Electrochimica Acta 54 (2009) 5986–5991

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Li diffusion in $LiNi_{0.5}Mn_{0.5}O_2$ thin film electrodes prepared by pulsed laser deposition

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ARTICLE INFO

Article history:
Received 20 October 2008
Received in revised form 22 February 2009
Accepted 23 February 2009
Available online 6 March 2009

Keywords:
Thin films
$LiNi_{0.5}Mn_{0.5}O_2$
Pulsed laser deposition
Li diffusion

ABSTRACT

Kinetic and transport parameters of Li ion during its extraction/insertion into thin film $LiNi_{0.5}Mn_{0.5}O_2$ free of binder and conductive additive were provided in this work. $LiNi_{0.5}Mn_{0.5}O_2$ thin film electrodes were grown on Au substrates by pulsed laser deposition (PLD) and post-annealed. The annealed films exhibit a pure layered phase with a high degree of crystallinity. Surface morphology and thin film thickness were investigated by field emission scanning electron microscopy (FESEM). The charge/discharge behavior and rate capability of the thin film electrodes were investigated on $Li/LiNi_{0.5}Mn_{0.5}O_2$ cells at different current densities. The kinetics of Li diffusion in these thin film electrodes were investigated by cyclic voltammetry (CV) and galvanostatic intermittent titration technique (GITT). CV was measured between 2.5 and 4.5 V at different scan rates from 0.1 to 2 mV/s. The apparent chemical diffusion coefficients of Li in the thin film electrode were calculated to be 3.13×10^{-13} cm^2/s for Li intercalation and 7.44×10^{-14} cm^2/s for Li deintercalation. The chemical diffusion coefficients of Li in the thin film electrode were determined to be in the range of 10^{-12}–10^{-16} cm^2/s at different cell potentials by GITT. It is found that the Li diffusivity is highly dependent on the cell potential.

1. Introduction

Although $LiCoO_2$ has been most widely used as cathode materials for lithium-ion batteries for the last 20 years, its high cost, toxicity and safety issues limit its further application in large scale batteries for power tools and hybrid cars which require high energy and power densities. Next-generation lithium-ion batteries are critically dependent on new lithium intercalation compounds that can store more energy and deliver it at higher powers than $LiCoO_2$, while being safer and cheaper. Recently, layered di- and tri-transition metal oxides with less or without Co have been extensively studied as potential cathode materials to replace $LiCoO_2$ [1–4]. Among these compounds, $LiNi_{0.5}Mn_{0.5}O_2$ is particularly interesting due to its low cost, improved safety and much larger reversible capacity compared to $LiCoO_2$ [1,2]. $LiNi_{0.5}Mn_{0.5}O_2$ is fundamentally different from $LiCoO_2$, in which only half of total Li can be deintercalated and intercalated corresponding to a capacity of about 140 mAh/g since removal of all Li from the $LiCoO_2$ lattice will lead to an unstable structure containing highly oxidized Co^{4+} ions [5]. In $LiNi_{0.5}Mn_{0.5}O_2$, Ni^{2+} acts as a double redox-active center while Mn^{4+} provides stability to the host structure. It was shown by Ohzuku and Makimura that $Li/LiNi_{0.5}Mn_{0.5}O_2$ cells could store about 200 mAh/g capacity in the potential range from 2.5 to 4.5 V at room temperature [2]. Unfortunately, this high reversible capacity can only be achieved at very slow charge/discharge current densities. This limited rate performance is attributed to the existence of Ni in the Li layer [6]. As shown in Fig. 1a, the well-ordered layer structure of $LiNi_{0.5}Mn_{0.5}O_2$ consists of layers of transition metal (TM = Ni and Mn) separated from Li layers by oxygen. Li ions are easy to move in this two dimensional diffusion channels between the strongly bonded TMO_2 layers. However, in all $LiNi_{0.5}Mn_{0.5}O_2$ synthesized by far, a large degree of cation disorder could always be found. As shown in Fig. 1b, in the less ordered layer structure of $LiNi_{0.5}Mn_{0.5}O_2$, a considerable amount of Li and Ni is exchanged between the Li layers and TM layers due to the similar size of Li^+ and Ni^{2+}. The introduction of Ni in the Li layers not only blocks the Li diffusion channels but also attract the neighboring TMO_2 layers, thus lowering the Li mobility [6]. Therefore, the rate performance of this material is highly dependent on the degree of Li/Ni intermixing. Several methods, such as introduction of Co ions in the TM layers [7], introduction of excess Li in the TM layers [8], and using molten salt synthesis route [6], have been developed to suppress the extent of Li/Ni intermixing in the layered $LiNi_{0.5}Mn_{0.5}O_2$ to improve the rate performance.

