

Electrochemical properties of diamond-like-carbon coated LiMn_2O_4 thin films for microbatteries

Hee-Soo Moon, Kwang-Sun Ji, Tae Jung Kim, Won-Il Cho^a, Young-Soo Yoon^a, Sung hoon Chung and Jong-Wan Park*
Division of Materials Science and Engineering, Hanyang University, 17 Haengdang-Dong, Seongdong-Ku, Seoul 133-791, Korea

^aKorea Institute of Science and Technology 39-1, Hawolok-Dong, Sungbuk-Ku, Seoul 136-791, Korea

There has been increasing interest in lithium rechargeable batteries, especially microbatteries, with the rapid development of portable electronic equipments and MEMS (Micro-Electro-Mechanical Systems) technology. In this study, lithium manganese oxide, which is a strong candidate for the battery material, is more abundant, stable in the ambient state and less toxic than the other oxides such as lithium nickel oxides and lithium cobalt oxides, was deposited by rf magnetron sputter. The effect of thermal treatment on the microstructure and electrode characteristics of the lithium manganese oxide cathode was investigated. In an electrochemical experiment using liquid electrolyte, half cell failure was caused by manganese dissolution, degradation of the electrolyte materials during charging/discharging process etc. In this research we focus on the interface reaction problem that would affect the cyclability and lifetime of the microbattery. In order to reduce the interface reaction during operation, we introduced a DLC (Diamond-like-Carbon) film that has high electrical resistivity, mechanical hardness and chemical stability. DLC films were deposited on sputtered lithium manganese oxide electrodes by ECRCVD (Electron Cyclotron Resonance Chemical Vapor Deposition). A DLC-top-layer 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.

Key words: Lithium rechargeable batteries, microbatteries, cathode, LiMn_2O_4 , rf magnetron sputtering.

Introduction

With the development of semiconductor technology and the demand for low power, battery-operated devices are on the rise, particularly in portable equipment requiring longer operation with higher reliability. Advances in the miniaturization of electronic devices and MEMS (Micro-Electro-Mechanical Systems) technology have reduced the current and power requirements of some of these devices to extremely low levels. This has made possible the use of thin film solid-state microbatteries as power sources for these devices. Therefore, it is important to develop long lasting and high-energy efficient thin film batteries that can be an integral part of MEMS. Over several decades, much research has been performed to achieve the 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 $\lambda\text{-MnO}_2$ framework [2, 3]. This system has a 4 V operating voltage versus a Li metal negative electrode and good electrochemical behavior is expected due to the favorable kinetics for fast Li ion diffusion through

the three dimensional channels of the $\lambda\text{-MnO}_2$ spinel structure. In general, to investigate electrochemical properties of cathode films a half-cell test method was employed using a liquid electrolyte such as 1 molar LiPF_6 or LiClO_4 in an organic solvent. In the case of LiMn_2O_4 , some problems such as liquid electrolyte decomposition [4] at high voltage and manganese ion dissolution [5] during the charging-discharging reaction occurred. These disadvantages cause problem with poor capacity of cathode film and suggest the need for further studies of the structure and electrochemical properties of this material in thin film form.

In this study, in order to improve the properties of the cathode film in liquid electrolyte diamond-like-carbon (DLC) films, which have high mechanical hardness and electrochemical stability [6], were deposited on sputtered LiMn_2O_4 by an electron cyclotron resonance chemical vapor deposition (ECRCVD) method. Furthermore, we investigated the effect of the DLC films on the electrochemical stability of the LiMn_2O_4 films.

Experimental

LiMn_2O_4 thin films were deposited by radio frequency magnetron sputtering. A 50 mm diameter LiMn_2O_4 target (99.97% purity) was purchased from Cerac. The chamber was evacuated to 6.7×10^{-4} Pa as a base pressure and the working pressure was maintained to

*Corresponding author:
Tel : +82-2-2290-0386
Fax: +82-2-2298-2850
E-mail: jwpark@hanyang.ac.kr

