

Characterization of protective-layer-coated LiMn_2O_4 cathode thin films

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Abstract

We introduced a post-annealing process for the preparation of spinel-phase LiMn_2O_4 . The annealed films had proper crystallinity and surface roughness. In order to reduce the interface reaction during operation, we introduced a diamond-like carbon (DLC) film. The DLC films were deposited on LiMn_2O_4 films by using electron cyclotron resonance chemical vapor deposition (ECRCVD). A DLC-coated LiMn_2O_4 film was more stable during the charging–discharging reaction and showed higher discharge capacity over a wide voltage window than the uncoated LiMn_2O_4 film.

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Keywords: LiMn_2O_4 ; DLC; Protective layer; rf magnetron sputtering; Lithium microbattery

1. Introduction

During several decades, many researchers have achieved new materials and fabrication techniques of cathode thin films for microbatteries [1]. Among many materials, LiMn_2O_4 thin film is particularly interesting, since it can reversibly intercalate one Li ion per mole, without altering the λ - MnO_2 framework [2]. In general, to investigate electrochemical properties of cathode films, half-cell test were carried out using liquid electrolyte like 1 M LiPF_6 or LiClO_4 in organic solvent. In the case of LiMn_2O_4 , some problems such as liquid electrolyte decomposition [3] at high voltages and manganese ion dissolution during charging–discharging reaction are occurring [4]. In this study, in order to improve electrode properties in liquid electrolyte, a diamond-like carbon (DLC) film, which has high mechanical hardness and chemical stability [5], was deposited on the LiMn_2O_4 .

2. Experimental

LiMn_2O_4 thin films were deposited by using rf magnetron sputtering. The working pressure was maintained to 10 mTorr with a forming gas of Ar and O_2 . Pt coated Si(1 0 0) wafers were used as substrates. The deposited films were annealed by a horizontal tube furnace in air. The DLC films were deposited

by using the electron cyclotron resonance chemical vapor deposition (ECRCVD) system with a gas mixture of CH_4 and H_2 at room temperature. The thicknesses of the annealed films and the DLC films were measured by using a surface profile system. The crystal structure of the fabricated films was analyzed by XRD. XPS was used to determine the change of elemental distributions and the chemical compositions of the films before and after the post-plasma treatment. Surface roughness and morphologies of the films were measured by AFM and FESEM. For electrochemical analysis, half-cells were made with 1 M solution of LiPF_6 in ethylene carbonate (EC)–dimethyl carbonate (DMC) (1:1 (v/v)) as an electrolyte.

3. Results and discussion

To obtain spinel-type LiMn_2O_4 thin film, we introduced a post-annealing process. The peak intensity of (1 1 1) became stronger with increasing annealing temperature (Fig. 1). The annealed films had preferred orientations of (1 1 1) without other orientations of LiMn_2O_4 . This is the unique structural property of thin-film LiMn_2O_4 . The film annealed at 700 °C had small-sized particles and a flatter surface, comparatively (Fig. 2a). Because the growth of LiMn_2O_4 particles was insufficient, the peak intensity of (1 1 1) was weak. When annealing temperature was 750 °C, the annealed LiMn_2O_4 was consisted by the particles of similar size about 100 nm. When the annealing temperature was increased to 800 °C, some of the spinel-phase LiMn_2O_4 particles were larger than

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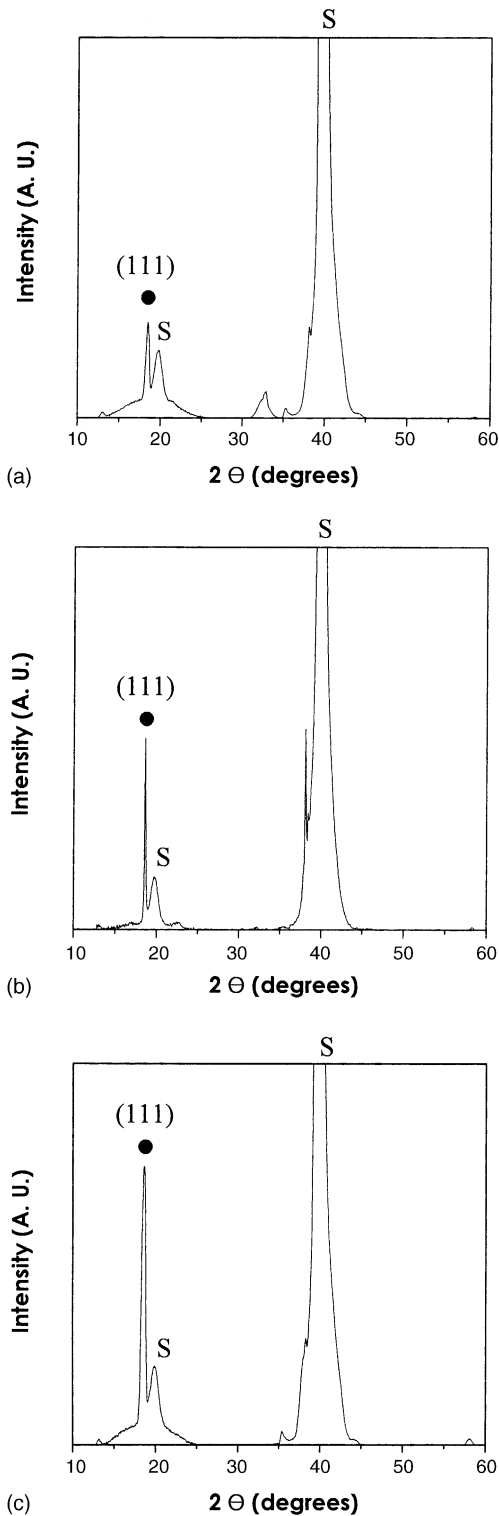


