Effect of target properties on deposition of lithium nickel cobalt oxide thin-films using RF magnetron sputtering

Duksu Kim[*], Mun-Kyu Kim, Jong-Tae Son, Ho-Gi Kim

*Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology,
373-1 Kusong-dong, Yusong-gu, Taejon 305-701, South Korea*

Abstract

Electrochemically active lithium nickel cobalt oxide thin-film has not been fabricated until now. To fabricate stoichiometric lithium nickel cobaltate films, a sputtering target of proper composition has been synthesized via a solid-state reaction. The films are deposited by RF magnetron sputtering at room temperature. As-deposited films show an amorphous structure. By varying the deposition conditions—such as the working pressures and deposition times—thin-films with different characteristics are produced. The relationship between physical characteristics and electrochemical properties is investigated. A crystallized thin-film prepared by an annealing method displays a good discharge capacity and cycle life. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Solid-state, thin-film microbatteries have been studied for various applications. The most promising applications are monolithic hybridization with CMOSRAM and combination with solar cells. The microbatteries can also be applied in microelectronics, sensors and MEMS [1–4]. With some exceptions, however, the actual application of microbatteries has not developed well. The uses are limited to thin-film devices due to the low capacities of the microbatteries.

Most research on thin-film cathodes has focused on lithium cobalt oxide. Films of lithium cobalt oxide have been fabricated by RF sputtering, laser ablation and the sol–gel method, but all the films have suffered from a low discharge capacity. The theoretical discharge capacity of a fully dense lithium cobaltate film is 65 $\mu Ah/(cm^2 \, \mu m)$ on extracting half of the lithium [5]. To overcome this limitation in discharge capacity, lithium nickelate and lithium nickel cobaltate films have been suggested as more promising candidates for cathode materials for microbatteries. Accordingly, there has been some research on thin-film $LiNiO_2$ and $LiNi_{0.5}Co_{0.5}O_2$ [6–8]. Most of these thin-films were not electrochemically active or showed poor properties. Using a soft-solution method [6], the deposited film is

electrochemically active but its surface morphology does not match industrial needs.

In previous work [9], by using a stoichiometric composition of lithium nickel oxide and lithium nickel cobalt oxide, the deposited thin-films were shown to have a lithium-deficient character (due to low sputtering yield and the light weight of lithium), when the fabrication was undertaken at room temperature. To prevent this non-homogeneity in the films, a customized composition of lithium nickel cobalt oxide target, which shows a lithium-rich phase, is used in the study reported here.

$LiNi_{0.5}Co_{0.5}O_2$ thin-films are deposited by the sputtering method using a specially manufactured $LiNi_{0.5}Co_{0.5}O_2$ target. The effect of sputtering conditions, such as the working pressure of the plasma and deposition time, are reviewed in terms of the basic film characteristics and associated electrochemical properties. The deposition process was performed at the ambient temperature. The fabricated films were expected to show an amorphous structure and more dense characteristics than films deposited at higher temperatures. To measure the density, the weight of each specimen was measured before and after the deposition process.

The amorphous thin-film deposited at room temperature is heat treated to achieve a crystalline structure. The annealing conditions for the crystalline thin-film are fixed. Other experiment variables, such as deposition and crystallization conditions are reviewed, elsewhere [9].

[*] Corresponding author. Tel.: +82-42-869-4152; fax: +82-42-869-8650.
E-mail address: coopdale@kornet.net (D. Kim).

2. Experimental

Experiments were performed in two stages: (1) manufacture of the sputtering target; (2) thin-film deposition by using the specially made target.

For the target-preparation experiments, powder synthesis by a solid-state reaction method were used due to the lithium-rich characteristics required in the final target composition. The excess of lithium in sputtering target is needed to fabricate the stoichiometric composition of the thin-films. Powders of $LiNi_{0.5}Co_{0.5}O_2$ were produced via a solid-state reaction between $LiNO_3$ (Kanto, 99.95%), $NiCO_3$ (Cerac, 99.5%) and $Co(NO_3)_2 \cdot 6H_2O$ (Strem, 99%) in mixing ratios of 1.05:0.5:0.5 and 1.1:0.5:0.5. The powders of the raw materials were ball-milled in a solvent and then in a mixer for 10 min to increase the homogeneity of the mixture. The milled powder was placed in a box furnace and pre-heated to 500 °C for 1 h. During the pre-heat treatment, the box furnace was filled with oxygen. Such treatment decreases the deficiency of lithium during the high-temperature process. The solid-state reaction was undertaken at 750 °C for 5 h, with a constant flow of oxygen at about 150 ml/min. After synthesis, the powders were characterized by physicochemical and electrochemical techniques to verify this composition and stoichiometry.

