Effect of chemical composition on rechargeable properties of LiNi_{1/3}Co_{1/3}Mn_{1/3}O_{2} cathode materials prepared by spray pyrolysis

Ryoma MINAMI, Takayuki KODERA and Takashi OGIHARA
Graduate School of Material Science and Engineering, University of Fukui, 3–9–1 Bunkyo, Fukui 910–8507, Japan

The market for lithium ion batteries has rapidly expanded because of the increase in demand for portable electronic devices. Lithium ion batteries are also expected to power electric vehicles (EVs) and hybrid electric vehicles (HEVs). LiCoO_{2} has been used as a potential cathode material for lithium ion batteries used in portable electronic devices. However, it has many disadvantages such as high cost, high toxicity, and low thermal stability. Therefore, it is not suitable as an energy source for EVs and HEVs. There are many other candidate cathode materials such as LiMn_{2}O_{4} and LiFePO_{4}. The layered LiNi_{1/3}Co_{1/3}Mn_{1/3}O_{2} cathode material has a high capacity (more 150 mAh/g) above 4.4 V. It has been reported that the rechargeable capacity of this cathode material is 160 mAh/g at the rate of 0.2 C and 200 mAh/g at the rate of 0.125 C in the voltage ranges of 2.5–4.4 and 2.8–4.6 V, respectively. However, the cycle stability of the LiNi_{1/3}Co_{1/3}Mn_{1/3}O_{2} cathode material is low because its crystal lattice volume increases upon extraction of Li. In the electrochemical reactions characteristic of the LiNi_{1/3}Co_{1/3}Mn_{1/3}O_{2} cathode material, Ni^{2+} and Co^{3+} are involved in redox reactions, while Mn^{4+} is involved in the structure stabilization of the cathode material. Therefore, the relation between chemical composition and rechargeable properties of the LiNi_{1/3}Co_{1/3}Mn_{1/3}O_{2} cathode material is an interesting subject for study. Santhanam et al. reported that the first discharge capacity of the LiNi_{0.3}Co_{0.3}Mn_{0.4}O_{2} cathode material was 136 mAh/g at the rate of 1 C and showed that the discharge capacity retention was 84% at the rate of 1 C after 40 cycles. In addition, they reported that this cathode material possessed superior electrochemical properties, enhanced structural stability and greater lithium diffusivity compared with the LiNi_{0.3}Co_{0.3}Mn_{0.4}O_{2} cathode material.

In this study, the LiNi_{1/3}Co_{1/3}Mn_{1/3}O_{2} cathode material was prepared by spray pyrolysis. The effects of chemical composition on the rechargeable properties of the material were investigated. Also examined were its powder characteristics.

2. Experimental procedure

LiNO_{3}, Ni(NO_{3})_{2}:6H_{2}O, Co(NO_{3})_{2}:6H_{2}O, Mn(NO_{3})_{2}:6H_{2}O were used as the starting materials for the synthesis of the LiNi_{1/3}Co_{1/3}Mn_{1/3}O_{2} cathode material. They were mixed in a molar ratio of 1:1:3:3:1:1:3 and dissolved in distilled water. The concentration of the aqueous solution was 1.0 mol/dm^{3}. A large-type spray pyrolysis apparatus (RH-2, OHKAWARA KAKOHKI) was used in this work. Figure 1 shows the schematic diagram of this apparatus. This apparatus consisted of a two-fluid nozzle, an electric furnace with an alumina tube (φ =...
30 mm; length = 1000 mm), and bag filters. The aqueous solution of metal nitrate was atomized using the two-fluid nozzle. The resulting mist was introduced into the electric furnace via air carrier gas and then pyrolyzed at 800°C. The flow rate of the carrier gas was 20 dm³/min. The obtained LiNi₁/₃Co₁/₃Mn₁/₃O₂ cathode material was then calcined at 800°C for 10 h in an electric furnace under air atmosphere.

