



Optimization of calcination temperature in preparation of a high capacity Li-rich solid-solution $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.18}\text{Co}_{0.03}\text{Mn}_{0.58}]\text{O}_2$ material and its cathode performance in lithium ion battery

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ABSTRACT

In our previous paper [12], it has been reported that $\text{Li}[\text{Ni}_{0.208}\text{Li}_{0.183}\text{Co}_{0.033}\text{Mn}_{0.575}]\text{O}_2$ Li-rich solid-solution layered oxide (LLO) cathode (Li_2MnO_3 (55%) - $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ (35%) - $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (10%)) possesses the best performance as cathode material among the examined LLO cathode materials of Li_2MnO_3 - $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ - $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ for lithium ion battery. In order to further improve its cathode performance, the calcination temperature was optimized in the range of 800–1100 °C. The cathode performance such as discharge capacity, discharge capacity retention and rate capability was improved with increasing the calcination temperature from 800 to 1000 °C, the best performance was obtained at 1000 °C and at more than 1000 °C, the cathode performance was degraded. The structural analysis with transmission electron microscope (TEM) and Rietveld analysis of XRD patterns indicated that the cation mixing between Li^+ ions on the 3a site and Ni^{2+} ions on the 3b site of the layered oxide structure (*R*-3m) is reduced significantly in the case of the LLO calcinated at 1000 °C, resulting in the improvement of cathode performance. In addition, the other LLOs having different compositions were also prepared at different calcination temperatures and their cathode performance was tested. The discharge capacity of $\text{Li}[\text{Ni}_{0.208}\text{Li}_{0.183}\text{Co}_{0.033}\text{Mn}_{0.575}]\text{O}_2$ was found to be the highest among all the LLOs examined in this study.

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1. Introduction

In recent years, Li-rich solid-solution layered oxide materials (LLOs) comprising layered LiMO_2 (*M*: transition metals) and Li_2MnO_3 have attracted much interest as a cathode material for lithium ion battery (LIB) because some materials exhibit capacities as high as 250 mAh g^{-1} in the voltage range of 2.0 and 4.8 V [1–6]. Because the Li_2MnO_3 structure can be reformulated with $\text{Li}[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2$, both of Li_2MnO_3 and LiMO_2 can be considered to be of layered α - NaFeO_2 -type rock salt structure. The structural compatibility between Li_2MnO_3 , which is electrochemically inactive and has a large theoretical capacity, and LiMO_2 , which is

electrochemically active but offers lower capacity, allows for the structural integration of these components at an atomic level. As a result, the electrochemically inactive Li_2MnO_3 can participate in the charge/discharge process after activation with oxygen release from the lattice during the charging process [7] and the capacity of LiMO_2 can be improved because the Li_2MnO_3 component acts to stabilize the layered structure of LiMO_2 when more than 50% of the Li^+ ions are deintercalated. These materials are charged to above 4.5 V (vs. Li/Li^+) to fully activate the Li_2MnO_3 component, and after activation, the cathodes are charged to 4.5 V to reach discharge capacities over 250 mAh g^{-1} [8–11]. In our previous study [12], in order to find the optimal composition of the LLOs exhibiting higher cathode performance, which are composed of Li_2MnO_3 , $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ and $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$, the selected 75 samples having different compositions were synthesized under identical preparation conditions except for the composition, and the dependence of the cathode performance of the individual materials on the percentages of

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Li_2MnO_3 , $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ and $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ in the LLO samples was examined in the viewpoints of discharge capacity, retention of discharge capacity, average discharge voltage, energy density and rate capability (Figs. S1–4). The results concluded that among the LLOs examined $\text{Li}[\text{Ni}_{0.208}\text{Li}_{0.183}\text{Co}_{0.033}\text{Mn}_{0.575}]\text{O}_2$ (Li_2MnO_3 (55%) - $\text{LiNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$ (35%) - $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (10%)) possesses the best composition as cathode material for LIBs. In this case, $\text{Li}[\text{Ni}_{0.208}\text{Li}_{0.183}\text{Co}_{0.033}\text{Mn}_{0.575}]\text{O}_2$ was synthesized only under the calcination condition of 900 °C for 12 h in air. Changing the calcination temperature can be expected to lead to a structural change and consequently a change in cathode performance. Therefore, in order to clarify the relationship between the calcination temperature in the preparation of LLOs and their cathode performance, in other words, between the degree of crystallinity of LLOs and the cathode performance, the LLO samples were synthesized at different calcination temperatures in the range of 800–1100 °C and their structural and cathode performance analyses were carried out in detail in this study.

