IMPROVEMENT ON ELECTRODE PERPORMANCE OF $Li_xCr_{0.07}Mn_{1.93}O_4$ THIN FILMS

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INTRODUCTIONS

$LiMn_2O_4$ is particularly interesting cathode material for microbattery, since it can reversibly intercalate one Li ion per mole, without altering the MnO_2 framework[1][2]. This system has a 4 V 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 Mn_2O_4 spinal structure. To prevent Mn dissolution in liquid electrolyte and Jahn-Teller distortion of $LiMn_2O_4$, we substituted Cr for Mn. We'll expect that Cr-substituted $LiMn_2O_4$ maintains MnO_2 framework, so cathode film has longer cycle life.

EXPERIMENTAL

$LiMn_2O_4$ thin films were deposited by radio frequency magnetron sputtering with 2-inch diameter of $LiMn_2O_4$ target (99.97% purity). The temperature for post annealing was 750˚C. The chamber was evacuated to 5.0 x 10^{-6} Torr as a base pressure and working pressure was maintained to 10 mTorr with a forming gas of Ar and O_2. RF power used during a process was 1.5 W/cm^2. Si wafers were used as substrate on which Pt was deposited as a current collector by D.C. sputtering. To substitute Cr ion, Cr_2O_3 pellets were placed on $LiMn_2O_4$ target during sputtering. Deposited films were annealed using a horizontal tube furnace. Compositions of films were analyzed by ICP and RBS. Surface roughness of the film before and after the heat treatment was measured by AFM. Surface morphologies of the films were obtained by FE-SEM. For electrochemical analysis, half cells were made with the lithium manganese oxide as cathode, the lithium metal as anode, and 1 M solution of $LiPF_6$ in EC-DMC(1:1) as electrolyte.

RESULTS

Before annealing, sputtered thin films had amorphous structure. To get spinel structure, post-annealing process was done in air[3]. After annealing, thickness of thin film was 200 nm. Annealed $LiMn_2O_4$ and Cr-substituted $LiMn_2O_4$ thin film have the same structure, spinel structure, and (111) preferred orientation. As Cr was substituted, grain size and surface roughness of substituted thin film smaller than that of $LiMn_2O_4$ film(Fig. 1). Fig. 2 is the discharge capacity of cathode thin films. Cathode area of cell was 0.86 cm^2 and Cut-off voltage and current density was 4.5-2.5 V and 100 μA/cm^2, respectively. Initial discharge capacity of $LiMn_2O_4$ thin film was larger than Cr-substituted $LiMn_2O_4$ thin film. However, as cycle number increased, discharge capacity fade of $LiMn_2O_4$ was rapidly decreased. In the case of cobalt substituted $LiMn_2O_4$, as cycle number increased, capacity fade rate decreased and higher constant values of discharge capacity than $LiMn_2O_4$ were obtained. We think that structural stability of MnO_2 was improved by the substituted Cr ions for Mn ions.

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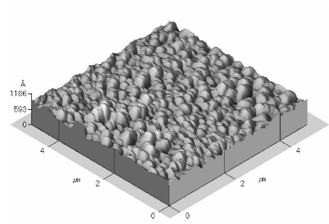
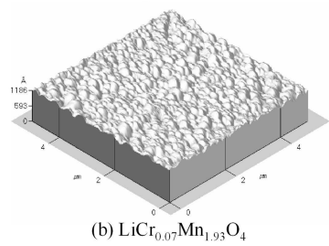


(a) $Li\ Mn_2O_4$

RMS roughness: 6.87 nm



(b) $LiCr_{0.07}Mn_{1.93}O_4$

RMS roughness: 5.67 nm

Figure 1. AFM images of the deposited films;
(a) $LiMn_2O_4$ and (b) $LiCr_{0.07}Mn_{1.93}O_4$

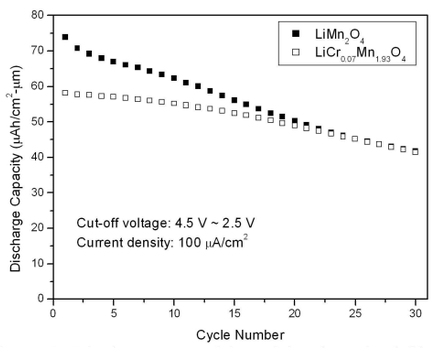


Figure 2. Discharge capacities of the deposited films.