The crystalline phases of the LiNi₁/₃Co₁/₃Mn₁/₃O₂ cathode material were identified by powder X-ray diffraction (XRD, Shimadzu, XRD-6100). The chemical composition was investigated by an inductively coupled plasma atomic emission spectrometer (ICP-AES, Hitachi hitec science, SPS-7800). The redox reactions by an inductively coupled plasma atomic emission spectrometer (JEOL, JSM-6390). The morphology and average particle size were determined using a scanning electron microscope (SEM, JEOL, JSM-6390). The chemical composition was investigated by an inductively coupled plasma atomic emission spectrometer (ICP-AES, Hitachi hitec science, SPS-7800). The redox reactions of LiNi₁/₃Co₁/₃Mn₁/₃O₂ cathode materials were investigated by cyclic voltammetry (CV, HOKUTO DENKO, HSV-100). The electrochemical properties were studied using a CR2032 coin cell. The LiNi₁/₃Co₁/₃Mn₁/₃O₂ cathode material was measured with a battery tester (Hosen, BTS2004) between 2.5 and 4.6 V.

3. Results

Figure 2 shows the XRD patterns of the LiNi₁/₃Co₁/₃Mn₁/₃O₂ cathode material that was calcined at 800°C. The crystal phases of all samples were identified as possessing a layered structure (space group: R-3m) even when the chemical composition of LiNi₁/₃Co₁/₃Mn₁/₃O₂ was change. Li₂MnO₃ was observed in the crystalline phases of the LiNi₁/₃Co₁/₃Mn₁/₃O₂, LiNi₀.₈₃Co₀.₁₃3Mn₀.₇₃₃O₂ and LiNi₀.₆₆Co₀.₃₄₃Mn₀.₆₆₃O₂ cathode materials. It is suggested that Mn is aligned consistently in the crystal lattice of these materials.8)

Table 1. Lattice parameters

| Material                  | a    | c    |
|---------------------------|------|------|
| LiNi₁/₃Co₁/₃Mn₁/₃O₂ (Reference) | 2.864 | 14.233 |
| LiNi₀.₆₆Co₀.₃₄₃Mn₀.₆₆₃O₂   | 2.872 | 14.271 |
| LiNi₀.₈₃Co₀.₁₃3Mn₀.₇₃₃O₂   | 2.889 | 14.223 |
| LiNi₀.₇₆Co₀.₂₄₃Mn₀.₄₆₆O₂   | 2.874 | 14.204 |

Table 2. Chemical composition

| Material                  | Li   | Ni   | Co   | Mn   |
|---------------------------|------|------|------|------|
| LiNi₀.₆₆Co₀.₃₄₃Mn₀.₆₆₃O₂  | 1.0  | 0.060 | 0.060 | 0.897 |
| LiNi₀.₈₃Co₀.₁₃3Mn₀.₇₃₃O₂  | 1.0  | 0.126 | 0.127 | 0.760 |
| LiNi₀.₇₆Co₀.₂₄₃Mn₀.₄₆₆O₂  | 1.0  | 0.191 | 0.190 | 0.631 |
| LiNi₁/₃Co₁/₃Mn₁/₃O₂      | 1.0  | 0.247 | 0.245 | 0.482 |
| LiNi₀.₆₆Co₀.₃₄₃Mn₀.₆₆₃O₂  | 1.0  | 0.304 | 0.305 | 0.336 |
| LiNi₁/₃Co₁/₃Mn₁/₃O₂      | 1.2  | 0.150 | 0.086 | 0.525 |

Figure 3 shows an SEM photograph of the LiNi₁/₃Co₁/₃Mn₁/₃O₂ cathode materials. Mn₁/₃O₂ cathode material. These have a spherical morphology, with a diameter of approximately 0.8 μm. In addition, the morphology and average particle size were not changed by any change in chemical composition.

Figure 4 shows the CV curves of the the LiNi₁/₃Co₁/₃Mn₁/₃O₂ cathode material. The oxidation peak is at 4.1 V, and the reduction peak is at 3.3 V. The oxidation peak is attributed to the extraction of lithium from the LiNi₁/₃Co₁/₃Mn₁/₃O₂ lattice. The redox reactions of LiNi₁/₃Co₁/₃Mn₁/₃O₂ cathode material calculated using XRD data. In particular, it was found that the lattice parameters of the e axis increased when the proportion of Mn was increased.

