Thin Solid Films 579 (2015) 81–88

Contents lists available at ScienceDirect

Thin Solid Films

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

# Fabrication of solid-state thin-film batteries using $LiMnPO_4$ thin films deposited by pulsed laser deposition

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ARTICLE INFO

*Article history:*
Received 9 March 2014
Received in revised form 15 January 2015
Accepted 13 February 2015
Available online 20 February 2015

*Keywords:*
Lithium manganese phosphate
All solid-state battery
Pulsed laser deposition
Chemical diffusion coefficient
Electronic conductivity
Olivine-type structure
Amorphous solid electrolyte

ABSTRACT

Solid-state thin-film batteries using $LiMnPO_4$ thin films as positive electrodes were fabricated and the electrochemical properties were characterized. The $LiMnPO_4$ thin films were deposited on Pt coated glass substrates by pulsed laser deposition. In-plane X-ray diffraction revealed that the $LiMnPO_4$ thin films were well crystallized and may have a texture with a (020) orientation. The deposition conditions were optimized; the substrate temperature was 600 °C and the argon pressure was 100 Pa. The electrochemical measurements indicate that the $LiMnPO_4$ films show charge and discharge peaks at 4.3 V and 4.1 V, respectively. The electrical conductivity of the $LiMnPO_4$ film was measured by impedance spectroscopy to be $2 \times 10^{-11}$ S cm$^{-1}$ at room temperature. The solid-state thin-film batteries that show excellent cycle stability were fabricated using the $LiMnPO_4$ thin film. Moreover, the chemical diffusion of the $LiMnPO_4$ thin film was studied by cyclic voltammetry. The chemical diffusion coefficient of the $LiMnPO_4$ thin film is estimated to be $3.0 \times 10^{-17}$ cm$^2$ s$^{-1}$, which is approximately four orders magnitude smaller than the $LiFePO_4$ thin films, and the capacity of the thin-film battery was gradually increased for 500 cycles.



## 1. Introduction

The olivine-type $LiMPO_4$ (M = Fe, Mn, Co) proposed by Padhi et al. [1] has been demonstrated to be a promising cathode material for rechargeable Li batteries. Among the olivine-type materials, $LiMnPO_4$ has attracted attention because it has a higher working potential (4.1 V vs. Li/Li$^+$) than $LiFePO_4$ [2,3]. Unfortunately, the rate performance of the olivine-type $LiMnPO_4$ is limited by its poor electronic conductivity [4,5]. Although carbon coating [6,7] and particle size reduction [8–10] have been demonstrated as effective strategies, further understanding of the intrinsic transport properties of $LiMnPO_4$ is required to reveal the factors that predominate the electrochemical properties. Thin-film electrodes are of great interest because they can serve as a simplified model to understand the electrochemical process of active materials [11]. Well-defined thin films are suitable for fundamental research since no binder and conductive additives are included. Moreover, thin-film cathode materials are also essential for all solid-state thin-film batteries (TFBs) [12–15]. Thin-film rechargeable Li batteries have numerous possible applications such as implantable medical devices, remote sensors, and smart cards [16–18].

Numerous studies on the growth of olivine $LiFePO_4$ thin films by radio-frequency (RF) magnetron sputtering [19,20,21], ion beam sputtering [22], pulsed laser deposition (PLD) [23–30], and electrostatic spray deposition (ESD) [31] have been reported. The $LiCoPO_4$ thin films have also been grown by RF magnetron sputtering [32–34], ESD [35], and a sol–gel method [36]. However, very few studies on $LiMnPO_4$ thin films have been reported, possibly due to the difficulty of structure and composition control. Ma and Qin [31] have authored the report on $LiMnPO_4$ thin-films, in which they have reported the application of ESD combined with a sol–gel method. The films were deposited on a stainless steel substrate and then post-annealed at 600 °C to obtain crystalline $LiMnPO_4$. The charge and discharge characteristics were confirmed using liquid electrolytes. The reversible capacity was less than 8 mAh g$^{-1}$, which is 5% of the theoretical capacity; however, fabrication of solid-state TFBs using $LiMnPO_4$ films has not been reported. ESD films usually have rough surface morphologies, which may cause short-circuit problems in the battery. Thus, physical vapor deposition techniques are preferred to obtain a dense film with uniform thickness.

