Charge–discharge properties of a layered-type Li(Ni,Co,Ti)O\(_2\) powder library

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Abstract

A powder library of layered Li(Ni,Co,Ti)O\(_2\) (Ni \(\leq 0.8\), Ti \(\leq 0.2\)) compounds was prepared by electrostatic spray deposition. From powder x-ray diffraction patterns, most of the powder library sintered at 700 °C was indexed as a single phase belonging to the space group R\(\overline{3}m\). These results were almost identical to those obtained from a study by combinatorial exploration. We investigated the charge–discharge characteristics of the Li(Ni,Co,Ti)O\(_2\) powder library in a voltage range from 4.2 to 2.8 V at 1 C and found favorable cycling properties in the LiNi\(_x\)Co\(_{0.9-x}\)Ti\(_{0.1}\)O\(_2\) (0 \(\leq x \leq 0.6\)) compounds.

Keywords: combinatorial chemistry, electrostatic spray deposition, lithium-ion secondary battery, layered structure

1. Introduction

Many research groups have studied LiM\(_2\)O\(_2\) (M=Co, Ni, Mn or Fe) compounds with layered \(\alpha\)-NaFeO\(_2\)-type structures as candidate cathode materials for lithium-ion secondary battery [1–4]. While LiCoO\(_2\) is commonly used for cathodes, it has serious drawbacks such as high toxicity and price. A number of researchers have sought to resolve these problems and improve the electrode properties by exploring various materials in which metal ions such as Ni\(^{3+}\), Mn\(^{3+}\), Al\(^{3+}\) or Ti\(^{3+}\) substitute for the Co ions at the octahedral site [5–9]. Other recent studies reported better cycle performance, higher thermal stability and lower discharge capacity in the layered Li(Ni,Co,Ti)O\(_2\) compounds than in Li(Ni,Co)O\(_2\) [10,11]. However, when those studies were conducted, the chemical compositions of the Li(Ni,Co,Ti)O\(_2\) system had only been reported for the shaded area shown in figure 1.

In previous works, our group used ‘M-ist Combi’, a high-throughput material exploration system based on the electrostatic spray deposition (ESD) method, to explore new candidate electrode materials in the layered Li(Ni,Co,Ti)O\(_2\) compounds. When studying the Li–Ni–Co–Ti oxide powder library prepared using the M-ist Combi system, we investigated the phase relation at 700 °C [12,13]. From the x-ray diffraction (XRD) patterns of the powder library, the single-phase layered Li(Ni,Co,Ti)O\(_2\) system had a wider composition region than that reported by Liu et al [10] and Arai et al [11] (see figure 1). In this study, we prepared Li(Ni,Co,Ti)O\(_2\) powders by conventional ESD method and...
The starting materials were LiNO$_2$. Experimental details evaluated the charge–discharge properties to clarify the effect of Ti$^{3+}$ substitution at the octahedral site.

### 2. Experimental details

The starting materials were LiNiO$_3$, Ni(NO$_3$)$_2$·6H$_2$O, Co(NO$_3$)$_2$·6H$_2$O and TiO$_2$ nanoslurry. The materials were dissolved or dispersed in a mixture of ethanol and butyl carbitol and their concentrations were adjusted to 0.2 mol l$^{-1}$. The mixing molar ratio of lithium and transition metals (Co, Ni and Ti) was set at 1.3 : 1 considering the volatilization of lithium in the sintering process. The initial compositions for preparing the powder library were adjusted to those represented by the solid circles in figure 1. The liquid mixed from the starting materials was atomized to a grounded reaction plate heated at 400 °C. Next, the deposited and dried...
powder library was heat-treated at 700 °C for 10 h in air. The sintered powder library was analyzed by powder XRD (Philips X’Pert-Pro) with CuKα radiation and by inductively coupled plasma atomic emission spectroscopy (ICP-AES Shimadzu ICPE-9000).

The charge–discharge properties of the as-prepared powder library were evaluated by a conventional procedure using three-electrode beaker cells at room temperature. The working electrode was prepared by mixing Li(Ni,Co,Ti)O2, acetylene black and polyvinylidene difluoride (PVdF) binder at a ratio of 85 : 10 : 5. The reference and counter electrodes were both made of lithium metal. The electrolyte used was 1 molL−1 LiClO4 dissolved in a mixture of ethylene carbonate and diethyl carbonate (EC : DEC = 1 : 1 by volume). The cell was assembled in an argon-filled glove box. Charge–discharge measurements were carried out at a current rate of 1 C in a voltage range from 2.8 to 4.2 V.