The sintering experiments were continued in two ways. One is using solid-state reacted power, and the other is using raw materials powder for easier processing. Synthesized powder was pressed isostatically using 0.5Φ mold at 2 t/1 mm pressure. The green density was generally more than 60% of its theoretical density. In general, the green compact had a thickness of 1 cm. To determine the theoretical density of lithium nickel cobalt oxide, the mixture rule was applied. Therefore, the density of the solid solution was the sum of the partial molar value of each constituent. The green body was sintered at 800 °C for 2 h in oxygen flowing at a rate of 150 ml/min. The same sintering procedure was used for the raw materials. To do reactive sintering, the sintering condition was slightly modified to produce a fully dense and oxide target. Therefore, two steps of heating were undertaken at 600 °C for 2 h and at 850 °C for 2 h. The lower temperature process ensures transformation to oxide, and higher one produced a final product with the required density.

The synthesized powder and the sintered body were characterized using conventional physicochemical techniques. For example, the microstructures of the powders were analyzed by means of SEM (Philips, XL30S) and PSA (Malvern, Mastersize X), while the crystal structure was determined by X-ray diffraction (Rigaku, D/max-IIIC) with 40 kV Cu Kα radiation and a scan rate of 4°/min over a 10–70° range. For the sintered body, the hard compact was crushed and ball-milled for 2 h to produce a powdered specimen. The composition of both powdered samples were measured by ICP (Jobin Yvon, Ultima-C). The density of the sintered body was calculated using the Archimedean method.

Thin-film deposition was performed by means of reactive RF magnetron sputtering at a power of 1.23 W/cm² and a frequency of 13.56 MHz. Prior to deposition, the chamber was taken to below 5×10^{-6} Torr pressure. The chamber was filled with a mixed gas of argon and oxygen (2:1) up to the desired pressure and then pre-sputtered for about 15 min to remove contaminants from the target surface and sustain a steady state of glow discharge. Deposition was carried out at room temperature with different working pressures, such as 5 and 10 mTorr on the Pt (800 Å) current-collector/Ti/SiO₂/Si (1 0 0) wafer for 1 h. Deposited thin-films showed an amorphous structure, and were, therefore, annealed at 700 °C for 10 min in an oxygen-filled quartz tube. Heating to the desired temperature was completed within 15 min and after treatment, the furnace-cooled.

The crystal structure of each thin-film was characterized by means of X-ray diffraction (Rigaku, D/max-rc) with Cu Kα radiation over the 10–70° range and by.

For electrochemical measurements, the $LiNi_xCo_{1-x}O_2$ thin-film was placed in an open beaker cell which contained 1 M $LiClO_4$ in propylene carbonate (PC) solution, and lithium foil for the counter and the reference electrodes. This cell was placed in argon-filled glove box, and charge–discharge tests were controlled with an EG and G electrochemical analysis system (Model 273A). Cell voltage was measured at a static current condition of 100 μAh/cm² and the cut-off voltages were 4.3 and 2.5 V. Impedance spectra of deposited films were measured in the range of 10^{-2} to 10^5 Hz with 5 mV$_{rms}$ amplitude (Solatron, 1260 Impedance/Gain Phase Analyzer).

3. Results and discussion

3.1. Powder and target-preparation

In case of thin-film deposition of $LiNi_xCo_{1-x}O_2$, the lithium deficiency occurred when the stoichiometric composition of target was used. Therefore, to overcome the non-stoichiometry in the films, a deliberately lithium-rich phase of the target was manufactured. The target-preparation step was divided into two experiments: (1) powder synthesis; (2) densification of prepared powders. There are many ways to synthesize lithium-rich powders, namely by solid-state reaction, sol–gel methods, and hydrothermal synthesis. In this work, the powder synthesis was not only confined to the powder, but also to the manufacture of the target of the powder. Therefore, to make a 4 in. sputtering target, about 300 g of powder are required. To synthesize this amount of powder, the only choice is the solid-state reaction. The starting raw materials exert a great influence on the properties of the produced powder, especially on the electrochemical properties. Lithium nitrate, nickel carbonate and cobalt nitrate were chosen as the constituents. These are widely used in the synthesis of lithium nickel cobaltate.

