



# Thin-film lithium batteries with 0.3–30 $\mu\text{m}$ thick $\text{LiCoO}_2$ films fabricated by high-rate pulsed laser deposition

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## ABSTRACT

High-rate pulsed laser deposition was applied to the preparation of thick  $\text{LiCoO}_2$  cathode films, which were then used in the fabrication of thin-film batteries. The deposition rate of the  $\text{LiCoO}_2$  films was 2–3  $\mu\text{m}/\text{h}$ . The thin-film batteries showed an increase in capacity up to 470  $\mu\text{Ah}/\text{cm}^2$  with increasing cathode film thickness. The rate dependence of discharge capacity was analyzed using a diffusion model in which the chemical diffusion coefficient of lithium in the cathode determines the dynamic capacity. For the initial stage of discharge, the chemical diffusion coefficient was estimated to be  $10^{-10} \text{ cm}^2/\text{s}$ . Conversely, the chemical diffusion coefficient decreases to  $\sim 10^{-12} \text{ cm}^2/\text{s}$  at the end of discharge. From the diffusion model, the available capacity was estimated as a function of cathode thickness. Crack formation inside the  $\text{LiCoO}_2$  film is also suggested as a cause of capacity limitation.

## 1. Introduction

Recently, all solid state thin-film batteries are attracting a great attention, since it will be a key energy component of the micro IT devices such as micro sensors, radio frequency identification tags, smart cards and drug delivery systems [1–3]. A merit of the all-solid-state battery is its wide temperature stability owing to the lack of organic electrolyte solution in it, which solves the safety issues of the conventional lithium battery and also enables the devices operating in tough environments from North-Pole to Sahara desert and also it is adapted to the reflow process of soldering [4]. Moreover, it can be fabricated in any place like the back of the solar cells or even in a silicon LSI device by using thin-film battery technologies.

For this purpose, however it is necessary to store the sufficient energy for operating the device within a limited space. For example, an energy density of  $\sim 15 \text{ mWh}/\text{cm}^2$  is required for a backup power supply of a real-time-clock application. Considering the theoretical capacity of  $\text{LiCoO}_2$  ( $69 \mu\text{Ah}/\text{cm}^2 \cdot \mu\text{m}$ ) and the average voltage 4 V, the thickness of  $54 \mu\text{m}$  is required for this application, which is one or two orders thicker than the typical thin-film batteries under study.

A simple way to increase capacity per unit area is to increase the thickness of the active materials as cathode and anode, although which has a theoretical limit due to the diffusion length in the operating time. Since the chemical diffusion coefficient ( $\tilde{D}$ ) of  $\text{Li}_x\text{CoO}_2$  ( $0.5 < x < 0.75$ ) is typically  $10^{-9}$ – $10^{-11} \text{ cm}^2/\text{s}$  [5], and assuming a typical diffusion time of 10 h, the diffusion length ( $l = \sqrt{\tilde{D}t}$ ) is roughly

estimated to be 6–60  $\mu\text{m}$ . Therefore, if thicker  $\text{LiCoO}_2$  films can be prepared, the areal capacity of their corresponding thin-film batteries would be expected to increase up to the theoretical limit of  $\tilde{D}$ .

In spite of this theoretical possibility, only a few works are known on the fabrication of the thin-film batteries with the thicker cathode  $> 1 \mu\text{m}$ , since it takes rather long period to fabricate the cell. Previously, Dudney et al. reported the electrochemical properties of a thin-film battery containing a 4.2- $\mu\text{m}$ -thick  $\text{LiCoO}_2$  cathode, which was prepared by a radio frequency (RF) magnetron sputtering [5,6]. Furthermore, Sasaki et al. have recently reported an investigation into thin-film batteries fabricated with  $\text{LiCoO}_2$  cathodes of 10–20  $\mu\text{m}$  of thickness prepared using RF and direct current (DC) convolution sputtering [7]. Trask et al. also reported thin-film batteries containing a 10- $\mu\text{m}$ -thick  $\text{LiCoO}_2$  prepared by a pulsed-DC sputtering [8]. Typical techniques used to prepare electrodes for thin-film batteries are RF and electron cyclotron resonance (ECR) magnetron sputtering [5,6,9–20]. However, our group has previously reported the preparation of thin-film batteries using pulsed laser deposition (PLD) [21–25]. Usually, the PLD technique is believed rather slow and employed to the preparation of high quality films as epitaxial ones [26]. However, recent development of high-energy and fast-repetition laser as well as the laser-scan PLD system enables to realize high-rate deposition of oxide films such as YBCO [27] and titanium carbonitride [28].

