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Electrochemical Properties of $LiNi_{0.50}Co_{0.25}Mn_{0.25}O_2$ Thin Film Cathodes Prepared by Pulsed Laser Deposition

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$LiNi_{0.50}Co_{0.25}Mn_{0.25}O_2$ thin film cathodes are successfully prepared by pulsed laser deposition technique with post-annealing treatment. The microstructure of the thin films is characterized by X-ray diffraction, environmental scanning electron microscopy, X-ray photoelectron spectroscopy and atomic force microscopy. The electrochemical performance of the thin film electrodes is evaluated by cyclic voltammetry and charge-discharge cycling tests. $LiNi_{0.50}Co_{0.25}Mn_{0.25}O_2$ thin film electrodes deliver good electrochemical performance. The initial discharge capacity of the thin film electrodes is 122 $mAhg^{-1}$ measured at a rate of 0.5C in the voltage range of 2.8–4.3 V. The coulombic efficiency is beyond 94% in addition to the first charge-discharge cycle. The chemical diffusion coefficients of lithium ions in the thin film electrodes are in the range of 10^{-11} – 10^{-13} cm^2s^{-1} determined by galvanostatic intermittent titration technique (GITT) method.

Keywords: $LiNi_{0.50}Co_{0.25}Mn_{0.25}O_2$, Thin film electrode, Lithium ion batteries, Electrochemical performance, Pulsed laser deposition

1. INTRODUCTION

$LiCoO_2$ cathode material has been widely used in commercial lithium-ion batteries because of its high theoretical capacity and excellent cycling stability [1]. However, the relatively high cost, toxicity and safety problems limit its further use in large-scale applications [2–3]. Recently, layered-structured compounds $LiNi_{1-x-y}Co_xMn_yO_2$ have been known as the promising cathode materials to replace $LiCoO_2$, owing to their promising electrochemical and safety characteristics [4–6]. $LiNi_{0.5}Co_{0.25}Mn_{0.25}O_2$ is expected to be a potential cathode material in the $LiNi_{1-x-y}Mn_xCo_yO_2$ oxides

family, due to its high initial discharge capacity (174 $mAhg^{-1}$) within the potential of 3–4.3 V (vs. Li^+/Li) [7–8]. The low content of Co is also beneficial to reduce the cost and toxicity. Researchers still focus on the study of $LiNi_{0.50}Co_{0.25}Mn_{0.25}O_2$ powders [7–9]. Nevertheless, to the best of our knowledge, there are no reports on $LiNi_{0.50}Co_{0.25}Mn_{0.25}O_2$ thin film electrodes.

Micro lithium ion batteries, consisting of thin film electrodes and electrolytes have been of great interest due to their potential applications as power sources for microelectronic devices [10]. As the development of microelectronic devices, the need to develop the micro batteries with high power and high energy density increases. Thin film cathodes of conventional active materials, such as $LiCoO_2$, have been reported to use well in thin film batteries [11–13]. However, the thin film cathodes do not meet the requirement. The thin film electrodes of the $LiNi_{1-x-y}Mn_xCo_yO_2$ oxides family have attracted more and more interest because of their excellent electrochemical performance. The $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ thin film electrodes [14, 15] have been reported that they presented a high discharge capacity of more than 120 $mAhg^{-1}$. Kim et al. recently have reported a $LiNi_{0.4}Co_{0.3}Mn_{0.3}O_2$ thin film electrode prepared by an aerosol deposition method. The $LiNi_{0.4}Co_{0.3}Mn_{0.3}O_2$ thin film electrode delivered an initial discharge capacity of 44.6 μAh cm^{-2} [16]. In the present work, $LiNi_{0.50}Co_{0.25}Mn_{0.25}O_2$ thin films are successfully prepared by pulsed laser deposition (PLD) technique. The electrochemical performance of $LiNi_{0.50}Co_{0.25}Mn_{0.25}O_2$ thin film electrodes is investigated in details. Furthermore, the lithium ion diffusion coefficients of thin film electrodes are also discussed.

