	3.7×10^{-10}	24
	A potential step	3.78×10^{-13}	25
	Nonheated	1.81×10^{-13}	
DC magnetron sputtering Pulsed laser deposition	Heated	2.0×10^{-11}	26
	An impedance	1.1×10^{-13} (insertion)	TW ^a
	Voltammetry	1.4×10^{-13} (extraction)	TW ^a
	A potential step	$(2.0-16.0) \times 10^{-13}$	TW ^a
	ITIC	5.93×10^{-14}	TW ^a
Nanoporous	A potential step	3×10^{-17} (insertion)	4 ^b
		4×10^{-17} (extraction)	4 ^b
Chemical vapor deposition	A potential step	2×10^{-15} (insertion)	4
		6×10^{-15} (extraction)	4
Nanoporous	Voltammetry	2×10^{-17} (insertion)	5 ^b
		4×10^{-15} (extraction)	5 ^b

^a TW, this work. ^b Chemical diffusion coefficient is obtained by taking into account the inner area of the electrode.

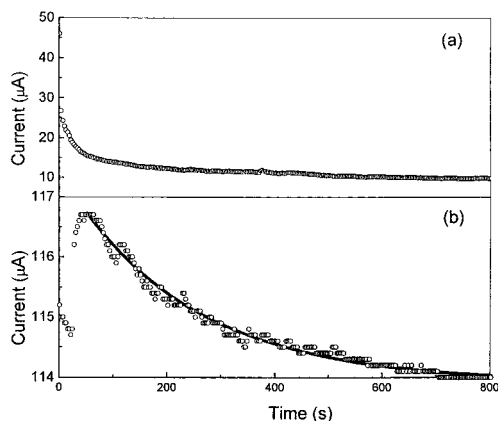


Figure 6. ITIC curves with the potential step from 0 to 1 V for (a) TiO₂ and (b) Li_xTiO₂. The solid line is the fit with equation: $113.92 \mu\text{A} + 3.09 \mu\text{A} \cdot \exp(-0.0043 \text{ s}^{-1}t)$.

to migrate through the Li_xTiO₂ film. Such an isothermal transient ionic current curve of Li ions for the Li_xTiO₂ is dependent on the stepping potential. Figure 7(a) and (b) present the ITIC curves during the potential stepping from 0 to 2 and 4 V, respectively. The τ value is smaller at larger applied potential, and is estimated to be 46 and 26 s at stepped potentials of 2 and 4 V, respectively. This result suggests the time-of-flight for Li ion to migrate through the TiO₂ film becomes shorter at higher applied potential. The relation of τ with the applied potential U can be expressed by the following equation:²⁸

$$U - U_{\text{eff}} = d^2/\mu\tau \quad (5)$$

where d is the thickness of Li_xTiO₂ film, U is the applied potential, U_{eff} is the average voltage drop due to space-charge effects, and μ is the approximate mobility of Li ions. Based on this equation, μ could be obtained by the relationship between U and $1/\tau$. As shown in Figure 8, the plot of U versus $1/\tau$ exhibits a linear dependence. From the obtained slope of a straight line, the mobility of Li ions μ is estimated to be $2.29 \times 10^{-12} \text{ cm}^2/\text{Vs}$.

The process of initial decrease in the ITIC curve is dominated by the formation of the Li ions accumulation layer near ion-blocking contacts. For such a process, the current decay can be described by the following equations from Faraday's law:²⁸

$$I(t) = S\sigma_{\text{dc}}U/d \exp(-\mu Ut/d^2) \quad (6)$$

where S is the contact area, and σ_{dc} is the conductivity. Equation

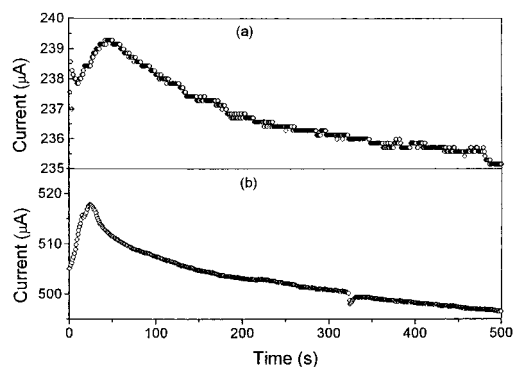


Figure 7. ITIC curves of Li_xTiO₂ with the potential step from (a) 0 to 2 V; and (b) 0 to 3 V.