Fig. 1. XRD patterns of the LiMn_2O_4 films with various annealing temperatures: (a) 700 °C; (b) 750 °C; (c) 800 °C. The annealing time was 120 min ('S' denotes substrate).

300 nm in diameter and had a broad size distribution. When the particle size is too large, lithium ions do not intercalate into the particles completely and another phase is formed on the particle surface, so discharge capacity of cathode will be

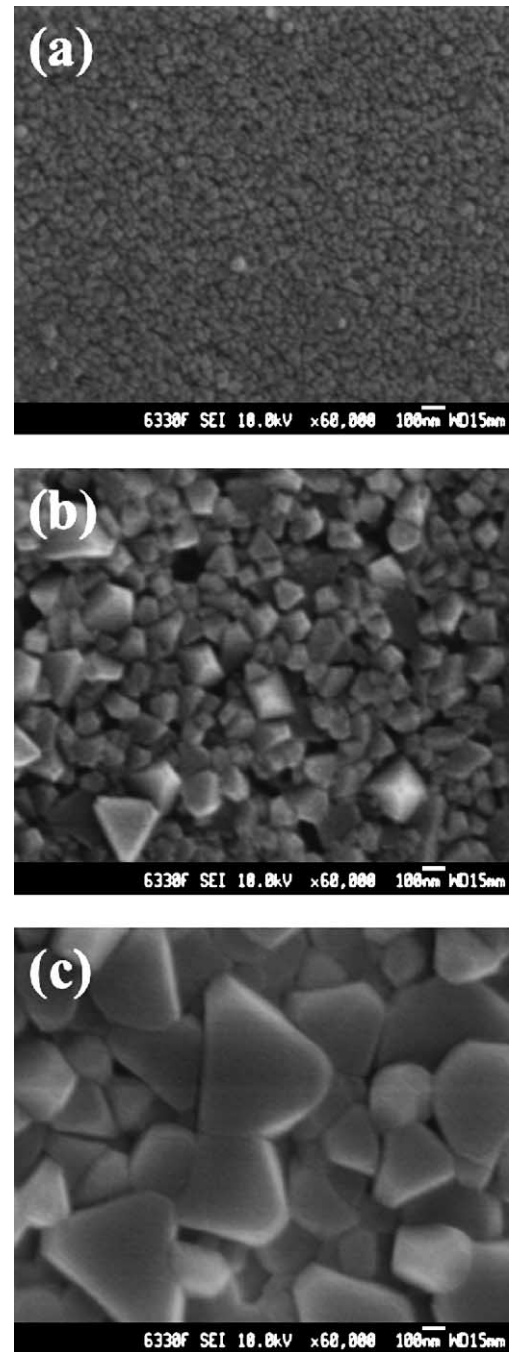


Fig. 2. FESEM images of the LiMn_2O_4 films with various annealing temperatures: (a) 700 °C; (b) 750 °C; (c) 800 °C. The annealing time was 120 min.

reduced [6]. This indicates that the film annealed at 750 °C is the optimized condition of the film for the proper particle size and the surface roughness.

