

Improved electrochemical properties of $\text{Li}_{1+x}(\text{Ni}_{0.3}\text{Co}_{0.4}\text{Mn}_{0.3})\text{O}_{2-\delta}$ ($x = 0, 0.03$ and 0.06) with lithium excess composition prepared by a spray drying method

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Abstract

Layered $\text{Li}_{1+x}(\text{Ni}_{0.3}\text{Co}_{0.4}\text{Mn}_{0.3})\text{O}_{2-\delta}$ ($x = 0, 0.03$ and 0.06) materials were synthesized through the different calcination times using the spray-dried precursor with the molar ratio of $\text{Li}/\text{Me} = 1.25$ ($\text{Me} = \text{transition metals}$). The physical and electrochemical properties of the lithium excess and the stoichiometric materials were examined using XRD, AAS, BET and galvanostatic electrochemical method. As results, the lithium excess $\text{Li}_{1.06}(\text{Ni}_{0.3}\text{Co}_{0.4}\text{Mn}_{0.3})\text{O}_{2-\delta}$ could show better electrochemical properties, such as discharge capacity, capacity retention and C rate ability, than those of the stoichiometric $\text{Li}_{1.00}(\text{Ni}_{0.3}\text{Co}_{0.4}\text{Mn}_{0.3})\text{O}_{2-\delta}$. In this paper, the effect of excess lithium on the electrochemical properties of $\text{Li}_{1+x}(\text{Ni}_{0.3}\text{Co}_{0.4}\text{Mn}_{0.3})\text{O}_{2-\delta}$ materials will be discussed based on the experimental results of ex situ X-ray diffraction, transmission electron microscopy (TEM) and galvanostatic intermittent titration technique (GITT)

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1. Introduction

LiCoO_2 is currently used as a positive electrode material for lithium rechargeable batteries due to its ease to production and acceptable specific capacity. However, the relatively high cost of the cobalt and the thermal instability of the charged positive electrode in electrolyte have lead to the study for other possible materials for lithium rechargeable batteries such as lithium nickel oxides, lithium manganese oxides, lithium iron phosphates and their substituted materials [1–5]. Recently, $\text{Li}(\text{Ni}_x\text{Co}_{1-2x}\text{Mn}_x)\text{O}_2$ ($0 \leq x \leq 1/2$) compounds, which are the solid solutions of $\text{LiNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$ and LiCoO_2 , have been introduced as promising positive electrode materials for lithium rechargeable batteries [6–8]. The valence states of Ni, Co and Mn ions in these compounds (e.g. $x = 1/3$ and $1/2$) were confirmed as divalent, trivalent and tetravalent, respectively, by XPS and XAFS [9,10]. The de-intercalation processes of lithium ions in

these compounds are basically accompanied by the redox processes of Ni and Co ions, while the tetravalent Mn ion remains electrochemically inactive during cycling.

On the other hand, the positive electrode materials with lithium excess compositions have been investigated to improve electrochemical performances of lithium rechargeable batteries. For example, the increase of capacity and the suppression of the phase transformation of LiCoO_2 during charge process were observed in the lithium excess $\text{Li}_{1+x}\text{CoO}_2$ [11,12]. Recently, our research group reported $\text{Li}_{1+x}(\text{Ni}_{1/2}\text{Mn}_{1/2})\text{O}_{2+\delta}$ ($x = 0$ and 0.13) materials prepared by an emulsion drying method and demonstrated that the lithium excess $\text{Li}_{1.13}(\text{Ni}_{1/2}\text{Mn}_{1/2})\text{O}_{2+\delta}$ material exhibited better electrochemical properties than those of the stoichiometric one [13]. Marinov Todorov and Numata [14] and Choi and Manthiram [15] also have investigated the electrochemical properties of $\text{Li}_{1+x}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ ($0 \leq x \leq 0.13$) materials with the molar ratio of Li/Me , respectively. They prepared metal hydroxides using co-precipitation method and obtained the final product with different molar ratios of Li/Me ($\text{Me} = \text{transition metals}$) by addition of appropriate amount of lithium salt to the metal hydroxides before calcination.