In the present study, a high-power, fast-repetition excimer laser is used to deposit both  $\text{LiCoO}_2$  film and solid electrolyte amorphous  $\text{a-Li}_3\text{PO}_4$  films. The  $\text{LiCoO}_2$  film thicknesses were varied in the range

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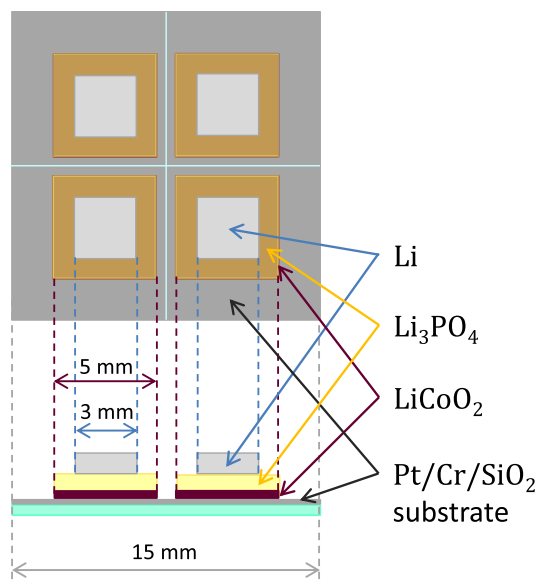


Fig. 1. Schematic representation of Li/Li<sub>3</sub>PO<sub>4</sub>/LiCoO<sub>2</sub> thin-film batteries on Pt/Cr/SiO<sub>2</sub> substrates.

0.3–30  $\mu\text{m}$ , which is close to the available limit calculated using the chemical diffusion coefficient of Li<sub>x</sub>CoO<sub>2</sub>. The structure of the LiCoO<sub>2</sub> films and the electrochemical properties of their corresponding thin-film batteries were investigated.

## 2. Experimental

### 2.1. Thin-film battery fabrication

Thin-film batteries consisting of LiCoO<sub>2</sub> films as a cathode, a-Li<sub>3</sub>PO<sub>4</sub> films as a solid electrolyte, and Li films as an anode (Li/Li<sub>3</sub>PO<sub>4</sub>/LiCoO<sub>2</sub>) were fabricated on SiO<sub>2</sub> substrates, where the Pt and Cr films were deposited as a current collector on the SiO<sub>2</sub> substrates (Pt/Cr/SiO<sub>2</sub>). Fig. 1 shows a schematic of Li/Li<sub>3</sub>PO<sub>4</sub>/LiCoO<sub>2</sub> thin-film batteries. The LiCoO<sub>2</sub> and Li<sub>3</sub>PO<sub>4</sub> films were deposited by PLD using an ArF excimer laser (Coherent, COMPexPro 205) with 193 nm wavelength. The laser power of 300 mJ and repetition frequency of 50 Hz were used. A Li<sub>1.2</sub>CoO<sub>2</sub> and Li<sub>3</sub>PO<sub>4</sub> targets of 25.4 mm diameter and 3 mm thickness were purchased from TOSHIMA Manufacturing Co., Ltd. The LiCoO<sub>2</sub> film was deposited on the substrate which was heated by a heater at 600 °C and the oxygen atmosphere pressure was 20 Pa. To prevent the exfoliation, initially the LiCoO<sub>2</sub> layer was deposited with repetition frequency of 10 Hz for 10 min. Without the buffer layer, LiCoO<sub>2</sub> film with thickness over 1  $\mu\text{m}$  was easy to exfoliate from the substrate after

the Li<sub>3</sub>PO<sub>4</sub> film deposition. The amorphous a-Li<sub>3</sub>PO<sub>4</sub> film was deposited on the LiCoO<sub>2</sub> film by PLD which was grown at room temperature in an oxygen atmosphere at 0.2 Pa. The LiCoO<sub>2</sub> and Li<sub>3</sub>PO<sub>4</sub> films were prepared in the same vacuum chamber to prevent the formation of a possible resistive layer on the surface of the LiCoO<sub>2</sub> film. The metallic Li anode was deposited by vacuum thermal evaporation on the Li<sub>3</sub>PO<sub>4</sub> film. Further details are given in the literature [22,23]. The morphologies and thicknesses of the thin-film batteries were investigated by field-emission scanning electron microscopy (FE-SEM, SU6600, Hitachi). After the electrochemical tests, the cross sections of the thin-film batteries were observed by FE-SEM.

### 2.2. Characterization of the films

X-ray diffraction (XRD) patterns of LiCoO<sub>2</sub> films deposited on Pt/Cr/SiO<sub>2</sub> substrates were recorded using an X-ray diffractometer (Rigaku, RINT-2100V) using CuK $\alpha$  radiation. The 2 $\theta$  scan range was 10–90° at a scan rate of 2.0°/min. Raman spectra of the LiCoO<sub>2</sub> films were obtained using micro-Raman spectrometer (Tokyo Instruments, Inc., Nanofinder30). A semiconductor laser was used for excitation at  $\sim$ 2  $\mu\text{W}$  output power. The wavelength of the laser was 532 nm.