1.3 Pa with a forming gas of Ar and O₂. The RF power used during the process was 1.5 W/cm². Si wafers were used as substrates and Pt was deposited on it in thickness of 200 nm as a current collector by D.C. sputtering. The deposited films were annealed in a horizontal tube furnace. To achieve the spinel structure, the temperature range for post annealing was above 700°C. The DLC films were deposited by a ECRCVD system (AsTex Model AX4505) using a gas mixture of CH₄ and H₂. The microwave power and temperature during deposition were fixed at 500 W and room temperature. The fabricated film thickness was measured by alpha-step, and the film structure was analyzed by an X-Ray Diffractometer (XRD). X-ray Photoelectron Spectroscopy (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 of the film before and after heat treatment was measured by Atomic Force Microscopy (AFM). Surface morphologies of the films were obtained by Field Emission Scanning Electron Microscopy (FE-SEM). For electrochemical analysis, half cells were made with the lithium manganese oxide as cathode, the lithium metal as anode, separator and 1 molar solution of LiPF₆ in ethylene carbonate (EC) – dimethyl carbonate (DMC) (1 : 1 in volume) as electrolyte. Using a cycle tester, charge-discharge experiments were performed at various cut-off voltages and current densities.

Results and Discussion

XRD patterns and FE-SEM images of annealed films are shown in Fig. 1 and Fig. 2. To use LiMn₂O₄ thin films as positive electrode for lithium microbatteries, the structure of the deposited films must be the spinel-type LiMn₂O₄. Because deposited films were amorphous, films were annealed in a horizontal tube furnace in air. At an annealing time of 120 minutes, the spinel LiMn₂O₄ (111) plane peak occurred above 700°C and as the annealing temperature increased above 700°C (111), the plane peak intensity became stronger. As shown in Fig. 2a, the film annealed at 700°C had small-sized crystallites and a flat surface comparatively. In this low-annealing-temperature condition, the growth of LiMn₂O₄ crystallites was insufficient, so the XRD peak of (111) plane of LiMn₂O₄ was weak. When the annealing temperature was 750°C, the film consisted of crystallites of a similar size of about 100 nm. However, when the annealing temperature was increased to 800°C, the spinel LiMn₂O₄ crystallites enlarged to over 300 nm in diameter and this size was more irregular (Fig. 2c). When the crystallite size was too large, lithium ions did not intercalate into the crystallite completely and another phase was formed on the electrode surface, and so the electrode capacity was reduced. This indicates that the film annealed at 750°C is the condition for optimum crystallite size and surface

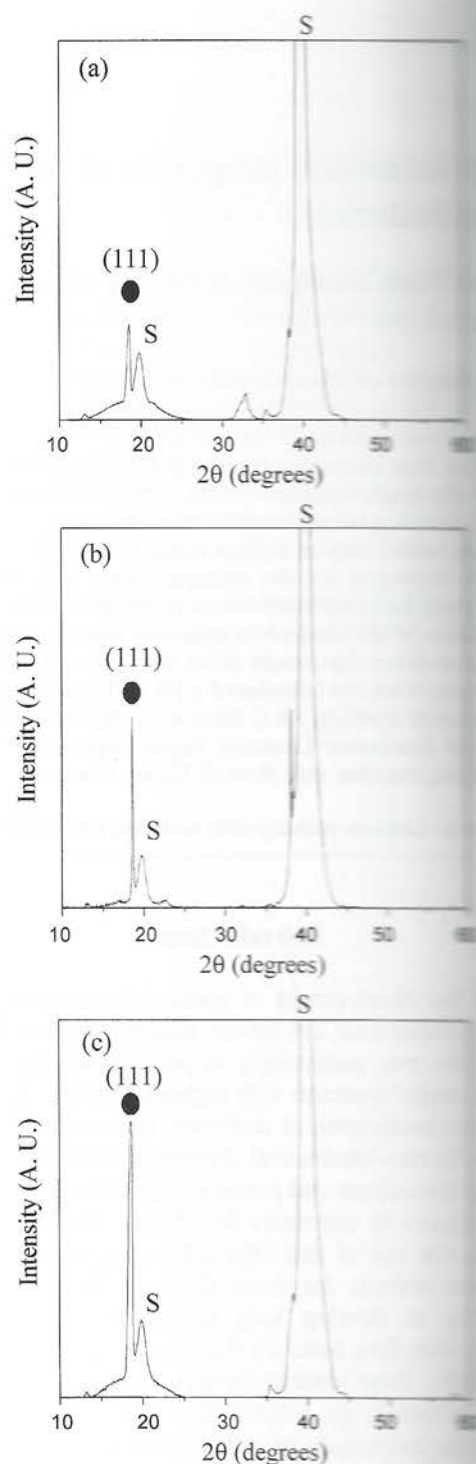


Fig. 1. XRD patterns of the LiMn₂O₄ films at various annealing temperatures (The annealing time was 120 minutes: (a) 700°C, (b) 750°C and (c) 800°C (S: substrate)).

