Preparation of Layered Li[$Ni_{1/3}Mn_{1/3}Co_{1/3}$]O_2 as a Cathode for Lithium Secondary Battery by Carbonate Coprecipitation Method

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Layered Li[$Mn_{1/3}Ni_{1/3}Co_{1/3}$]O_2 cathode material was synthesized by carbonate coprecipitation method. SEM observation and X-ray diffraction experiment showed that the material with spherical particle morphology was successfully synthesized by the method. The cathode material delivered 180 mAh/g as an initial discharge capacity at 0.2 mA/cm^2 and showed high average capacity retention ratio of 99.85%/cycle over 40 cycles.

In 1991, Sony firstly introduced $LiCoO_2$ as a cathode material for the commercial lithium ion secondary battery. After that, this intercalation compound is using as a major cathode material for the lithium ion secondary battery. However, it is well known that the cobalt ingredient is relatively expensive and toxic element. Moreover, its practical capacity is restricted to a half of theoretical capacity because it shows structural degradation when it is charged above 4.2 V vs Li.[1] These drawbacks, therefore, promoted intensive studies to find suitable alternative cathode materials. In recent year, Ohzuku et al. reported that Li[$Ni_{1/3}Mn_{1/3}Co_{1/3}$]O_2 as a promising alternative cathode material.[2] The cathode has isostructure of α-$NaFeO_2$, i.e., layered hexagonal structure, and shows stable electrochemical performance even it cycles above 4.5 V vs Li.[2] And it also shows milder thermal behavior than other layered cathode materials such as $LiNiO_2$ and $LiCoO_2$ at the charged state.[3] Moreover, the cost of cathode also can be reduced by substituting Mn and Ni for Co. Thus, this solid solution could be one of the promising cathode materials.

In the solid solution system, it is very important to make homogeneous cathode materials because the electrochemical behaviors depend on the mixed state of transition-metal ions materials. However, it is difficult to prepare homogeneously mixed solid solution materials usually. Therefore, to obtain homogeneous cathode materials with high performance, a homogeneously substitutable process should be selected. Generally, homogeneous precursor can be obtained by solution method such as hydroxide coprecipitation method,[2] ultra sonic spray pyrolysis method,[4] and spray drying method.[5] In our previous work,[6] we successfully introduced one of the simplest synthetic method, viz. carbonate coprecipitation method, to prepare a homogeneously substituted cathode materials. When we used this method, homogeneous material can be readily obtained with relatively low cost as well as in short preparation time. Furthermore, particle size and/or shape also can be controlled through the method.

In this study, therefore, we applied carbonate coprecipitation method as a synthetic route for preparing the layered Li[$Ni_{1/3}Mn_{1/3}Co_{1/3}$]O_2 with spherical particle shape. It is the first attempt to apply carbonate coprecipitation process to preparing this material. And, we reported structural and electrochemical properties of Li[$Ni_{1/3}Mn_{1/3}Co_{1/3}$]O_2.

In order to prepare mixed carbonate precursor by carbonate coprecipitation, we selected $MnSO_4\cdot4$–$5H_2O$, $NiSO_4\cdot6H_2O$, $CoSO_4\cdot7H_2O$, and Na_2CO_3 as starting materials. The detailed precipitation route was well described in our previous work.[4] The coprecipitated carbonate powder, hereafter referred as a precursor, was preheated at 500 °C for 5 h in air. After calcinations, we applied EDTA titration to decide exact amount of transition metal ions in the preheated powder. To make Li[$Ni_{1/3}Mn_{1/3}Co_{1/3}$]O_2 powder, a stoichiometric amount of lithium was mixed with the preheated powder and calcined at 950 °C for 12 h in air.

X-ray diffraction data of the precursor and the calcined powder were carefully collected in the 2θ range of 10 to 80° using Cu Kα radiation of a Rigaku Rint 1000 diffractormeter. The lattice parameters of the calcined powder were calculated by least square method using eight highest diffraction lines. The chemical composition of the synthesized powder was determined by an inductively coupled plasma spectrometer (ICP:SPS 7800, Seiko instruments, Japan). Scanning electron microscopy (SEM : JSM-5300E, JEOL, Japan) was carried out to confirm the morphologies of the precursor and the synthesized cathode material.

The electrochemical characterizations were carried out using the CR-2032-type coin cell. A cathode was prepared by pressing active material film, which is consist of 20-mg active material and 12-mg conducting binder (Teflonized acetylene black), on the stainless steel mesh. The coin type cell was composed of the cathode, the lithium foil as an anode, and 1 M $LiPF_6$–EC/DMC (1:2 in volume) as an electrolyte. The electrochemical cycling tests were performed at room temperature.

The structure of the precursor prepared by carbonate coprecipitation was investigated by X-ray diffraction experiment. As shown in Figure 1a, the XRD pattern of the precursor can be in-

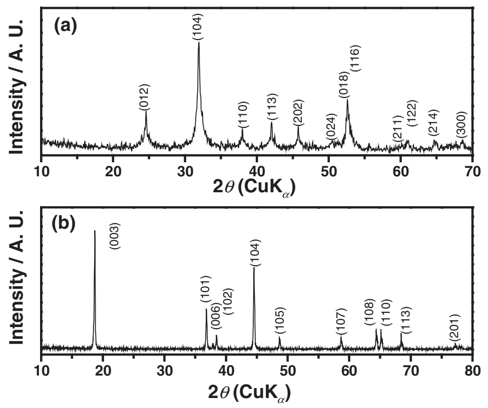

Figure 1. X-ray diffraction patterns for (a) coprecipitated powder and (b) synthesized Li[$Mn_{1/3}Ni_{1/3}Co_{1/3}$]O_2 compound.

