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Fabrication of Lithium Nickel Cobaltate Thin-film for the Cathode Material of Microbattery

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ABSTRACTS

Electrochemically active lithium nickel cobalt oxide thin-film was not fabricated until now. The thin-film was deposited by RF magnetron sputtering at room temperature, and its initial phase was amorphous. By varying deposition condition, the different characteristics of thin-film were achieved. Using electrochemical analyses, the relationship between physical and electrochemical characteristics was identified. Crystallized thin-film by RTA (Rapid Thermal Annealing) was shown a good capacity and cycle property.

Key words : Lithium nickel cobaltate, Microbattery, Cathode, RF magnetron sputtering

1. Introduction

Solid-state thin-film micro battery has been studied for various application fields. The most promising applications are the monolithic hybridization with CMOSRAM and combination with solar cells. Also, these micro batteries can be applied to microelectronics, sensor, and MEMS. [1-4] One of the promising candidates of thin-film cathode [5-7] was lithium nickelate and lithium nickel cobaltate. The research about thin-film $LiNiO_2$ and $LiNi_{0.5}Co_{0.5}O_2$ was undergone in a few numbers, [8-10] but the most of thin-film was not electrochemically active. Via soft-solution method, [8] the deposited film was electrochemically active but its surface shape does not match the industrial needs.

In this study, $LiNi_{0.5}Co_{0.5}O_2$ thin-films are deposited by sputtering method using stoichiometric $LiNi_{0.5}Co_{0.5}O_2$ target. The effects of sputtering conditions, such as the working pressure of plasma, flow rate of source gases, deposition time, and sputtering power, are reviewed on the basic film characteristics and their electrochemical properties. As deposited amorphous thin-film is heat treated to achieve crystalline structure. Therefore, the annealing conditions for the crystalline thin-film were defined.

2. Experimental

To synthesize target material for sputtering, powder with the composition of $LiNi_{0.5}Co_{0.5}O_2$ was produced by the solid-state reaction between $LiNO_3$ (Kanto, 99.95%), $NiCO_3$ (Cerac, 99.5%), $Co(NO_3)_2 \cdot 6H_2O$ (Strem, 99%) in the ratio of 1.05 : 0.5 : 0.5 and 1.1 : 0.5 : 0.5. Synthesized powder was pressed isostatically and its green body was sintered at 750°C for 5 hours with uniaxially pressed at 25 MPa in flowing oxygen atmosphere (150 ml/min).

Thin-film deposition was deposited at room temperature and in the argon and oxygen atmosphere (2 : 1) with the different working pressure, such as 1 mtorr, 5 mtorr, and 10 mtorr on the commercial Pt (800 Å) current collector/Ti/SiO_2/Si (100) wafer using RF magnetron sputter at 1.23 W/cm^2 power for 1 hour. The deposited thin-film was an amorphous structure, therefore annealed at 650, 750, and 800 °C for 10 minutes in the oxygen environment using RTA (Rapid Thermal Annealing) system.

For the electrochemical measurements, the $LiNi_xCo_{1-x}O_2$ thin-film was placed in an open beaker cell containing 1 M $LiClO_4$ in Propylene Carbonate (PC) solution, and lithium foil for counter and reference electrodes, respectively. This cell was put in argon filled glove box, and charge-discharge tests were controlled with an EG&G electrochemical analysis system (Model 273A).

3. Results and discussion

Prepared powder from the solid-state reaction with different mixing ratio was shown in Fig. 1. Its particle size was 1.3 μm and 1.0 μm for 1.05 : 0.5 : 0.1 and 1.1 : 0.5 : 0.5, respectively. In case of the mixing ratio of 1.05 : 0.5 : 0.5, the powder was spherical shape, and for 1.1 : 0.5 : 0.5 was monodispersed but hard agglomerated form. Both powders showed a good hexagonal structure (R3m), and no other impurity phases appeared in the XRD analyses (Fig. 2). The green density of sintering powder was over 65%, and the density of sintered body was over 90% of theoretical density. Compositional change of the samples, during sintering, was measured and presented at Table 1. The non-stoichiometry