Figure 3. SEM photograph of LiNi₁/₃Co₁/₃Mn₁/₃O₂ cathode materials.

Fig. 3. SEM photograph of LiNi₁/₃Co₁/₃Mn₁/₃O₂ cathode materials.

Fig. 2. XRD patterns of LiNi₁/₃Co₁/₃Mn₁/₃O₂ cathode materials.

Fig. 4. CV curves of LiNi₁/₃Co₁/₃Mn₁/₃O₂ cathode materials.
and oxidation of the Co and Ni ions.\textsuperscript{4)}

Figure 5 shows the first charge and discharge curves of the LiNi\textsubscript{1/3}Co\textsubscript{1/3}Mn\textsubscript{1/3}O\textsubscript{2} cathode material. The first discharge capacity was 140 mAh/g at the rate of 1C. As the chemical percentages of Ni and Co were decreased, the discharge capacity of LiNi\textsubscript{1/3}Co\textsubscript{1/3}Mn\textsubscript{1/3}O\textsubscript{2} cathode materials also decreased. On the other hand, the discharge capacity of the Li\textsubscript{1.2}Ni\textsubscript{0.175}Co\textsubscript{0.1}Mn\textsubscript{0.525}O\textsubscript{2} cathode material had the highest discharge capacity of 197 mAh/g at the rate of 1C. The discharge capacity of the Li\textsubscript{1.2}Ni\textsubscript{0.175}Co\textsubscript{0.1}Mn\textsubscript{0.525}O\textsubscript{2} cathode material was thus 1.4 times that of the LiNi\textsubscript{1/3}Co\textsubscript{1/3}Mn\textsubscript{1/3}O\textsubscript{2} cathode material.

Figure 6 shows the relation between cycle number and discharge capacity of the LiNi\textsubscript{1/3}Co\textsubscript{1/3}Mn\textsubscript{1/3}O\textsubscript{2} cathode material. After 30 cycles, the discharge capacity retention was 52\% at the rate of 1C. On the other hand, for the Li\textsubscript{1.2}Ni\textsubscript{0.175}Co\textsubscript{0.1}Mn\textsubscript{0.525}O\textsubscript{2} cathode material it was 69\% at the rate of 1C after 30 cycles.

4. Discussion

We investigated the relation between chemical composition and rechargeable properties of the LiNi\textsubscript{1/3}Co\textsubscript{1/3}Mn\textsubscript{1/3}O\textsubscript{2} cathode material. As the chemical proportions of Ni and Co were decreased, the retention rate was increased, but the discharge capacity decreased. It is suggested that as the quantity of Mn was increased, the crystal lattice volume became smaller with the removal of Li. This result corresponded to the assumptions of Cho et al. that Mn\textsuperscript{3+} is involved in the structure stabilization of the LiNi\textsubscript{1/3}Co\textsubscript{1/3}Mn\textsubscript{1/3}O\textsubscript{2} cathode material.\textsuperscript{12} From the results of the study of electrochemical property reported by Santhanam et al., the first discharge capacity of the LiNi\textsubscript{0.3}Co\textsubscript{0.3}Mn\textsubscript{0.4}O\textsubscript{2} cathode material was 136 mAh/g and had 84\% retention at the rate of 1C. However, the electrochemical properties in our study were generally found to be different from those observed by Santhanam et al. In our study, the first discharge capacity of the LiNi\textsubscript{0.3}Co\textsubscript{0.3}Mn\textsubscript{0.4}O\textsubscript{2} cathode material was 147 mAh/g and had 56\% retention at the rate of 1C. Furthermore the discharge capacity of the LiNi\textsubscript{1/3}Co\textsubscript{1/3}Mn\textsubscript{1/3}O\textsubscript{2} cathode material was lower than 100 mAh/g. As the chemical fractions of Ni and Co were decreased, the discharge capacity became lower than 100 mAh/g.