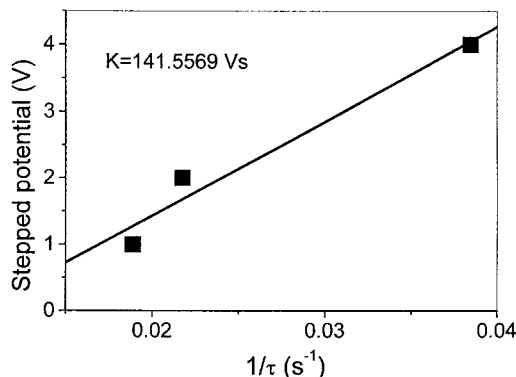


Figure 8. The stepped potential versus $1/\tau$ during the ITIC measurements. The solid line is the fit with a linear relationship.

6 is used to fit the measured current starting at time equal τ . As shown in Figure 6(b), the time dependence of the measured current is well fitted by eq 6, and the μ value is calculated to be $1.39 \times 10^{-12} \text{ cm}^2/\text{Vs}$, which is lower than the value we previously estimated. The underestimated μ is caused by the fact that the effective voltage over the film is taken to be applied voltage U in eq 6, and the voltage drop across the film is neglected.

According to the Einstein relation,³⁴

$$D_0 = \kappa T \mu / q \quad (7)$$

where κ is Boltzmann's constant, T is the absolute temperature, q is the electron charge, and D_0 is the diffusion constant. By using the μ values just given, the D_0 value is calculated to be $5.93 \times 10^{-14} \text{ cm}^2/\text{s}$ in the ITIC measurement by the potential stepping from 0 V to a finite value.

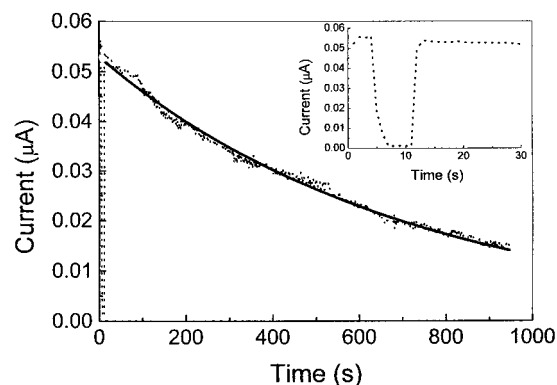


Figure 9. ITIC curves of Li_xTiO₂ with the potential step from 2 to 0 V. The solid line is the fit with equation: $0.003 \mu\text{A} + 0.05 \mu\text{A} \cdot \exp(-0.001 \text{ s}^{-1}t)$.

Further verification to the transport behavior of Li ions can be gained by examining the ITIC curve during the potential stepping from a finite value to zero. After the applied potentials disappear and turn to 0 V, the ions accumulated near an ion-blocking contact will redistribute in the film. This process seems reversible, with the potential stepping from 0 V to a specified potential. But during the potential stepping from a specified potential to 0 V, the diffusion of the Li ion is driven by the concentration gradient of Li ion in the film, instead of the applied field. Figures 9 and 10 show the ITIC curves of Li_xTiO₂ film with the potential stepping from 2 and 3 to 0 V, respectively. It can be seen that the current near zero is in the region 0–10 s. This result suggests that the Li ions do not reach the opposite contact in the start period. When Li ions diffuse to an ion-blocking contact, the current is generated. Meanwhile, the Li ion accumulation layer is also formed. In other words, the Li ions accumulated by the pre-polarization are released to the bulk of film after the applied potential turn to zero, and Li ions in the bulk are redistributed by the free-field diffusion. The origin of the current decay is rather complicated, but the accumulation formation should play an important role in decreasing the ion flow at the interface between Li_xTiO₂ film and the contact. As shown in Figures 9 and 10, we found that the current decreases with exponential decay, with decay times of 1000 and 400 s for the pre-polarized potentials of 2 and 3 V applied for 10 min, respectively. Considering the redistribution of the ions is via free-field diffusion through the sample, we simply assume that the decay times are the effective diffusion times (t_{eff}). The diffusin coefficient D_0 can be expressed by

$$D_0 = d^2 / \pi t_{\text{eff}} \quad (8)$$

the diffusion coefficient is estimated to be ~ 1.03 and $2.58 \times 10^{-13} \text{ cm}^2/\text{Vs}$ for the pre-polarized potentials 2 and 3 V, respectively. A little difference between both D_0 values should be related to the different concentration gradient of Li ion in the film between the pre-polarized potentials of 2 and 3 V. The former value agrees unexpectedly well with the results of cyclic voltammetry measurements, but is twice as large as those estimated by the potential stepping from zero to a finite potential. The overestimated D_0 value may be mainly due to our simple assumption of the decay time equal to the effective diffusion time.

