

Improvement of cyclability of LiMn_2O_4 thin films by transition-metal substitution

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Abstract

To improve structural and electrochemical properties of LiMn_2O_4 thin films, cobalt ions were substituted for manganese ions by a co-sputtering method. The annealed films had the spinel-phase, which had a preferred orientation of (1 1 1). Compositions of the films were nearly the stoichiometric LiMn_2O_4 and $\text{LiCo}_{0.26}\text{Mn}_{1.74}\text{O}_4$, respectively. In the electrochemical test, the discharge capacity of the $\text{LiCo}_{0.26}\text{Mn}_{1.74}\text{O}_4$ film was lower than that of the LiMn_2O_4 film. However, cyclability of the $\text{LiCo}_{0.26}\text{Mn}_{1.74}\text{O}_4$ film was better than that of the LiMn_2O_4 film. The cobalt ions effectively improved the structural and electrochemical properties of the spinel-phase LiMn_2O_4 thin films.

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1. Introduction

Advances in micro-electro-mechanical systems (MEMS) 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 micro-batteries as power sources for these devices. Therefore, it is important to develop long-lasting and high-energy efficient microbatteries that can be an integral part of MEMS. LiMn_2O_4 is a particularly interesting cathode material for microbatteries, since it can reversibly intercalate lithium ions, without altering the MnO_2 framework [1]. However, LiMn_2O_4 has some problems such as a dissolution of Mn ions during intercalation reaction and an instability of delithiated spinel electrode [2]. One of the solutions of these problems is transition-metal substitution for manganese in the spinel. Many researchers worked to improve the electrochemical properties of LiMn_2O_4 by metal substitution [3,4]. In this work, to prevent Mn dissolution in liquid electrolyte and Jahn–Teller distortion of the LiMn_2O_4 , we substituted cobalt for manganese.

2. Experimental

LiMn_2O_4 thin films were deposited by using radio frequency (rf) magnetron sputtering with LiMn_2O_4 target.

The working pressure was maintained to 10 mTorr with a forming gas of Ar and O_2 . The rf power used during a process was 1.5 W/cm^2 . B-doped p-type Si(1 0 0) wafers were used as substrate on which Pt was deposited in thickness of 2000 Å as a current collector by dc sputtering. To substitute cobalt ion, 1 cm diameter Co_3O_4 pellets were placed on the LiMn_2O_4 target during sputtering. Deposited films were annealed using a horizontal tube furnace. Compositions of films were analyzed by ICP and AES. Surface morphologies and roughness of the film were measured by FE-SEM and AFM. For electrochemical analysis, half-cells were made with the annealed thin films as a cathode, the lithium metal as an anode, and 1 M solution of LiPF_6 in EC–DMC (1:1) as an electrolyte.

3. Results and discussion

In order to make the spinel structure, a post-annealing process was introduced [5]. The composition of films were nearly the stoichiometric LiMn_2O_4 and $\text{LiCo}_{0.26}\text{Mn}_{1.74}\text{O}_4$, respectively. These films had almost the same structure. The cobalt-ion doping did not affect the crystal structure of LiMn_2O_4 . These films had preferred orientation of (1 1 1) with small intensity of (2 2 2).

As shown in Fig. 1, the surface roughness of the $\text{LiCo}_{0.26}\text{Mn}_{1.74}\text{O}_4$ film was larger than that of the LiMn_2O_4 film. The higher value of the roughness is more favorable for intercalation reactions because the higher surface roughness of the film assured that a higher surface area is in contact with liquid electrolyte [3].

