Optimization of Lithium in $\text{Li}_{1+x}[\text{Mn}_{0.720}\text{Ni}_{0.175}\text{Co}_{0.105}]\text{O}_2$ as a Cathode Material for Lithium Ion Battery

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ABSTRACT

Different amounts of excess lithium in the range of $x = 0 \sim 0.3$ were added to $\text{Li}_{1+x}[\text{Mn}_{0.720}\text{Ni}_{0.175}\text{Co}_{0.105}]\text{O}_2$ cathode materials synthesized using the co-precipitation method to investigate its microstructure and electrochemical properties. Pure layered structure without impurities was confirmed in the XRD pattern analysis and increasing peak intensity of Li_2MnO_3 was observed along with the addition of over 0.2 mol Li. The initial discharge capacity of the stoichiometric composition was determined to be 246 mAh/g, while the discharge capacity of the addition of 0.1 mol Li was obtained to be 241 mAh/g, which was not significantly different from that of the stoichiometric composition. However, the discharge capacities decreased dramatically after the addition of 0.2 and 0.3 mol Li to 162 mAh/g and 146 mAh/g, respectively. In the rate capability test, the active $\text{Li}_{1+x}[\text{Mn}_{0.720}\text{Ni}_{0.175}\text{Co}_{0.105}]\text{O}_2$ cathode material of the stoichiometric composition showed a dramatic decrease in its discharge capacity with increasing C-rate, as evidenced by the result that the discharge capacity at 5C was 13% compared with 0.1C. On the other hand, the discharge capacity of compositions containing excess lithium was improved at higher current rates. The cycling test showed that the composition containing an excess of 0.1 mol Li had the most outstanding capacity retention.

Keywords : Li_2MnO_3 , Co-precipitation, Lithium ion battery, Li excess, Cathode material

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1. Introduction

Research on lithium secondary battery is being actively conducted as there is an increasing demand on batteries with high power and high energy density for the applications of HEV and EV. The active LiCoO_2 cathode material of lithium secondary batteries is used widely for IT application at present because it has an outstanding charge/discharge cycling performance and its mass production is simple as it can be easily synthesized.^{1,2)} However, the high cost and low thermal stability of one of the starting materials, Co, as well as the environmental problems caused by its toxicity, LiCoO_2 still lacks to meet the criteria to be used as a cathode material for large-scale lithium secondary battery

for electric vehicles and energy storage system, etc. Thus, numerous studies are being conducted to develop new active cathode materials to replace LiCoO_2 .¹⁻⁵⁾ Some studies have reported findings of improvement of thermal stability and capacity characteristics with the replacement of Co with other transition metals such as Mn and Ni.³⁾ In particular, when compounds such as Li_2MnO_3 and LiMO_2 ($M = \text{Mn, Ni and Co}$) are charged with over 4.6 V, they show a high capacity of over 200 mAh/g. Also, because they are more economical since they can partially replace the relatively more expensive Co, they are seen as potential candidates to be used as the new active cathode materials for next generation lithium secondary battery.⁶⁻⁸⁾

However, there is a problem of irreversible capacity caused during the initial charge and discharge as well as the dramatic reduction in capacity shown during charge/discharge cycling test. Therefore, many studies are being

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performed to improve the rate capability and cycle properties by stabilizing the surface of electrodes or changing the composition ratio of the metal ions. In particular, a recent study reported that treating the surface of the cathode material particles with insulating substances such as acid, fluorinate, TiO_2 , Al_2O_3 , AlPO_4 , and ZrO_2 , helped reduce the irreversible capacity during charge and discharge and improve not only the rate capability but also the cycle performance.⁹⁻¹⁴ Other than this method, there have been reports of improvement in the rate capability and cycle performance through the prevention of Ni/Li substitution in Li-layer by adding excess lithium to $\text{Li}_{1+x}\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$. Furthermore, excess Li in B-site of the ABO_2 lattice is reported to enhance the electrochemical performance. In case of the LiCoO_2 , excess Li is known to prevent the monoclinic distortion during charge.¹⁵

Therefore, stoichiometric $\text{Li}[\text{Mn}_{0.720}\text{Ni}_{0.175}\text{Co}_{0.105}]\text{O}_2$ as the basic composition was investigated in terms of its microstructure and electrochemical properties that occurred with additions of different amounts of excess lithium.

2. Experimental

The metal precursors of $\text{Li}_{1+x}[\text{Mn}_{0.720}\text{Ni}_{0.175}\text{Co}_{0.105}]\text{O}_2$ cathode material were prepared via a co-precipitation method using $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, and $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ as starting materials. At the same time, NaOH and NH_4OH as chelating agents were fed into the reactor in appropriate amounts and pH was maintained in the range of 11-11.5 during the process. After co-precipitation, $(\text{Ni}, \text{Co}, \text{Mn})(\text{OH})_2$ precursors were filtered, washed five times by distilled water, and then dried at 100°C for 24 h. An ethanol was added into the mixture of the precursor and lithium hydroxide to be a mud-like state. Subsequently, the mixture was preheated at 500°C for 5 h and then, calcined at 900°C for 3 h in air.