2. EXPERIMENTAL PART

The target was prepared by using $LiNi_{0.50}Co_{0.25}Mn_{0.25}O_2$ powders with 5 wt% excess Li_2O to compensate for Li loss during the deposition and heat treatment processes of thin films. $LiNi_{0.50}Co_{0.25}Mn_{0.25}O_2$ thin films were deposited on $Pt/Ti/SiO_2/Si$ substrates at ambient temperature in an O_2 atmosphere of 50 mTorr for 60 min by PLD technique using a KrF excimer laser (300 mJ, 10 Hz). The thicknesses of Pt current collector layer and Ti buffer layer were 150 and 100 nm, respectively. The as-prepared thin films were then annealed at 450 ºC for 3 h with a constant heating rate of 2 $ºCmin^{-1}$ in air to improve crystallization. The microstructure of $LiNi_{0.50}Co_{0.25}Mn_{0.25}O_2$ thin films was characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), environmental scanning electron microscopy (ESEM) and atomic force microscopy (AFM).

A two-electrode cell test equipment with lithium metal foil as the counter electrode was used in the electrochemical measurements. Constant current charge/discharge measurements were conducted using an Arbin (BT-2000) battery testing system. Cyclic voltammetry (CV) measurements were carried out using a Zaher Elektrik IM6 electrochemical workstation between 2.8 and 4.3 V versus Li/Li^+ with a scan rate of 1 mVs^{-1}. Galvanostatic intermittent titration technique (GITT) measurements were performed after 5 charge–discharge cycles. The cell was charged at a current density of 10 μAcm^{-2} for 10 min followed by an open circuit relaxation for 2 h. The procedure was continued until the cell voltage reached a given value. All experiments were performed in an Ar-filled glove box. 1 M $LiClO_4$ in propylene carbonate (PC) was used as the electrolyte.

3. RESULTS AND DISCUSSION

The X-ray diffraction pattern of the $LiNi_{0.50}Co_{0.25}Mn_{0.25}O_2$ thin film annealed at 450 ºC is shown in Fig. 1. The pattern displays a dominant peak at about 18.7º, indicating a (003) axis preferred growth of the thin film. The slightly intensive dominant peak suggests that the annealed thin film possesses a partially amorphous structure.

The ESEM images of the annealed $LiNi_{0.50}Co_{0.25}Mn_{0.25}O_2$ thin film are shown in Fig. 2. The surface of the annealed thin film is slightly smooth with an average grain size of about 50 nm. The thin film exhibits the columnar structure observed from the cross-section ESEM image (Fig. 2b). The thickness of the thin film is estimated to be about 280 nm.

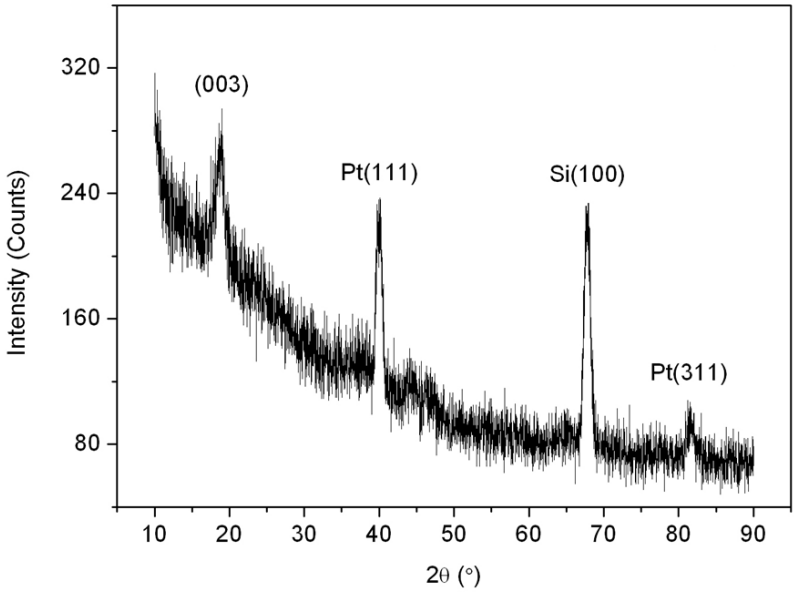

Figure 1. XRD pattern of $LiNi_{0.50}Co_{0.25}Mn_{0.25}O_2$ thin film.

