Novel Synthesis Method for Preparing Layered $Li[Mn_{1/2}Ni_{1/2}]O_2$ as a Cathode Material for Lithium Ion Secondary Battery

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We introduced a novel synthesis method, carbonate coprecipitation, for preparing $Li[Mn_{1/2}Ni_{1/2}]O_2$ cathode. XRD experiment and ICP spectroscopy revealed that the cathode was successfully synthesized by the method. The cathode delivered discharge capacities of 151, 171.6, and 186.2 mAh/g at cut-off voltages 4.4, 4.5, and 4.6 V (vs Li/Li^+), respectively. And the cathode retained 99.56% discharge capacity of the initial one at the 30th cycle with cut-off voltage 4.4 V (vs Li/Li^+).

Because of the high cost and toxicity of $LiCoO_2$, layered lithiated transition metal oxides have been extensively studied as an alternative cathode material. Recently, a layered transition metal oxide with hexagonal structure, $Li[Ni_{1/2}Mn_{1/2}]O_2$, was introduced by Ohzuku et al. as a promising cathode material to replace $LiCoO_2$.[1] The combination of nickel and manganese can provide advantages such as lower cost and less toxicity than $LiCoO_2$. Moreover, this compound showed good electrochemical performance.[1,2] Although $Li[Mn_{1/2}Ni_{1/2}]O_2$ is an attractive cathode material, the material has a difficulty to prepare. In order to produce the cathode successfully, therefore, a proper synthesis route should be selected.

Here, we introduced a novel synthesis method named carbonate coprecipitation to prepare $Li[Mn_{1/2}Ni_{1/2}]O_2$. To our knowledge, it is the first try to synthesize the cathode material using carbonate coprecipitation. In this paper, we reported structural and electrochemical properties for the synthesized $Li[Mn_{1/2}Ni_{1/2}]O_2$.

Firstly, we synthesized a transition metal carbonate powder, $Mn_{1/2}Ni_{1/2}CO_3$, using $MnSO_4 \cdot 4\text{–}5H_2O$, $NiSO_4 \cdot 6H_2O$, and Na_2CO_3 by a coprecipitation route. The detailed precipitation route was well described in our previous work.[3] The coprecipitated carbonate powder, here after referred as a precursor, was pre-heated at 500 °C for 5 h in air. After pre-heating, we applied EDTA titration to decide exact amount of transition metal ions in the pre-heated powder. To make $Li[Mn_{1/2}Ni_{1/2}]O_2$ powder, a stoichiometric amount of lithium was mixed with the pre-heated powder and calcined at 850 °C for 15 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 eleven highest diffraction lines. The chemical composition of the synthesized $Li[Mn_{1/2}Ni_{1/2}]O_2$ powder was determined by an inductively coupled plasma spectrometer (ICP: SPS 7800, Seiko instruments, Japan). The specific surface area was measured using a Micromeritics Gemini 2375 (USA) by the BET method. Scanning electron microscopy (SEM: JSM-5300E, JEOL, Japan) was carried out to observe the morphologies of 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. Cyclic voltammetry study was conducted using a three-electrode cell with 1 M $LiPF_6$–EC/DMC (1:2 in volume) as electrolyte and lithium foil was used as both counter electrode and reference. CV experiments were carried out at a scan speed of 0.1 mV/s between 2.8 and 4.6 V (vs Li/Li^+).

In order to investigate the structure of the mixed carbonate precursor and synthesized layered $Li[Mn_{1/2}Ni_{1/2}]O_2$ cathode material obtained by carbonate coprecipitation, X-ray diffraction experiment was applied. As shown in Figure 1a, the XRD pattern of the precursor could be indexed as transition metal carbonate with hexagonal structure (space group 167; $R\bar{3}c$). The XRD experiment revealed that the carbonate precursor was successfully formed by precipitation process.

Figure 1b shows X-ray diffraction pattern of $Li[Mn_{1/2}Ni_{1/2}]O_2$. All diffraction lines could be indexed as the α-$NaFeO_2$ structure with a space group 166 ($R\bar{3}m$). Although the peaks separation of (006), (102), and (108), (110) were not so clear, the XRD pattern revealed that this material has typical hexagonal structure. The calculated lattice parameters a and c were 2.8846(1) Å and 14.2756(16) Å, respectively. The calculated lattice parameters agreed well with other literature.[4] It is well known that the c/a ratio and intensity ratio of (003)/(104) are closely related to hexagonal setting. The higher values for c/a and (003)/(104) intensity ratio indicate good hexagonal ordering. The pattern shows 4.948 of c/a which agree well with reported values[0,1] and high integrated intensity ratio (003)/(104)

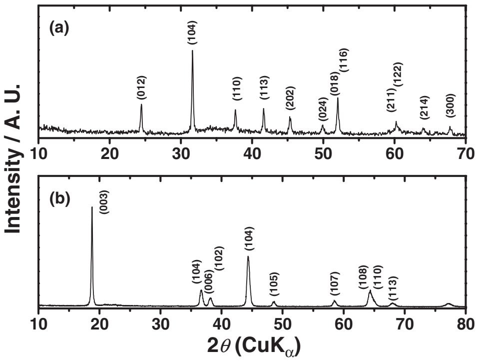

Figure 1. X-ray diffraction patterns for (a) coprecipitated powder and (b) synthesized $Li[Mn_{1/2}Ni_{1/2}]O_2$ compound.

