Li-ion diffusion kinetics in LiFePO$_4$ thin film prepared by radio frequency magnetron sputtering

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ABSTRACT

LiFePO$_4$ thin films were prepared by radio frequency (RF) magnetron sputtering and were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM) and atomic force microscope (AFM). Li-ion chemical diffusion coefficients, $\tilde{D}_{Li}$, were measured by potentiostatic intermittent titration technique (PITT), electrochemical impedance spectroscopy (EIS), and cyclic voltammetry (CV). The effects of Ag content, film thickness, and film orientation on the electrochemical performance and Li-ion chemical diffusion coefficients of the LiFePO$_4$ thin films were investigated. $\tilde{D}_{Li}$ values were measured using the liquid electrolyte and the solid electrolyte, and the obtained values were discussed. The $\tilde{D}_{Li}$ values by PITT and EIS were in the range of 10^{-14} to 10^{-12} and 10^{-15} to 10^{-12} cm^2 s^{-1}, respectively and that by CV was in the order of 10^{-14} cm^2 s^{-1}.

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1. Introduction

Since first reported by Padhi et al. [1,2], olivine-type lithium iron phosphate, LiFePO$_4$, is of increasing interest as a candidate cathode material for Li-ion batteries from both economic and environmental points of view since iron is more abundant, cheaper, and less toxic than other transition metals. The main problem restricting the practical application of LiFePO$_4$ in Li-ion batteries is poor rate capability. It is conventionally accepted that the rate problem of LiFePO$_4$ material comes mainly from its low electronic conductivity and low lithium ion diffusion mobility. The first-principle calculations [3,4] and atomistic modeling techniques [5] showed that Li-ions diffuse in the LiFePO$_4$ lattice through one-dimensional channels. Although theoretical calculation showed that the intrinsic ionic diffusion rate is as high as 10^{-8} to 10^{-7} cm^2 s^{-1}, the one-dimensional channels are easy to be blocked by defects and impurities [3]. Recently, Sauvage et al. [6] and Delacourt et al. [7] inferred from the AC/DC studies that the ionic conductivity of pure LiFePO$_4$ is lower than its electronic conductivity. More recently, DC measurements on the single crystal LiFePO$_4$ showed that the performance of pure LiFePO$_4$ is limited by ionic conduction rather than electronic conduction [8,9].

Since the kinetics of Li-ion diffusion through LiFePO$_4$ plays an important role in its rate capability. It is, therefore, very important to determine the Li-ion chemical diffusion coefficients, $\tilde{D}_{Li}$, in order to clarify the intrinsic limiting factors of electrochemical performance. There was much literature on the determination of Li-ions chemical diffusion coefficients in LiCoO$_2$ and LiMn$_2$O$_4$. However, little is available on LiFePO$_4$. The $\tilde{D}_{Li}$ values reported by Prosini et al. [10] were in a wide range of 10^{-17} to 10^{-14} cm^2 s^{-1}, which were determined by galvanostatic intermittent titration technique (GITT) and electrochemical impedance spectroscopy (EIS) for the LiFePO$_4$/C composite electrode with a poly-tetra fluoro ethylene binder. However, the Li-ions diffusion kinetics have proved to be affected by the incorporation of carbon [11]. Compared with the LiFePO$_4$/C-binder composite electrodes, thin film electrodes seem to be more appropriate for the measurement of the chemical diffusion coefficient since it is conducting additive and binder free, and have a well-defined geometry and good contact with the current collector.

In our present work, LiFePO$_4$ thin films were prepared by radio frequency (RF) magnetron sputtering method. Li-ion chemical diffusion coefficients, $\tilde{D}_{Li}$, were measured by potentiostatic intermittent titration technique (PITT), EIS, and cyclic voltammetry (CV). The effects of the Ag additive, the film thickness, and the film orientation on $\tilde{D}_{Li}$ were investigated.