roughness. To investigate the characteristics of LiMn₂O₄ thin films as a function of annealing conditions, the annealing temperature was held at 750°C and the annealing time was varied from 60 minutes to 240 minutes. Figure 3 shows XRD patterns of deposited films as a function of annealing time. As the annealing

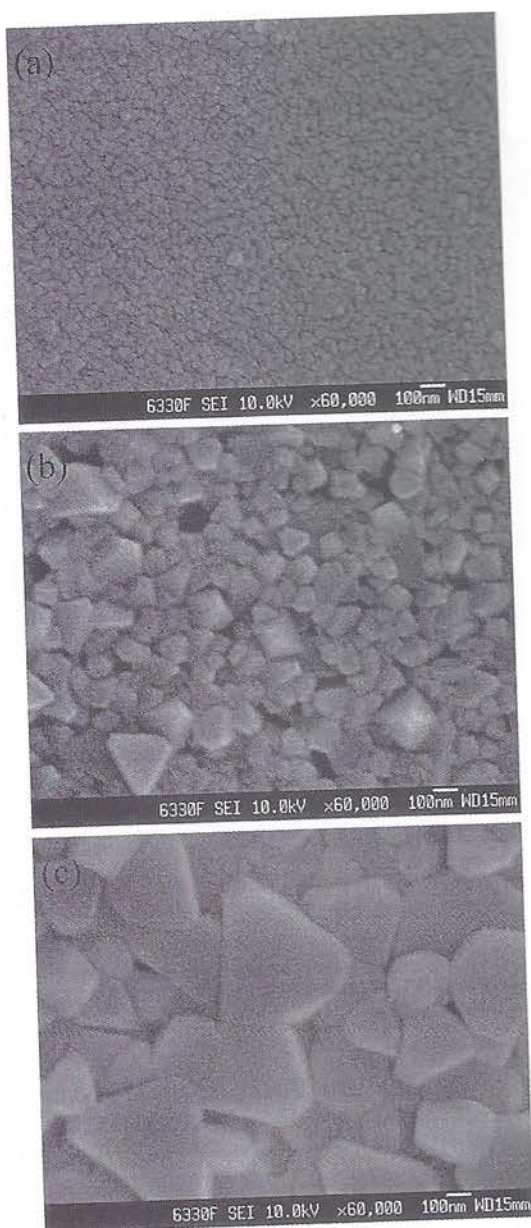


Fig. 2. FESEM images of the LiMn_2O_4 films at various annealing temperatures (The annealing time was 120 minutes); (a) 700°C, (b) 750°C and (c) 800°C.

time increased, the peak intensity of the spinel LiMn_2O_4 (111) plane became higher. Unlike LiMn_2O_4 powder, other orientations did not appear in the annealed LiMn_2O_4 thin films. Thus the annealed films had preferred orientation in the [111] direction.

To prevent the electrode/liquid electrolyte reaction, diamond-like-carbon (DLC) films were deposited on the annealed LiMn_2O_4 thin films as protective top layers by ECRCVD. Because thick DLC films on electrode thin films may cause lithium-ion blocking, the thickness of the DLC films must be thin enough for lithium ions to pass through DLC films without blocking. Figure 4 is XPS survey spectra of LiMn_2O_4 and DLC-top-layer LiMn_2O_4 . The thickness of DLC film was 600 nm. In Fig. 4a, XPS peaks of O and Mn were