3. Results and discussion

3.1. Powder preparation and particle properties

Figure 2 shows the XRD patterns of the prepared powder library. All the samples were indexed as layered α-NaFeO2-type structures (space group R3m). However, some nickel-rich compounds had small amounts of Li2CO3. This impurity phase was eliminated by washing the sintered powder samples with ultrapure water (see figure 3). LiTiO2-type compounds with a rock salt structure were also observed in the cobalt-rich region with 20% Ti included at the octahedral site. We suspected, however, some overlap between the XRD peaks of Li(Ni,Co,Ti)O2 and LiTiO2-type compounds as the XRD peaks of the layered structure shift to low angles with increasing nickel content. This hindered the detection of LiTiO2 from the XRD pattern in Li–Ni–Co–Ti oxides doped with 20% Ti.

Figure 4 shows the intensity ratio of the I003 and I104 peaks in the powder library. The decrease in this ratio is mostly attributed to the cation mixing in the crystal structure [14]. This effect increases with increasing Ni and Ti concentrations in the layered structure when the amount of Ni exceeded 50% of the transition metals. A Ni3+ reduction is considered more likely than a Co3+ reduction, and Ti4+ is considered to stimulate Ni3+ reduction because of the charge balance.

The studied powder contained excess lithium, and the ratio of the transition metal concentrations corresponded to that of the initial mixing ratio. Table 1 shows the chemical composition of the powder library measured using ICP-AES. The excess lithium can be attributed to the Li2CO3 phase detected by XRD. As mentioned above, washing with ultrapure water eliminated the Li2CO3. These findings agree
with our previous results [13], and in this study we have also characterized the electrochemical properties of the powder library.

3.2. Electrochemical behavior

Figure 5 shows the charge–discharge curves of LiNi$_{1-x}$Co$_{0.6-x}$Ti$_x$O$_2$ (x = 0, 0.1, 0.2). As the titanium content increased, the first discharge capacity decreased. Ti$^{4+}$ is considered to be inactive in the range of voltages applied in this study (2.8–4.2 V). LiNi$_{0.4}$Co$_{0.6-x}$Ti$_x$O$_2$ (x = 0.1) exhibited the best cycle performance among these samples. Moreover, the discharge curves of the Ti-substituted sample had flatter plateaus than those of LiNi$_{0.4}$Co$_{0.6}$O$_2$. Similar phenomena were observed in the other samples. Figure 6 shows the charge–discharge properties of the Li(Ni,Co,Ti)O$_2$ library. Li(Ni,Co,Ti)O$_2$ exhibited a better cycle performance and a lower first discharge capacity than Li(Ni,Co)O$_2$. Particularly favorable characteristics were observed for the LiNi$_{1-x}$Co$_{0.9-x}$Ti$_{0.1}$O$_2$ ($0 \leq x \leq 0.6$) composition region.

4. Conclusions

We prepared layered Li(Ni,Co,Ti)O$_2$ (Ni $\leq 0.8$, Ti $\leq 0.2$) compounds by the conventional ESD method. From the XRD and ICP-AES results, the composition region of the single-phase layered Li(Ni,Co,Ti)O$_2$ system was consistent with our previous reports. Li(Ni,Co,Ti)O$_2$ exhibited a better cycle performance and a lower first discharge capacity than Li(Ni,Co)O$_2$. Particularly favorable characteristics were observed for the LiNi$_{1-x}$Co$_{0.9-x}$Ti$_{0.1}$O$_2$ ($0 \leq x \leq 0.6$) compounds.

References

[1] Mizushima K, Jones P C, Wiseman P J and Goodenough J B 1980 Mater. Res. Bull. 15 783
[2] Thomas M, David W, Goodenough J and Groves P 1985 Mater. Res. Bull. 20 1137
[3] Reimers J, Fuller E, Rossen E and Dahn J 1993 J. Electrochem. Soc. 140 3396
[4] Sakurai Y, Arai H, Okada S and Yamaki J 1997 J. Power Sources 68 711
[5] Delmas C and Saadoun I 1992 Solid State Ion. 53 370
[6] Kinoshita A, Yanagida K, Yanagida A, Kida Y, Funahashi A, Nohma T and Yonezu I 2001 J. Power Sources 102 283
[7] Nayoze C, Ansart F, Laberty C, Sarrias J and Rousset A 2001 J. Power Sources 99 54
[8] Wang H, Jang Y, Huang B, Sadoway D and Chiang Y 1999 J. Power Sources 81 594
[9] Huang W and Frech R 1996 Solid State Ion. 86 395
[10] Liu H, Li J, Zhang Z, Gong Z and Yang Y 2004 Electrochim. Acta 49 1151
[11] Arai H, Tsuda M and Sakurai Y 2000 J. Power Sources 90 76
[12] Fujimoto K, Kato T, Ito S, Inoue S and Watanabe M 2006 Solid State Ion. 177 2639
[13] Fujimoto K, Onoda K and Ito S 2008 Mater. Res. Soc. Symp. Proc. 1024E 1024-A01-03
[14] Morales J, Vicente C P and Tirado J L 1990 Mater. Res. Bull. 25 623