Studying of the kinetic parameters which control the rate performance of the Li intercalation electrodes is crucial for their optimization in lithium-ion batteries. Li diffusion in the electrodes is a key factor that determines the rate at which a battery can be charged and discharged. With increasing interest in high power

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doi:10.1016/j.electacta.2009.02.071

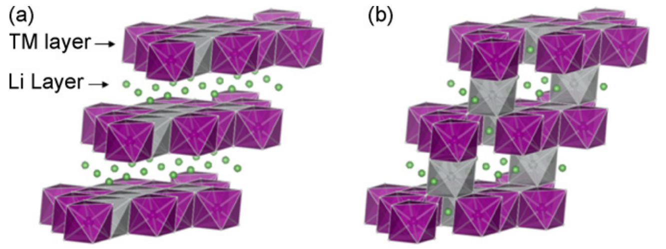

Fig. 1. (a) Ideal ordered layered structure of $LiNi_{0.5}Mn_{0.5}O_2$ without Li/Ni intermixing, and (b) less ordered layered structure of $LiNi_{0.5}Mn_{0.5}O_2$ with a high degree of Li/Ni intermixing.

density, the kinetics of Li diffusion in intercalation electrodes has become an important topic. However, for $LiNi_{0.5}Mn_{0.5}O_2$ electrodes, only few studies about Li diffusion in this material have been carried out on the composite electrodes, consisting of the active material, carbon black and binder [9,10]. Due to many variables involved, it is difficult to reveal the intrinsic properties of the active material. Thin film electrodes are ideal samples for studying the intrinsic properties of electrode materials due to their well-defined geometries and pure active materials. Therefore, a study of Li intercalation/deintercation rates together with the determination of the Li diffusivity using the $LiNi_{0.5}Mn_{0.5}O_2$ thin film electrode would provide more insights into the material's performance.

To evaluate the solid-state diffusion coefficient of Li ion in various Li insertion anodes and cathodes, four major electroanalytical techniques, SSCV, PITT, GITT and EIS, are frequently employed. As discussed by Levi and Aurbach [11], these four major electroanalytical techniques can be divided into two groups: (1) large-amplitude techniques (CV), and (2) small-amplitude techniques (differential techniques, PITT, GITT, EIS). As shown in the above mentioned review paper, the characteristic time-invariant functions for these four techniques have been defined, and the diffusion time constant can be presented as a combination of one of these functions with the differential intercalation capacity. In this way, all the time-invariant functions are connected, thus demonstrating correlation between these techniques [11].

In this work, layered $LiNi_{0.5}Mn_{0.5}O_2$ thin films are prepared by pulsed laser deposition (PLD) on Au substrate. Galvanostatic static charge/discharge measurements were performed on the $Li/LiNi_{0.5}Mn_{0.5}O_2$ cells at different current densities. Li diffusion in the $LiNi_{0.5}Mn_{0.5}O_2$ thin film electrodes was investigated by cyclic voltammetry (CV) and galvanostatic intermittent titration technique (GITT).

2. Experimental

$LiNi_{0.5}Mn_{0.5}O_2$ thin films were deposited on the Au substrates by PLD in a vacuum chamber at a base pressure less than 10^{-5} Torr. The target was prepared by sintering a mixture of LiOH (99%, Alfa Aeser), NiO and MnO_2 at 1000 °C in air for 12 h. To compensate the Li loss during the sintering and deposition, excess LiOH was added leading to a Li/(Ni + Mn) ratio of 1.5 in the mixture. A Lambada Physik KrF excimer laser with wavelength 248 nm was used in the deposition. The laser fluence and repletion rate were controlled at 2 J/cm^2 and at 10 Hz, respectively. The thin films were deposited at a substrate temperature of 550 °C with an oxygen partial pressure of 2 Torr. Post-annealing of thin films was conducted in the furnace with an oxygen flow at a temperature of 800 °C for 3 h.