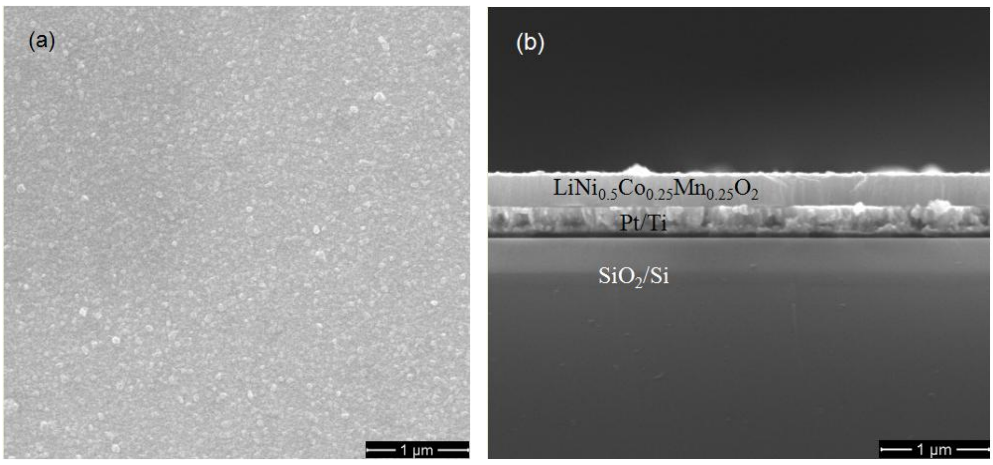

Figure 2. ESEM surface and cross-section images of $LiNi_{0.50}Co_{0.25}Mn_{0.25}O_2$ thin film: (a) surface image, (b) cross-section image.

The typical three-dimensional AFM image of the surface topography of the $LiNi_{0.50}Co_{0.25}Mn_{0.25}O_2$ thin film is shown in Fig. 3. Uniform microstructure and grain size distribution can be observed in $LiNi_{0.50}Co_{0.25}Mn_{0.25}O_2$ thin film. In order to study surface roughness, RMS (Root Mean Square) average roughness of the thin film was measured. RMS roughness determined from randomly selected regions is 18.5 nm, indicating that the obtained thin film has a relatively regular topography.

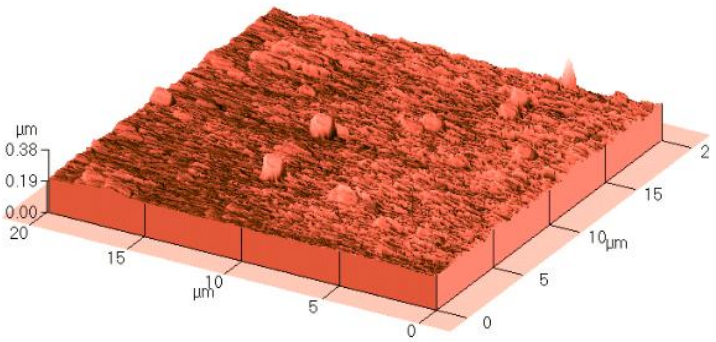

Figure 3. AFM image of the surface topography of $LiNi_{0.50}Co_{0.25}Mn_{0.25}O_2$ thin film.