Powders prepared by the solid-state reaction using two different mixing ratios are shown in Fig. 1. The average
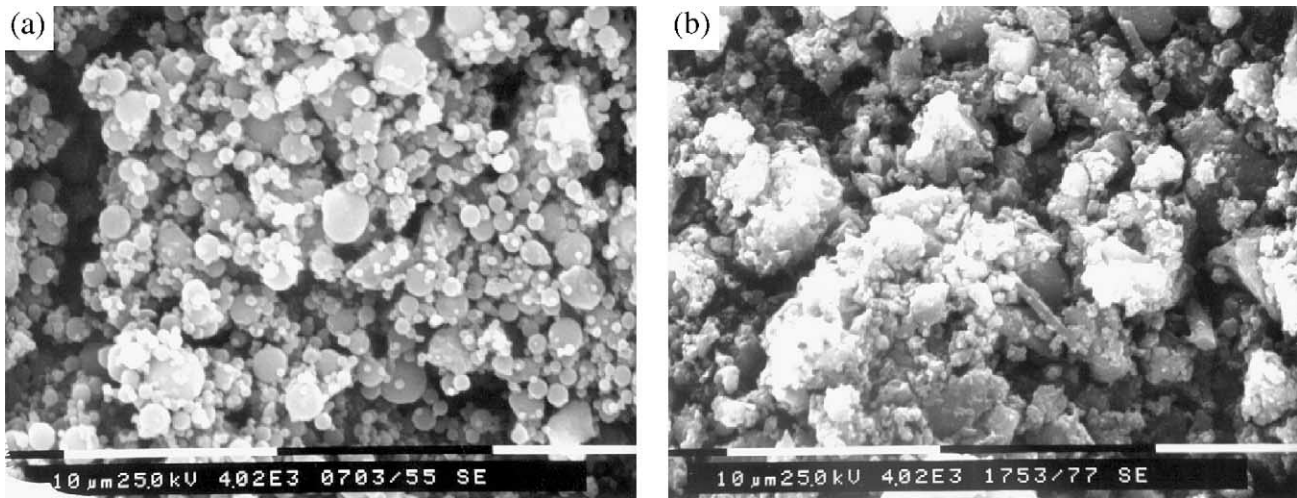
Fig. 1. SEM images of powders from a solid-state reaction (750 °C for 5 h) between lithium nitrate, nickel carbonate and cobalt nitrate in the ratio: (a) 1.05:0.5:0.5 and (b) 1.1:0.5:0.5.

particle size is 1.3 and 1.0 μm for 1.05:0.5:0.5 and 1.1:0.5:0.5 mixing ratios of the lithium, nickel and cobalt source materials, respectively. In case of the 1.05:0.5:0.5 ratio, the powder has a near-spherical shape, but for the 1.1:0.5:0.5 ratio is monodispersed in a hard agglomerated form. Both powders show a good hexagonal structure (R3m). No impurity phases are found with the 1.05:0.5:0.5 mixing ratio (Fig. 2). By contrast, the mixing ratio of 1.1:0.5:0.5 display a peak which corresponds to lithium carbonate. The carbonate phase is induced from the lithium-rich components in the raw materials. The agglomerated structure seen in the SEM image originates from the formation of lithium carbonate during the high-temperature process. The formation energy of lithium carbonate is smaller than that of lithium nickel cobalt oxide. Thus, during the synthesis, lithium carbonate is produced before the oxide phase. Also, the lower melting point of lithium carbonate (720 °C) assists agglomeration. From a microscopic view, the powder using a 1.05:0.5:0.5 ratio is preferred for the manufacture of the sputtering target due to its homogeneous properties and lack of agglomeration. The density of the sputtering target is generally about 70% of the theoretical value. Therefore, densification is not the key factor in the sintering process. Moreover, the composition of the sintered body should contain more lithium to fabricate stoichiometric films in the later process.

