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Preparation of $LiMn_2O_4$ cathode thin films for thin film lithium secondary batteries by a mist CVD process

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ABSTRACT

$LiMn_2O_4$ cathode thin films for thin film lithium secondary batteries were prepared by using so-called the "mist CVD process", employing an aqueous solution of lithium acetate and manganese acetate, as the source of Li and Mn, respectively. The aqueous solution of starting materials was ultrasonically atomized to form mist particles, and mists were transferred by nitrogen gas to silica glass substrate to form thin films. FE-SEM observation revealed that thin films obtained by this process were dense and smooth, and thin films with a thickness of about 750 nm were obtained. The electrochemical cell with the thin films obtained by sintering at 700 °C exhibited a capacity of about 80 mAh/g, and the cell showed good cycling performance during 10 cycles.

1. Introduction

There is a rapidly growing need for all-solid-state thin-film lithium batteries as micropower sources for RF-IC tags, smart cards, medical devices, microelectric mechanical systems, wireless sensors, robots and so on [1]. For the fabrication of thin film batteries, physical vapor processes, such as sputtering and PVD process, have been used [1–8]. However, those physical vapor processes have some disadvantages such as usage of vacuum system or difficulty in control of chemical composition and large area coating. Thus, solution processes like sol–gel process have been proposed to prepare thin film electrode and electrolyte materials [9–12]. In the solution processes, large area and good quality, or nano-structured thin films can be prepared. In addition, chemical compositions of thin films can be easily controlled, and rather thick films are easily obtained in the solution processes. Thus, the solution process is very attractive for the development of thin film batteries. From the viewpoint of the load to the environment, an aqueous solution process is more favorable.

On the other hand, $LiMn_2O_4$ with spinel-type structure is one of the most attractive candidates to substitute commercial $LiCoO_2$ positive electrode, because spinel $LiMn_2O_4$, which has a theoretical charge storage capacity of 148 mAh/g, has the advantages of low-cost, environmental friendliness, and high abundance [13]. Thin films of $LiMn_2O_4$ have been prepared by several processes, such as pulsed laser deposition [8,14,15], RF magnetron sputtering [16,17], electrostatic spraying [18,19], and sol–gel process [20,21]. Solution processes such as electrostatic spraying and sol–gel process are very attractive for good control of the chemical composition. However, these processes often use organic solvents, and a process with aqueous solution is more favorable.

In the present study, $LiMn_2O_4$ thin films were prepared by using so called a "mist CVD process" [22,23]. In the mist CVD process, aqueous solution is used for the precursor solution. Aqueous solution of starting materials is ultrasonically atomized to form mist particles with a size of about 3 μm, and mists are transferred by a carrier gas to the substrate to form thin films. The mists were supplied onto a heated substrate through a linear shaped nozzle, and the substrate was scanned for the formation of thin films with a certain area. This process is similar to the ultrasonic spray pyrolysis, or ultrasonic spray deposition processes [24,25]. However, the configuration in the mist CVD process is believed to allow the formation of thin films with uniform thickness [22,23]. In addition, this process is operated at atmospheric conditions, and

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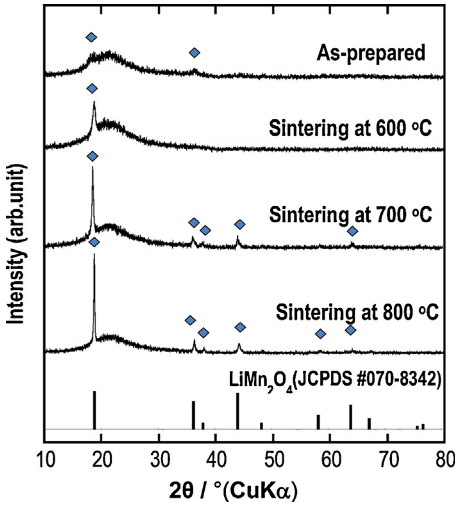

Fig. 1. XRD patterns of the as-prepared film with the substrate temperature of 200 °C, and that of the films obtained by the subsequent heat treatment at 600, 700 and 800 °C.

aqueous solutions can be used for the source. Thus, this process possesses advantages of safety, cost-effectiveness, light load to the environment, and multiplicity of applying to a lot of materials.