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From these previous researches, it is expected that the excess lithium in the layered cathode materials plays an important role and can improve the electrochemical properties. In this paper, we prepared $\text{Li}_{1+x}(\text{Ni}_{0.3}\text{Co}_{0.4}\text{Mn}_{0.3})\text{O}_{2-\delta}$ materials ($0 \leq x \leq 0.06$) as positive electrode materials. The precursor was prepared from the solution with the molar ratio of $\text{Li}/\text{Me} = 1.25$ using a spray drying method and the ratio of Li/Me in the final product was changed from 1.00 to 1.06 through different calcination times at 950°C . The physical and electrochemical properties of the prepared $\text{Li}_{1+x}(\text{Ni}_{0.3}\text{Co}_{0.4}\text{Mn}_{0.3})\text{O}_{2-\delta}$ materials and the effects of excess lithium on the electrochemical properties were investigated.

2. Experimental

$\text{Li}_{1+x}(\text{Ni}_{0.3}\text{Co}_{0.4}\text{Mn}_{0.3})\text{O}_{2-\delta}$ ($x = 0, 0.03$ and 0.06) materials were synthesized using the spray-dried precursor with the molar ratio of $\text{Li}/\text{Me} = 1.25$. To prepare the precursor, LiNO_3 and $\text{Me}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ ($\text{Me} = \text{Ni}, \text{Co}$ and Mn) with a molar ratio of $\text{Li}/\text{Me} = 1.25$ were dissolved into distilled water, and this stock solution was fed into a spray drying instrument (SD-1000, TOKYO RIKAKIKAI Co., Ltd.). The spray-dried powder was burned out at 400°C for 6 h in air and the obtained powder was pelletized before main calcination. The final three $\text{Li}_{1+x}(\text{Ni}_{0.3}\text{Co}_{0.4}\text{Mn}_{0.3})\text{O}_{2-\delta}$ ($x = 0, 0.03$ and 0.06) materials were synthesized at 950°C for 24, 12 and 3 h in air, respectively. To remove unreacted Li ingredient, the calcined materials were thoroughly washed with distilled water for several times and vacuum-dried at 120°C for overnight. The chemical compositions of the final products were analyzed by an atomic absorption spectroscopy (AAS, Analyst 300, Perkin-Elmer).

X-ray diffractometry (XRD, Rigaku Rint 2200) was employed to determine the structure of the synthesized materials. The diffracted data of the materials were collected from 10° to 80° in 2θ with a step size of 0.03° . The lattice parameters for the materials were calculated by the least squares method using 10 main diffraction peaks based on a hexagonal structure ($R\bar{3}m$). The particle morphologies and the distributions of transition metals of the materials were observed using scanning electron microscopy (SEM, JSM-5300E, JEOL, Japan) and energy dispersive X-ray analysis (S-2300, Hitachi, Japan), respectively. The specific surface areas of the materials were measured using the B. E. T. method (BEL SORP MINI, BEL JAPAN Inc.). Prior to measuring surface areas, the materials were dried for 24 h in vacuum oven.

For the electrochemical characterizations, the positive electrode was prepared as follows. The synthesized material, acetylene black and polyvinylidene fluoride (80:10:10 in weight) were mixed in *N*-methylpyrrolidinon. Then the obtained slurry was spread on Al foil and dried at 80°C for several hours. From 5 to 10 mg of the synthesized material was loaded onto 16 mm in diameter Al disc after roll-pressing and punching. The positive electrode was then dried at 120°C for 1 day in vacuum state. A 2032 type of coin cell consisted of the prepared positive electrode, lithium metal foil as a negative electrode and 1 M LiPF_6 in ethylene carbonate (EC)–diethylene carbonate (DEC) (1:2 in volume) as an electrolyte. The cell was charged and discharged

by a galvanostatic method at 25°C between several voltage windows. To calculate the chemical diffusion coefficients, \bar{D}_{Li^+} , of the synthesized materials, the galvanostatic intermittent titration technique (GITT) was employed. A constant current flux was supplied to the cell for a given time followed by open circuit for 8 h. For observation of the structural changes of the materials, TEM was performed on the materials after repetitive electrochemical cycling between 4.5 and 2.8 V versus Li^0 and ex situ XRD data were also collected during the initial charge process with a step of 0.1 mol Li extraction.

