Single crystal synthesis, crystal structure and electrochemical property of spinel-type LiCoMnO₄ as 5 V positive electrode materials

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Micrometer-sized single crystals of spinel-type LiCoMnO₄ were synthesized by heating a mixture of LiOH·H₂O, CoCl₂, and MnCl₂ with a molar ratio of Li:Co:Mn = 1.5:1:1 at 750°C. X-ray diffraction (XRD) pattern and scanning electron microscopic (SEM) image showed that LiCoMnO₄ has cubic spinel structure with well-formed octahedral crystal shapes. The size of the obtained LiCoMnO₄ single crystal particles was about 1–3 μm. Rietveld analysis using power XRD data confirmed the cubic spinel-type structure with space group Fd-3m, and the lattice parameter of a = 8.05812(14) Å. The tetrahedral 8a site was occupied by both Li and Co atoms with the occupancy values of Li/Co = 0.958/0.042. Electrochemical measurement exhibited the reversible Li⁺ ion extraction and insertion reactions at high potentials. The discharge profile with the discharge capacity of 107 mAh g⁻¹ showed three voltage plateaus at 5.1, 4.9, and 3.9 V; the former two corresponded to the redox reaction of Co³⁺/Co⁴⁺ and the latter was to the redox reaction of Mn⁴⁺/Mn³⁺, respectively.

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2.2 Electrochemical Properties

Electrochemical Li-ion extraction and insertion properties were evaluated using the CR2032-type coin cells at 25°C. The working electrode was made from a mixture of the sample (5 mg), acetylene black (5 mg), and polytetrafluoroethylene (PTFE) (1 mg) powder. Aluminum mesh having a diameter of 15 mm was used as a current collector. The counter electrode was a Li foil having a thickness of 0.2 mm. The separator was a microporous polypropylene sheet. A solution of 1 M LiPF6 in a 1:1 mixture by volume of ethylene carbonate (EC) and diethyl carbonate (DEC) (Kishida Chemical Co., Ltd.) was used as the electrolyte. The cells were constructed in an argon-filled glove box. Electrochemical charge and discharge cycle tests were carried out at a constant current density of 10 mA g⁻¹ for 24 h, and then discharged to 3.0 V at the same current density.

3. Results and discussion

3.1 Synthesis

Figure 1 shows the powder XRD pattern of the LiCoMnO₄ sample prepared by a flux method at 750°C in air. The pattern showed high crystallinity and was well indexed to be a single phase of the spinel-type structure having a cubic crystal system and space group Fd-3m. The well-formed octahedral shaped single-crystal morphology of LiCoMnO₄ with well-developed {111} faces can be observed in the SEM photographs, as shown in Fig. 2. The size of the obtained LiCoMnO₄ single crystal particles was about 1–3 μm. Chemical formula, determined by ICP-AES analysis, was Li₀.₉₇Co₁.₀₀Mn₁.₀₃O₄, which suggested the nearly stoichiometric composition.

We can speculate on the present synthetic route of the spinel crystals as follows. The starting chlorides and lithium hydroxide partly melt by heating above 650°C. Because these chlorides are unstable in air at these temperatures, the oxidation reaction should then proceed. Then, LiCoMnO₄ would precipitate together with the crystal growth.

We tried to synthesize larger single crystals of LiCoMnO₄ by changing the flux materials and the flux-content, and synthetic temperatures, unfortunately these experiments were failures. In the case of the use of LiCl as a flux material, the crystal size was achieved to be 100 μm, but the chemical composition was considerably shifted to the lithium-poor one, as reported previously.⁹ On the other hand, the lithium-rich starting composition resulted in the production of Li₂MnO₃ phase.

3.2 Crystal structure of LiCoMnO₄

The crystal structure of LiCoMnO₄ was refined by Rietveld method using the powder XRD data with an initial structure model of [(Li₁₋ₓCoₓ)₀.₆₆(Co₁₋ₓMnₓ)Liₓ]₀.₆₆O₄ and space group Fd-3m (No. 227), as previously reported.³ In the present refinement, the chemical formula was fixed to be Li₀.₉₇Co₁.₀₀Mn₁.₀₃O₄ analyzed by ICP-AES.

Figure 3 shows the observed, calculated, and difference patterns for the Rietveld refinement of LiCoMnO₄. The resultant R-values reached Rwp = 16.9% and R₁ = 11.1%, with a fit indicator of S = Rwp/R₁ = 1.38. This result accorded with the observed XRD and calculated XRD patterns well. The refined atomic coordinates are listed in Table 1. The lattice parameter of the sample was refined to be a = 8.05812(14) Å. This lattice parameter was similar to the reported values for the LiCoMnO₄ powder samples.⁵ The occupation value of the Co atom in 8a site was determined to be about 4%. This value was comparable to the reported value (7%) of the sample prepared by a solid state synthetic route.⁷

3.3 Electrochemical properties

Figure 4 represents the charge and discharge curves of the LiCoMnO₄ sample for the initial three cycles with a constant current density of 10 mA g⁻¹. It was confirmed that the Li-ion extraction and insertion reactions occurred in the LiCoMnO₄ single crystal samples having the crystal size of several micrometers. The discharge capacity was achieved to be 107 mAh g⁻¹ in the second cycle, which was about 74% of the theoretical capacity of 145 mAh g⁻¹. The obtained capacity was well consist-

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**Figure 1.** Powder XRD pattern of the LiCoMnO₄ single crystal sample synthesized by a flux method.

**Figure 2.** SEM images of the LiCoMnO₄ single crystal sample.
The irreversible capacity was probably due to the decomposition of the electrolyte at high potentials. The Li-ion extraction and insertion potentials were carefully examined by the dQ/dE plots of the LiCoMnO₄ sample, as shown in Fig. 5. Three oxidation and reduction peaks were observed in this figure. Two peaks at 5.1 and 4.9 V were attributed to be the redox reactions of Co³⁺/Co⁴⁺, suggesting the lithium-site ordering in the intermediate composition.¹¹ On the other hand, the peak at 3.9 V corresponded to the redox reaction of Mn³⁺/Mn⁴⁺, such as LiMn₂O₄ and LiNi₀.₄Mn₁.₆O₄.¹² This fact indicated the existence of Mn³⁺ ions in the sample, and well consistent with the chemical composition determined by both the ICP-AES and structure analyses.

4. Conclusion

In summary, we successfully synthesized micrometer-sized single crystals of spinel-type LiCoMnO₄ by a flux method at 750°C in air. The well-formed and high crystallinity LiCoMnO₄ sample was first synthesized in the present study. The crystal structure was refined by Rietveld analysis using powder XRD data. The electrochemical measurement revealed the Li-ion extraction and insertion properties of the sample. The rate capability and charge and discharge cycling properties are now investigating in the all solid-state lithium ion battery configuration, and will be published in the near future.

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