Research Article

Structural and Electrochemical Properties of Lithium Nickel Oxide Thin Films

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LiNiO₂ thin films were fabricated by RF magnetron sputtering. The microstructure of the films was determined by X-ray diffraction and field-emission scanning electron microscopy. The electrochemical properties were investigated with a battery cycler using coin-type half-cells. The LiNiO₂ thin films annealed below 500°C had the surface carbonate. The results suggest that surface carbonate interrupted the Li intercalation and deintercalation during charge/discharge. Although the annealing process enhanced the crystallization of LiNiO₂, the capacity did not increase. When the annealing temperature was increased to 600°C, the FeCrNiO₄ oxide phase was generated and the discharge capacity decreased due to an oxygen deficiency in the LiNiO₂ thin film. The ZrO₂-coated LiNiO₂ thin film provided an improved discharge capacity compared to bare LiNiO₂ thin film suggesting that the improved electrochemical characteristic may be attributed to the inhibition of surface carbonate by ZrO₂ coating layer.

1. Introduction

In an attempt to miniaturize high performance portable electronic equipment, batteries with high power and energy density are required. Thin film batteries have been developed in an attempt to satisfy this requirement [1–3]; however, improving the performance of the cathode films is critical for advancing the use of electrochemical thin film batteries. Among the possible materials that could be used for a cathode film, LiCoO₂, owing to its high theoretical specific capacity and ease of preparation, is a promising candidate [4–6]. However, the high cost and toxicity of cobalt limit the use of LiCoO₂ in thin film batteries. Therefore, it is necessary to develop less expensive cathode materials for thin film battery applications. LiNiO₂ has emerged as a useful cathode material owing to its low cost and high energy density [7–10].

In the current study, LiNiO₂ thin films were deposited by using RF magnetron sputtering. The microstructure of the films was measured by X-ray diffraction and field-emission scanning electron microscopy. Finally, the electrochemical

properties were investigated with a battery cycler using coin-type half-cells, in the potential range of 3.0 V–4.2 V.

2. Experimental

Bare and ZrO₂-coated LiNiO₂ thin films have been deposited onto stainless steel (STS 304) foil substrates held at a distance of 6 cm away from the target. The STS304 substrate was ultrasonically cleaned with acetone, alcohol, and distilled water in that order. The LiNiO₂ and ZrO₂ targets were made by Pascal Co. (Japan). A base vacuum of 5×10^{-6} Torr was obtained with a cryopump. Gas flow rate of Ar/O₂ was 4/1 with a total gas flow amount of 150 sccm. Deposition pressure was maintained at 2×10^{-3} Torr during deposition. The LiNiO₂ target was presputtered for 30 min and the deposition time was 360 min at 100 W RF power. ZrO₂ coating layer was deposited for 10 min at 100 W RF power. Figures 1(a) and 1(b) show the surface and cross-section images of bare LiNiO₂ thin film deposited on Si wafer substrate. As seen in Figure 1(a),

FIGURE 1: FE-SEM images of (a) surface and (b) cross-section images of LiNiO_2 thin film deposited on Si wafer substrate.

FIGURE 2: XRD patterns of (a) as-deposited, (b) 400°C, (c) 500°C, and (d) 600°C annealed LiNiO_2 thin films. The annealing time was 10 minutes.

a uniform distribution of clusters of ~ 50 nm was seen. The calculated deposition rates of LiNiO_2 were approximately 1.7 nm/min. The deposited thin films were annealed from 400°C to 600°C in air to obtain the crystalline film.

The structure of the LiNiO_2 thin films was investigated by X-ray diffractometry (XRD, Rigaku, Miniflex). The XRD measurements were performed using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) and phase identification was made by comparing the diffraction patterns with the JCPDS references. The morphology of the deposited films was studied by field-emission scanning electron microscopy (FE-SEM, Jeol, JSM-6701F).

In order to examine the electrochemical properties of cathode thin films, coin-type cells were assembled with lithium foils as the counter and reference electrode and 1M LiPF_6 in ethylene carbonate (EC):diethyl carbonate (DEC) (1:1, vol.%) electrolytic solution. The charge-discharge test was carried out with a battery cycler (Won A Tech,

WDCS3000s) at a constant current density of $5 \mu\text{A}/\text{cm}^2$ in the potential range of 3.0–4.2 V.