Cycle voltammetry measurements were performed in the voltage range 2.8 – 4.3 V at a scan rate of 1 mVs^{-1}. The cyclic voltammograms of the $LiNi_{0.50}Co_{0.25}Mn_{0.25}O_2$ thin film electrodes for the first three cycles are shown in Fig. 4. The curves exhibit a couple of well-defined anodic and cathodic peaks located at about 3.8 V and 3.5 V. This is a typical characteristic attributed to the deintercalation/intercalation process of Li^+ ions in $LiNi_{0.50}Co_{0.25}Mn_{0.25}O_2$ cathode material [9]. It can be seen that the cathodic and anodic peaks exhibit a tiny shift during the second and third cycles, suggesting better cycle stability of the film electrode after the first cycle.

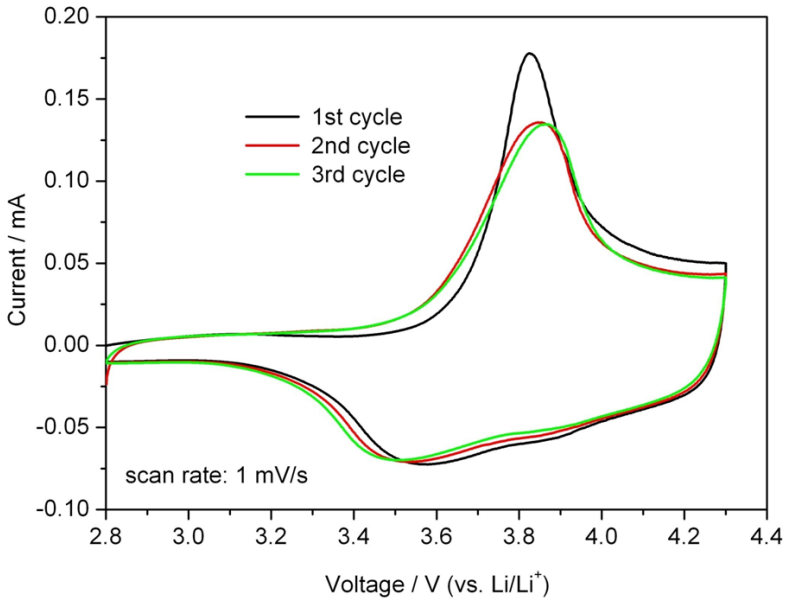

Figure 4. The cyclic voltammograms of $LiNi_{0.50}Co_{0.25}Mn_{0.25}O_2$ thin film electrodes tested at a scan rate of 1 mVs^{-1}.

Fig. 5 shows the charge/discharge curves and the cycle performance of the $LiNi_{0.50}Co_{0.25}Mn_{0.25}O_2$ thin film electrodes. The constant current charge/discharge tests of the $Li/LiNi_{0.50}Co_{0.25}Mn_{0.25}O_2$ cell were carried out at a constant current density of 10 μAcm^{-2} (0.5C rate, 1C = 160 mAg^{-1}) in the voltage range of 2.8 – 4.3 V. The initial charge and discharge specific capacities are 143 and 122 $mAhg^{-1}$, respectively. The specific capacities were calculated assuming a density of 4.81 gcm^{-3}. The discharge specific capacity is comparable to that of the $LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$ film electrodes [14]. The initial discharge specific capacity is about 130 $mAhg^{-1}$ measured between 2.5 and 4.5 V at a current density of 7.8 μAcm^{-2} (0.24C rate). The coulombic efficiency (Fig. 5b) is beyond 94% in addition to the first charge-discharge cycle. This reveals good reversibility of lithium intercalation/deintercalation reactions in the thin film electrodes. The $LiNi_{0.50}Co_{0.25}Mn_{0.25}O_2$ thin film electrodes deliver a relatively good cycle performance. The discharge capacity retention is 83% after 25 cycles.

