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Synthesis and Electrochemical Performance of LiNi$_x$Ti$_y$O$_2$ as a New Positive Electrode Material


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**Introduction**

Layered LiNi$_x$Ti$_y$O$_2$ containing Ni$^{2+}$ and Ti$^{4+}$, which has a similar composition and structure to LiNi$_x$Mn$_{2-x}$O$_2$, is a potential positive electrode material for rechargeable lithium batteries. However, it has been reported that it is impossible to prepare this compound by simple calcination. Recently, Kang et al. have reported layered Li$_{0.5}$Ni$_{0.4}$Ti$_{0.1}$O$_2$ synthesized by ion exchange. We decided it would be desirable to prepare Li-Ni-Ti oxide with Ni/Ti=1, as it is known that LiNi$_x$Mn$_{1-x}$O$_2$ exhibits good electrochemical performance when the Ni/Mn molar ratio is close to 1. So, we set the Ni/Ti starting ratio at 1 and employed ion exchange with layered NaNi$_{0.5}$Ti$_{0.5}$O$_2$ as a precursor to prepare layered LiNi$_x$Ti$_y$O$_2$. In this paper, we report the electrochemical performance and other results for the obtained Li-Ni-Ti oxide.

**Synthesis**

The layered NaNi$_{0.5}$Ti$_{0.5}$O$_2$ was synthesized by calcination. We mixed NaNi$_{0.4}$Ti$_{0.6}$O$_2$ and LiNO$_3$, and then heated this mixture at 270 °C for 3 h in an argon atmosphere. After this heat treatment, the reaction mixture was washed with distilled water and acetone, and then filtered and dried at 80 °C in air. Hereafter, we denote the precursor NaNi$_{0.4}$Ti$_{0.6}$O$_2$ as ‘precursor’ and the sample after ion exchange as ‘Li-type sample’.

**Results and Discussion**

The nominal composition of the precursor was Na$_{3.88}$Ni$_{0.4}$Ti$_{0.6}$O$_{2.07}$ (the excess sodium and oxygen was caused by the excess Na$_2$CO$_3$). The XRD analysis confirmed that precursor with a layer structure was obtained; although there was a small amount of impurity phase NiO.

The composition of the Li-type sample was Li$_{1.0}$Na$_{0.4}$Ni$_{0.4}$Ti$_{0.6}$O$_{2.0}$. The Li-type sample was yellow-green in color, suggesting low conductivity. Fig. 1 shows the XRD pattern of the Li-type sample. The pattern was indexed in a space group of R-3m, showing that a layered compound was obtained.

Figs. 2(a) and (b) show Ni and Ti K-edge XANES spectra, respectively. The Ni K-edge spectra of the precursor and Li-type sample were similar to that of the Ni$^{2+}$ reference, NiO. This suggests that the nickel was divalent. The Ti K-edge spectra of the precursor and Li-type sample were similar. Although the peak shape of the Ti$^{4+}$ reference, rutile-type TiO$_2$, was different from those of our samples, all the spectra had pre-edges at about 4.968 keV, and the maximum peak energies were also similar. Accordingly, we assumed the existence of tetravalent titanium.

Fig. 3 shows charge/discharge curves for the Li-type sample, which we obtained using a coin cell with a metallic lithium negative electrode. The first charge and discharge capacities were about 120 and 66 mAh g$^{-1}$, respectively. There was a large irreversible capacity within the first cycle. The second discharge capacity was even smaller than the first, and the cyclability required improvement.

**References**

1) Y. Makimura and T. Ohzuku, J. Power Sources, 119-121, 156 (2003).