3.3. Discussion

The ITIC measurements of Li_xTiO₂ films were carried out by stepping from a finite potential to 0 V and from 0 V to a

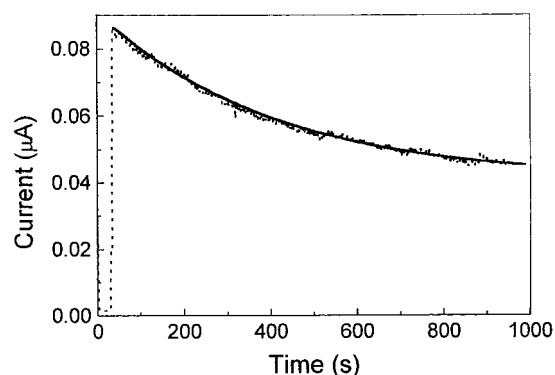


Figure 10. ITIC curves of Li_xTiO₂ with the potential step from 3 to 0 V. The solid line is the fit with equation: $0.041 \mu\text{A} + 0.045 \mu\text{A} \cdot \exp(-0.0025 \text{ s}^{-1}t)$.

finite potential. Two kinds of diffusion processes of Li ion, both driven by an applied field and by the concentration gradient, were observed. Our results estimate the diffusion constant to be $5.93 \times 10^{-14} \text{ cm}^2/\text{s}$ for the potential stepping from 0 V to a finite potential. A larger diffusion constant is estimated in the case of higher applied field from the potential step in the electrochemical measurement. However, the process of insertion of Li ions into the TiO₂ film electrode, as determined by cyclic voltammogram measurements and potential steps, takes place at a more negative potential than the flat band potential, and via the diffusion of Li ions with higher concentrations at the solid/electrolyte interface into TiO₂ film. Thus, both the applied field and concentration gradient effects impact on the Li ion movement as determined by the electrochemical measurements. Compared with the diffusion constant estimated by the ITIC measurement, the overestimated diffusion constant by the electrochemical measurement may be caused by using the projected electrode area instead of the active electrode area in the electrochemical equations. Because it is difficult to measure the active electrode area of the film, the diffusion constant estimated by the ITIC measurement has the advantage of relative accuracy. Thus, our results provide three kinds of diffusion mechanisms for Li ion into TiO₂ film, in which the movements of Li ion are driven by an applied field and the concentration gradient as well as by both of them.

It should be noted that the transfer coefficients are estimated to be close to 0.07 for the insertion and extraction processes in the cyclic voltammogram experiments. This value is one order of magnitude lower than that reported by Lindström et al.⁵ They suggested that the charge transfer of nanoporous TiO₂ film electrode exhibits metallic behavior with the transfer coefficients between 0.3 and 0.7, and higher density of surface states may exist in the TiO₂ during the redox process. However, the lower transfer coefficients of TiO₂ fabricated by pulsed laser deposition could be due to the characteristic feature of semiconductor electrodes with a large energy band gap, and imply no evidence for the higher density traps in the TiO₂ film. In addition, the current decreases with exponential decay in the ITIC measurement, which means that few traps are experimentally observed in the TiO₂ film. Thus, our results give important evidence that pulsed laser deposition is a powerful method to fabricate a high-quality TiO₂ film.

4. Conclusions

Electrochemical and isothermal transient ionic current methods have successfully been employed for the investigation of Li ion diffusion in anatase TiO₂ films, which are fabricated by

pulsed laser deposition. The diffusion constants of Li ion are calculated to be 1.12 and 1.39×10^{-13} cm²/s for both insertion and extraction processes, respectively, by the cyclic voltammograms. However, potential step measurements show that the diffusion constant is dependent on the applied potential and is found in the range $1.95\text{--}16.0 \times 10^{-13}$ cm²/s for the insertion of Li ions in TiO₂ film electrode. The ITIC measurements estimate that the diffusion constant of Li ion is 5.93×10^{-14} cm²/s. Our results show that a high-quality anatase TiO₂ film without experimentally observed traps has successfully been fabricated by pulsed laser deposition.

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