The average green density of the sintering powder is more than 60% in case of using synthesized material. For the raw material powders, about 50% of the relative density is achieved. The density of the sintered body is 75% of the theoretical density in the case of pressureless sintering using synthesized powder with a 1.05:0.5:0.5 ratio. The densities of the green and sintered bodies for the various sintering conditions are given in Table 1. The target using raw material powder is too fragile to handle, therefore the manufactured target from raw materials is unusable. Accordingly, the direct sintering from the raw materials was excluded from further characterizations such as compositional and electrochemical analyses. By using synthesized powders, the sputtering target has a desirable density but, as denoted before, the key constraint in the target is the lithium content.

The compositional change during sintering was measured and the results are presented in Table 2. The compositional
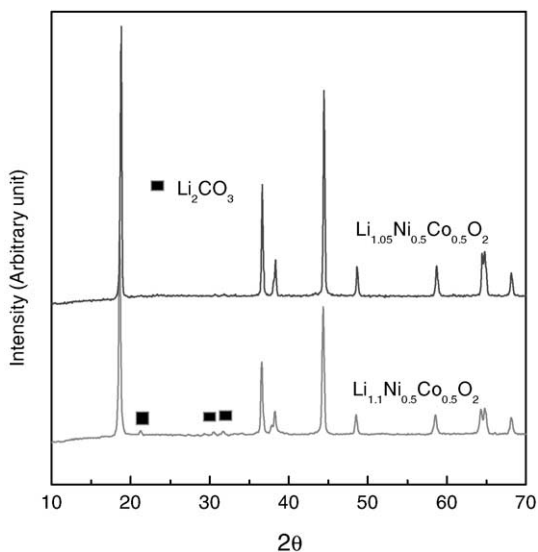

Fig. 2. XRD diffraction patterns from solid-state reaction between lithium nitrate, nickel carbonate and cobalt nitrate with different mixing ratios.

Table 1
Relative densities of green and sintered bodies for different sintering conditions

	Green body	Sintered body
Synthesized powder (1.05:0.5:0.5)	59.4	76.1
Synthesized powder (1.1:0.5:0.5)	56.3	65.2
Raw material powder (1.05:0.5:0.5)	50.1	63.1
Raw material powder (1.1:0.5:0.5)	49.3	59.6

Table 2
Compositional analyses of as-synthesized powders and sintered body using ICP and X-ray methods

	ICP	X-ray[a]
Synthesized powder (1.05:0.5:0.5)	0.01	0.02
Synthesized powder (1.1:0.5:0.5)	−0.02	0.0
Sintered body (1.05:0.5:0.5)	0.01	0.02
Sintered body (1.1:0.5:0.5)	0.05	0.04

[a] X-ray: $R = 4/3((1.6 - Y^2)/Y^2)$, $Y = 1 - x$ in $Li_{1-x}(Ni_{0.5}Co_{0.5})_{1+x}O_2$.

analyses were obtained by ICP and empirical X-ray methods [10]. There is very little deficiency of lithium in the case of either mixing ratio due to the addition of cobalt. The 1.1:0.5:0.5 mixing ratio shows an excess of lithium in the synthesized powder, but after sintering, the more evaporation of lithium takes place than with the other ratio. This deficiency results from the formation of lithium carbonate during the synthesis process. Decomposition and melting of lithium carbonate in the densified body causes the evaporation of lithium and the lower relative density (65%). Loosely-bonded lithium ions are also separated from the lithium–nickel–cobalt matrix by the heat of decomposition and melting. Differential scanning calorimetry showed an exothermic peak at around 720 °C, which was caused by the melting and decomposition of lithium carbonate.

The electrochemical properties of synthesized powders and powders from the crushing of sintered bodies were measured using three-electrode half-cell methods. The capacity performance of the synthesized powders and crushed for a mixing ratio of 1.05:0.5:0.5 is shown in Fig. 3(a). The cycle retention of both powders is stabilized by the addition of cobalt even for the high-temperature process of sintering. By contrast, the lithium-rich powders show a fall in capacity at the initial stage of cycling (Fig. 3(b)). This performance is due to the non-homogeneity of the powders.

