Low-temperature synthesis of LiCoO$_2$ with eutectic of lithium precursors via the solid-state reaction method

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ABSTRACT
Lithium cobalt oxide powders have been prepared via the solid-state reaction method at lower temperatures (650 and 750°C) and in a shorter time (2 h). The eutectic effects of LiOH·H$_2$O and Li$_2$CO$_3$ salts on the formation of LiCoO$_2$ was investigated. The effects of the molar ratio of LiOH·H$_2$O to Li$_2$CO$_3$, the sintering temperature and the molar ratio of Li/Co on the physicochemical properties of LiCoO$_2$ powders were examined, especially, by powder X-ray diffraction (XRD), scanning electron microscopy (SEM) and charge-discharge cycling tests. LiCoO$_2$ prepared at 750°C and 2 h with a molar ratio (9:1) between these of LiOH·H$_2$O and Li$_2$CO$_3$ showed the best electrochemical properties (discharge capacity 98.3 mAh/g$^{-1}$ and capacity retention 80.7% after 50 cycles at 1C).

1. Introduction
LiCoO$_2$ has been widely applied in the manufacture of lithium-ion batteries since its electrochemical lithium insertion/extraction reactions were found by Goodenough et al. [1]. Although many studies on LiMn$_2$O$_4$, LiNiO$_2$, and LiFePO$_4$ as alternative cathode materials for LIBs (lithium-ion batteries) have been carried out in recent decades, layered LiCoO$_2$ is still the preferred cathode material for LIBs at present because of its superior cycle performances, ease of preparation, and high energy density.

Commercial LiCoO$_2$ is commonly prepared via the solid-state reaction method using cobalt compounds (e.g., Co$_3$O$_4$) and lithium compounds (e.g., Li$_2$CO$_3$) as starting materials [2]. To obtain an α-NaFeO$_2$ material (known as HT-LiCoO$_2$), high-temperature heating (> 850°C) and a long holding time (> 12 h) are required, which results in irregular morphology, broad particle-size distribution of the powder and high energy costs [3]. Lower temperature heating has been reported to result in a low-temperature phase (LT-LiCoO$_2$) with its capacity limited mainly to the lower voltage range and with inferior electrochemical performance [4–6].

A number of low-temperature techniques have been developed, including the sol–gel [7–9], coprecipitation [10], hydrothermal synthesis [11,12], high-energy ball milling pretreatment [13] and molten-salt synthesis method [2,14–16]. Most of these methods can produce materials with finer powder and improve the electrochemical properties as compared with the normal solid-state reaction method. They are generally complex, however, unable to achieve high-volume production without difficulty under existing industrial conditions.

In consideration of commercial application, it is important to develop an efficient low-temperature solid-state synthesis method by which HT-LiCoO$_2$ can be prepared without affecting its electrochemical properties. These properties are generally highly sensitive to the preparation method as well as to the phase crystallinity, purity, morphology and particle size of the products. Most solid-state reaction methods employ a single lithium precursor component, and the formation of LiCoO$_2$ depends on the solid-state reaction between the lithium precursor and cobalt precursor materials. With the use of two different lithium precursors, LiOH·H$_2$O and Li$_2$CO$_3$, in this study, melting of the lithium precursors occurred at lower temperatures due to the melting point depression effect. The appearance of the liquid phase can enhance the homogenous mixture of reactants and make it increase the contact area for reactions. The diffusion rate of the lithium ions is much higher, moreover, than in a solid-state reaction. These advantages have created high expectations that use of two lithium compounds as lithium precursors may accelerate the formation of LiCoO$_2$ at reduced sintering temperatures.

In this study, we have carried out synthesis and characterization of HT-LiCoO$_2$ powders via solid-state reaction using LiOH·H$_2$O and Li$_2$CO$_3$ as lithium precursors. The effects of such process parameters as the molar ratio of LiOH·H$_2$O to Li$_2$CO$_3$, the sintering temperature and...
the molar ratio of Li/Co on the physicochemical and electrochemical properties were investigated.

2. Experimental

Co(OH)$_2$ (Assay(Co):60.4%, Mitsuwa), LiOH-H$_2$O (99.0%, Nacalai Tesque) and Li$_2$CO$_3$ (99.0%, Nacalai Tesque) were used as starting materials. The molar ratios of LiOH-H$_2$O to Li$_2$CO$_3$ were set at different values (5:5, 8.43:1.57, 9:1, etc.). LiOH-H$_2$O and Li$_2$CO$_3$ with a molar ratio of 8.43:1.57 is a eutectic composition with a melting point of 434°C. After mixing the materials in two mortars with pestles, the mixtures were sintered at 650 or 750°C for 2 h in air, respectively. The heating rate was 5°C min$^{-1}$ for both sintering procedures.