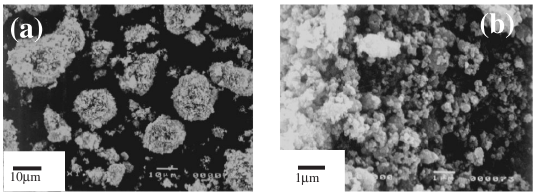

Figure 2. SEM Photographs for (a) macromorphology and (b) micromorphology of synthesized Li[$Mn_{1/2}Ni_{1/2}$]O_2 compound.

of 1.96. These high values indicate less disorder in the hexagonal structure. The chemical composition of synthesized Li[$Mn_{1/2}$-$Ni_{1/2}$]O_2 was determined by ICP spectroscopy technique. The chemical composition can be represent as $Li_{1.02}$[$Mn_{0.503}$-$Ni_{0.497}$]O_2 that composition is almost same as target one. Therefore, we can consider that the layered cathode was successfully synthesized by carbonate coprecipitation method.

We observed micro- and macromorphologies of Li[$Ni_{1/2}$-$Mn_{1/2}$]O_2, at different magnifications. Figure 2b shows micromorphology of the material. The size of primary particles is 0.1–0.2 μm in diameter. These small primary particles are aggregated each other. The aggregated particles are 12–15 μm in diameter as in Figure 2a. The specific surface area measurement revealed that the cathode has large specific surface area of 7.6 m^2/g. The relatively large surface area without any grinding process can be explained by small primary particles.

Figure 3 shows typical cyclic voltammogram of the first five cycles of Li[$Mn_{1/2}Ni_{1/2}$]O_2. As shown in the Figure 3, major oxidation peak shifted to the lower voltage and shows reproducible redox peaks in subsequent cycles. The material shows smaller ΔV (0.148 V) than previous reported paper.[6,7] It means that our sample leads smaller hysteresis than others. In the cycle voltammogram, there is no extra peak around 3 V (vs Li/Li^+) indicating that manganese in our synthesized material is not in 3+ state.[8]

The electrochemical performances of Li[$Mn_{1/2}Ni_{1/2}$]O_2 were investigated at room temperature with various cut-off voltages 4.4, 4.5, and 4.6 V (vs Li/Li^+) at applied current density of 0.2 mA/cm^2 (20 mA/g). Figure 4 shows the initial charge/discharge curves and specific discharge capacities as a function of cycle number. The obtained initial discharge capacities were 151, 171.6, and 186.2 mAh/g at cut-off voltages 4.4, 4.5, and 4.6 V (vs Li/Li^+), respectively. The material showed negligible capacity loss upon repeated cycling. The retained discharge capacities after 30th cycle were 99.56, 96.07, and 95.39% of initial one at cut-off voltages 4.4, 4.5, and 4.6 V (vs Li/Li^+), respectively. It is notable that the cell can deliver high retainable discharge capacity even it tested at severe experimental condition, viz. high cutoff voltage of 4.6 V (vs Li/Li^+). Therefore, we could synthesized Li[$Mn_{1/2}Ni_{1/2}$]O_2 with good electrochemical properties by carbonate coprecipitation route at relatively low calcination temperature of 850 °C.

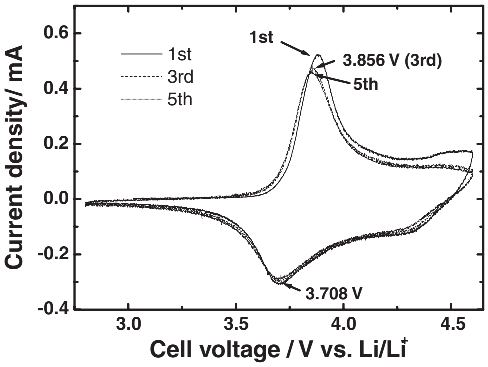

Figure 3. Cyclic voltammogram of Li[$Mn_{1/2}Ni_{1/2}$]O_2.

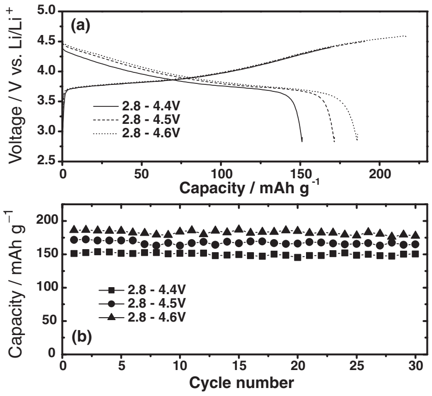

Figure 4. (a) Initial charge/discharge curves and (b) charge/discharge capacities as a function of cycle number for the synthesized Li[$Mn_{1/2}Ni_{1/2}$]O_2 compound at various cutoff voltages.

In order to investigate the rate capability of the Li[$Mn_{1/2}$-$Ni_{1/2}$]O_2 cathode material, the cell was charged at 0.1 C and various C-rates of 0.5, 1, and 2 C were applied to the electrode in the voltage range 2.8 to 4.5 V (vs Li/Li^+). The C-rates were calculated using first discharge capacity (170 mAh/g) as a theoretical capacity. Obtained discharge capacities were gradually decreased with increasing C-rate. When 2 C was applied to electrode, the electrode could deliver highly retained discharge capacity of 138 mAh/g, which is correspond to 80.95% of theoretical capacity. As shown above, the cathode material show good rate capability, which can be due provably to nature of the Li[$Mn_{1/2}Ni_{1/2}$]O_2 cathode such as large surface area and low hysteresis.

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