Comparison of the Electrochemical Properties of Layered Structure Li[Ni$_x$Co$_y$Mn$_{1-x-y}$]O$_2$ (x = 1/3, 0.5, 0.6, 0.7, 0.8, and 0.85) Cathode Material for Lithium-Ion Batteries

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Introduction

Rechargeable lithium-ion batteries have become a common power source for portable electronic devices due to their high energy density, high voltage, and long cycle life. The widespread use of these batteries in the automobile industry requires further improvements of their energy density and safety. **[1-4]**

Li[Ni$_{1-x-y}$Co$_x$Mn$_y$]O$_2$ materials (1-x-y $\geq$ 0.5) deliver higher capacities than Li[Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$]O$_2$ due to the higher Ni content, which is the main active redox species (Ni$^{2+}\leftrightarrow$Ni^{4+}) in the host structure. The thermal stability of Li[Ni$_{1-x-y}$Co$_x$Mn$_y$]O$_2$ is also directly related to the Ni content. In other words, the relationship between capacity and safety is a trade-off. It is well known that Ni provides a high capacity but poor thermal stability, while Mn maintains an outstanding cycle life and safety. Also, Co offers increased electronic conductivity resulting in an excellent rate capability. Hence, the intrinsic properties of Li[Ni$_{1-x-y}$Co$_x$Mn$_y$]O$_2$ materials strongly depend on the amounts of the metal ions (Ni, Co, Mn). However, the relationships between the compositions and the capacity and thermal stability in layered lithium metal oxides have not been systematically studied.

In this report, we intensively studied the effects of the transition metal composition on the electrochemical properties and the structural and thermal stabilities of Li[Ni$_x$Co$_y$Mn$_{1-x-y}$]O$_2$ (x:y:1-x-y = 1/3:1/3:1/3, 0.5:0.2:0.3, 0.6:0.2:0.2, 0.70:0.15:0.15, 0.8:0.1:0.1, and 0.85:0.075:0.075, hereafter defined as x = 1/3, 0.5, 0.6, 0.7, 0.8, and 0.85, respectively).

Experimental

Spherical [Ni$_x$Co$_y$Mn$_{1-x-y}$](OH)$_2$ precursors (x=1/3, 0.5, 0.6, 0.7, 0.8, and 0.85) were synthesized via the co-precipitation method.

The appropriate amounts of NiSO$_4$·6H$_2$O, CoSO$_4$·7H$_2$O, and MnSO$_4$·5H$_2$O were used as the starting materials for the synthesis of [Ni$_x$Co$_y$Mn$_{1-x-y}$](OH)$_2$. An aqueous solution of NiSO$_4$·6H$_2$O, CoSO$_4$·7H$_2$O, and MnSO$_4$·5H$_2$O with a concentration of 2.0 mol L^{-1} was pumped into a continuously stirred tank reactor (CSTR, 4 L) under a N$_2$ atmosphere. Concurrently, a 4.0 mol L^{-1} NaOH solution (aq.) and the desired amount of NH$_4$OH solution (aq.) as a chelating agent were separately pumped into the reactor. The concentration of the solution, pH, temperature, and stirring speed of the mixture in the reactor were carefully controlled. The precursor powders were obtained through filtering, washing, and drying in a vacuum oven overnight. Li[Ni$_x$Co$_y$Mn$_{1-x-y}$]O$_2$ (x=1/3, 0.5, 0.6, 0.7, 0.8, and 0.85) were prepared by thoroughly mixing the precursor [Ni$_x$Co$_y$Mn$_{1-x-y}$](OH)$_2$ with LiOH·H$_2$O followed by calcination at various temperatures for 15 hrs: 950 °C for Li[Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$]O$_2$, 950 °C for Li[Ni$_{0.5}$Co$_{0.2}$Mn$_{0.3}$]O$_2$, 900 °C for Li[Ni$_{0.6}$Co$_{0.2}$Mn$_{0.2}$]O$_2$, 850 °C for Li[Ni$_{0.7}$Co$_{0.15}$Mn$_{0.15}$]O$_2$, 780 °C for Li[Ni$_{0.8}$Co$_{0.1}$Mn$_{0.1}$]O$_2$, and 750 °C for Li[Ni$_{0.85}$Co$_{0.075}$Mn$_{0.075}$]O$_2$.

Powder X-ray diffraction (XRD, Rint-2000, Rigaku, Japan) using Cu-Kα radiation was performed to identify the crystal structure of the synthesized material. The thermal stability of the electrochemically delithiated positive electrode material was evaluated with differential scanning calorimetry (DSC, NETZSCH-TA4, Germany).

Electrochemical properties of the synthesized Li[Ni$_x$Co$_y$Mn$_{1-x-y}$]O$_2$ were evaluated using a 2032-type coin type cell.

Results and discussion

Fig. 1 shows the X-ray powder diffraction patterns of the prepared Li[Ni$_x$Co$_y$Mn$_{1-x-y}$]O$_2$ (x=1/3, 0.5, 0.6, 0.7, 0.8, and 0.85) powders. All of the powders exhibited a well-defined layer structure based on a hexagonal a-NaFeO$_2$ structure with a $R\bar{3}m$ space group and no impurity phases.

The thermal stabilities of electrochemically delithiated wet Li[Ni$_x$Co$_y$Mn$_{1-x-y}$]O$_2$ (x=1/3, 0.5, 0.6, 0.7, 0.8, and 0.85) electrodes were evaluated by differential scanning calorimetry (DSC). As can be seen in Fig. 2, the exothermic reaction peak temperature gradually shifted to lower temperatures accompanied with higher heat generation as the Ni content increased
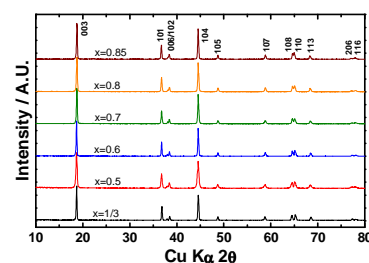

Figure 1. Powder XRD patterns of as-prepared Li[Ni$_x$Co$_y$Mn$_z$]O$_2$ (x =1/3, 0.5, 0.6, 0.7, 0.8, and 0.85).
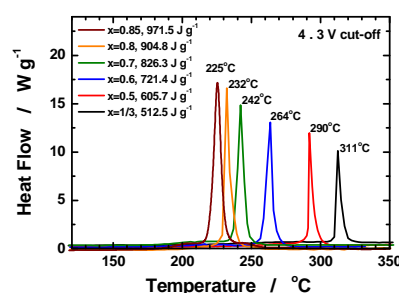

Figure 2. DSC results of the Li$_{1-\delta}$[Ni$_x$Co$_y$Mn$_{1-x-y}$]O$_2$ (x =1/3, 0.5, 0.6, 0.7, 0.8, and 0.85).

Acknowledgments

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