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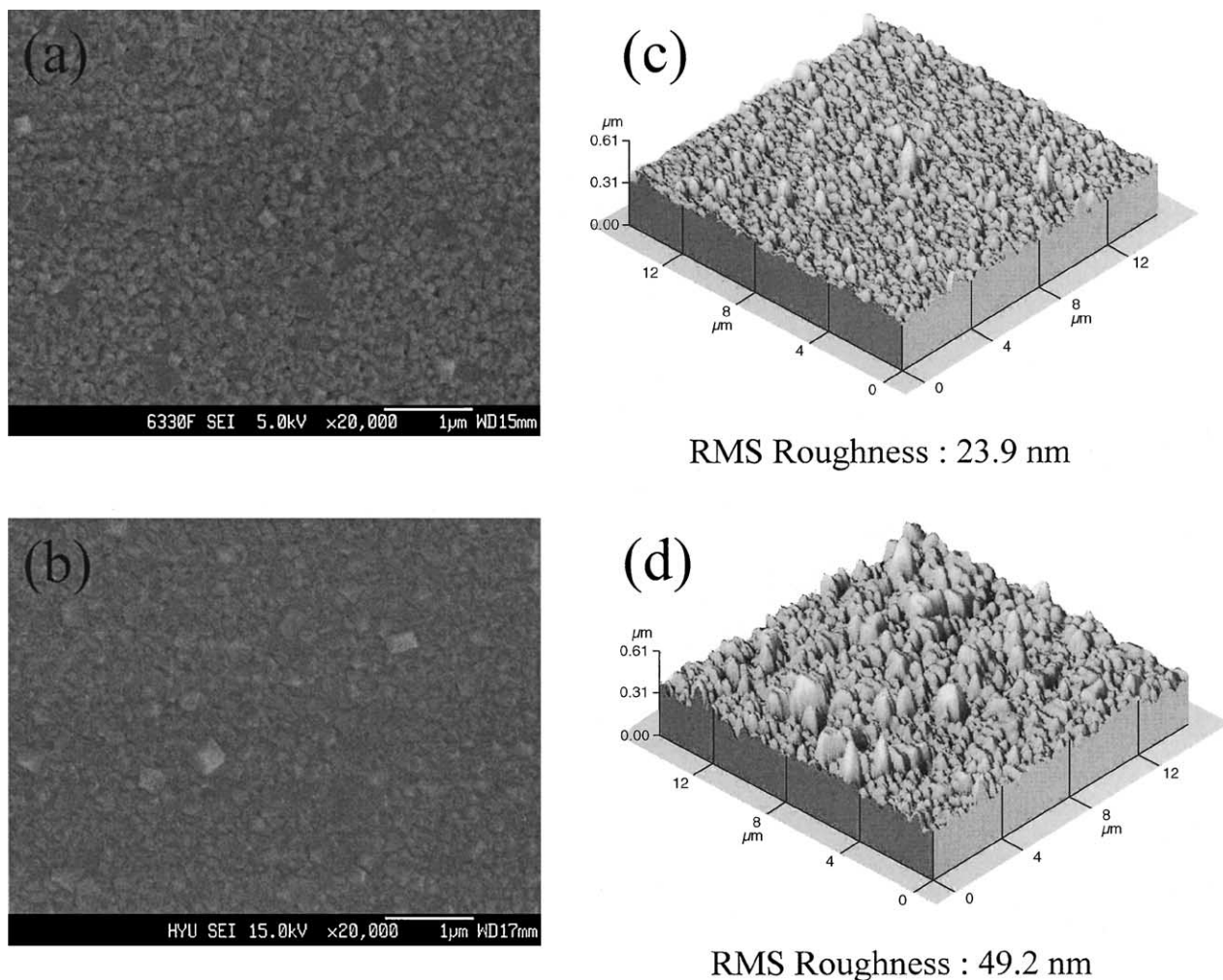


Fig. 1. FE-SEM image of (a) LiMn_2O_4 and (b) $\text{LiCo}_{0.26}\text{Mn}_{1.74}\text{O}_4$. AFM images of (c) LiMn_2O_4 and (d) $\text{LiCo}_{0.26}\text{Mn}_{1.74}\text{O}_4$ after annealing process.

Fig. 2 shows results of the half-cell tests. In the case of the LiMn_2O_4 film, the plateau existed at around 3.5 V. The reason of this phenomenon is not understood. After the first charge step, both films had same voltage–time profiles. Fig. 2(c) shows the discharge capacity of both the films. When voltage was below 3.0 V, the spinel-phase LiMn_2O_4 was transformed to tetragonal phase (Jahn–Teller distortion). This phase transformation was irreversible, so capacity fading occurred. However, in spite of the Jahn–Teller distortion, the $\text{LiCo}_{0.26}\text{Mn}_{1.74}\text{O}_4$ film shows good cycle retention. These results mean that cobalt ions contribute in the solidity of the spinel frameworks during cycling.

Fig. 3 shows the discharge capacity of both films in the voltage window from 4.2 to 3.8 V. The first discharge capacity of the LiMn_2O_4 film was higher than that of the $\text{LiCo}_{0.26}\text{Mn}_{1.74}\text{O}_4$ film. Generally, transition-metal-substituted LiMn_2O_4 electrodes have lower discharge capacity than LiMn_2O_4 because Mn^{3+} ions, which are oxidized when Li^+ ions intercalate into LiMn_2O_4 , are reduced by transition-metal ions substitution. This fact is applicable for our thin

films. However, the capacity fade of the LiMn_2O_4 was faster than that of the $\text{LiCo}_{0.26}\text{Mn}_{1.74}\text{O}_4$ film. This result shows that the cyclability of the LiMn_2O_4 film is improved by cobalt-ion substitution.

As shown in Fig. 4, when the cycle number was about 100, a Li_2MnO_3 phase occurred in the XRD pattern and peak intensity of the Li_2MnO_3 increased as the cycle number increased. As increased impurity phase in the cycled film, the discharge capacity of the film decreased.

