Preparation of Polycrystalline HT-$LiCoO_2$ Using Molten Salt Synthesis Method at 280 °C

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Polycrystalline HT-$LiCoO_2$ powders with homogeneous size distribution have been synthesized at 280 °C by the molten salt synthesis method using 0.59 $LiNO_3$–0.41 LiOH as a flux. These powders exhibit a good electrochemical behavior without further heat treatment at higher temperatures.

The researches on $LiCoO_2$ have been intensified over the past 10 years in view of their applications as a cathode material in lithium-ion batteries. Of these, the synthesis of HT-$LiCoO_2$ is carried out by the solid-state reaction process involving mechanical mixing of lithium and cobalt salts followed by firing for over 24 h above 800 °C. This process inevitably leads to the abnormal grain growth and poor control of stoichiometry. In this regard, many attempts have been made to synthesize HT-$LiCoO_2$ powders at lower temperatures.[1–6] However, the problems concerning the electrochemical properties still remain and a further heating at higher temperatures is required to enhance them. For the viewpoints of practical applications, therefore, it is important to search for a process to prepare HT-$LiCoO_2$ powders, exhibiting good electrochemical properties without further heat treatment.

Molten salt synthesis (MSS) method has been reported to be one of the effective methods to prepare a single-phase powder.[7] Yang et al. has prepared spinel $Li_4Mn_5O_{12}$ by MSS method using γ-MnO_2, β-MnO_2, hollandite, and birnessite as manganese sources, and $LiNO_3$ as a flux.[8] In a previous study, we have synthesized HT-$LiCoO_2$ at 400 °C using 0.58 LiOH–0.42 LiCl fulx.[9] This led us to conclude that HT-$LiCoO_2$ can be prepared at much lower temperatures if a suitable flux with low melting point is provided. In this study, we have selected the eutectic mixture of 0.59 $LiNO_3$–0.41 LiOH (mp = 183 °C) as the flux. As far as we know, this flux has the lowest melting point among various lithium salts, and we propose that polycrystalline HT-$LiCoO_2$ powders with a good electrochemical performance can be prepared at 280 °C.

The relative amount of flux and cobalt ion (= total Li ions/total Co ions) was set to 14. Appropriate amounts of $LiNO_3$ and $LiOH{\cdot}H_2O$ were roughly mixed with a mortar and pestle and heated at 280 °C in air. Then $CoCl_2{\cdot}6H_2O$ was poured into the melt. After heating, the obtained powders were cooled to ambient temperature and washed with water. TG–DTA (Dupont SDT 2960) was simultaneously performed on the starting mixture. The obtained powders were identified by XRD method using a MAC science MXP3A-HF diffractometer employing Cu Kα radiation. The scan data were collected at a rate of 0.026°/s in the 2θ range of 15–100°. The crystal structure was refined by the Rietveld method using the Fullprof program.[10] Field emission scanning electron microscopy (FE-SEM, S-4300) was taken to ensure the morphology. The electrochemical characteristics were studied using a two-electrode cell. The working electrode, which was consisted of 15 mg of $LiCoO_2$ (75 wt% by mass), acetylene black (15 wt%) and PTFE (10 wt%), was pressed and then vacuum dried at 120 °C for 24 h. The lithium metal and polypropylene film was used as the counter electrode and separator, respectively. The electrolyte used was 1 M $LiPF_6$ in 1:1 ethylene carbonate/dimethyl carbonate solution. The cells were tested using a constant current of 0.5 mA/cm^2 at the voltage ranges of 4.2–2.8 V with the Arbin charge/discharge cycler (BT 2042).

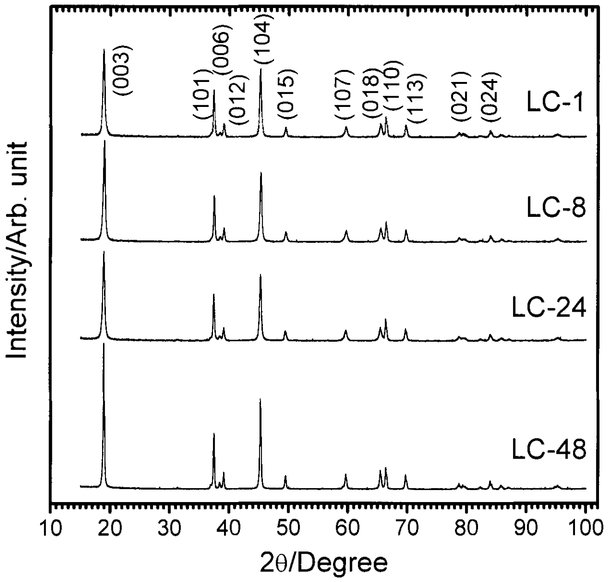

Figure 1. Powder XRD patterns of the samples prepared at 280 °C for various lengths of duration time in air.

