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Electrochemical characteristics of $LiNiO_2$ and $LiCoO_2$ as a positive material for lithium secondary batteries

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Abstract

The discharge characteristics of lithium nickel oxides have been improved by investigating their synthesizing conditions, such as their raw materials and heat-treating conditions. Lithium hydroxide (LiOH) and nickel hydroxide ($Ni(OH)_2$) were found to be appropriate raw materials, and 750 °C in oxygen atmosphere was the most suitable heat-treating condition. Lithium nickel oxide synthesized under these suitable conditions showed a greater discharge capacity of more than 190 mAh/g than that of lithium cobalt oxide. The existence of lithium carbonate (Li_2CO_3) was detected, by the Fourier-transform infrared spectroscopy method, in lithium nickel oxide heat-treated in air. This suggests that the existence of Li_2CO_3 adversely affected the discharge characteristics of lithium nickel oxides.

Keywords: Secondary lithium batteries; Nickel oxide; Cobalt oxide

1. Introduction

Increased demand for secondary batteries with high energy density has accompanied the advancement of electronic devices. As a result, the research and development of ambient-temperature lithium secondary batteries has been intensified. Recently, lithium secondary batteries using a carbon negative electrode have attracted considerable interest in terms of providing safety and a long cycle life.

Lithium cobalt oxide ($LiCoO_2$) and lithium nickel oxide ($LiNiO_2$) are promising compounds for use as a positive electrode material in lithium secondary batteries using a carbon negative electrode, because they show a very high discharge potential and contain lithium in their structure before charging the carbon negative electrode [1–3]. The conditions for synthesizing $LiNiO_2$ are said to be more complicated than those for $LiCoO_2$ [4], but $LiNiO_2$ offers an advantage in terms of the availability of natural resources and cost.

In this paper, we have investigated suitable conditions for synthesizing $LiNiO_2$, such as raw materials, heat-treating temperature and atmosphere. Materials were also examined in terms of their crystal structure, composition and other physical properties. These conditions and properties have been related to the electrochemical characteristics.

2. Experimental

$LiCoO_2$ was prepared from lithium carbonate (Li_2CO_3) and cobalt carbonate ($CoCO_3$) by heat-treating at 850 °C for 20 h, and $LiNiO_2$ was prepared by heat-treating lithium compounds and nickel compounds in air or oxygen atmosphere between 650 and 850 °C. A mixture of $LiCoO_2$ or $LiNiO_2$, carbon and binder was used as the positive electrode. Charge/discharge tests were carried out in three-electrode experimental cells using lithium metal as the counter and reference electrodes. The charge/discharge current density was 0.25 mA/cm^2 and the potential range was from 3.0 to 4.3 V (versus Li/Li^+).

The crystal structures of these samples were characterized by powder X-ray diffraction (XRD). The existence of by-products was confirmed by Fourier-transform infrared spectroscopy (FT-IR).

3. Results and discussion

3.1. Raw materials

In order to select suitable raw materials for synthesizing $LiNiO_2$, we synthesized lithium nickel oxides from various lithium compounds and nickel compounds, lithium hydroxide (LiOH), Li_2CO_3, nickel hydroxide

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($Ni(OH)_2$), nickel carbonate ($NiCO_3$) and nickel oxide (NiO).

Fig. 1 shows the discharge characteristics of $LiCoO_2$ and lithium nickel oxides synthesized from these compounds. They were heat-treated at 850 °C for 20 h in air. We selected this condition as the first screening because it is a well-known method for synthesizing $LiCoO_2$. Although lithium nickel oxides showed a smaller discharge capacity than that of $LiCoO_2$, LiOH and $Ni(OH)_2$ were considered to be the appropriate raw materials. It was also found from the results of XRD patterns that lithium nickel oxides which showed poor discharge characteristics had similar crystal structures to that of $Li_2Ni_8O_{10}$ (JCPDS No. 23-362), and lithium nickel oxide prepared from LiOH and $Ni(OH)_2$ had a similar XRD pattern to that of $LiNiO_2$ (JCPDS No. 9-63).

3.2. Heat-treating temperature

Fig. 2 shows the discharge characteristics of $LiCoO_2$ and lithium nickel oxides prepared from LiOH and $Ni(OH)_2$ at 650, 750 and 850 °C. Lithium nickel oxide heat-treated at 750 °C showed nearly the same discharge capacity as that of $LiCoO_2$ while the discharge potential was lower than that of $LiCoO_2$.

The composition of these oxides was determined by the results of chemical analysis. The composition of lithium cobalt oxide prepared at 850 °C and lithium

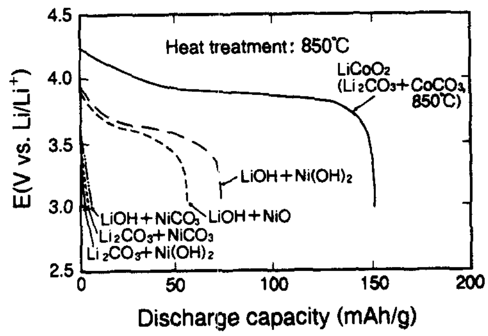

Fig. 1. Discharge characteristics of $LiCoO_2$ and some lithium nickel oxides electrodes; current density = 0.25 mA/cm^2.

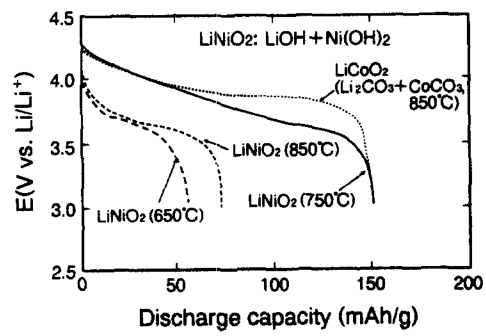

Fig. 2. Discharge characteristics of some lithium nickel oxides and $LiCoO_2$ electrodes; current density = 0.25 mA/cm^2.