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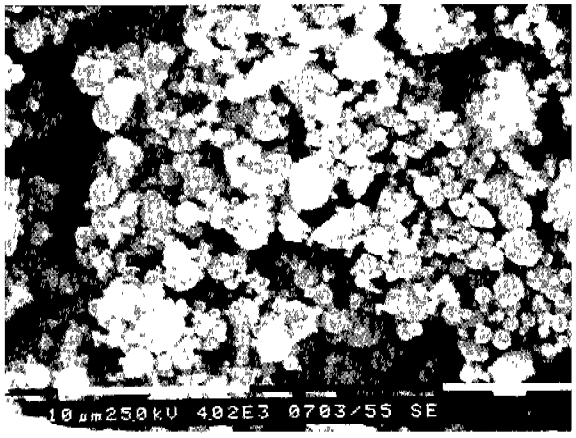
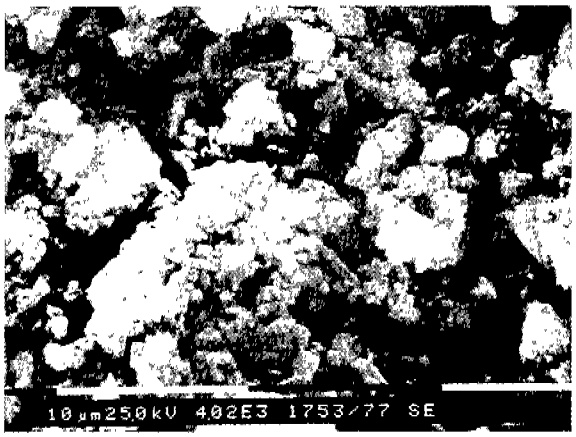


(a)



(b)

Fig. 1. SEM images of the powders from solid-state reaction between lithium nitrate, nickel carbonate, and cobalt nitrate in the ratio of (a) 1.05 : 0.5 : 0.5 and (b) 1.1 : 0.5 : 0.5 at 750°C for 5 h.

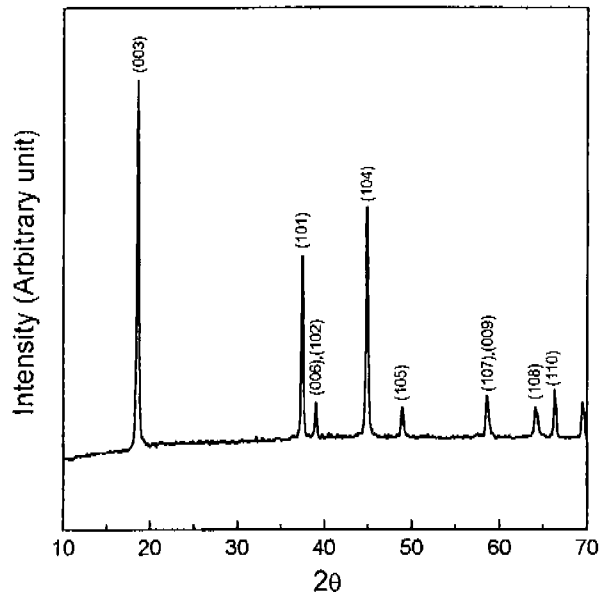


Fig. 2. X-ray diffraction pattern of the powders prepared by solid-state reaction.

Table 1. ICP and X-ray Analyses of Solid-state Reacted Powder and Sintered Body

	Solid-state reaction	Sintered body
X-ray*	0.02	0.02
ICP	0.01	0.02

*X-ray: R = $4/3((1.6\text{-}Y)^2/Y^2)$, Y = 1-x in $Li_{1-x}(NiCo)_{1+x}O_2$[11]

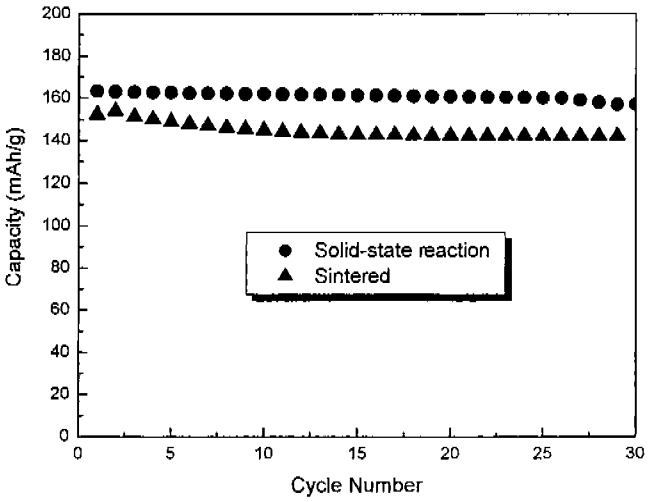


Fig. 3. Capacity retentions of the solid-state reacted powder and sintered one.

