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Exploration of layered-type pseudo four-component Li–Ni–Co–Ti oxides

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Abstract

A series of layered-type pseudo four-component Li–Ni–Co–Ti oxides were prepared to explore optimal cathode materials for a lithium-ion secondary battery. The new layered-type compounds were prepared using a combinatorial material-preparation system based on electrostatic spray deposition (the ‘‘M-ist Combi’’ system), and combinatorial powder X-ray diffraction. The composition region of the new compounds ($Li_{\alpha}(Ni_xCo_yTi_z)O_2$ ($\alpha \sim 1$, $0 \le x \le 1$, $0 \le y \le 1$, $z \sim 0.2$, $x + y + z = 1.0$)) was found to be wider than the composition region previously reported ($LiNi_{0.8-y}Co_{0.2}Ti_yO_2$ ($0 \le y \le 0.1$)).

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Keywords: Combinatorial chemistry; Powder preparation; Layered-type structure; Electrode materials

1. Introduction

The positive electrodes for secondary lithium-ion batteries are usually made from the layered-type structure $LiCoO_2$. This compound has drawbacks, however, as it is toxic and requires the use of cobalt, an expensive material. Many researchers have tried to find alternative positive electrode compounds and overcome the current dependence on $LiCoO_2$ for the production of lithium-ion rechargeable batteries. $LiNi_{0.8}Co_{0.2}O_2$ [1,2], $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ [3–5] has recently been found to possess electrochemical and safety characteristics comparable or superior to those $LiCoO_2$, and thus is regarded as one of the most promising alternatives.

In this study we focused on the layered-type Li–Ni–Co–Ti oxides, as Li–Ni–Ti [6–8] and some of the Li–Ni–Co–Ti [9,10] compounds have been confirmed to have excellent electrode properties and to perform well as cathode materials. Layered-type Li–Ni–Ti compounds have been obtained in the range of $Li_xNi_{1-y}Ti_yO_2$ ($x \sim 1$, $0.1 \le y \le 0.55$). Layered-type Li–Ni–Co–Ti compounds, on the other hand, have only been reported in the range of $LiNi_{0.8-y}Co_{0.2}Ti_yO_2$ ($0 \le y \le 0.1$). Our group speculated that with a combinatorial process, it may be possible to use these layered-type Li–Ni–Co–Ti compounds to quickly prepare not only this tie line, but also a wider composition region throughout the entire range. We therefore applied the combinatorial process to obtain the information on a series of single phase layered-type pseudo four-component Li–Ni–Co–Ti compounds.

In an effort to find a series of single phase layered-type Li–Ni–Co–Ti oxides, we used the M-ist Combi system to prepare a series of pseudo four-component Li–Ni–Co–Ti oxides and then identified the oxides with a combinatorial powder X-ray diffractometer.

2. Experimental

A Li–Ni–Co–Ti oxide powder library was prepared using the M-ist Combi system based on a method of electrostatic spray deposition. Fig. 1 illustrates the M-ist Combi system apparatus. The main components were a multi-liquid feed unit, high-voltage power supply, triaxial robot system, and PC control unit. The starting materials