3. Results and Discussion

Figure 2 shows the XRD patterns of as-deposited and annealed LiNiO_2 thin films at various temperatures at 10 min. Crystallization peaks of LiNiO_2 were not seen in the as-deposited films. However, the XRD pattern of the 400°C annealed film exhibited broad (104) LiNiO_2 and lithium carbonate (Li_2CO_3) reflection peaks. The degree of crystallization of LiNiO_2 was enhanced at 500°C because the (104) reflection became stronger as the annealing temperature was increased. The intensity of the Li_2CO_3 peak also increased. However, after annealing at 600°C, the reflection peaks of LiNiO_2 and Li_2CO_3 disappeared and impurity peaks of NiCrFeO_4 , which was considered an oxide layer of the STS304 substrate, were observed (Figure 2(d)).

FIGURE 3: FE-SEM images of LiNiO_2 thin film with various annealing temperatures at (a) 400°C , (b) 500°C , and (c) 600°C , respectively. The annealing time was 10 minutes.

Surface images of the annealed LiNiO_2 thin films are shown in Figure 3. The 400°C annealed film had a rough surface with no cracks and some surface impurities (Figure 3(a)). When the annealing temperature was increased to 500°C , the size of the surface impurities grew and became angular. After annealing at 600°C , complete removal of the surface impurities was achieved and the surface had a smooth morphology compared with that of the 400°C annealed film. The XRD (Figure 2) and FE-SEM (Figure 3) results suggest that the angulated surface impurity, which disappeared at an annealing temperature of 600°C , was lithium carbonate (Li_2CO_3).

Figure 4 shows the initial discharge curves of the as-deposited and annealed LiNiO_2 thin films. All of these films were tested at a current density of $5\ \mu\text{A}/\text{cm}^2$ between 3.0 V and 4.2 V and a plateau was observed in the 400°C annealed films. When the annealing temperature was increased to 500°C , the plateau was more clearly exhibited and indicated a phase transition of crystalline LiNiO_2 [11, 12]; the discharge capacity, however, did not increase. These results suggest that the surface carbonate interrupts the lithium intercalation and deintercalation during charge/discharge, affecting the discharge capacity. The 600°C annealed films exhibited a lower initial discharge capacity compared with the other annealed films. This may be attributed to the formation of an intermediate oxide layer between the substrate and

FIGURE 4: Initial discharge curves of LiNiO_2 thin film with various annealing temperatures. The annealing time was 10 minutes.

active material film. The intermediate oxide layer that formed may lead to an oxygen deficiency in the annealed LiNiO_2 thin films. In order for the LiNiO_2 film to obtain good electrochemical characteristics, the deposited LiNiO_2 thin

FIGURE 5: XRD patterns of (a) noncoated and (b) ZrO_2 -coated LiNiO_2 thin films. The films were annealed in 10 min at 500°C .

FIGURE 6: (a) Initial discharge behavior and (b) cyclic performance of LiNiO_2 thin films. The films were annealed in 10 min at 500°C .

films should be annealed at a temperature that prevents the formation of an intermediate oxide layer. In addition, it is necessary to remove the surface carbonate. It has been previously reported that surface coatings enhance the electrochemical properties of cathode materials without sacrificing the specific capacity of the respective cathode [13].

Figure 5 shows the XRD patterns of bare and ZrO_2 -coated LiNiO_2 thin films annealed at 500°C for 10 min. As seen in Figure 5(a), the diffraction peak of the surface carbonate disappeared in the coated thin film, suggesting that the ZrO_2 coating prevents the formation of surface carbonate during the annealing process.

Figure 6 shows the first discharge curves and cycle stability of bare and ZrO_2 -coated LiNiO_2 thin films. As seen in Figures 6(a) and 6(b), a single plateau was observed in both of the films, corresponding to the phase transition of crystalline LiNiO_2 . Therefore, this would indicate that both films are crystallized. However, the first discharge capacity

is slightly different such that the first discharge capacity of ZrO_2 -coated film is higher than that of the bare LiNiO_2 thin film. The capacity retention rate is similar in both thin films as seen in Figure 6(b).