In order to fabricate the electrode, a cathode material, super pure black (SPB) as conductive materials, and poly vinylidene fluoride (PVDF) as a binder, were slurried with *n*-methyl pyrrolidone (NMP) solvent in the ratio of 84 : 8 : 8 (wt %). The slurry after blending was coated on an aluminum current collector foil and dried at 100°C for 12 h.

X-ray diffraction analysis was employed to confirm the crystal structure and impurities in the synthesized active material, using an X-pert PW3830 (Philips Co.) with $\text{Cu K}\alpha$ radiation under conditions of 40 kV and 30 mA. In addition, a field emission scanning electron microscope (FE-SEM, S-4800, Hitachi Co.) was used to observe

the particle size and surface morphology.

For electrochemical measurements, the electrodes was pressed ($600\text{--}800 \text{ kg/cm}^2$) and punched into 15 mm diameter disks. The cells were assembled in 2032 coin type cell by stacking a lithium anode, polypropylene separator (Celgard®3501), liquid electrolyte consisted of 1 M LiPF_6 in 1 : 1 ethylene carbonate (EC) : dimethyl carbonate (DEC) and a cathode in turn. The cells were constructed in a dry room (dew point below 55°C) and aged for 12 h before the first charge to ensure full absorption of electrolyte into the electrodes.

The electrochemical performances were measured by a battery cycler (TOCAT-3100, TOYO System). $\text{Li}/\text{Li}_{1+x}[\text{Mn}_{0.720}\text{Ni}_{0.175}\text{Co}_{0.105}]\text{O}_2$ cathode electrode was charged and discharged in the voltage range of 2.0-4.6 V by the constant current (CC) - constant voltage (CV) method. Rate capability was evaluated at current rates of 0.1 C, 1 C, 2 C and 5 C while the cycling performance was tested at a current rate of 1 C at room temperature. EIS was measured for the discharged cell using an IM6 (ZAHNER, Germany) in the frequency range of 1 Hz~1 MHz at 10 mV of amplitude, and cyclic voltammogram (CV) was operated at 0.1 mV/s between 2.0 V and 4.6 V at room temperature.

3. Results and Discussion

Fig. 1 shows the X-ray diffraction patterns of the $\text{Li}_{1+x}[\text{Mn}_{0.720}\text{Ni}_{0.175}\text{Co}_{0.105}]\text{O}_2$ cathode material according to the additions of different amounts of lithium. The powder was observed to have accurately matched the peaks of (003), (101) and (104), the peaks of hexagonal $\alpha\text{-NaFeO}_2$ structure, which is the R-3m space group. Also, we confirmed that pure layered structures formed well due to clear separation of (018) and (110) without any

Fig. 1. XRD patterns of $\text{Li}_{1+x}[\text{Mn}_{0.720}\text{Ni}_{0.175}\text{Co}_{0.105}]\text{O}_2$ ($x = 0, 0.1, 0.2, 0.3$) cathode material.

impurities. In addition, from the peak near 21° , a peak that represented Li_2MnO_3 of the C2/m space group with a monoclinic structure, we confirmed that the peak intensity increased along with the increasing additions of excess lithium after 0.2 mol. This showed similar tendencies with previously reported data in literature.¹⁵⁾

Fig. 2 are FE-SEM images of the active $\text{Li}_{1+x}[\text{Mn}_{0.720}\text{Ni}_{0.175}\text{Co}_{0.105}]\text{O}_2$ cathode material calcined at 900°C for 3 h. From Fig. 2(a) and (b), we confirmed that particles smaller than 500 nm grouped together in a relatively uniform distribution pattern with Li additions of up to 0.1 mol. When more than 0.2 mol Li were added, however, angular rod-shaped particles of over 2 μm in size were observed and the size of the particles increased to 5 μm with the addition of 0.3 mol Li. These angular rod-shaped particles are believed to be associated with the growth of Li_2MnO_3 that occurs with the increasing additions of excess lithium in the XRD diffraction pattern.

Fig. 3 shows the results of CV measured at the scanning speed of 0.1 mVs^{-1} to determine the reversibility of oxidation-reduction reaction of $\text{Li}_{1+x}[\text{Mn}_{0.720}\text{Ni}_{0.175}\text{Co}_{0.105}]\text{O}_2$ electrode. Oxidation-reduction reactions were observed to be the same in all compositions and other side reactions were not observed. An oxidation-reduction peak was

observed near 3.7–4.2 V. However, unlike the composition with addition of less than 0.1 mol Li, the reaction area became smaller with a reduction in peak strength and broadening of its width when over 0.2 mol Li were added. This represents that there was a reduction in the capacity. This CV measurement result corresponds to the initial charge and discharge results shown in Fig. 4.