2. Experimental

The LiFePO$_4$ powder was prepared by solid-state reactions of stoichiometric Li$_2$CO$_3$, FeC$_2$O$_4$·2H$_2$O and (NH$_4$)$_2$HPO$_4$ at 700 °C for

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6 h in an Ar/H$_2$ mixture (2%H$_2$). LiFePO$_4$ thin films were deposited on the polished Al$_2$O$_3$ substrates (8 mm × 8 mm) by RF magnetron sputtering. Au was pre-deposited on the substrates by RF magnetron sputtering in pure Ar for 15 min as the current collector. For comparison, LiFePO$_4$ thin films were also deposited on the Au substrates and on the NASICON-type glass ceramics electrolyte plates (Li$_{1+x+y}$Al$_x$Ti$_{2-x}$Si$_y$P$_{3-y}$O$_{12}$ (LATSP)) (supplied by OHARA Inc., Japan), followed by Au sputtering as the current collector. The target (50 mm in diameter) used for sputtering was prepared by cold pressing the LiFePO$_4$ powder and the LiFePO$_4$ powders with 5 and 10 wt.% Ag. LiFePO$_4$ was sputtered for 1–3 h in pure Ar with a working pressure of 2 Pa. The power used for LiFePO$_4$ sputtering was 50 W, and the distance between the substrate and the target was 10 cm. Prior to LiFePO$_4$ sputtering, the target was pre-sputtered for 15 min under the same conditions in order to eliminate the impurities from the surface of the target. The as-prepared LiFePO$_4$ thin films were annealed at 700 °C (unless otherwise stated) for 1 h in the Ar/H$_2$ mixture (2%H$_2$) to improve crystallization. The crystal structure of the films was characterized by X-ray diffraction (XRD) using a RINT2000/PC diffractometer with Cu-K$_\alpha$ radiation. The surface and cross-sectional morphologies of the films were observed by scanning electron microscopy (SEM) using a Hitachi S-4000 and by atomic force microscope (AFM) using a Nanoscale Hybrid Microscope VN-8010. The composition of the thin films was determined by inductively coupled RF plasma (ICP) spectroscopy, using a Shimadzu ICPS-1000IV spectrometer.

Electrochemical measurements for the LiFePO$_4$ thin films were performed using three-electrode beaker cells. The cells were assembled in an Ar-filled glove box using Li foils as both the counter and the reference electrodes. The electrolyte used was 1 M LiClO$_4$ in a mixture of ethylene carbonate (EC)/diethylene carbonate (DEC) (1:1 in volume). Galvanostatic cycling of the cells was carried out at a current density of 1 µA between 3 and 4 V for three cycles before chemical diffusion coefficient measurements. CV was performed between 2.7 and 4.2 V at scan rates ranging from 0.1 to 20 mV s^{-1} using a Solartron 1287 electrochemical interface. For the PITT measurements, a potential step of 10 mV was applied and the current was recorded as a function of time. The procedure was repeated between 3.4 and 3.6 V. EIS measurements were conducted at various electrode potentials by applying an AC signal of 10 mV amplitude over the frequency range from 1 MHz to 1 mHz using a Solartron 1287 electrochemical interface combined with a Solartron 1260 frequency response analyzer. The electrochemical measurements were carried out at 20 °C.

3. Results and discussion

Fig. 1 shows the XRD patterns of the LiFePO$_4$ thin films deposited on Al$_2$O$_3$/Au substrates by RF magnetron sputtering for 3 h using the LiFePO$_4$ target containing 10 wt.% Ag. For comparison, the XRD patterns of the LiFePO$_4$ powder are also given in this figure. It is obvious that the peaks of the powder are dominated by the LiFePO$_4$ diffraction peaks, even though a small satellite can be seen at around 2θ = 30°. The origin of the small peak is unclear. It may be attributed to the formation of some iron phosphates. However, it should not exert obvious effect on the preparation of LiFePO$_4$ thin film since it is at a low content. Note that the LiFePO$_4$ thin film exhibits a (0 2 0) preferred orientation after annealing at 700 °C for 1 h. A (1 2 0) preferred orientation was also observed for the pulsed laser deposition (PLD) prepared LiFePO$_4$ thin film [6]. No Ag diffraction peaks can be observed, indicating low Ag content in the film. It is suggested that the Ag is in the form of neutral metal since the film was deposited and annealed under an inert atmosphere. It is also difficult for Ag$^+$ to substitute Li$^+$ or Fe^{2+} in the LiFePO$_4$ lattice because of the larger radius of Ag$^+$. It was found that the Ag in the LiFePO$_4$/Ag thin film deposited by PLD from a LiFePO$_4$/Ag target was also in a metal-
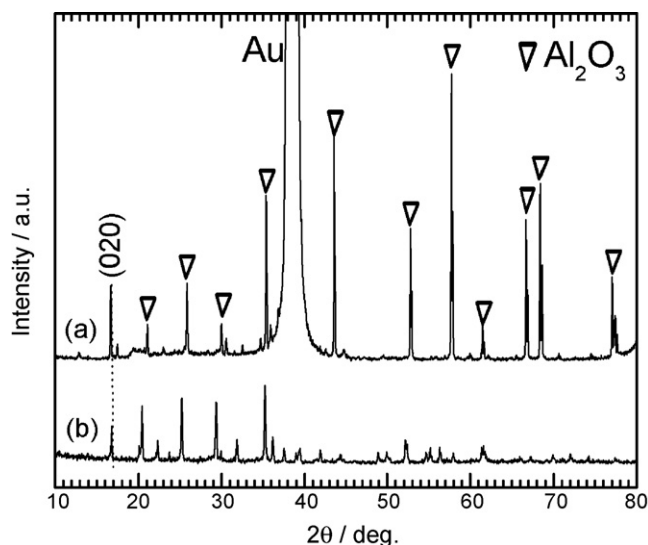