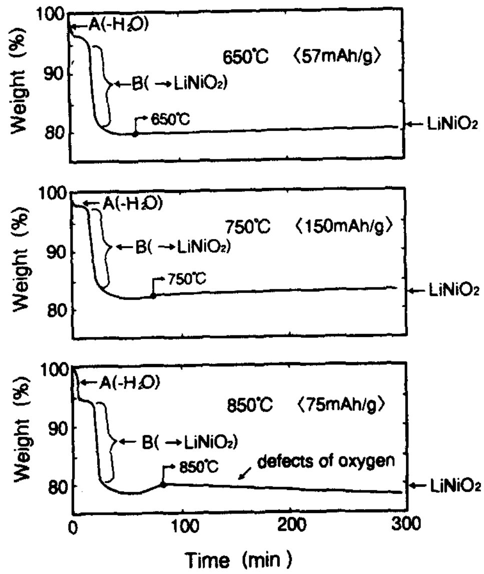

Fig. 3. Thermogravimetric analysis of LiOH and $Ni(OH)_2$: (A) dehydration from raw materials, and (B) $LiOH + Ni(OH)_2 + 0.25O_2 \rightarrow LiNiO_2 + 1.5H_2O$.

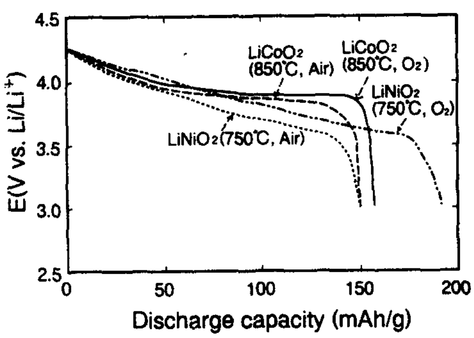

Fig. 4. Discharge characteristics of $LiNiO_2$ and $LiCoO_2$, synthesized in air and oxygen; current density = 0.25 mA/cm^2.

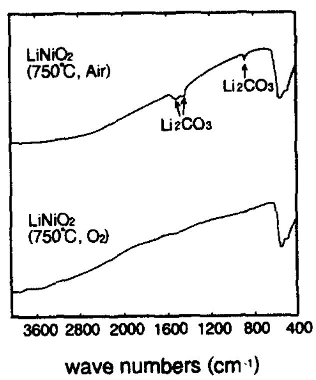

Fig. 5. Fourier-transform infrared spectra of $LiNiO_2$ heat-treated in air and oxygen.

nickel oxides prepared at 650 and 750 °C was very close to $LiCoO_{2.0}$ and $LiNiO_{2.0}$, respectively. On the other hand, the composition of lithium nickel oxides prepared at 850 °C was $LiNiO_{1.8}$.

Fig. 3 shows the results of thermogravimetric analysis of LiOH and $Ni(OH)_2$ heat-treated from room temperature to 650, 750 or 850 °C. The temperature was kept after having reached the temperatures indicated in Fig. 3. In the case of 850 °C, a decrease in weight was confirmed. This was considered to be caused by the defect of oxygen in the lithium nickel oxide.

3.3. Heat-treating atmosphere

In order to examine the influence of the heat-treating atmosphere, $LiCoO_2$ and $LiNiO_2$ were synthesized in oxygen atmosphere. As a result, $LiNiO_2$ heat-treated in oxygen showed much better discharge characteristics than in air, although $LiCoO_2$ showed a similar discharge capacity in air and oxygen. $LiNiO_2$ heat-treated in oxygen showed a discharge capacity of more than 190 mAh/g, which was greater than that of $LiCoO_2$ as shown in Fig. 4.

Fig. 5 shows the FT-IR spectra of $LiNiO_2$ heat-treated at 750 °C in air and oxygen atmosphere. The peaks for Li_2CO_3 were much more obvious in $LiNiO_2$ prepared in air than in oxygen. This suggested that the existence of Li_2CO_3 had some influence on the composition and discharge characteristics of $LiNiO_2$.

4. Conclusions

The relation between the conditions for synthesizing $LiNiO_2$ and its electrochemical characteristics was investigated. LiOH and $Ni(OH)_2$ were found to be appropriate raw materials, and 750 °C in oxygen were the most suitable heat-treating conditions. $LiNiO_2$ synthesized under these suitable conditions showed a greater discharge capacity (more than 190 mAh/g) than that of $LiCoO_2$. The existence of Li_2CO_3 was detected in $LiNiO_2$ heat-treated in air by the FT-IR method. This suggested that the existence of Li_2CO_3 adversely affected the discharge characteristics of $LiNiO_2$.

References

[1] K. Mizushima, P.C. Jones, P.C. Wiseman and J.B. Goodenough, *Mater. Res. Bull., 15* (1980) 783.

[2] J.R. Dahn, U. von Sacken and C.A. Michel, *Solid State Ionics, 44* (1990) 87.

[3] T. Ohzuku, A. Ueda and M. Nagayama, *J. Electrochem. Soc., 140* (1993) 1862.

[4] H. Kurokawa, M. Uehara, M. Fujimoto, M. Takahashi, T. Nohma, K. Nishio and T. Saito, *Ext. Abstr., 60th Meet. Japan Electrochemical Society, Tokyo, Japan, 1993*, p. 175.