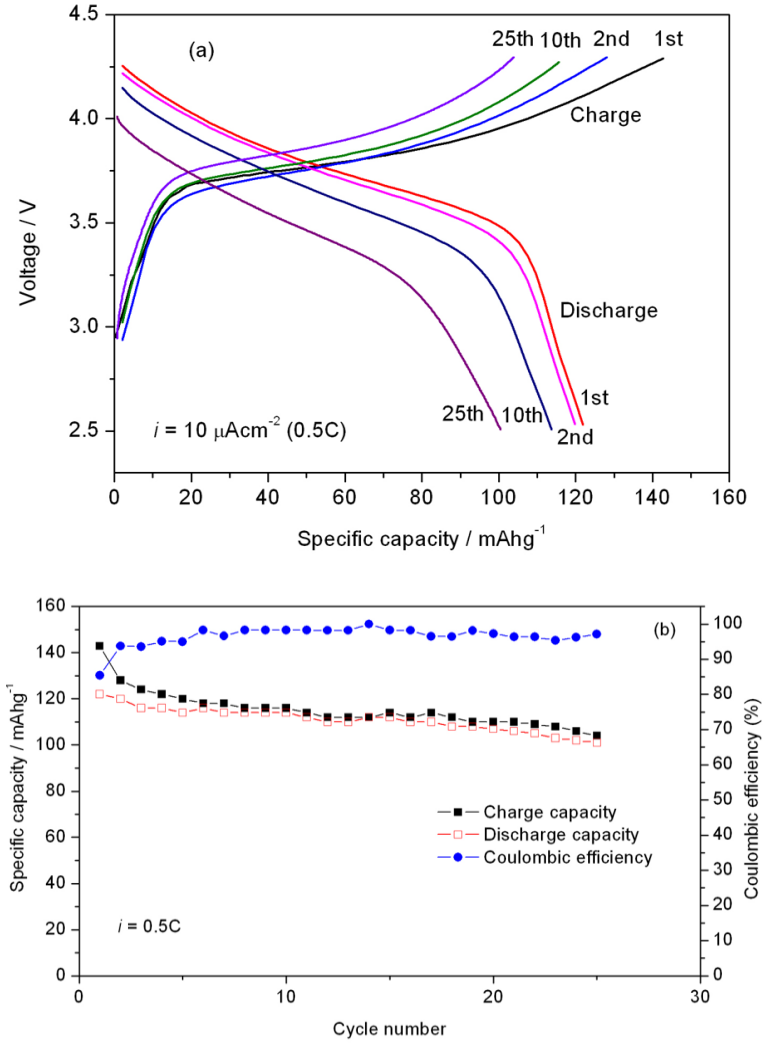

Figure 5. The charge/discharge curves (a) and cycle performance (b) for $LiNi_{0.50}Co_{0.25}Mn_{0.25}O_2$ thin film electrodes.

However, the capacities are lower than the $LiNi_{0.50}Co_{0.25}Mn_{0.25}O_2$ composite electrode [7, 8]. The low capacities can be ascribed to the following reasons. The thin films are free of conducting agent, and the active area for electrochemical reactions is much smaller than that of the composite electrode in the liquid electrolyte. The partially amorphous structure of the $LiNi_{0.50}Co_{0.25}Mn_{0.25}O_2$ thin film electrodes is also an important factor resulting in their low capacities. In addition, Li deficiency in thin films may be one of reasons resulting in low capacities. In order to confirm the lithium deficiency of thin film electrodes, XPS analysis was used. Prior to collecting the XPS data, the surface (about 40 nm thickness) of $LiNi_{0.50}Co_{0.25}Mn_{0.25}O_2$ thin films was etched by ion beam sputtering to remove any surface contaminations. The molar ratio of Ni/Co/Mn is near 2:1:1 obtained from XPS analysis (see Fig.6). The molar composition of lithium in the thin films is 21.76%, indicating the loss of part of lithium during the deposition and heat treatment processes for the thin films.