2. Experimental procedure

$LiMn_2O_4$ cathode thin films were prepared with the mist CVD process (equipments were provided by TOUKI Co. Ltd., Japan), employing the precursor solution of 0.033 M lithium acetate and 0.06 M manganese acetate, as the source of Li and Mn, respectively. Silica glass or Au-coated silica glass was used for substrates. The solution was ultrasonically atomized, and the aerosol particles were supplied onto a substrate through a linear shaped nozzle, using N_2 carrier gas at a flow rate of 8 L/min. The substrate was placed on a heating stage, and the temperature of the stage was 200 °C in the present study. The distance between the substrate and the nozzle is about 1 mm. The stage was scanned at a speed of 0.05 mm/s, and the scanning process was repeated for 8 times. Deposition time was about 30–40 min for 8 scans. The obtained thin films were further heat-treated at 600–800 °C for 1 h.

The film surface and cross section were examined using a field emission type scanning electron microscopy (FE-SEM, S-4500; Hitachi Ltd.). X-ray diffraction (XRD) patterns were recorded using an X-ray diffractometer (XRD-6000, Shimadzu) with Cu Kα radiation. The XRD patterns were measured in the $2\theta/\theta$ mode.

Electrochemical behavior of $LiMn_2O_4$ thin film prepared on Au/SiO_2 substrate was examined by a three electrode beaker cell using Li as the counter and reference electrodes, and 1 M $LiPF_6$/(EC-DEC) as liquid electrolyte.

3. Results and discussion

Fig. 1 presents XRD patterns of the as-prepared film with the substrate temperature of 200 °C, and that of the films obtained by the sintering of the as-prepared film at 600, 700 and 800 °C. The halo pattern observed in the all samples is background from the glass substrate. In the as-deposited film with substrate temperature of 200 °C, precipitation of $LiMn_2O_4$ with spinel structure was confirmed. The precursor in the mist must be thermally decomposed at 200 °C on the substrate, and the decomposition should result in the crystallization at this temperature in the present process. With a subsequent heat treatment up to 800 °C, the degree of crystallization in the films gradually increased with the increase of the sintering temperature. However, loss of lithium with a high temperature heat-treatment is often observed in lithium-containing oxides. Thus, the sample sintered at 700 °C was used for the electrochemical characterization.

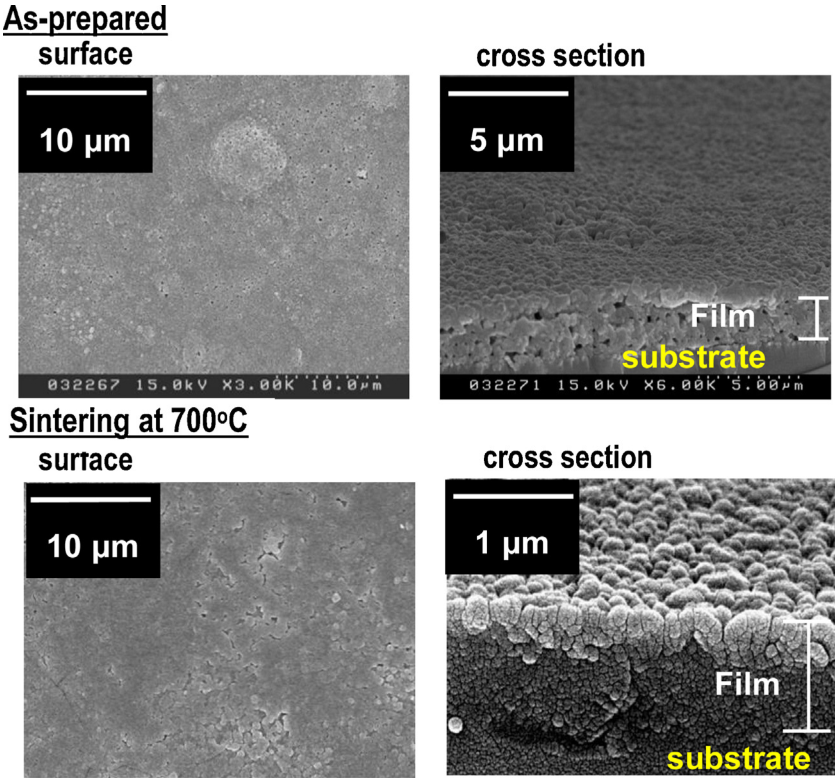

Fig. 2. FE-SEM images of the as-prepared film and heat-treated one at 700 °C.