To prevent the electrode–liquid electrolyte reaction, we deposited DLC film on the 750 °C-annealed film. Thicknesses of the DLC and LiMn_2O_4 films were about 60 and 200 nm, respectively. After the DLC film was deposited, the XPS peaks of O and Mn (Fig. 3a) disappeared and only the XPS peak of C from DLC was detected (Fig. 3b). And, after

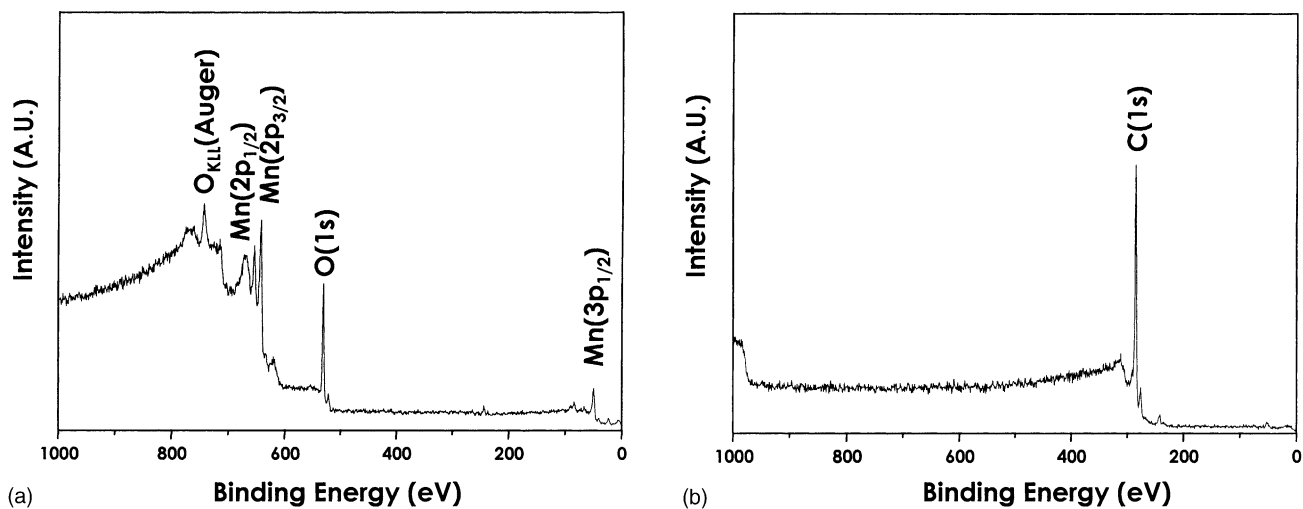
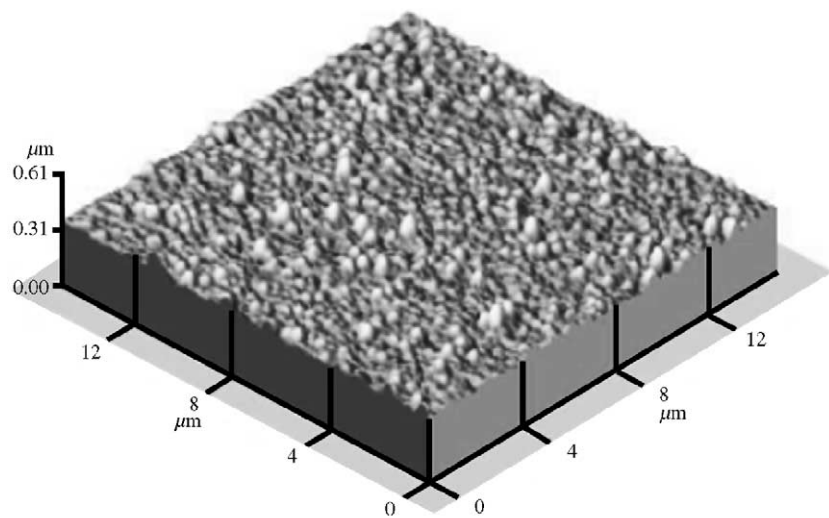
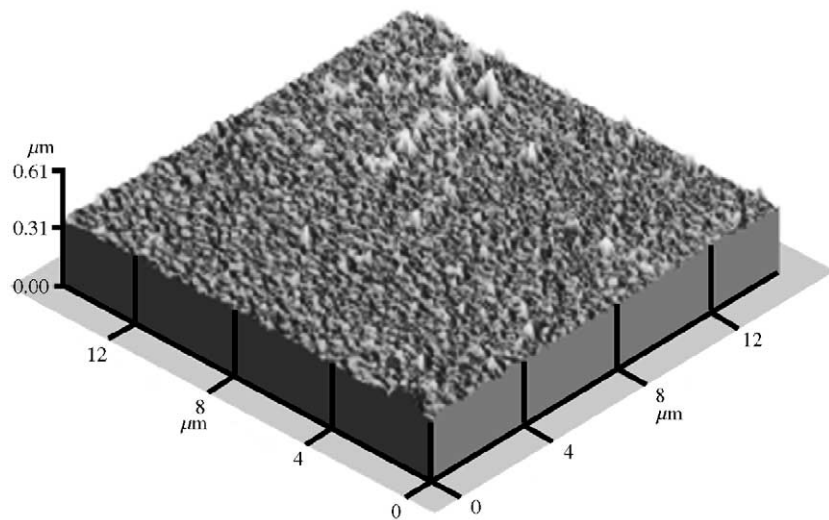