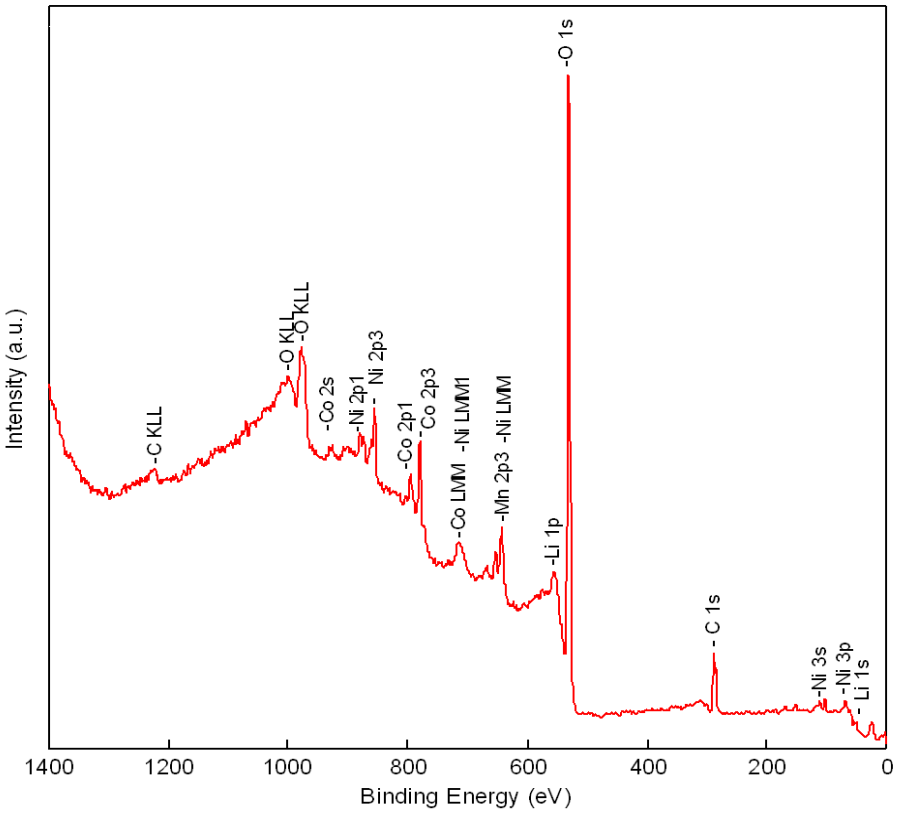

Figure 6. XPS spectrum of $LiNi_{0.50}Co_{0.25}Mn_{0.25}O_2$ thin films.

To investigate the diffusion coefficients of lithium ion in $LiNi_{0.50}Co_{0.25}Mn_{0.25}O_2$ thin film electrodes, GITT measurements were performed after the cell had been cycled between 2.8 V and 4.3 V for 5 times. Fig. 7a shows the variation of the cell voltage for a single titration at 3.703 V. The relation of the cell voltage against $\tau^{1/2}$ is linear during the time period τ under an applied constant current density. Thus, the diffusion coefficient of lithium ions in $LiNi_{0.50}Co_{0.25}Mn_{0.25}O_2$ thin film electrodes can be determined by Eq. 1 [17]

$$D_{\mathrm{Li}} = \frac{4}{\pi\tau} L^2 \left(\frac{\Delta E_s}{\Delta E_\tau}\right)^2 \quad \left(\tau \le L^2 / D_{\mathrm{Li}}\right) \qquad (1)$$

where D_{Li} (cm^2s^{-1}) represents the Li-ion diffusion coefficient. L (cm) is the thickness of the thin film electrodes. ΔE_s and ΔE_τ are the change of equilibrium voltage for a single titration and the total change of cell voltage (after subtracting the IR drop).

The Li-ion diffusion coefficients, D_{Li}, calculated using Eq. 1 as a function of the cell voltage is shown in Fig. 7b. The values of D_{Li} in $LiNi_{0.50}Co_{0.25}Mn_{0.25}O_2$ thin film electrodes are in the range of $10^{-11} - 10^{-13}$ cm^2s^{-1}. The D_{Li} values in this study are in agreement with results obtained in $LiCoO_2$ [18] and $LiNi_{0.5}Mn_{0.5}O_2$ [19] thin film electrodes.