4. Conclusions

To improve electrochemical and structural stability of the spinel-phase LiMn_2O_4 thin films, cobalt ions substitute for manganese ions in the LiMn_2O_4 thin films. The crystal structures of the undoped and doped films are almost same structure. Both films had preferred orientation of (1 1 1). In the half-cell test, the $\text{LiCo}_{0.26}\text{Mn}_{1.74}\text{O}_4$ film had lower discharge capacity than that of the LiMn_2O_4 film.

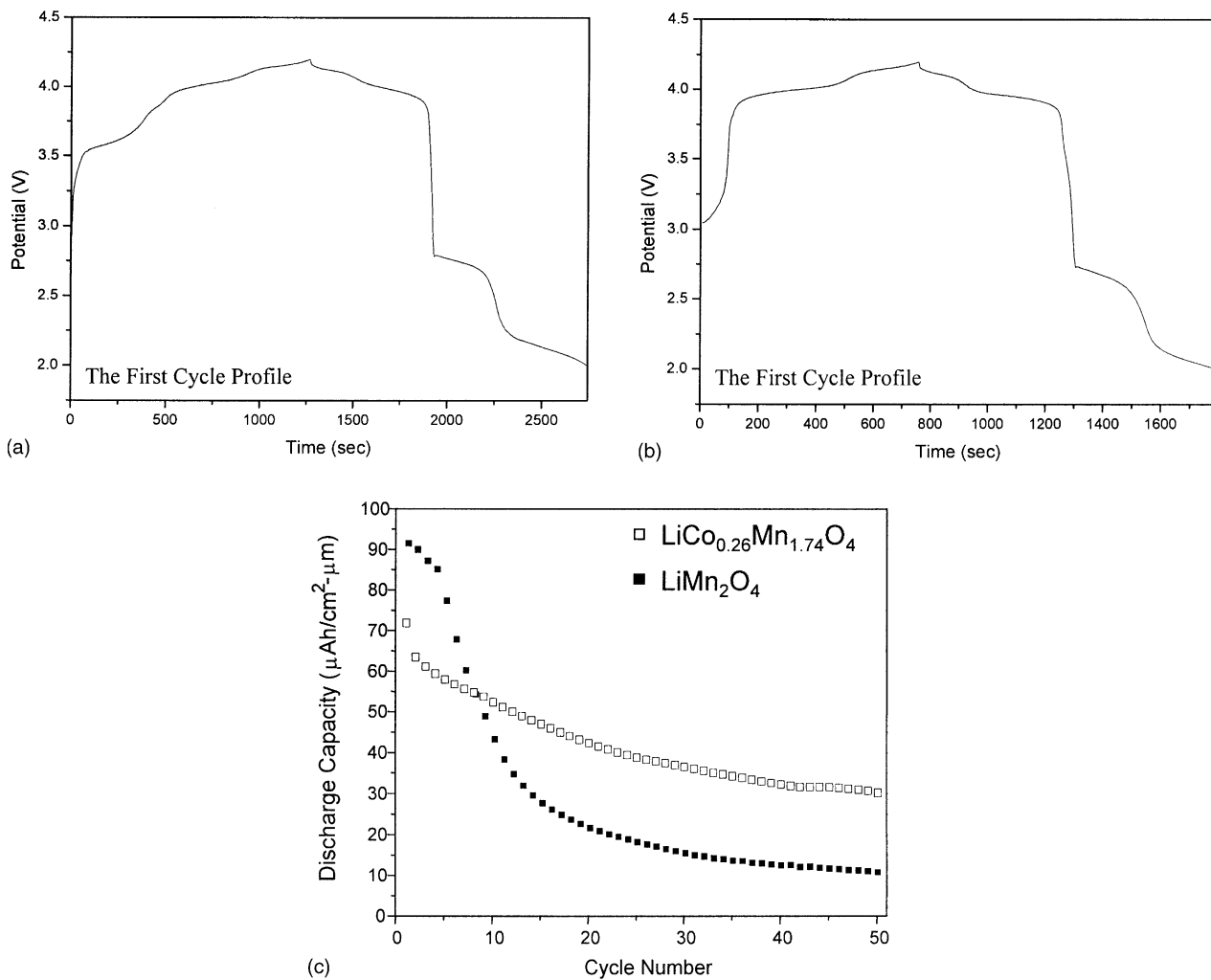


Fig. 2. First cycle profiles of the LiMn_2O_4 (a) and $\text{LiCo}_{0.26}\text{Mn}_{1.74}\text{O}_4$ (b) and discharge capacities of the films (c) (voltage window: 4.2–2.0 V; current density: $100 \mu\text{A}/\text{cm}^2$).