### 2.3. Electrochemical measurements

The thin-film batteries were characterized by cyclic voltammetry (CV) and constant current (CC) charge-discharge measurements. A thin-film battery was placed in a vacuum-tight vessel with electrical feed-through. The sample was kept under vacuum during the measurement by evacuating with a rotary pump. A potentio/galvanostat (BioLogic, SP-150) was used for the electrochemical tests. CV measurements were performed between 3.0 and 4.4 V at sweep rates from 0.03 to 1 mV/s. The constant current charge-discharge experiments were performed between 3.0 and 4.4 V at current densities from 1  $\mu\text{A}/\text{cm}^2$  to 1 mA/cm<sup>2</sup>.

## 3. Results and discussion

The deposition rates for the LiCoO<sub>2</sub> and Li<sub>3</sub>PO<sub>4</sub> films are summarized in Table 1. In the present high-rate PLD system, the deposition rate for LiCoO<sub>2</sub> reaches 2.2 to 3.4  $\mu\text{m}/\text{h}$ , which is 10- to 15-times higher than that of our previous PLD system (0.22  $\mu\text{m}/\text{h}$ ) [22], where the fourth harmonic of Nd: YAG laser ( $\lambda = 266$  nm) was used with 60 mJ and 10 Hz. The deposition rate for the a-Li<sub>3</sub>PO<sub>4</sub> solid electrolyte is  $\sim$ 5 to 7.2  $\mu\text{m}/\text{h}$ , which is 10- to 14-times higher than that of our previous system (0.5  $\mu\text{m}/\text{h}$ ) [22], where the ArF excimer laser was used with 150 mJ and 5 Hz.

LiCoO<sub>2</sub> has a high absorption coefficient in the ultraviolet range because its band edge is around 300 nm (4.13 eV) [29]. Thus, laser ablation is effective with both the 266 and 193 nm lasers. In contrast, high-quality a-Li<sub>3</sub>PO<sub>4</sub> thin films can only be deposited using the 193 nm

Table 1

Deposition rates for (a) the LiCoO<sub>2</sub> cathode and (b) the Li<sub>3</sub>PO<sub>4</sub> solid electrolyte for the thin-film batteries using the high-rate PLD system (ArF, 300 mJ, 50 Hz) and the previous PLD system (Nd: YAG, 60 mJ, 10 Hz and ArF, 150 mJ, 5 Hz).

Samples	Thickness	Laser	Laser power at the entrance of chamber	Laser fluence	Time	Rate
(a) LiCoO <sub>2</sub>						
TFB50	0.32 $\mu\text{m}$	ArF, 300 mJ, 50 Hz	110 $\pm$ 10 mJ	1.8 J/cm <sup>2</sup>	0.1 h	3.2 $\mu\text{m}/\text{h}$
TFB48	2.2 $\mu\text{m}$	ArF, 300 mJ, 50 Hz	83 $\pm$ 13 mJ	1.4 J/cm <sup>2</sup>	1 h	2.2 $\mu\text{m}/\text{h}$
TFB49	6.7 $\mu\text{m}$	ArF, 300 mJ, 50 Hz	82 $\pm$ 12 mJ	1.4 J/cm <sup>2</sup>	3 h	2.2 $\mu\text{m}/\text{h}$
TFB45	27 $\mu\text{m}$	ArF, 300 mJ, 50 Hz	94 $\pm$ 14 mJ	1.6 J/cm <sup>2</sup>	8 h	3.4 $\mu\text{m}/\text{h}$
TFB01	0.15 $\mu\text{m}$	Nd:YAG, 60 mJ, 10 Hz	N/A	4 J/cm <sup>2</sup>	0.67 h	0.22 $\mu\text{m}/\text{h}$ [22]
(b) Li <sub>3</sub> PO <sub>4</sub>						
TFB50	2.4 $\mu\text{m}$	ArF, 300 mJ, 50 Hz	110 $\pm$ 10 mJ	1.8 J/cm <sup>2</sup>	0.33 h	7.2 $\mu\text{m}/\text{h}$
TFB48	3.2 $\mu\text{m}$	ArF, 300 mJ, 50 Hz	81 $\pm$ 12 mJ	1.4 J/cm <sup>2</sup>	0.5 h	6.4 $\mu\text{m}/\text{h}$
TFB49	3.3 $\mu\text{m}$	ArF, 300 mJ, 50 Hz	79 $\pm$ 12 mJ	1.3 J/cm <sup>2</sup>	0.67 h	5.0 $\mu\text{m}/\text{h}$
TFB45	5.0 $\mu\text{m}$	ArF, 300 mJ, 50 Hz	92 $\pm$ 12 mJ	1.5 J/cm <sup>2</sup>	1 h	5.0 $\mu\text{m}/\text{h}$
TFB01	2.0 $\mu\text{m}$	ArF, 150 mJ, 5 Hz	N/A	5 J/cm <sup>2</sup>	4 h	0.5 $\mu\text{m}/\text{h}$ [22]

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