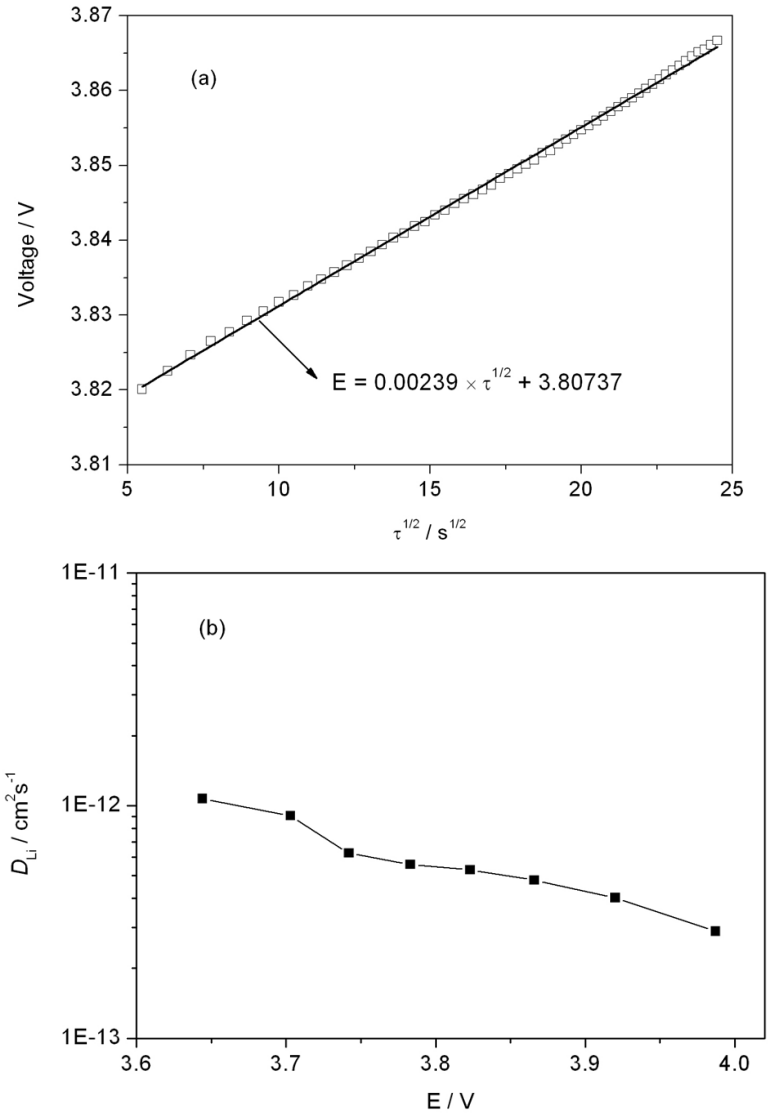

Figure 7. (a) The variation of cell voltage vs. $\tau^{1/2}$ during the time period τ on application of the current pulse for a single titration at 3.703 V, and (b) the diffusion coefficients of Li^+ ions in $LiNi_{0.50}Co_{0.25}Mn_{0.25}O_2$ thin film electrodes.

4. CONCLUSIONS

Layered $LiNi_{0.50}Co_{0.25}Mn_{0.25}O_2$ thin film electrodes have been successfully prepared by pulsed laser deposition technique. The microstructure and electrochemical properties of thin film electrodes have been investigated. $LiNi_{0.50}Co_{0.25}Mn_{0.25}O_2$ thin film electrodes exhibit good electrochemical performance. The first discharge specific capacity is 122 $mAhg^{-1}$ tested at a rate of 0.5C in the voltage range of 2.8 – 4.3 V. The coulombic efficiency is beyond 94% except the first charge-discharge cycle, and the capacity retention ratio is 83% after 25 charge-discharge cycles. The Li-ion diffusion coefficients in $LiNi_{0.50}Co_{0.25}Mn_{0.25}O_2$ thin film electrodes are in the range of 10^{-11} – 10^{-13} cm^2s^{-1} obtained by GITT method.

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