Fig. 3. XPS survey spectra of: (a) LiMn_2O_4 ; (b) DLC-coated LiMn_2O_4 .



(a) RMS Roughness : 157 \AA



(b) RMS Roughness : 117 \AA

Fig. 4. AFM images of: (a) LiMn_2O_4 ; (b) DLC-coated LiMn_2O_4 .

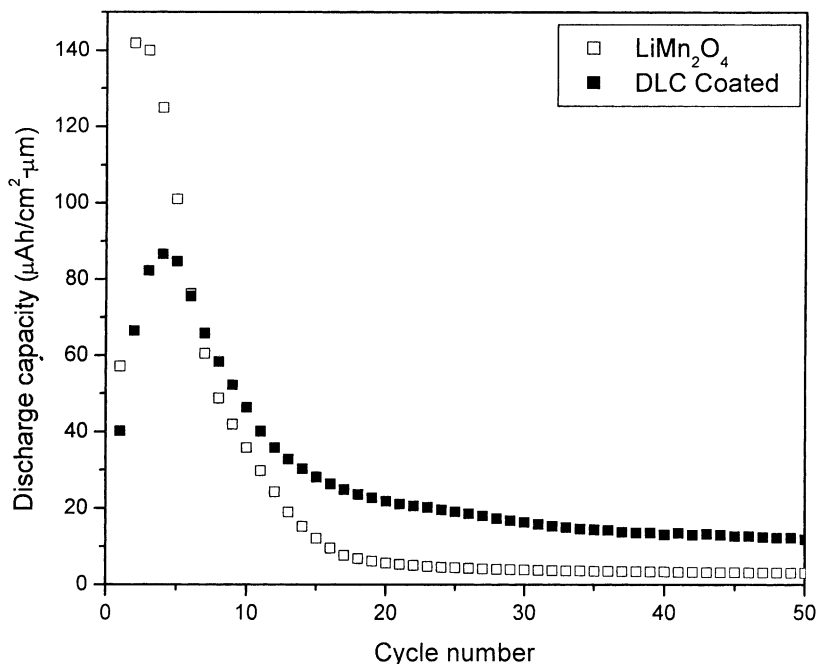


Fig. 5. Discharge capacity of the films (voltage window, 2.0–4.2 V; current density, 50 $\mu\text{A}/\text{cm}^2$).

the DLC film was coated on the cathode film, the surface roughness was reduced (Fig. 4). These results show the DLC film is deposited on the LiMn_2O_4 thin film completely and uniformly.

To investigate improvement of the electrochemical properties, we performed a half-cell test in a stressful environment such as wide voltage range (from 2.0 to 4.2 V) and high current density ($50 \mu\text{A}/\text{cm}^2$). In the case of both cathode films, the discharge capacity increased in the early cycles (Fig. 5). We guess that the excess lithium ions inserted in the pores of the thin film and/or plated on Pt current collector exposed to the liquid electrolyte. After the initial cycle stage, the discharge capacity decreased with increasing cycle number until reaching a constant value of capacity. In the DLC-coated LiMn_2O_4 film, the capacity fade rate was slower and the discharge capacity value at the 50th cycle was higher than the LiMn_2O_4 film. In our experiment, we could not prevent the irreversible phase transformation (Jahn-Teller distortion). However, the DLC film on cathode films prevent from Mn dissolution into the liquid electrolyte by prevention of the direct contact with electrolyte and electrode.

4. Conclusions

To improve the electrochemical stability of the spinel-phase LiMn_2O_4 films in the liquid electrolyte, the DLC films

were deposited on the cathode electrode films by ECRCVD. When half-cell tests were done with the DLC-coated LiMn_2O_4 film as the working electrode, the cyclability was improved and the capacity loss was reduced. This fact means that the DLC film prevents electrode–electrolyte reaction because the electrode cannot contact liquid electrolyte directly. We suggest that the DLC film as an electrode surface coating is one possible method of improving the cathode films.

Acknowledgements

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