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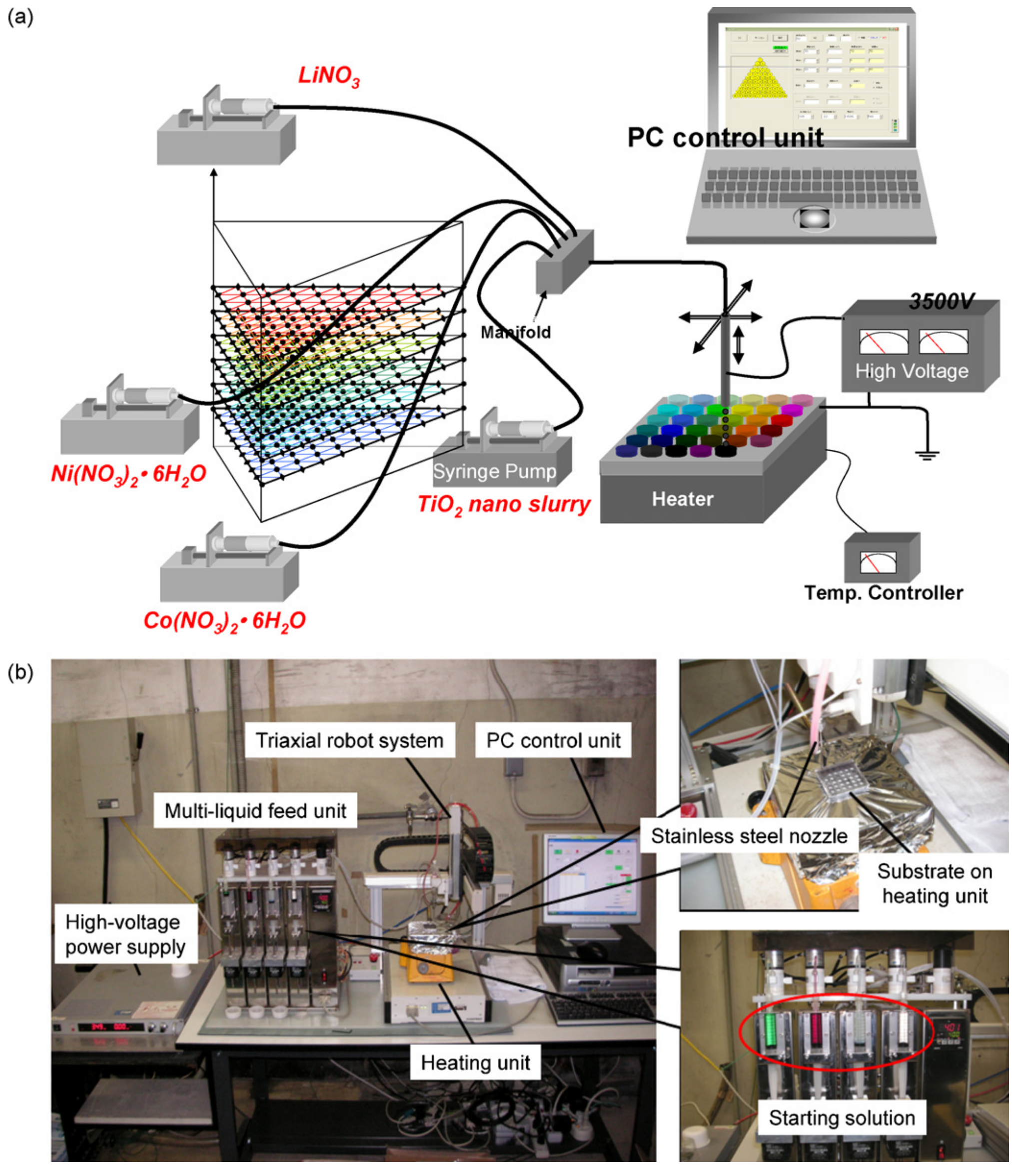

Fig. 1. Schematic image (a) and photograph (b) of the M-ist Combi system based on an electrostatic atomization method.

were $LiNO_3$, $Ni(NO_3)_2{\cdot}6H_2O$, $Co(NO_3)_2{\cdot}6H_2O$ and TiO_2 nano-slurry. The materials were dissolved in a mixture of ethanol and butyl carbitol at mixture ratios controlled by the feed speeds of the syringe pumps used to dispense them. The liquid mixture of starting materials in the manifold was fed to a stainless steel nozzle charged with a high-voltage and atomized from the top of the nozzle onto a substrate heated at 400 °C. Once the materials were deposited, they were heat-treated at 700 °C for 5 h in atmospheric air and evaluated by a combinatorial powder X-ray diffractometer. The diffractometer was equipped with a slidable X–Y stage and a position-sensitive proportional counter (PSPC). These components enabled the device to obtain the diffraction pattern without a scanning detector, within a brief period of only about 2 min per pattern. Once the X-ray diffraction patterns were analyzed, reaction phase diagrams were established and the chemical components of the heat-treated library were analyzed by ICP emission spectroscopy.

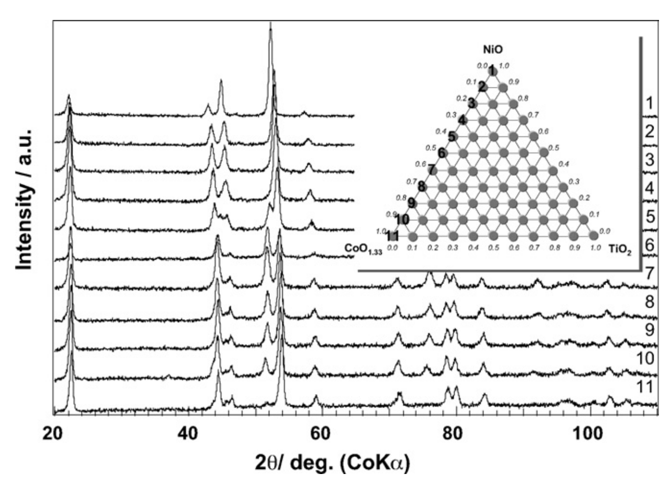

Fig. 2. Powder X-ray diffraction patterns of Li:($Ni_x + Co_y + Ti_z$) = 50:50 ($0 \le x \le 1$, $0 \le y \le 1$, $z = 0$, $x + y + z = 1$) in the initial condition after heat treatment at 700 °C for 5 h.