On the other hand, the first discharge capacity of lithium-excess Li\textsubscript{1.2}Ni\textsubscript{0.175}Co\textsubscript{0.1}Mn\textsubscript{0.525}O\textsubscript{2} was 260 mAh/g. We also investigated the electrochemical properties of the lithium-excess Li\textsubscript{1.2}Ni\textsubscript{0.175}Co\textsubscript{0.1}Mn\textsubscript{0.525}O\textsubscript{2} to compare them with the properties of the LiNi\textsubscript{1/3}Co\textsubscript{1/3}Mn\textsubscript{1/3}O\textsubscript{2} cathode material. The first discharge capacity of the Li\textsubscript{1.2}Ni\textsubscript{0.175}Co\textsubscript{0.1}Mn\textsubscript{0.525}O\textsubscript{2} cathode material thus showed a high discharge capacity. The volume of the crystal lattice of Li\textsubscript{1.2}Ni\textsubscript{0.175}Co\textsubscript{0.1}Mn\textsubscript{0.525}O\textsubscript{2} after extraction of Li ion was small, and therefore, the chemical proportion of Mn was increased. As a result, the Li\textsubscript{1.2}Ni\textsubscript{0.175}Co\textsubscript{0.1}Mn\textsubscript{0.525}O\textsubscript{2} cathode material exhibited the best cycle performance.

5. Conclusion

LiNi\textsubscript{1/3}Co\textsubscript{1/3}Mn\textsubscript{1/3}O\textsubscript{2} cathode material was successfully synthesized by spray pyrolysis. They possessed a spherical morphology and a layered structure (space group: R-3m). The average particle size was approximately 0.8 \textmu m. The chemical composition affected rechargeable capacity and cycle stability. The change in the crystal lattice volume of Li\textsubscript{1.2}Ni\textsubscript{0.175}Co\textsubscript{0.1}Mn\textsubscript{0.525}O\textsubscript{2} after extraction of Li ion was small, and therefore, the chemical proportion of Mn was increased. As a result, the Li\textsubscript{1.2}Ni\textsubscript{0.175}Co\textsubscript{0.1}Mn\textsubscript{0.525}O\textsubscript{2} cathode material exhibited the best cycle performance.

References

1) C. Villevielle, M. V. Thournout, J. Scoyer, C. Tessier, J. O. Fourcade, J. C. Jumas and L. Monconduit, \textit{Electrochem. Acta}, 55, 7080–7084 (2010).
2) Y. Yao, H. Liu, G. Li, H. Peng and K. Chen, \textit{Electrochim. Acta}, 113, 340–345 (2013).
3) S. J. Jin, K. S. Park, M. H. Cho, C. H. Song, A. M. Stephan and K. S. Nahm, \textit{Solid State Ionics}, 177, 105–112 (2006).
4) C. Wu, X. Fang, X. Guo, Y. Mao, J. Ma, C. Zhao, Z. Wang and L. Chen, \textit{J. Power Sources}, 231, 44–49 (2013).
5) Z. Tang, Z. Wang, X. Li and W. Peng, \textit{J. Power Sources}, 208, 237–241 (2012).
6) J. Wang, Q. Zhang, X. Li, Z. Wang, K. Zhang, H. Guo, G. Yan, B. Huang and Z. He, \textit{Electrochem. Commun.}, 36, 6–9 (2013).
7) A. Awarke, S. Lauer, S. Pischinger and M. Wittjer, \textit{J. Power Sources}, 196, 405–411 (2011).
8) R. Santhanam, P. Jones, A. Sumana and B. Rambaba, \textit{J. Power Sources}, 195, 7391–7396 (2010).
9) N. Yabuuchi and T. Oizuki, \textit{J. Power Sources}, 171, 119–121 (2003).
10) K. M. Shaju, G. V. Subba Rao and B. V. R. Chowdari, \textit{Electrochem. Acta}, 48, 145–151 (2002).
11) J. M. Kim and H. T. Chung, \textit{Electrochim. Acta}, 49, 937–944 (2004).
12) T. H. Cho, Y. Shiosaki and H. Noguchi, \textit{J. Power Sources}, 159, 1322–1327 (2006).
13) S. K. Martha, J. Nanda, G. M. Veith and N. J. Dudney, \textit{J. Power Sources}, 190, 220–226 (2012).