of lithium nickelate was calculated from the X-ray peak to peak ratio using empirical ways.[11] By assuming Ni and Co was not depleted during the high temperature process, the empirical way of calculating the lithium deficiency of lithium nickelate was applied to the lithium nickel cobaltate. From ICP analyses and X-ray calculation, the deficiency of lithium was hardly occurred in both cases by the addition of cobalt.

The electrochemical properties of synthesized powder and crushed powder from the sintered body were also measured (Fig. 3). The cycle retention of both powders was stabilized by the addition of cobalt even after the high temperature process like sintering.

The deposited thin-film had an amorphous structure and smooth surface, and the grain size was approximately 20 nm. In Fig. 4, the surface morphology and cross-sectional view of deposited film was shown. At the 10 mtorr working pressure, the density and thickness were higher than 5 mtorr case. For the ratio of source gases, in case of argon only environment showed the highest deposition rate, but the film characteristics was poor (Fig. 5). Due to the low deposition rate of lithium and its lightweight, it is reported that deposited film showed the deficiency of lithium.[9] Therefore, without oxygen present in the plasma, more lithium deficiency would be expected, and that caused the lower initial discharge capacity. Deposited film showed a good cycle retention property and about 90% of initial discharge capacity after 100 cycles (Fig. 6). The nominal discharge capacity of fully dense $LiNi_{0.5}Co_{0.5}O_2$ cathode electrode is

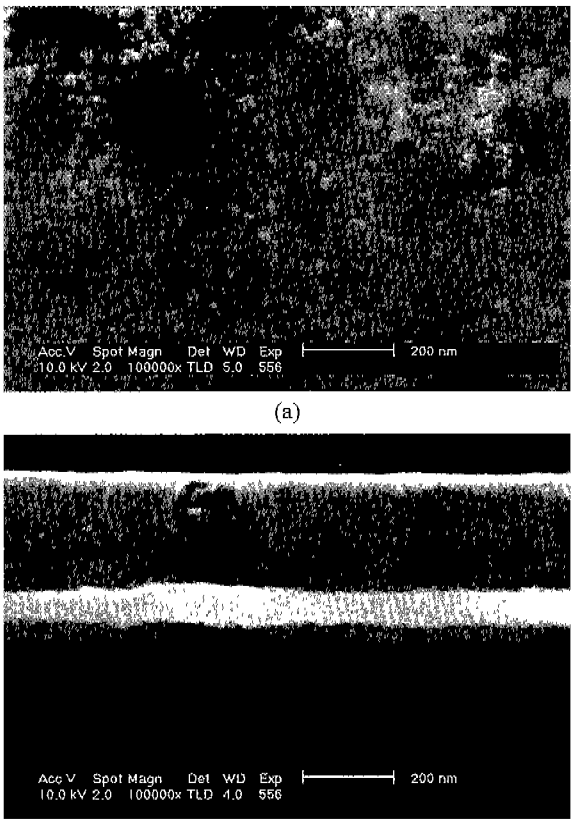


Fig. 4. Surface morphology and cross-sectional view of deposited thin-film with 5 mtorr of Ar and O_2 (4 : 1) on Pt (800 Å)/Ti/SiO_2/Si (100) at 1.23 W/cm^2 sputtering power for 1 h.

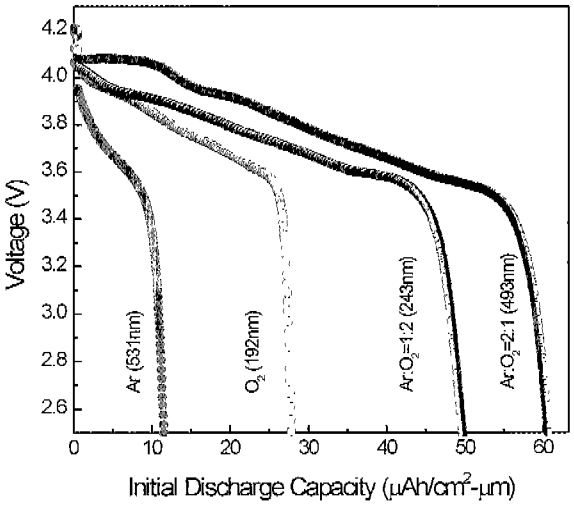


Fig. 5. Initial discharge plots of the thin-films using different mixing gas ratios.