Structure and crystallinity of the thin films were investigated using a Shimadzu XRD-6000 X-ray diffractometer (XRD) with Cu Kα radiation. Surface morphology of the thin films was characterized using a Hitachi S-4100 field emission scanning electron microscopy (FESEM). Thin film thickness was estimated from FESEM images of the cross-sections of thin films deposited on the SiO_2/Si substrate.

Electrochemical experiments were conducted using a Solartron 1287 cell test system. The Swagelok type cells consist of a Li-metal foil counter electrode, a $LiNi_{0.5}Mn_{0.5}O_2$ thin film working electrode with an active area of approximately 0.785 cm^2, and 1 M $LiPF_6$ in EC/DEC (1/1, vol%) as the electrolyte. Galvanostatic charge/discharge measurements were carried out in the potential range between 2.5 and 4.3 V with a constant current density (2–20 μA/cm^2). CV measurements were carried out in the potential range between 2.5 and 4.5 V at different scan rates from 0.1 to 2 mV/s. For the GITT measurements, the cells were charged at a current density of 15.7 μA/cm^2 for 200 s followed by an open circuit relaxation for 1 h.

3. Results and discussion

We have already shown that phase pure $LiNi_{0.5}Mn_{0.5}O_2$ thin films with layered structure can be prepared on the Au substrates by PLD [12]. Fig. 2 shows the XRD spectra of the pure $LiNi_{0.5}Mn_{0.5}O_2$ deposited on the Au substrate and of the target. The XRD spectrum of the target can be indexed based on the α-$NaFeO_2$ structure with space group R-3m. The existence of doublets at (0 0 6)/(1 0 2) and (1 0 8)/(1 1 0) clearly indicates the layered structure of the target. There is a strong (0 0 3) reflection peak from the $LiNi_{0.5}Mn_{0.5}O_2$ film can be observed. Other reflections such as (1 0 1), (1 0 4) and (1 1 0) are very weak or cannot be observed in the XRD spectrum due to the strong reflection peaks from the Au substrate.

Fig. 3 shows FESEM micrographs of the top view of the $LiNi_{0.5}Mn_{0.5}O_2$ film on the Au substrate and cross-sectional view of the $LiNi_{0.5}Mn_{0.5}O_2$ film on the SiO_2/Si substrate. The film is composed of dense grains with an average grain size of about 100–200 nm. The spherical shaped grains developed on the Au substrate are similar to those observed in the layered $LiCoO_2$ and $LiNi_{0.8}Co_{0.2}O_2$ films grown by PLD [13,14]. From the cross-sectional view of the film on the SiO_2/Si substrate, the film thickness is estimated to be about 500 nm.

Galvanostatic charge/discharge measurements were performed on the $Li/LiNi_{0.5}Mn_{0.5}O_2$ cells. Fig. 4a shows the typical charge/discharge curves of the $LiNi_{0.5}Mn_{0.5}O_2$ film in the potential range between 2.5 and 4.3 V at a constant current density of 2 μA/cm^2. Upon charge, the cell voltage steeply jumps to about 3.7 V then slowly increases to 4.3 V. Similar behavior can be observed for the discharge process. The charge/discharge behavior and the reversible capacity of the $LiNi_{0.5}Mn_{0.5}O_2$ film are in good agreement with those of composite electrodes in literature [1,2]. Fig. 4b

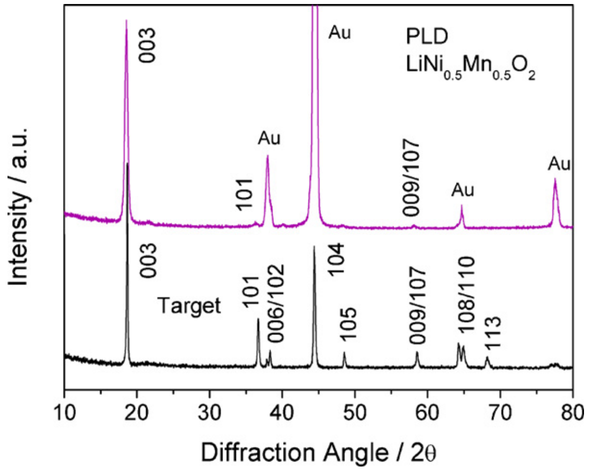

Fig. 2. XRD spectra of the $LiNi_{0.5}Mn_{0.5}O_2$ thin film and the $LiNi_{0.5}Mn_{0.5}O_2$ target.