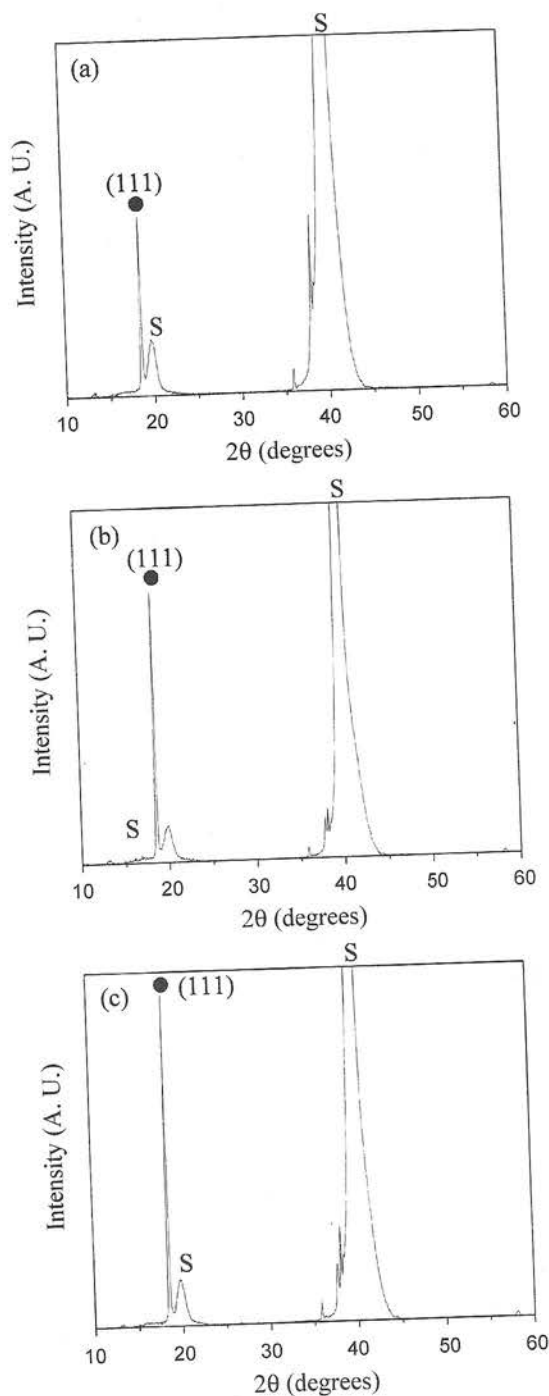


Fig. 3. XRD patterns of the LiMn_2O_4 films at various annealing times (The annealing temperature was 750°C); (a) 60 minutes, (b) 180 minutes, and (c) 240 minutes (S; substrate).

detected and an XPS peak from Li was not detected because of its small content in the film. After the DLC film was deposited, XPS peaks of O and Mn disappeared and only the XPS peak of C from the DLC was detected (Fig. 4b). This result shows that the DLC film is deposited on LiMn_2O_4 film completely and uniformly.

Figure 5 shows the discharge capacities of the LiMn_2O_4 film and DLC-top-layer LiMn_2O_4 film. The

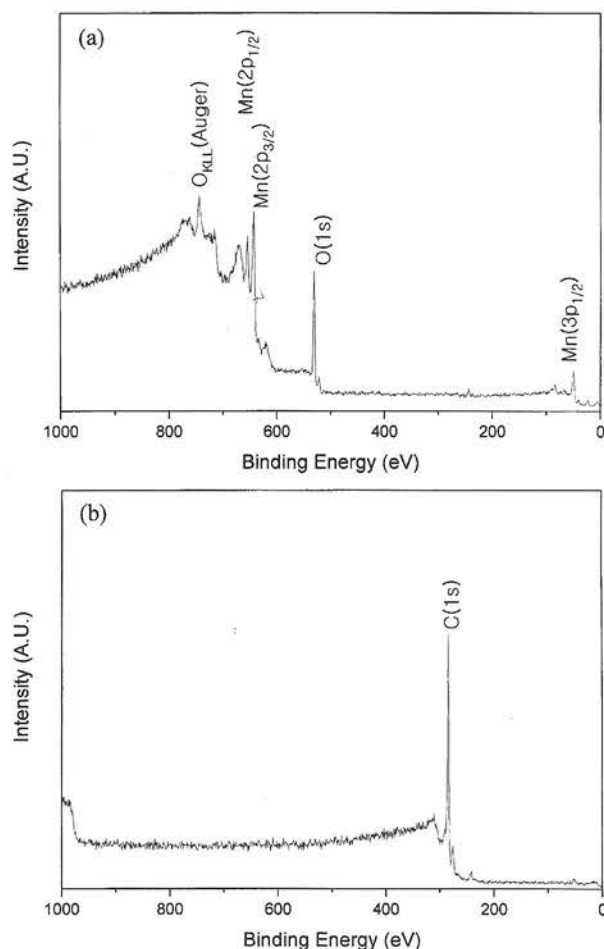


Fig. 4. XPS survey spectra of LiMn₂O₄(a) and DLC-top-layer-LiMn₂O₄(b).