Fig. 4 is the voltage profiles of the initial charge and discharge of $\text{Li}_{1+x}[\text{Mn}_{0.720}\text{Ni}_{0.175}\text{Co}_{0.105}]\text{O}_2$ electrode measured at a 0.1 C in the voltage range of 2–4.6 V. The discharge capacity of the stoichiometric composition was determined to be 246 mAh/g, while the discharge capacity after the addition of 0.1 mol Li was 241 mAh/g. However, after the additions of 0.2 and 0.3 mol of Li, the discharge capacities decreased dramatically to 162 mAh/g and 146 mAh/g, respectively, and the initial charge-discharge efficiencies were determined to be 56% and 58%, respectively, which were deemed significantly low. Such reduction in the initial charge and discharge efficiency is believed to have a close association with Li_2MnO_3 . When charged over 4.5 V, Li_2MnO_3 is activated and the two lithium ions are removed from Li_2MnO_3 with concomitant loss of oxygen resulting in the formation of Li_2O and MnO_2 . However, only one lithium ion is reinserted into

Fig. 2. Morphologies of $\text{Li}_{1+x}[\text{Mn}_{0.720}\text{Ni}_{0.175}\text{Co}_{0.105}]\text{O}_2$ powders as function of excess lithium with (a) stoichiometric amount, (b) 0.1 mol excess, (c) 0.2 mol excess and (d) 0.3 mol excess.

Fig. 3. Cyclic voltammograms of $\text{Li}_{1+x}[\text{Mn}_{0.720}\text{Ni}_{0.175}\text{Co}_{0.105}]\text{O}_2$ electrode with (a) stoichiometric amount, (b) 0.1 mol excess, (c) 0.2 mol excess and (d) 0.3 mol excess.

Fig. 4. Initial charge/discharge voltage profiles of $\text{Li}_{1+x}[\text{Mn}_{0.720}\text{Ni}_{0.175}\text{Co}_{0.105}]\text{O}_2$ electrode with different excess lithium amounts operated between 2.0 and 4.6 V at 0.1 C rate. (a) stoichiometric amount, (b) 0.1 mol excess, (c) 0.2 mol excess and (d) 0.3 mol excess.

MnO_2 during discharge, which causes such irreversible capacity. Thus, the reaction region of Li_2MnO_3 becomes

wider with increasing additions of excess lithium, which is believed to be the cause of significant reduction in the

initial charge and discharge efficiency.

Fig. 5 shows the rate capability of the $\text{Li}_{1+x}[\text{Mn}_{0.720}\text{Ni}_{0.175}\text{Co}_{0.105}]\text{O}_2$ electrode at 0.1C, 1C, 2C and 5C. The stoichiometric composition showed a dramatic decrease in the discharge capacity with increasing C-rate. This could be explained by the fact that Ni moves to the Li layer due to the oxygen produced during the initial charging and interferes with the diffusion path of Li, causing low rate capability. On the other hand, in compositions with additions of excess Li, significant improvement of rate capability even at the high C-rate was observed. The reason for the improved rate capability is believed to be attributed to the prevention of substitution of Li with Ni due to excess Li, which facilitates Li diffusion path during charging and discharging.¹⁶⁾

Fig. 6 shows the charge/discharge cycling performance of the $\text{Li}_{1+x}[\text{Mn}_{0.720}\text{Ni}_{0.175}\text{Co}_{0.105}]\text{O}_2$ electrode according to the amount of lithium additions at 1 C. The stoichiometric composition without an addition of excess Li showed a gradual decrease in the discharge capacity from the initial capacity of 183 mAh/g to 150 mAh/g after 30 cycles,

Fig. 5. Rate capability of $\text{Li}_{1+x}[\text{Mn}_{0.720}\text{Ni}_{0.175}\text{Co}_{0.105}]\text{O}_2$ electrode with different excess lithium amounts operated at the 0.1 C, 1 C, 2 C and 5 C rates.

Fig. 6. Cycle performances of $\text{Li}_{1+x}[\text{Mn}_{0.720}\text{Ni}_{0.175}\text{Co}_{0.105}]\text{O}_2$ electrode with different excess lithium amounts operated between 2.0 and 4.6 V at 1 C rate.

whereas the composition with an addition of 0.1 mol Li showed almost no change in the discharge capacity for up to 30 cycles. However, with the increasing amount of Li addition, the discharge capacity was dramatically reduced after 15 cycles. The discharge capacity with an addition of 0.1 mol Li, however, somewhat increased after 24 cycles. This phenomenon could be explained by the reason that the temperature of the cycling test room after 24 cycle might be slightly changed and affect its charge/discharge cycling performance.

4. Conclusions

The electrochemical properties of $\text{Li}_{1+x}[\text{Mn}_{0.720}\text{Ni}_{0.175}\text{Co}_{0.105}]\text{O}_2$ according to the additions of different amounts of lithium were investigated. The composition with an addition of 0.1 mol Li showed the most outstanding rate capability and cycle performance. Additions of over 0.2 mol Li expanded the reaction area of Li_2MnO_3 , which increased the irreversible capacity, and there was a dramatic reduction in capacity with an increase in the number of cycles.

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