2. Experimental

2.1. Preparation of LLOs

$\text{Li}[\text{Ni}_{0.18}\text{Li}_{0.20}\text{Co}_{0.03}\text{Mn}_{0.58}]\text{O}_2$ was synthesized by a coprecipitation procedure using the following commercially available reagents: nickel sulfate hexahydrate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, 99%, Kanto Chemical Co., Inc. (Kanto), Japan), manganese sulfate monohydrate ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$, 99%, Kanto), cobalt sulfate heptahydrate ($\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, 99%, Wako Pure Chemical Industries, Ltd. (Wako), Japan) and sodium carbonate (Na_2CO_3 , 99.8%, Wako). All of the reagents were used without further purification. In order to obtain a Li_2MnO_3 (65%) - $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ (25%) - $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (10%) solid solution cathode material (Ni:Co:Mn = 0.158:0.033:0.592 (atomic ratio)), 40.4 mmol $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, 8.4 mmol $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ and 151.2 mmol $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ were dissolved in 100 mL H_2O . Next, 80 mL of 2 M Na_2CO_3 solution was added at a speed of $0.5 \text{ cm}^3 \text{ s}^{-1}$ into the transition metal ion solution at 60 °C. During the whole synthesis, the pH was kept at 7.5 by adding 1.4 wt% the NH_4OH solution. The resulting precipitates of the transition metal carbonates were filtered. They were dried under vacuum at 100 °C for 5 h after they were washed several times with hot water until the filtrate exhibited neutral pH during the washing process. After that, to compensate for any possible loss of Li element during sintering at 800–1100 °C by evaporating Li element, an excess (7.0%) of lithium carbonate (Li_2CO_3 , 98%, Kano Chemical Co., Inc., Japan) was mixed with the transition metal carbonate using a wet planetary ball-milling machine with a Teflon jar (67 mL) containing Teflon balls (diameter 1.5 cm, 88 balls) and acetone (80 mL) at ambient temperature at a speed of 300 rpm for 3 h. After the ball milling, the mixture was dried under vacuum at 120 °C for 5 h. A pellet (diameter: 2 mm) of the dried mixture was formed using 30 kN of pressure. Then, the pellet was sintered at 800–1100 °C for 12 h in air, quenched with liquid N_2 and ground with a mortar to obtain the particles used to prepare the cathode films on an Al current collector. We used an excess (7.0%) of Li_2CO_3 to compensate for any possible loss of Li element during sintering at 800–1100 °C. How much excess of Li_2CO_3 should be mixed with transition metal oxides to form $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.18}\text{Co}_{0.03}\text{Mn}_{0.58}]\text{O}_2$ in the examined range of temperature was examined and finally it was found that the optimal excess percentage is 7%. We examined the different composition of Li_2MnO_3 - $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ - $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ solid solution cathode materials. Among the cathode materials examined, 7% excess of Li_2CO_3 was not enough to provide the samples in which the measured compositions are close to the nominal value at the higher calcining temperatures. How much excess of Li_2CO_3

should be used in the higher calcining temperatures depends on the composition of Li_2MnO_3 - $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ - $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ solid solution cathode materials. When the LLO samples having different compositions were synthesized, the Ni/Co/Mn molar ratios of their starting materials that were added to a water of 100 mL at the first step were controlled according to their target composition. In this case, the total concentration of the transition metal ions was kept to be 2 M. In the preparation of LLOs having a composition other than $\text{Li}[\text{Ni}_{0.18}\text{Li}_{0.20}\text{Co}_{0.03}\text{Mn}_{0.58}]\text{O}_2$, depending on the Ni/Co/Mn molar ratio in LLOs, adequate amounts of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ and $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ were dissolved in water, and they were prepared in the same way as mentioned above.

2.2. Characterization of synthesized cathode materials

Powder X-ray diffractometry (pXRD) measurements were performed using CuK_α radiation (Rigaku RINT-Ultima III; $\lambda = 0.15418 \text{ nm}$) at an increment of 0.02° at diffraction angles ranging from 20 to 80° . An obliquely finished Si crystal (non-reflective Si plate) was used as the sample holder to minimize the background noise. The average sizes and shapes of the particles of cathode materials were evaluated with a field-emission scanning electron microscope (FE-SEM, S-4000, Hitachi). The Li:Ni:Co:Mn elemental ratios of the synthesized cathode materials were determined by ICP-MS using an Agilent, 7700x spectrometer. The elemental analysis results with ICP-MS for the LLOs prepared at different calcination temperatures were virtually the same as their nominal formula (Table S1).

A 200 kV transmission electron microscope (TEM and/or STEM, JEM-2100F, JEOL) equipped with two aberration correctors (CEOS GmbH) for the image- and probe-forming lens systems and an X-ray energy-dispersive spectrometer (JED-2300T, JEOL) were used for compositional analysis of the particle surfaces. Both aberration correctors were optimized to realize the point-to-point resolutions of TEM and scanning transmission electron microscopy (STEM) as 1.3 and 1.1 Å, respectively. A probe convergence angle of 29 mrad and a high-angle annular-dark-field (HAADF) detector with an inner angle greater than 100 mrad were used for HAADF-STEM observation. HAADF-STEM was used to perform microscopic observation of the morphologies and particle sizes of the samples. The samples for the HAADF-STEM analysis were prepared by dropping a methanol suspension of the sample powder onto a commercial TEM grid coated with a polymer film. The sample was thoroughly dried in a vacuum prior to observation. Brunauer-Emmett-Teller (BET) surface areas of the cathode particles were measured with a surface area instrument (TriStar 3000, Micromeritics Instrument Corporation).

2.3. Cell preparation and electrochemical tests

1 g of an accurately weighed cathode material, 0.121 g of acetylene black (AB, DENKA BLACK, Denki Kagaku Kogyo Ltd., Japan) and 0.084 g of polyvinylidene difluoride (PVdF, KF Polymer #9130, 13 wt% in N-methyl-2-pyrrolidone (NMP), Kureha, Japan) were mixed in NMP (anhydrous 99.5%, Sigma-Aldrich) with a planetary mixing equipment (Mazerustar, KK-250S, KURABO, Japan) until a homogenous mixture was formed; the mixture (30–40 wt% solid matter) had a suitable viscosity for coating the cathode films to preserve the weight % of the cathode material: AB: PVdF = 83: 10: 7 in the prepared cathode films. The mixture was coated using a doctor-blade coater (100 μm gap) on the Al current collector. The mixture thin film on the Al was dried at 130 °C for 5 h in a vacuum drying oven. The loading of the cathode materials on the Al current collector was 2.0–3.0 mg cm^{-2} . The resulting cathode/Al contained a 200 mm^2 stainless steel mesh as the current collector under

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