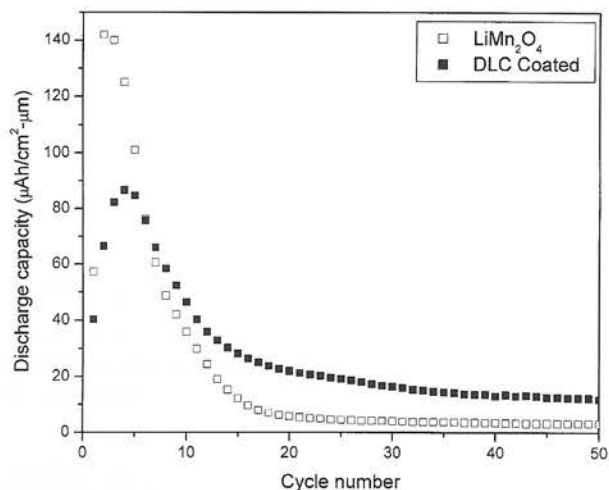


Fig. 5. Discharge capacity of LiMn₂O₄ and DLC-top-layer-LiMn₂O₄ thin films; the cut off voltage and current density were 4.2~2.0 V and 50 μA/cm².

cut-off voltage and current density were 4.2~2.0 V and 50 μA/cm² respectively. In the case of both cathode films, the discharge capacity increased in the early cycles because of the excess lithium ions inserted in the

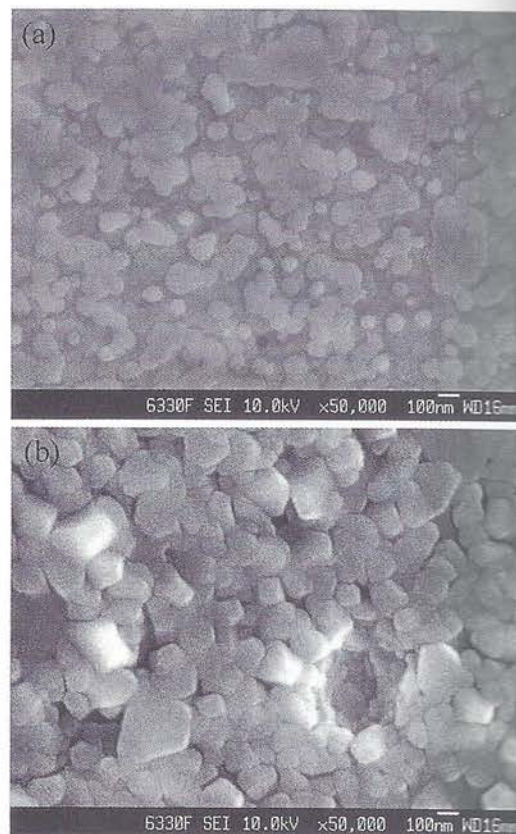


Fig. 6. FESEM images of the LiMn₂O₄ films(a) and DLC-top-layer-LiMn₂O₄(b) after half cell test.

pores of the thin film and/or the 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 the capacity. In the DLC-top-layer LiMn₂O₄ thin film, the capacity fade rate was slower and the discharge capacity value at the 50 th cycle was higher than the bare LiMn₂O₄ thin film. The origin of the capacity loss of LiMn₂O₄ is as follows. First, because of wide voltage window, a part of spinel LiMn₂O₄ phase was transformed to the tetragonal Li₂Mn₂O₄ phase during discharging process (Jahn-Teller distortion). This phase transformation was irreversible, so the tetragonal phase remained after the half cell was fully charged and this phase induced capacity fade. Second, the manganese ions in the cathode film were dissolved into the liquid electrolyte during the charging/discharging process. In our experiment, we could not prevent the irreversible phase transformation but the capacity loss was reduced as the DLC films introduced. The surface morphologies of the cathode films are shown in Fig. 6 and Fig. 7. As shown in Fig. 6, the surface of the LiMn₂O₄ film (Fig. 6a) was covered with a passivation film that interrupted the lithium ion transition from electrolyte to electrode and vice versa during the charging/discharging process [7]. In the AFM images (Figure 7), the LiMn₂O₄ film was flattened while the

