

# CHARACTERISTICS OF COBALT SUBSTITUTED LITHIUM MANGANESE OXIDE THIN FILM FOR MICROBATTERY

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## INTRODUCTION

Demand for low power, battery operation device's on the rise, particularly in portable equipment requiring longer operation with higher reliability. Advances in the miniaturization of electronic device 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 as an integral part of MEMS.  $\text{LiMn}_2\text{O}_4$  is particularly interesting cathode material for microbattery, since it can reversibly intercalate one Li ion per mole, without altering the  $\text{MnO}_2$  framework[1][2]. This system has a 4V operating voltage versus Li metal negative electrode and good electrochemical behavior is expected due to the favorable kinetics for fast Li ion diffusion through the three dimensional channel of the  $\text{Mn}_2\text{O}_4$  spinel structure. To prevent from Mn dissolution in liquid electrolyte and Jahn-Teller distortion of  $\text{LiMn}_2\text{O}_4$ , we substituted cobalt for manganese. We'll expect that cobalt substituted  $\text{LiMn}_2\text{O}_4$  maintains  $\text{MnO}_2$  framework, so cathode film has more long cycle life.

## EXPERIMENTAL

$\text{LiMn}_2\text{O}_4$  thin films were deposited by radio frequency magnetron sputtering. 2-inch diameter of  $\text{LiMn}_2\text{O}_4$  target(99.97% purity) was purchased from Cerac. The temperature for post annealing was 750 °C. The chamber was evacuated to  $5.0 \times 10^{-6}$  Torr as a base pressure and working pressure was maintained to 10 mTorr with a forming gas of Ar and  $\text{O}_2$ . RF power used during a process was  $1.5\text{W}/\text{cm}^2$ . Si wafers were used as substrate and Pt was deposited on it in thickness of 2000 Å as a current collector by D.C. sputtering. To substitute cobalt ion,  $\text{Co}_3\text{O}_4$  pellet put on  $\text{LiMn}_2\text{O}_4$  target. Deposited films were annealed by a horizontal tube furnace. Fabricated film thickness was measured by alpha-step(500, TENCOR), and film structure was analyzed by X-ray diffractometer(RINT 2000, RIGAKU). Composition of films were analyzed by AES(PHI-670, Perkin-Elmer). Surface roughness of the film before and after heat treatment was measured by atomic force microscopy(AP0190, AutoProbe CP Multitask Microscopy). Surface morphologies of the films were obtained by field emission scanning electron microscopy(JES 6340F, JEOL). For electrochemical analysis, half cells were made with the lithium manganese oxide as cathode, the lithium metal as anode, and 1 M

solution of  $\text{LiPF}_6$  in EC-DMC(1:1) as electrolyte. Using cycle tester(WBCS 3000, WON A TECH) charge-discharge experiments were performed by various cut-off voltages and current densities.

## RESULTS AND DISCUSSION

Before annealing, sputtered thin film was amorphous structure. To get spinel structure, post-annealing process was done in air. After annealing, thickness of thin film was 2300 Å. As shown in Fig. 1, annealed  $\text{LiMn}_2\text{O}_4$  and cobalt substituted  $\text{LiMn}_2\text{O}_4$  thin film have same structure, spinel structure, and (111) of preferred orientation. As cobalt was substituted, grain size and surface roughness of substituted thin film larger than that of  $\text{LiMn}_2\text{O}_4$  film(Fig. 2). Fig. 3 is discharge capacity of cathode thin films we made. Cathode area of cell was  $0.86 \text{ cm}^2$  and Cut-off voltage and current density was 4.2-2.0 V and  $50 \mu\text{A}/\text{cm}^2$ , respectively. Initial discharge capacity of  $\text{LiMn}_2\text{O}_4$  thin film was larger than cobalt substituted  $\text{LiMn}_2\text{O}_4$  thin film. But as cycle number increased, discharge capacity fade of  $\text{LiMn}_2\text{O}_4$  was rapidly decreased. In the case of cobalt substituted  $\text{LiMn}_2\text{O}_4$ , as cycle number increased, capacity fade rate decreased and approached higher constant value of discharge capacity than  $\text{LiMn}_2\text{O}_4$ . We think that structural stability of  $\text{MnO}_2$  was improved by substituted cobalt ions for manganese ions.

## REFERENCES

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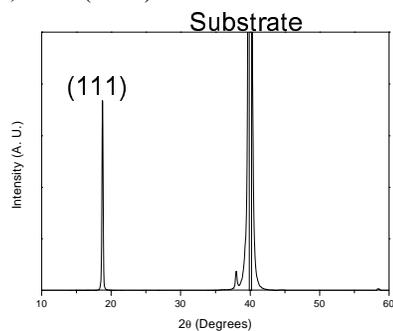


Figure 1. XRD pattern of cobalt substituted  $\text{LiMn}_2\text{O}_4$  thin film.

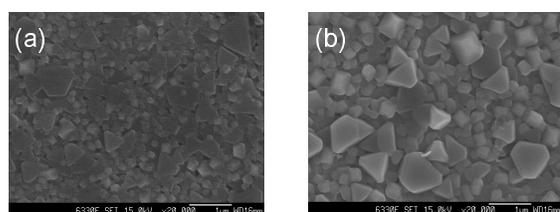


Figure 2. FE-SEM images of  $\text{LiMn}_2\text{O}_4$ (a) and cobalt substituted  $\text{LiMn}_2\text{O}_4$  thin film(b).

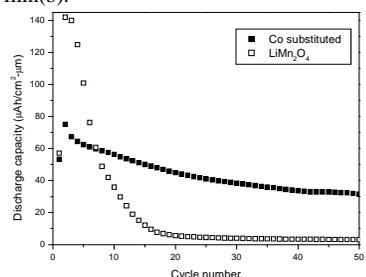


Figure 3. Discharge capacity of  $\text{LiMn}_2\text{O}_4$  and cobalt substituted  $\text{LiMn}_2\text{O}_4$  thin film.