In this paper, we report the deposition of carbon-free $LiMnPO_4$ thin films on Pt coated $SiO_2$ glass substrates using a pulsed laser deposition (PLD) technique. One of the most important characteristics in PLD is the ability to realize stoichiometric transfer of ablated material from multi-component targets. This arises from the non-equilibrium nature of the laser ablation process due to absorption of high laser energy density by a small volume of a target material. Since the $LiMnPO_4$ is a multicomponent oxide, PLD is suitable technique for thin-film deposition. Another advantage of PLD is the ability to operate with various background

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http://dx.doi.org/10.1016/j.tsf.2015.02.041

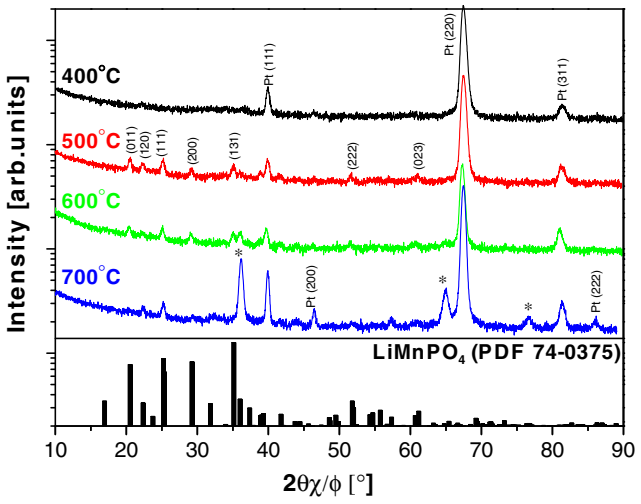


**Fig. 1.** In-plane X-ray diffraction patterns for $LiMnPO_4$ thin films deposited at substrate temperatures of 400, 500, 600, and 700 °C at 100 Pa Ar pressure. Asterisk (*) shows peaks probably due to manganese oxide.

pressures of gases. Actually, the $LiMnPO_4$ thin films were sensitive to the process gases and the pressure, which were optimized to obtain the best electrochemical properties. The crystal structure, lattice vibration, surface morphology, and electrochemical performance of the $LiMnPO_4$ thin films were characterized. The solid–solid interface between the electrodes and the solid electrolyte is essential for the solid-state battery. A good contact between cathode and solid electrolyte is achieved by sequential PLD process using exchanging different target materials [37]. All solid-state TFBs were fabricated using the $LiMnPO_4$ film as the positive electrode. The TFBs were tested between 3.5 and 4.5 V vs. $Li/Li^+$, and demonstrated excellent cycle performance for 500 cycles.

## 2. Experimental details

The $LiMnPO_4$ powder was prepared by hydrothermal reaction at 150 °C for 12 h. The starting chemicals were lithium hydroxide monohydrate ($LiOH \cdot H_2O$), manganese acetate tetrahydrate ($Mn(CH_3COO)_2 \cdot 4H_2O$), and ammonium dihydrogen phosphate ($NH_4H_2PO_4$). The chemicals were placed into an autoclave with distilled water. The molar ratio of Mn and $H_2O$ was 1:15, and the molar ratio of Li, Mn, and P in the precursor solution was set to 1.75:1.0:1.1. The $LiMnPO_4$ powder was ground by wet ball-milling with ethanol and then pressed into 1.66-mm-thick pellets with a diameter of 20 mm using a hydrostatic press. The pellet was then sintered at 800 °C for 10 h in Ar atmosphere. The relative density of the target was 97% of the theoretical density (3.44 g $cm^{-3}$) of $LiMnPO_4$. The composition ratio of the target was Li:Mn:P = 1.02:1.0:0.97 measured by inductive coupled plasma–optical emission spectrometry (ICP-OES, Perkin Elmer Optima 3300XL).

$LiMnPO_4$ thin films were grown on $Pt/Cr/SiO_2$ substrates (Sendai Sekiei Glass) by PLD. The fourth harmonic of a Nd:YAG laser (Spectra-Physics, LAB-150) was used with laser energy of 1.58 J $cm^{-2}$. The working pressure of Ar gas was fixed between 2 and 100 Pa after evacuating the chamber to $2 \times 10^{-4}$ Pa, and the substrate temperature was set to 400, 500, 600, and 700 °C. The crystal structure of the $LiMnPO_4$ thin films was characterized by X-ray diffraction (XRD, Rigaku, SmartLab 90TF) using Cu $K_\alpha$ radiation, and in-plane measurements with $2\theta\chi/\phi$ geometry were used. The lattice vibration of the film was analyzed by Fourier transform infrared (FTIR) spectroscopy (Perkin-Elmer, Spectrum GX). The FTIR spectra were measured by an attenuated total reflectance method. The surface morphology of the thin-films was observed by a field emission scanning electron microscope (FE-SEM, Hitachi S-4800). The operating voltage of the FE-SEM was 2.0 kV. The composition ratio of the $LiMnPO_4$ thin film was measured by ICP-OES analysis. The $LiMnPO_4$ film was dissolved with aqua regia. Reference solutions were made by diluting the Li, Mn and P standard solutions (Wako Pure Chemical).