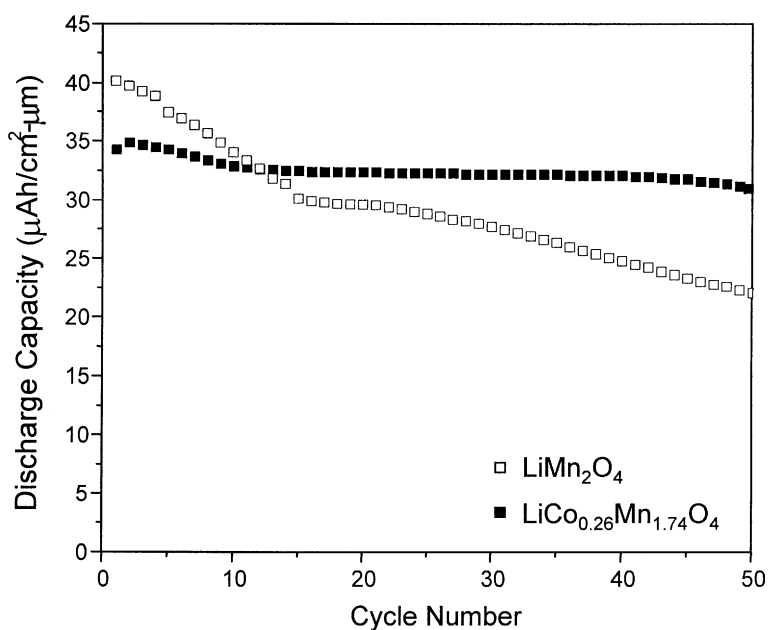


Fig. 3. Discharge capacities of the films (voltage window: 4.2–3.8 V, current density: $100 \mu\text{A}/\text{cm}^2$).

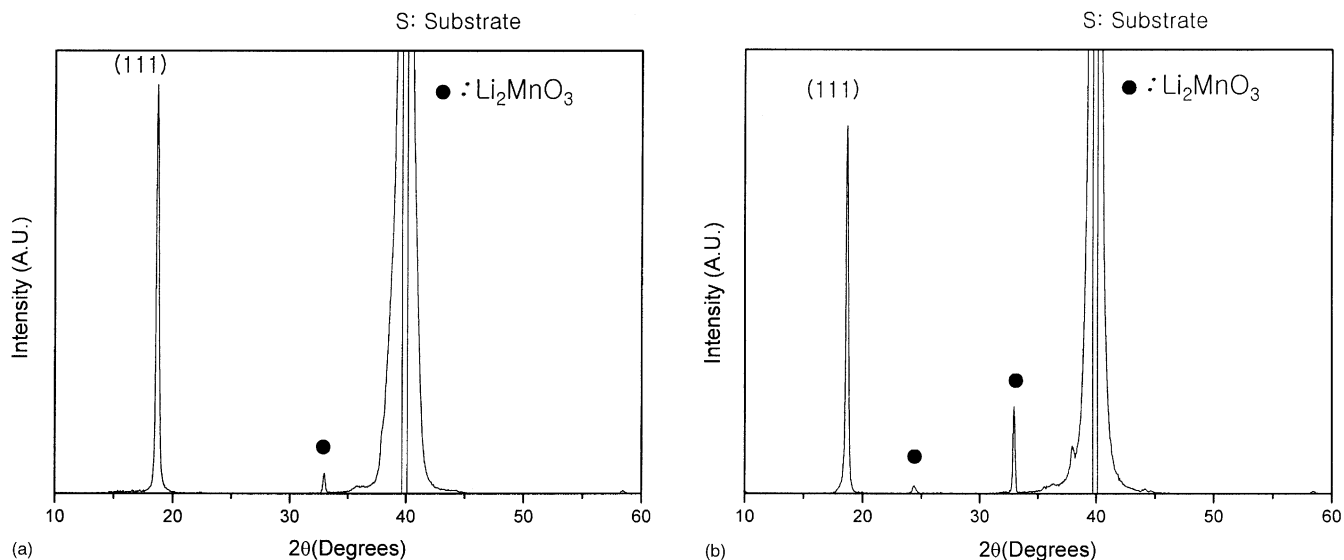


Fig. 4. XRD patterns of the cycled films: (a) LiMn_2O_4 and (b) $\text{LiCo}_{0.26}\text{Mn}_{1.74}\text{O}_4$ (after 100 cycles).

However, the capacity retention of the $\text{LiCo}_{0.26}\text{Mn}_{1.74}\text{O}_4$ film is better than that of the LiMn_2O_4 film. The cobalt ions modified the spinel thin films effectively and improved the electrochemical properties of the LiMn_2O_4 thin films for microbatteries.

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