3.2. Thin-film deposition

As-deposited thin-films at room temperature using the specially manufactured sputtering target have amorphous structures, a smooth surface, and grains of 20 nm. The surface morphology and a cross-sectional view of such a film is shown in Fig. 4. The film was deposited at a working pressure of 5 mTorr for 1 h using a 1.05:0.5:0.5 mixing ratio for the synthesized powder target. By changing the working pressure to 10 mTorr, both the density and the thickness became greater. The film density was roughly measured by weighing the film before and after deposition. The film thickness changed from 254 (4.23 nm/min) to 493 nm (8.21 nm/min). Using various sputtering targets, such as a synthesized powder target and a raw material powder target, the change in film thickness was less than that caused by increasing the sputtering pressure. A discrepancy in the film density was found with the various targets. This feature was generated by changing the density of the target from 76 to
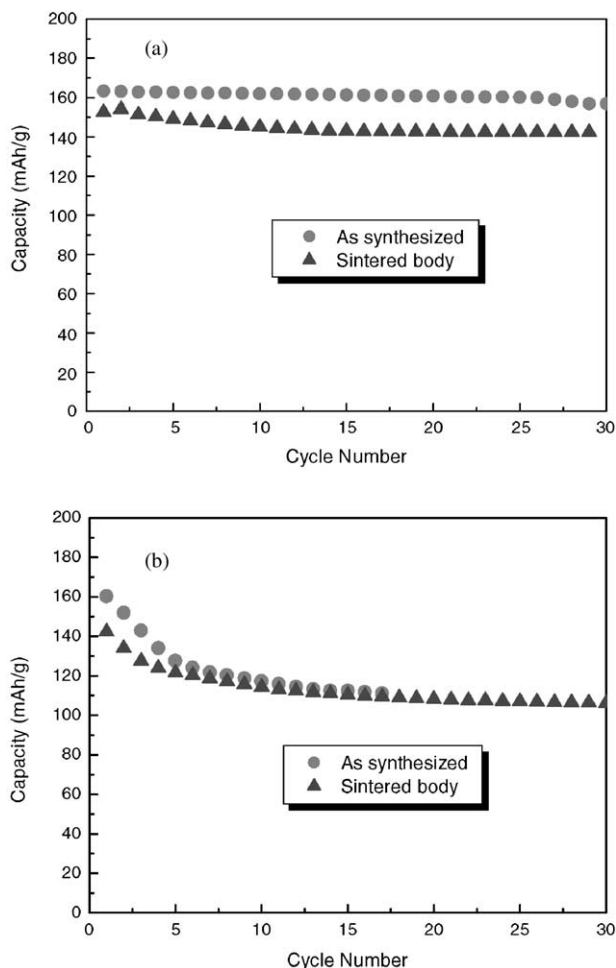

Fig. 3. Capacity retention of as-synthesized powder and powder obtained by crushing sintered bodies with mixing ratio of (a) 1.05:0.5:0.5; (b) 1.1:0.5:0.5 for the lithium, nickel and cobalt source materials.

60%. The densest thin-film in this experiment was 90% of its theoretical density, which was prepared using a 1.05:0.5:0.5 synthesized powder target. The coarsest film was 60% of the theoretical density and was prepared from a 1.1:0.5:0.5 raw material powder target. From the approximate density of the film, the theoretical discharge capacities can be calculated. A fully dense lithium nickel cobalt oxide thin-film yeilds 68 μAh/(cm² μm) on extracting half of the lithium. Therefore, the calculated discharge capacity for a 90 and 60% relative density film is 61.2 and 40.8 μAh/(cm² μm), respectively.

Since, as-deposited thin-films show amorphous characteristics, the films were annealed at 700 °C for 10 min using an RTA (rapid thermal annealing) system. After annealing, the films were fully crystallized to the R3m structure, as for previous powders and no impurity phases were found. All electrochemical tests of thin-films were conducted after the crystallization step.