4. Summary

LiNiO_2 thin films were fabricated by RF magnetron sputtering. Crystallization began at annealing temperatures above 400°C ; however, the films that were annealed below 500°C exhibited surface carbonate (in the form of Li_2CO_3) identified by XRD. Surface carbonate interrupts the Li intercalation and deintercalation during charge/discharge and therefore the capacity did not increase, although the degree of LiNiO_2 crystallization was enhanced. When the annealing temperature was increased to 600°C , the FeCrNiO_4 oxide phase was generated and the discharge capacity decreased due to

the oxygen deficiency in the LiNiO_2 thin film. The ZrO_2 -coated LiNiO_2 thin film provided an improved discharge capacity compared to the bare LiNiO_2 thin film at an annealing temperature of 500°C . Therefore, the improvement in electrochemical characteristics can be attributed to the inhibition of surface carbonate by the ZrO_2 coating layer.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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References

- [1] Y. Iriyama, C. Yada, T. Abe, Z. Ogumi, and K. Kikuchi, "A new kind of all-solid-state thin-film-type lithium-ion battery developed by applying a D.C. high voltage," *Electrochemistry Communications*, vol. 8, no. 8, pp. 1287–1291, 2006.
- [2] S. J. Lee, H. K. Baik, and S. M. Lee, "An all-solid-state thin film battery using LISIPON electrolyte and Si-V negative electrode films," *Electrochemistry Communications*, vol. 5, no. 1, pp. 32–35, 2003.
- [3] Y. J. Kim, H. Kim, B. Kim et al., "Electrochemical stability of thin-film LiCoO_2 cathodes by aluminum-oxide coating," *Chemistry of Materials*, vol. 15, no. 7, pp. 1505–1511, 2003.
- [4] G. G. Amatucci, J. M. Tarascon, and L. C. Klein, " CoO_2 , the end member of the Li_xCoO_2 solid solution," *Journal of The Electrochemical Society*, vol. 143, no. 3, pp. 1114–1123, 1996.
- [5] K. Edstrom, T. Gustafsson, and J. O. Thomas, "The cathode-electrolyte interface in the Li-ion battery," *Electrochimica Acta*, vol. 50, no. 2-3, pp. 397–403, 2004.
- [6] J. H. Kim, M. Y. Eom, S. W. Noh, and D. W. Shin, "Performance optimization of all-solid-state lithium ion batteries using a $\text{Li}_2\text{S-P}_2\text{S}_5$ solid electrolyte and LiCoO_2 cathode," *Electronic Materials Letters*, vol. 8, pp. 209–213, 2012.
- [7] H. Arai, S. Okada, H. Ohtsuka, M. Ichimura, and J. Yamaki, "Characterization and cathode performance of $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$ prepared with the excess lithium method," *Solid State Ionics*, vol. 80, pp. 261–269, 1995.
- [8] S. H. Ju, J. H. Kim, and Y. C. Kang, "Electrochemical properties of $\text{LiNi}_{0.8}\text{Co}_{0.2-x}\text{Al}_x\text{O}_2$ ($0 \leq x \leq 0.1$) cathode particles prepared by spray pyrolysis from the spray solutions with and without organic additives," *Metals and Materials International*, vol. 16, no. 2, pp. 299–303, 2010.
- [9] S. N. Kwon, J. Song, and D. R. Mumm, "Effects of cathode fabrication conditions and cycling on the electrochemical performance of LiNiO_2 synthesized by combustion and calcination," *Ceramics International*, vol. 37, no. 5, pp. 1543–1548, 2011.
- [10] M. Y. Song, C. K. Park, H. R. Park, and D. R. Mumm, "Variations in the electrochemical properties of metallic elements-substituted LiNiO_2 cathodes with preparation and cathode fabrication conditions," *Electronic Materials Letters*, vol. 8, no. 1, pp. 37–42, 2012.
- [11] J. Cho, T. Kim, Y. J. Kim, and B. Park, "High-performance ZrO_2 -coated LiNiO_2 cathode material," *Electrochemical and Solid-State Letters*, vol. 4, no. 10, pp. A159–A161, 2001.
- [12] E. Endo, T. Yasuda, K. Yamaura, A. Kita, and K. Sekai, " LiNiO_2 electrode modified by plasma chemical vapor deposition for higher voltage performance," *Journal of Power Sources*, vol. 93, no. 1-2, pp. 87–92, 2001.
- [13] J. Kim, C. S. Johnson, J. T. Vaughey et al., "The electrochemical stability of spinel electrodes coated with ZrO_2 , Al_2O_3 , and SiO_2 from colloidal suspensions," *Journal of the Electrochemical Society*, vol. 151, no. 10, pp. A1755–A1761, 2004.