3. Results and discussion

3.1. Powder characteristics

As shown in Table 1, the chemical analysis by AAS indicated that calcination of the spray-dried precursor ($\text{Li}/\text{Me} = 1.25$) at 950°C for different periods resulted in a change of chemical compositions of the final products, that is, $\text{Li}_{1.06}(\text{Ni}_{0.32}\text{Co}_{0.40}\text{Mn}_{0.28})\text{O}_{2-\delta}$, $\text{Li}_{1.03}(\text{Ni}_{0.32}\text{Co}_{0.40}\text{Mn}_{0.28})\text{O}_{2-\delta}$ and $\text{Li}_{1.00}(\text{Ni}_{0.32}\text{Co}_{0.40}\text{Mn}_{0.28})\text{O}_{2-\delta}$ materials were obtained. The decrease in Li/Me ratio is probably due to lithium evaporation at such a high calcination temperature for prolonged calcination time as reported in our laboratory [13]. Note that the chemical composition of prepared material will be represented to be $\text{Li}_{1+x}(\text{Ni}_{0.3}\text{Co}_{0.4}\text{Mn}_{0.3})\text{O}_{2-\delta}$ for convenience. Fig. 1 shows the XRD patterns for $\text{Li}_{1+x}(\text{Ni}_{0.3}\text{Co}_{0.4}\text{Mn}_{0.3})\text{O}_{2-\delta}$ ($x = 0, 0.03$ and 0.06) materials. All the prepared materials could be identified as $\alpha\text{-NaFeO}_2$ structure with the space group of $R\bar{3}m$ because all the XRD patterns accorded well with a typical hexagonal pattern and showed a clear split between (1 0 8) and (1 1 0) peaks. The lattice parameters a_{hex} and c_{hex} decreased as the value x in $\text{Li}_{1+x}(\text{Ni}_{0.3}\text{Co}_{0.4}\text{Mn}_{0.3})\text{O}_{2-\delta}$ increased as shown in Table 1. The similar phenomenon was observed in the lithium excess layered transition material oxides [14–16]. The decrease in the lattice parameters with increasing the amount of excess lithium may be caused by the occurring of oxy-

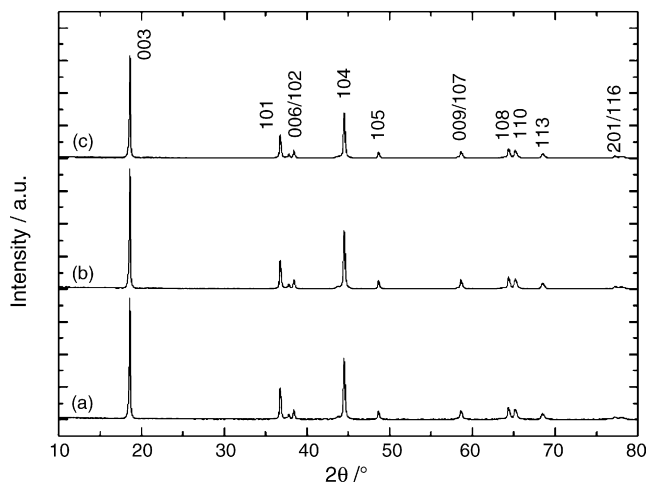


Fig. 1. XRD patterns of $\text{Li}_{1+x}(\text{Ni}_{0.3}\text{Co}_{0.4}\text{Mn}_{0.3})\text{O}_{2-\delta}$ ($x = 0, 0.03$ and 0.06) materials calcined at 950°C for (a) 3 h, (b) 12 h and (c) 24 h after burning out at 400°C for 6 h in air.

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