Thermogravimetry and differential thermal analysis (TG/DTA, Hitachi STA7000) were used to monitor the thermal evolution of the precursors in air at a heating rate of 10°C min$^{-1}$. The crystal structure of as-prepared LiCoO$_2$ powders was identified by X-ray diffractometer (XRD, Shimadzu 6100) with Cu Kα radiation ($\lambda = 1.5418$ Å). The diffraction patterns were recorded at room temperature (25°C) in the 2θ range from 10° to 80°. Particle morphology was

Figure 1. X-ray diffraction patterns of LiCoO$_2$ prepared from LiOH-H$_2$O and Li$_2$CO$_3$ at different molar ratios and Li/Co with a molar ratio of 1.0.

Figure 2. The intensity ratios of the (311) peak of Co$_3$O$_4$ to the (003) peak of LiCoO$_2$ prepared from LiOH-H$_2$O and Li$_2$CO$_3$ at different molar ratios in Figure 1.
examined using a scanning electron microscope (SEM, Hitachi S-2600HS). The densities of the prepared powders were measured using a gas pycnometer (Shimadzu Accupyc 1330).

Electrochemical measurement of the product was performed using Tom cells. The cathode mixture consisted of LiCoO$_2$, Acetylene Black (AB) and polyvinylidene difluoride (PVDF) in a weight ratio of 8:1:1. A sheet of aluminum foil was coated with cathode slurry and dried in a drying oven at 120°C for 1 h. Circular cathodes (Φ = 16 mm) were punched out and pressed at 2 Mpa for 10 min. The cathodes were then kept under vacuum for 24 h at room temperature. The lithium metal foil was used as a reference and as counter electrodes. The electrolyte was 1 mol dm$^{-3}$ LiPF$_6$/PC+ DME (1:1 in volume). After assembling Tom cells in an argon-filled glove box, the charge-discharge tests were carried out at room temperature using HJ1001SM8A and SJ1001SD8 (Hokuto Denko Co.). In the first five cycles, a 0.2C-rate was applied in the voltage range between 3.0V and 4.1V. The current was then increased to a 1C-rate (130 mAg$^{-1}$ was assumed to be the 1C-rate).

3. Results and discussion

3.1. Effects of the molar ratio of LiOH·H$_2$O to Li$_2$CO$_3$

XRD patterns of the as-sintered mixtures of precursors with different molar ratios of LiOH·H$_2$O to Li$_2$CO$_3$ at 650°C for 2 h are shown in Figure 1. As seen in Figure 1, the LiCoO$_2$ phase was formed and

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**Figure 3.** TG (−) and DTA (−) curves of a mixture of LiOH·H$_2$O and Li$_2$CO$_3$ in an eutectic composition.

![Figure 4](image-url)  
**Figure 4.** TG (−) and DTA (−) curves of pure Co(OH)$_2$ and a mixture of Co(OH)$_2$ and lithium salts at which LiOH·H$_2$O and Li$_2$CO$_3$ are in an eutectic composition with Li/Co at a molar ratio of 1.05.
the Co$_3$O$_4$ phase was also detected in all the samples. The intensity ratio of the (311) peak of Co$_3$O$_4$ to the (003) peak of LiCoO$_2$ are presented in Figure 2. The intensity ratio depends on the molar percentage of LiOH·H$_2$O in the lithium precursors, as shown in Figure 2. It seems to decrease with increases in the molar percentage of LiOH·H$_2$O, and it increased dramatically at above 90% of LiOH·H$_2$O. It should be noticed that the variation tendency of the intensity ratio is similar to that of the phase diagram [17] of LiOH·H$_2$O and Li$_2$CO$_3$ with the molar percentage of LiOH·H$_2$O varying from 0 to 1. That is to say, it indicates that the degree of completeness of the reaction has a relationship with the liquidus temperature of the lithium precursors. Lithium salt compositions with lower liquidus temperatures can form liquid of lithium salts at lower temperatures during the

Table 1. Lattice parameters and densities of LiCoO$_2$ powders prepared at 650°C/2 h with different molar ratios of lithium precursors.

| Molar ratios of LiOH·H$_2$O:Li$_2$CO$_3$ | $I_{003}/I_{104}$ | FWHM | a (Å) | c (Å) | c/a | Density (g cm$^{-3}$) |
|----------------------------------------|------------------|-------|-------|------|-----|---------------------|
| 0:1                                    | 2.43             | 0.41  | 2.8109| 14.0388 | 4.994 | 4.5484             |
| 5:5                                    | 3.11             | 0.37  | 2.8133| 14.0463 | 4.993 | 4.4589             |
| 8.43:1.57                              | 3.24             | 0.39  | 2.8121| 14.0712 | 5.001 | 4.4763             |
| 9:1                                    | 2.61             | 0.40  | 2.8162| 14.0681 | 4.995 | 4.4423             |
| 1:0                                    | 2.47             | 0.45  | 2.8108| 14.0507 | 4.999 | 4.4987             |

Figure 5. TG (--) and DTA (--) curves of a mixture of Co(OH)$_2$ and Li$_2$CO$_3$ and a mixture of Co(OH)$_2$ and LiOH·H$_2$O. The molar ratio of Li/Co is 1.05.