The initial discharge capacities of the thin-films from the various sputtering targets are shown in Fig. 5. From these results, the densest thin-film, which was prepared with a
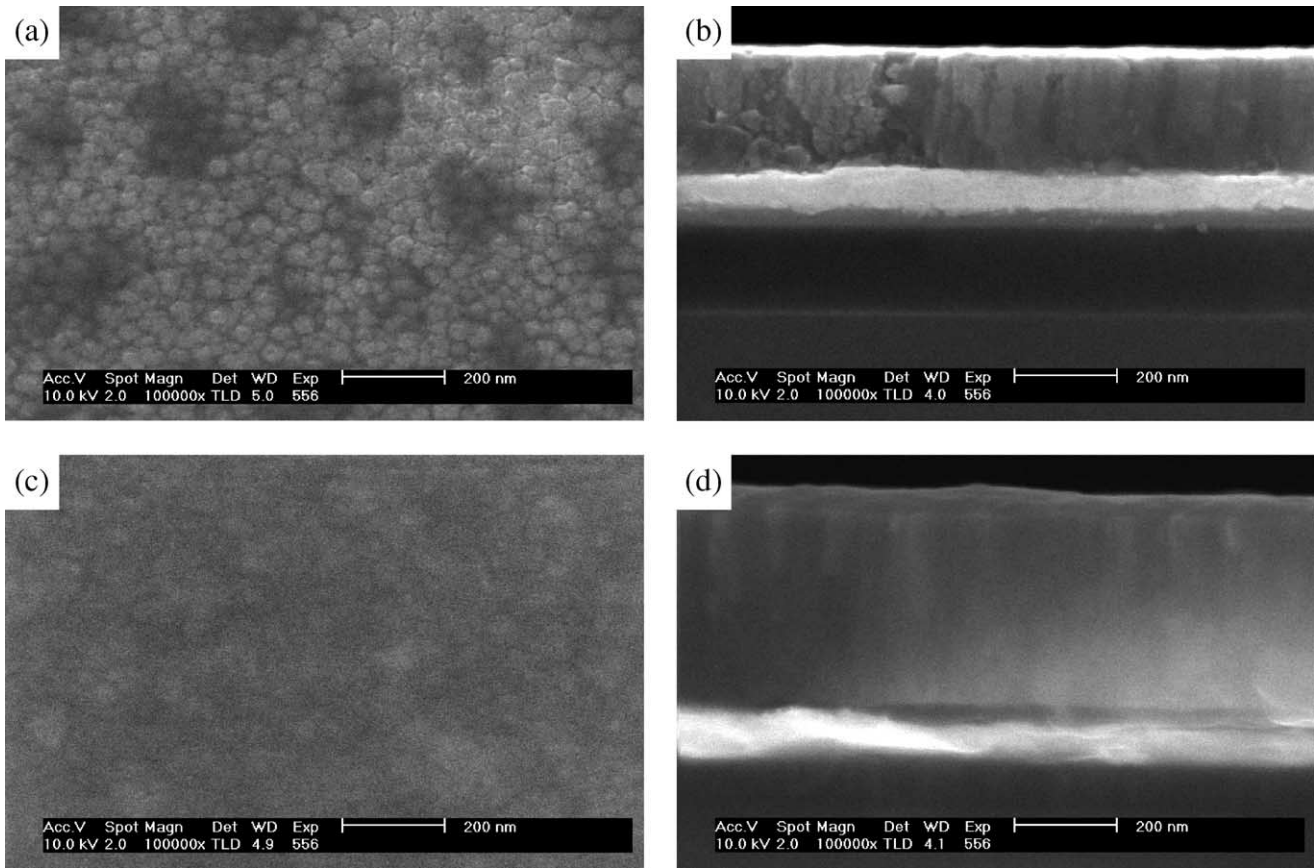
Fig. 4. Surface morphology (a, c) and cross-sectional view (b, d) of as-deposited thin-film with 5 mTorr (a, b) and 10 mTorr (c, d) of Ar and O_2 (2:1) on Pt (500 Å)/SiO$_2$/Si (1 0 0) at 1.23 W/cm^2 sputtering power for 1 h using a target of synthesized powders in ratio 1.05:0.5:0.5.

