

Synthesis and Electrochemical Performance of LiNi_{0.5}Ti_{0.5}O₂ as a New Positive Electrode Material

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Introduction

Layered LiNi_{0.5}Ti_{0.5}O₂ containing Ni²⁺ and Ti⁴⁺, which has a similar composition and structure to LiNi_{0.5}Mn_{0.5}O₂,^{1,2)} 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.³⁾ Recently, Kang et al. have reported layered Li_{0.9}Ni_{0.45}Ti_{0.55}O₂ synthesized by ion exchange.⁴⁾ We decided it would be desirable to prepare Li-Ni-Ti oxide with Ni/Ti=1, as it is known that LiNi_{0.5}Mn_{0.5}O₂ exhibits good electrochemical performance when the Ni/Mn molar ratio is close to 1.¹⁾ So, we set the Ni/Ti starting ratio at 1 and employed ion exchange with layered NaNi_{0.5}Ti_{0.5}O₂ as a precursor to prepare layered LiNi_{0.5}Ti_{0.5}O₂.^{5,6)} 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}O₂ was synthesized by calcination.⁷⁾ We mixed NaNi_{0.5}Ti_{0.5}O₂ and LiNO₃, 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_{0.5}Ti_{0.5}O₂ as 'precursor' and the sample after ion exchange as 'Li-type sample'.

Results and Discussion

The nominal composition of the precursor was Na_{1.08}Ni_{0.49}Ti_{0.51}O_{2.07} (the excess sodium and oxygen was caused by the excess Na₂CO₃). 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_{0.80}Na_{0.12}Ni_{0.49}Ti_{0.51}O_{1.98}. 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 Ni²⁺ 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 Ti⁴⁺ reference, rutile-type TiO₂, 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

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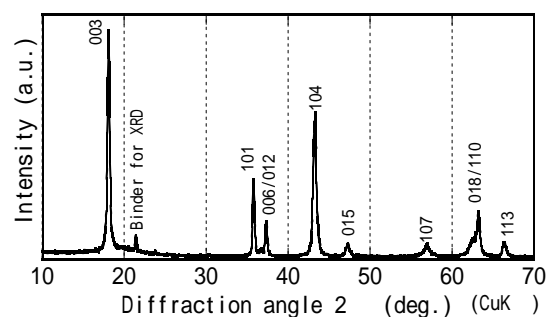


Fig. 1. XRD pattern of the Li-type sample.

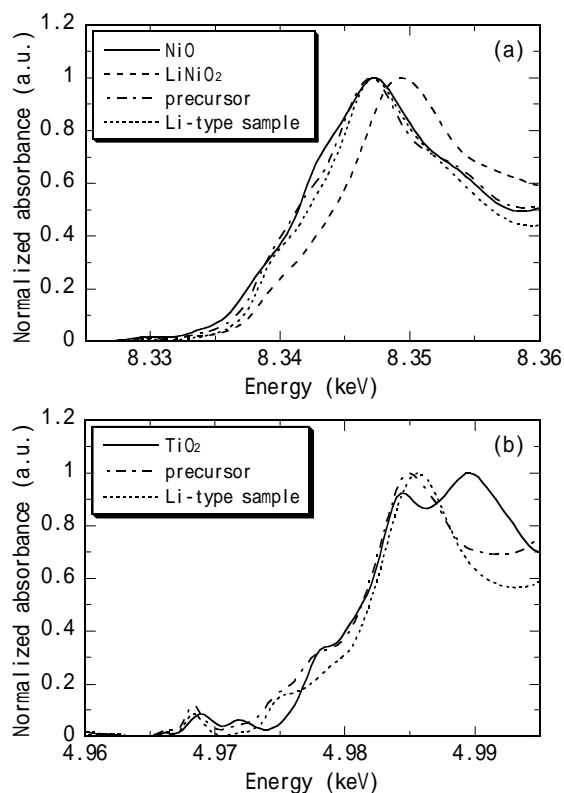


Fig. 2. (a) Ni K-edge and (b) Ti K-edge XANES spectra of the precursor and Li-type sample.

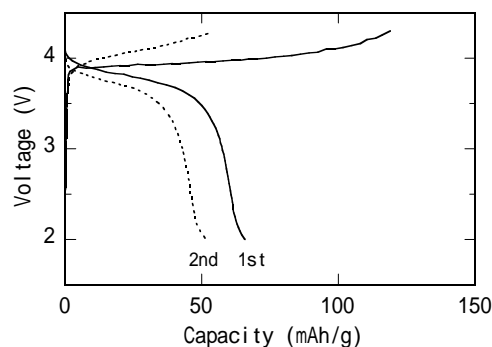


Fig. 3. Charge/discharge curves of the Li-type sample at voltages of 2.0~4.3 V with a current density of 0.1 mA cm⁻².