Fig. 1. XRD patterns of (a) LiFePO$_4$ thin films sputtered on Al$_2$O$_3$/Au using the LiFePO$_4$ target with 10 wt.% Ag for 3 h and (b) LiFePO$_4$ powder. The film was annealed at 700 °C for 1 h.

lic state [12]. The ICP results showed that the Ag contents in the LiFePO$_4$ thin film were 4.88 wt.% from the LiFePO$_4$ target with 5 wt.% Ag and 6.24 wt.% from that with 10 wt.% Ag target. The composition of the film is around Li$_{0.97}$FePO$_4$ as analyzed by ICP. Fig. 2 shows the XRD patterns of the LiFePO$_4$ thin films sputtered for 1 h on Au substrate from the target with 5 wt.% Ag. Note that before annealing the film is amorphous. Unlike that on the Al$_2$O$_3$/Au substrate, the film on Au substrate exhibits a random orientation when annealed under the same conditions. It is clear that the orientation of the film depends on the substrate used.

Fig. 3 shows the SEM and AFM images of LiFePO$_4$ thin film sputtered for 2 h on the Al$_2$O$_3$ substrate followed by annealed at 700 °C for 1 h using the target with 10 wt.% Ag. From Fig. 3(a) and (c), it is clear that the film is uniform and crack free. The film is also dense enough for the kinetics characterization as shown in Fig. 3(b). The thicknesses of the films after 1, 2 and 3 h sputtering are estimated to be about 0.4, 0.8 and 1.3 µm, respectively, from cross-sectional view of the film.
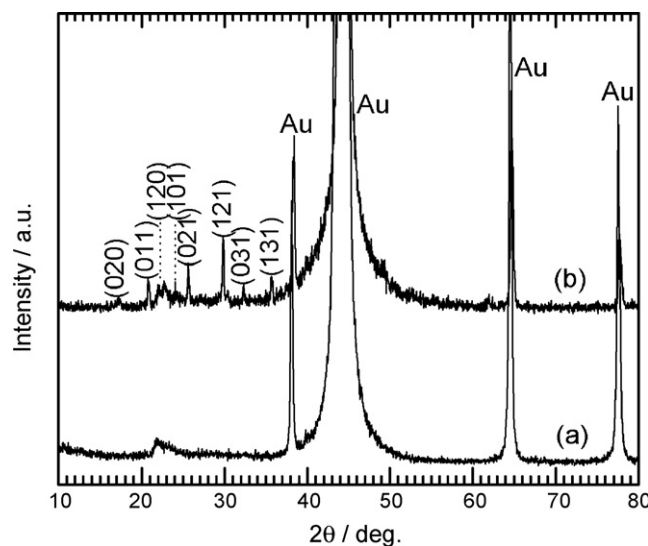

Fig. 2. XRD patterns of LiFePO$_4$ thin films sputtered on Au for 1 h using the LiFePO$_4$ target with 5 wt.% Ag: (a) As-deposited and (b) after annealing at 700 °C for 1 h.