1.05:0.5:0.5 synthesized powder target, is seen to reach its theoretical value of discharge capacity. On the other hand, films which were deposited using a 1.1:0.5:0.5 synthesized powder target, give 50 µAh/(cm^2 µm) and the calculated value is 56 µAh/(cm^2 µm). This disparity with the calculated value is due to lithium deficiency within the target, as shown in Table 2. In case of a raw material powder target, the discharge capacity abruptly decreases from the calculated value. Compositional analyses for the raw material powder targets were not carried out, but the significant drop in the discharge capacity is not induced by a decrease in film density. Therefore, from the capacity drop, an increase in non-homogeneity and non-stoichiometry in the film prepared from a raw material powder target can be inferred. Due
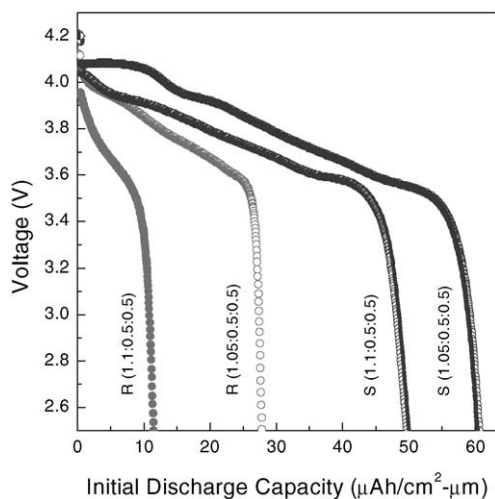

Fig. 5. Initial discharge capacities of thin-films using various conditions of sputtering target. R stands for raw material powder target, S for synthesized powder target.
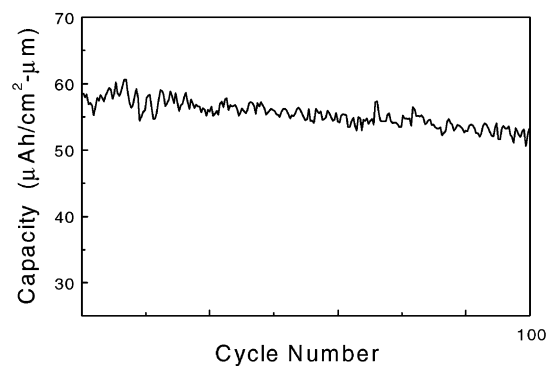

Fig. 6. Cycle retention test on thin-film fabricated with 10 mTorr of Ar and O_2 (2:1) on Pt (500 Å)/SiO$_2$/Si (1 0 0) at 1.23 W/cm^2 sputtering power for 1 h using a target of synthesized powders in ratio of 1.05:0.5:0.5.

to the low deposition rate of lithium and its light weight, deposited films generally show a deficiency of lithium [6]. Hence, the non-homogeneity and non-stoichiometry in the raw material powder target is enlarged during the deposition process and the results in a severe drop in capacity of fabricated thin-films show a severe drop in capacity.

The densest deposited film showed a good cycle retention property and maintained about 90% of initial discharge capacity even after 100 cycles (Fig. 6). From this, the electrochemically active and good characteristic thin-film can be fabricated using 1.05:0.5:0.5 synthesized powder target.

4. Conclusions

Electrochemically active lithium nickel cobalt oxide thin-film has not been fabricated using the RF sputtering method. Lithium non-stoichiometry is increased during the process of deposition. Hence, in this work, a specially designed sputtering target has been manufactured. To compensate for the lithium deficiency, a lithium-rich characteristic powder is synthesized and sintered in an oxygen atmosphere. For the manufacturing process, plain, reactive sintering of raw material powders is applied. The lithium-rich composition is tested for two conditions, 1.05:0.5:0.5 and 1.1:0.5:0.5 for lithium nitrate, nickel carbonate, and cobalt nitrate. By the addition of cobalt, the lithium deficiency is sustained even for the high-temperature sintering process. In case of the lithium-richer composition, 1.1:0.5:0.5, the synthesized powder shows lithium carbonate, which is excess. Lithium carbonate plays a role in the agglomerate and increases the non-stoichiometry. The raw material powder target is too fragile for practical use. Using these manufactured targets,

lithium nickel cobalt oxide thin-films have been fabricated. In case of a 1.05:0.5:0.5 synthesized powder target, the film density is 90% of the theoretical value, and the calculated initial discharge capacity is obtained. In other cases, non-homogeneity and non-stoichiometry are increased during the thin-film deposition process, and poor electrochemical properties are obtained.

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