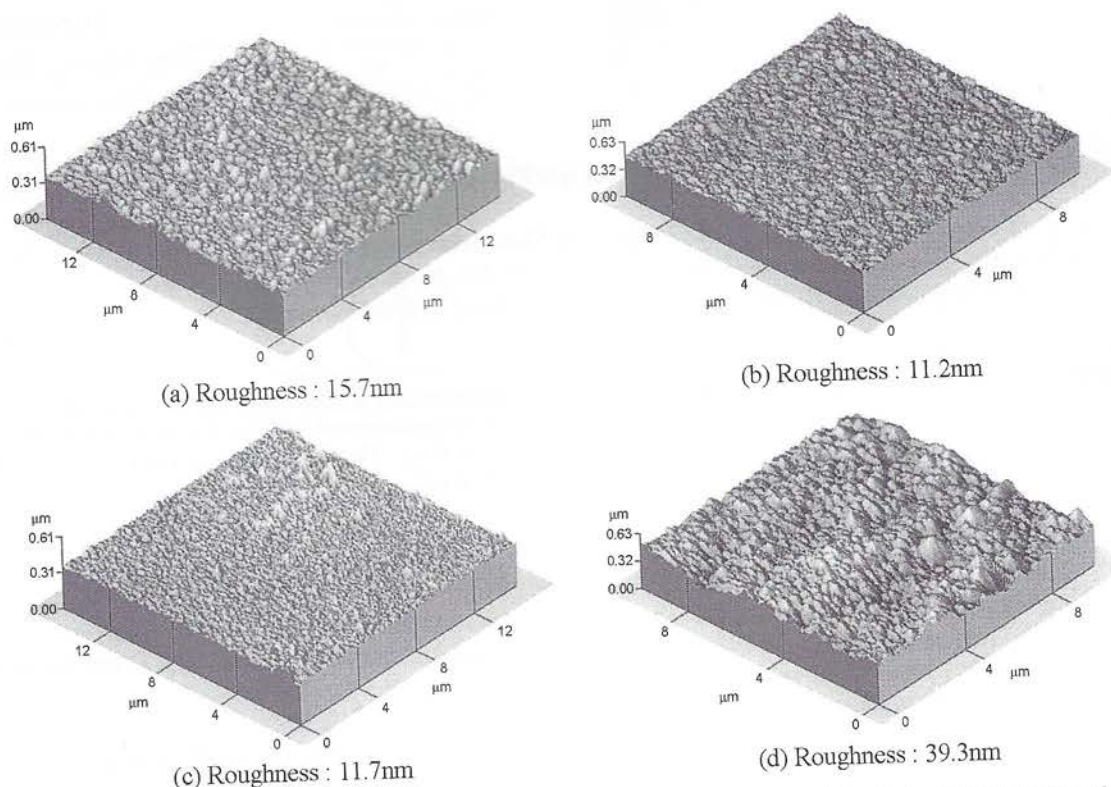


Fig. 7. AFM topography of before (a) and after (b) half-cell test of the bare LiMn_2O_4 film and before (c) and after (d) half cell-test of the DLC-top-layer- LiMn_2O_4 thin films.

DLC-top-layer LiMn_2O_4 film became rougher after the cycle test. This fact showed that the passivation film on the LiMn_2O_4 film reduced the surface roughness during cycle test.

These results mean that the DLC films on electrodes prevent direct contact of the electrode with the liquid electrolyte and reduce the dissolution reaction of manganese ions in the cathode thin films.

Conclusions

In order to use LiMn_2O_4 thin film cathodes for lithium microbatteries, the films were deposited by radio frequency magnetron sputter and annealed in air. When the annealing temperature and time were above 750°C and 1 hr respectively, spinel-phase LiMn_2O_4 thin films were fabricated. To improve the electrochemical stability of the fabricated films in the liquid electrolyte, DLC films, which have good electrochemical stability and mechanical properties, were deposited on the cathode electrode films by ECRCVD. A phase transformation during cycling caused an irreversibility of the lithium intercalation/deintercalation reaction. When half-cell tests were done with the DLC-top-layer LiMn_2O_4 film as the working electrode, cyclability was improved

and 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 DLC as an electrode surface coating is one possible methods of improving this cathode.

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