62 μAh/cm^2-μm in case of 50% of lithium extraction.[12] Therefore, the deposited film showed its theoretical capacity, and a bit coarser than theoretical density. During cycling test, if the physical aspect such as density induced the drop of capacity from ideal value, the non-reversible

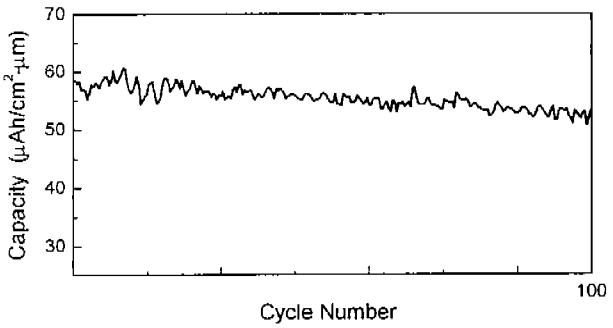


Fig. 6. Cycle retention test on the thin-film.

capacity should not be increased like this one. Therefore, the non-stoichiometries due to chemical aspect like lithium deficiency were present on the films different deposition conditions.

By changing deposition time from 60 minutes to 120 minutes, the preferred orientation was changed from (003) to (104) on the crystallized film. Crystallization of the different deposition timed sample was undergone at 750 °C for 10 minutes using RTA (Rapid Thermal Annealing) system. The preferred orientation change during the crystallization may be induced by the thermal mismatch of substrate and deposited film. Due to low thermal conductivity of oxide film, the substrate temperature was higher than the deposited film. Therefore, in the thicker film, the larger temperature difference between surface and the interface (deposited film/substrate) would be developed. The upper part of deposited film suffered longitudinal tensile stress, and the lower part was applied to the compressive stress. These stresses would be key factor to the preferred orientation aligning to (104). Applied longitudinal stresses make the more open structure, (003) plan, be aligned to surface normal during the crystallization process. To relive the applied stresses, the film structure would transform to more open structure during the crystallization process. Compared to

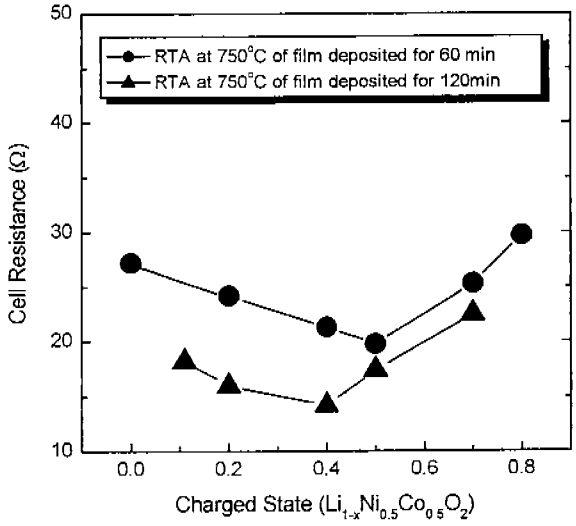


Fig. 7. Cell resistances during initial charging state.

(003) oriented grain, the layered structure in (104) orientation, which was key plane to lithium movement, was surface normal to deposition plane. Therefore, the cell resistance of (104) preferred orientation was expected to lower value than (003) oriented plane due to the easier lithium de-intercalation and intercalation. From the impedance spectra analyses of thin-films, the (104) oriented structure showed lower cell resistance (Fig. 7).

4. Conclusion

Electrochemically active lithium nickel cobalt oxide thin-film was fabricated using RF sputtering method. The characteristics of the deposited film were varied by changing the source gas ratios and deposition time. In the argon only deposition atmosphere, the deposition of film was good, but its electrochemical property was not good enough. However, in the proper mixing ratio of argon and oxygen (2 : 1), the film thickness and the electrochemical property was hold. For the deposition time, the thicker film showed different preferred orientation after crystallization. The (104) preferred orientation was expected to show lower cell resistance, and this was verified from the impedance spectra analyses.

Acknowledgement

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