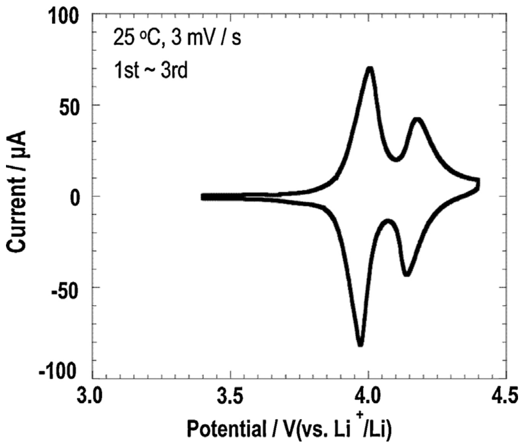

Fig. 3. Cyclic voltammogram recorded at a scan rate of 3 mV/s for the $LiMn_2O_4$ thin film heat-treated at 700 °C.

Fig. 2 portrays FE-SEM images of the as-prepared film and sintered one at 700 °C. FE-SEM observation revealed that the thin films were dense and smooth, and the grain size of the films was around 200–300 nm. Thickness of the as-prepared film was about 1 μm, and the thinness of the film was decreased to about 750 nm after sintering at 700 °C. However, no cracks were observed on the surface of the sintered thin film.

Fig. 3 portrays cyclic voltammogram recorded at a scan rate of 3 mV/s for the $LiMn_2O_4$ thin film heat-treated at 700 °C. The CV result proves that the prepared film can be electrochemically oxidized and reduced in the cell using 1 M $LiPF_6$/(EC-DEC) as an electrolyte. The CV consists of two pairs of symmetrical redox peaks, which are characteristic of the $LiMn_2O_4$ spinel during the two step intercalation/de-intercalation process: the first anodic and cathodic peaks at around 4 V correspond to Li ion extraction/ insertion between $LiMn_2O_4$ and $Li_{0.5}Mn_2O_4$, and the second anodic and cathodic peaks at around 4.15 V correspond to Li ion extraction between $Li_{0.5}Mn_2O_4$ and λ-MnO_2 [26].

Fig. 4 shows the charge–discharge curves of a cell using the $LiMn_2O_4$ thin film heat-treated at 700 °C, up to the 10th cycle. The current density employed in the present study was 0.05 mA/cm^2, and the cell was charged to 4.2 V, and discharged to 3.5 V. In the charge–discharge processes, typical plateaus at 4.15 V and 3.95 V (vs. Li^+/Li) for $LiMn_2O_4$ were observed, which are in agreement with the reduction potentials observed for the cyclic voltammogram. The initial discharge capacity was about 80 mAh/g, and the cell showed good cycling performance during 10 cycles. Discharge capacities of the thin films were rather small compared with the theoretical charge storage capacity [13]. Lack of crystallinity, or lithium content, or poor electron conductivity can be reason for the small capacity.

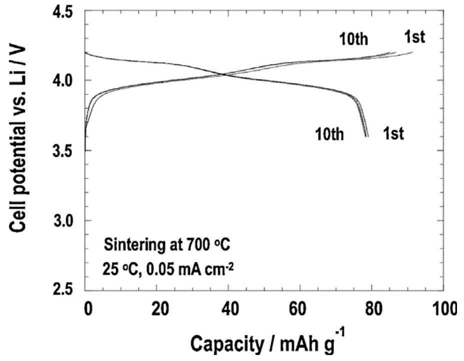

Fig. 4. Charge–discharge curves of a cell using the $LiMn_2O_4$ thin film heat-treated at 700 °C, up to the 10th cycle.

The mist-CVD process in the present study only uses an aqueous solution of lithium acetate and manganese acetate as a precursor solution. Since this process is very simple, and can be conducted under the ambient atmosphere, this process is expected to be easily applied for thin films of other cathode, anode and electrolyte materials for lithium batteries.

4. Conclusions

We demonstrated that $LiMn_2O_4$ thin films were prepared by using so called the “mist CVD process”, employing the aqueous solution of lithium acetate and manganese acetate, as the precursor solution. FE-SEM observation revealed that thin films obtained by this process were dense and smooth, and thin films with a thickness of about 750 nm were obtained. In the XRD measurement, precipitation of $LiMn_2O_4$ with spinel structure was confirmed in the as-deposited film with substrate temperature of 200 °C. With a subsequent heat treatment up to 800 °C, the crystallinity of the film was increased. The cell with the thin films obtained by sintering at 700 °C exhibited a capacity of about 80 mAh/g, and the cell showed good cycling performance during 10 cycles.

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