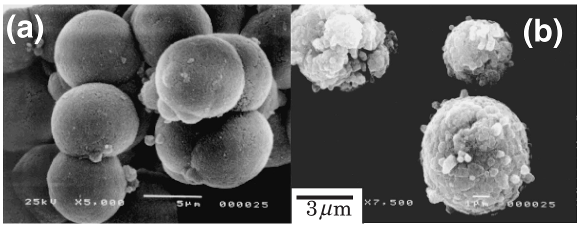

Figure 2. SEM Photographs for (a) coprecipitated powder and (b) synthesized Li[$Mn_{1/3}Ni_{1/3}Co_{1/3}$]O_2 compound.

dexed as transition metal carbonate with hexagonal structure (space group 167; R-3c). We think that broad peaks of XRD pattern are due to the mixture of transition metal carbonates such as $MnCO_3$, $NiCO_3$, and $CoCO_3$. As shown in Figure 2a, the morphology of the precursor is homogeneous spherical shape with about 5 µm in diameter. Therefore, we could prepare transition metal carbonate precursor by coprecipitation process successfully.

Li[$Ni_{1/3}Mn_{1/3}Co_{1/3}$]O_2 cathode material was synthesized with preheated powder and lithium hydroxide through calcination of the mixture at 950 °C for 12 h in air. Figure 2b shows morphology of the material. The primary particles are less than 1 µm and the particles aggregate each other to form spherical secondary particles with about 5 µm in diameter. The chemical composition of synthesized the Li[$Ni_{1/3}Mn_{1/3}Co_{1/3}$]O_2 cathode material was determined by I.C.P spectroscopy technique. The chemical composition can be represent as $Li_{1.02}[Mn_{0.335}Ni_{0.336}Co_{0.329}]O_2$ that is almost the same as we designed value. Figure 1b shows X-ray diffraction pattern of the material. All diffraction lines could be indexed as the α-$NaFeO_2$ structure with a space group 166 (R-3m). As can be seen in the Figure 1b, there are no observable impurity phases in the whole scan range. The intensity ratio of the (003)/(104) diffraction lines is higher than 1.45 and (108) and (110) diffraction peaks were clearly separated, which means that this material has well-ordered hexagonal structure. The calculated unit cell constants *a* and *c* were 2.8604(6) and 14.2453(29) Å, respectively. The calculated lattice parameters are agreed well with other literatures.[2,7] The c/a ratio is 4.98 that is closed to the ratio of $LiCoO_2$. Therefore, we could synthesize Li[$Ni_{1/3}Mn_{1/3}Co_{1/3}$]O_2 cathode material with hexagonal structure and homogeneous particle distribution using the coprecipitation method.

The electrochemical properties of Li[$Ni_{1/3}Mn_{1/3}Co_{1/3}$]O_2 was performed at a room temperature in the voltage range from 3.0 to 4.6 V with an applied current density of 0.2 mA/cm^2 (20 mA/g). Figure 3 shows the initial charge/discharge curves and charge/discharge capacities up to the 40th cycle. There was no extra plateau below 3.5 V during discharge stage. This result implies that Mn ions are inactive during electrochemical operation.[8] This material delivered high discharge capacity over 180 mAh/g at the initial discharge stage and the capacity retained over than 170 mAh/g up to the 40th cycle in spite of severe charge–discharge condition, viz. the high cut-off voltage. The average capacity retention ratio, which was suggested in our previous study,[9] was over than 99.85%/cycle. Therefore, we could synthesized Li[$Ni_{1/3}Mn_{1/3}Co_{1/3}$]O_2 with good electrochemical properties by coprecipitation method.

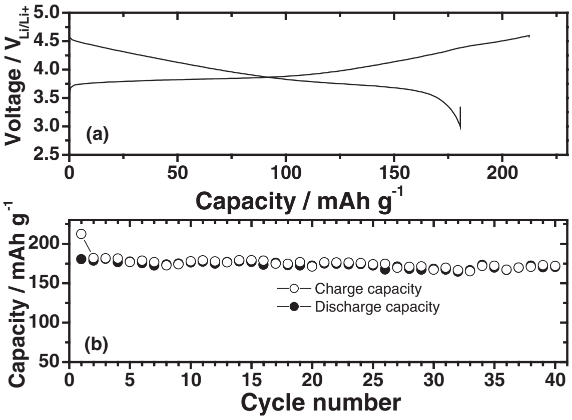

Figure 3. (a) Initial charge/discharge curves and (b) charge/discharge capacities as a function of cycle number for the synthesized Li[$Mn_{1/3}Ni_{1/3}Co_{1/3}$]O_2 compound.

To confirm the dependence of capacity on applied current density of the material, the cell was charged at 0.2 mA/cm^2 and then discharged at various current densities of 0.2 mA/cm^2 (20 mA/g), 0.65 mA/cm^2 (65 mA/g), 1.3 mA/cm^2 (130 mA/g), and 3.6 mA/cm^2 (360 mA/g). The discharge capacities were gradually decreased with increasing applied current density. When high current density of 3.6 mA/cm^2, which is 18 times higher than initial one, was applied to the cell, the cathode could deliver discharge capacity about 85% compared with the capacity when we applied 0.2 mA/cm^2 to the cell.

We have successfully demonstrated new synthesis route named carbonate coprecipitation method for preparing the layered Li[$Mn_{1/3}Ni_{1/3}Co_{1/3}$]O_2 cathode material. The cathode material synthesized by the method showed spherical particle morphology as well as homogeneous particle distribution and delivered 180 mAh/g as an initial discharge capacity and showed good capacity retention ratio over 99.85%/cycle up to the 40th cycle. Therefore, we think that the carbonate coprecipitation process could be one of effective techniques to prepare cathode materials with solid solution.

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