An appropriate heating temperature was determined by TG–DTA. When the starting mixture was heated up to 300 °C, the weight loss was around 29.5%, corresponding to the dehydration of water (calcd 20.2%) and the oxidation of $CoCl_2$ by nitrate ion, such as $CoCl_2 + LiNO_3 \rightarrow LiCoO_2 + NO(\uparrow) + Cl_2(\uparrow)$ (calcd 9.9%). The endothermic peak was shown at 190 °C on the DTA curve, resulting from the melting of lithium salts; $LiNO_3$–LiOH (solid) → $LiNO_3$–LiOH (melt). As the temperature increases, the abrupt weight loss due to the evaporation of lithium salts could be observed above 500 °C. Figure 1 shows the XRD patterns of the powders prepared at 280 °C for various lengths of duration time in air (referred to LC–duration time (h)). Surprisingly, even after firing for 1 h, the sample shows the characteristic lines of HT-$LiCoO_2$ with small amounts of Co_3O_4 (< 1%). HT-$LiCoO_2$ is distinguished by the high intensity of the (003) line and clear splitting between the (006)/(012) and (018)/(110) from LT-$LiCoO_2$. These structural features can be clearly seen in all samples and refined by the space group *R*3*m*. In the refinement, the hypothesis of the pres-

Table 1. Unit cell parameter, absolute coordinate, Bragg factor, and bond distances of HT-$LiCoO_2$ prepared by MSS method at 280 °C

Sample	*a* (Å)	*c* (Å)	*c/a*	O(z)	B_{Li}	B_{Co}	B_O	R_B	Li-O(Å)	Co-O(Å)
LC-1	2.8160(2)	14.062(1)	4.994	0.2615(3)	1.2(4)	0.58(7)	0.6(1)	2.72	2.103(3)	1.914(2)
LC-8	2.8159(2)	14.058(1)	4.992	0.2621(3)	1.4(3)	0.62(6)	0.7(1)	2.55	2.108(2)	1.910(2)
LC-24	2.8160(2)	14.058(1)	4.992	0.2616(3)	1.1(3)	0.60(7)	0.7(1)	2.50	2.103(3)	1.913(2)
LC-48	2.8152(1)	14.056(1)	4.993	0.2606(3)	1.5(3)	0.43(5)	0.5(1)	2.21	2.094(2)	1.920(2)

ence of a fraction of Co ions in lithium site was ruled out since the fits lead to a negative occupancy. The unit cell parameter, absolute coordinate, isotropic thermal parameter, Bragg factor, and bond distances of HT-$LiCoO_2$ are listed in Table 1. The refined cell parameters of *a* and *c* well correspond to the values of 2.8161(5) and 14.0536(5) Å obtained from the single crystal.[11] The reaction intermediates, $Co(OH)_2$ and CoOOH, as appeared in the synthesis of HT-$LiCoO_2$ using 0.58 LiOH–0.42 LiCl flux, were not detected. This indicates that they quickly change into HT-$LiCoO_2$. In fact, CoOOH is known to transform into the spinel Co_3O_4 on heating at around 300 °C. That is, the formation of stable Co_3O_4 could be avoided by lowering the synthesis temperature.

Figure 2 illustrates the evolution of the specific capacity as a function of the number of cycles. The first-discharge capacity increases from 90 to 111 mAh/g as the reaction times increases from 1 to 48 h. Although the capacity of LC-1 slowly fades away, it shows noticeable capacities. More importantly, it is worthy to note that HT-$LiCoO_2$ with good cyclability can be prepared at 280 °C for 48 h. The discharge capacity of the Li/LC-48 cell was decreased to 100 mAh/g after 20 cycles. Actually, one of the most significant problems of low temperature synthesis is that HT-$LiCoO_2$ powders should be annealed at higher temperatures to impart an enhanced electrochemical property. Figure 3 shows that HT-$LiCoO_2$ powders consist of hexagonal crystallites. Even the reaction time increases, the crystallite size was approximately 200 nm for the samples of LC-1 to LC-24. For LC-48, the crystallites were grown up to around 1 μm. In any case, it is important to note that MSS method facilitates the formation of HT-$LiCoO_2$ powder with a uniform morphology.

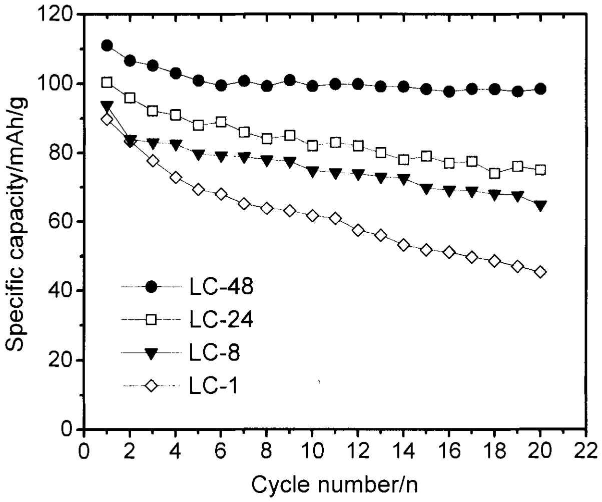

Figure 2. Evolution of discharge capacity as a function of cycle numbers.

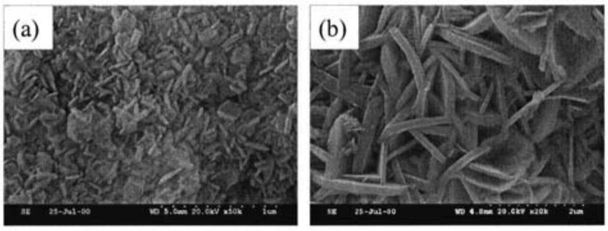

Figure 3. FE-SEM images of (a) LC-8 and (b) LC-48.

In conclusion, the MSS method has been shown the effective method to yield polycrystalline HT-$LiCoO_2$ with uniform size distribution at 280 °C. The phase analysis by XRD and FE-SEM shows that the hexagonal HT-$LiCoO_2$ powders are immediately formed in the flux since the reaction path is comparable to the solution routes.

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