The electrochemical properties of the $LiMnPO_4$ thin films were evaluated by cyclic voltammetry (CV) using a potentiostat (Bio-Logic, SP-150). A three-electrode cell was assembled in an Ar filled grove box using $LiMnPO_4$ thin films as the positive electrode. Lithium metal was used for the counter and reference electrodes, and 1 mol $L^{-1}$ of $LiPF_6$ was dissolved in ethylene carbonate–dimethyl carbonate (1:1 vol, Kishida Chemical) as the liquid electrolyte. The area of the $LiMnPO_4$ film was 0.56 $cm^2$, and the average thickness of the film was ca. 50 nm. The cell was tested by CV measurement in the range of 3.5–4.4 V vs. $Li/Li^+$ with a scan rate of 20 mV $min^{-1}$.

All solid-state TFBs, which consisted of $Li/Li_3PO_4/LiMnPO_4$, were deposited on a $Pt/Cr/SiO_2$ substrate. The conditions under which the $LiMnPO_4$ layer was deposited onto the $Pt/Cr/SiO_2$ substrate were 600 °C substrate temperature in Ar atmosphere of 100 Pa for 1 h using Nd:YAG laser. The amorphous $Li_3PO_4$ solid electrolyte was deposited at room temperature in $O_2$ atmosphere at 0.2 Pa for 3 h using an ArF excimer laser, and the Li film was deposited by thermal evaporation. Details of the $Li_3PO_4$ and Li depositions have been reported in a previous

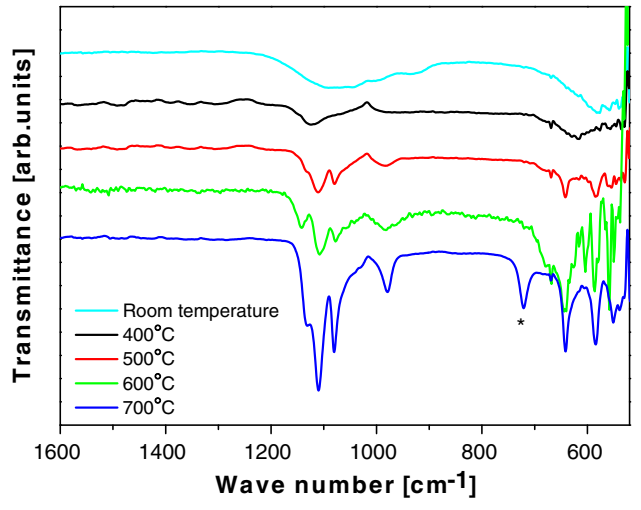


**Fig. 2.** FTIR spectra for $LiMnPO_4$ thin films at different substrate temperatures at 100 Pa Ar pressure. Asterisk (*) shows a peak from manganese oxide.

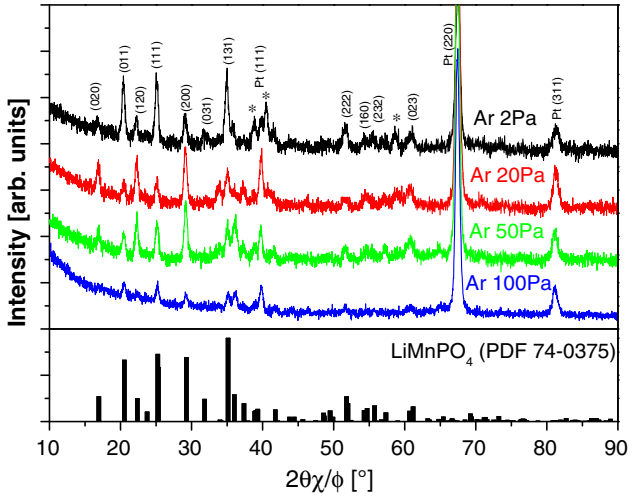


**Fig. 3.** In-plane X-ray diffraction patterns for $LiMnPO_4$ thin films under different atmospheric pressures at a substrate temperature of 600 °C. Asterisk (*) shows peaks probably due to manganese oxide.