Figure 6. X-ray diffraction patterns of the LiCoO$_2$ prepared from LiOH·H$_2$O and Li$_2$CO$_3$ at different molar ratios Li/Co at 650°C for 2 h and at a molar ratio of 1.05.
sintering process, which contributes to a larger contact area and a more homogenous mixture of reactants. Since the diffusion rate of lithium ions into cobalt precursors is also higher in the liquid phase, moreover, the formation reaction of LiCoO$_2$ is more efficient and the residual unreacted Co$_3$O$_4$ is also reduced during the short reaction time.

Figure 3 shows the TG-DTA curves of the mixture of LiOH·H$_2$O and Li$_2$CO$_3$ in the eutectic composition. The dehydration of LiOH·H$_2$O occurred at around 100°C, and the appearance of the endothermic peak at around 425°C is ascribed to the melting of the LiOH-Li$_2$CO$_3$ binary eutectic.

The TG-DTA curves of Co(OH)$_2$ and the mixture of Co(OH)$_2$ and lithium salts in which LiOH·H$_2$O and Li$_2$CO$_3$ are in the eutectic composition are given in Figure 4. The TG-DTA curves of the mixture of Co(OH)$_2$ and Li$_2$CO$_3$ and the mixture of Co(OH)$_2$ and LiOH·H$_2$O are given in Figure 5. The molar ratio of Li/Co is 1.05 for all mixtures. The exothermic peak at 204°C in Figure 4 is due to the decomposition of Co(OH)$_2$ into Co$_3$O$_4$. And the exothermic peaks at 202, 184 and 179°C in Figures 4 and 5 represent the decomposition temperatures of Li$_2$CO$_3$, LiOH·H$_2$O and the two together in a mixture, respectively. The endothermic peaks at around 420°C are observed in Figures 4 and 5, and they are associated with the co-melting of LiOH·H$_2$O and Li$_2$CO$_3$. Since there is no exothermic peak above 420°C, the sharp endothermic peak at 425°C in Figure 3 indicates that the reaction between Co(OH)$_2$ and the melting of lithium precursors take place at the eutectic temperature. The appearance of the lithium melt enhances the formation of LiCoO$_2$, which explains why the residual unreacted Co$_3$O$_4$ is reduced in the mixture of LiOH·H$_2$O and Li$_2$CO$_3$ as the lithium source. In the case of the reaction between

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Figure 7. SEM images of the LiCoO$_2$ powders prepared from LiOH·H$_2$O and Li$_2$CO$_3$ at different molar ratios at 650°C for 2 h. (a) 0:1, (b) 5:5, (c) 8.43:1.57, (d) 9:1, (e) 1:0.
Co(OH)$_2$ and Li$_2$CO$_3$ alone in Figure 5, there is no obvious peak or drop in the TG-DTA curves. This means that the Li$_2$CO$_3$ did not react with Co(OH)$_2$ until the temperature reached 500°C. With the weight loss rate of pure Co(OH)$_2$ at 500°C used as a reference value, the weight loss of the mixture should be 9.6% at 500°C, assuming that no decomposition of Li$_2$CO$_3$ occurred. The experimental weight loss is 19.0%, however, which indicates that Li$_2$CO$_3$ already takes part in some reactions which cause weight loss at below 500°C despite the high decomposition temperature. We know from the TG-DTA results that Co(OH)$_2$ begins to decompose at rather low temperatures and that the decomposition temperature can be reduced when LiOH·H$_2$O is present in the mixture. The reaction between the cobalt and lithium precursors may have been enhanced as the melt of lithium salts formed, as evidenced by the exothermic peak and weight loss that followed the eutectic endothermic peak at around 420°C. As some LiOH·H$_2$O will be transformed into Li$_2$CO$_3$ during sintering in air, the molar ratios of LiOH·H$_2$O to Li$_2$CO$_3$ will be changed from the initial molar ratios. This causes the lowest intensity ratio between the (311) peak of Co$_3$O$_4$ and the (003) peak of LiCoO$_2$ in Figure 2 to appear at 9:1 rather than 8.43:1.57 of the exact eutectic composition molar ratio.

### 3.2. Effect of the molar ratio of Li/Co

Considering the evaporation loss of lithium ions during the heating process, the molar ratio of Li/Co was raised to 1.05 for the following sintering processes: When the molar ratio of Li/Co was 1.0, the unreacted Co$_3$O$_4$ remained in all the products, as shown in Figure 1, but when the molar ratio of Li/Co was increased to 1.05, the peaks of unreacted Co$_3$O$_4$ disappeared from almost all the products, as shown in Figure 6. Five molar ratios of LiOH·H$_2$O to Li$_2$CO$_3$ were selected to prepare LiCoO$_2$. These were 1:0 (denoted as MR-1), 5:5 (MR-2), 8.43:1.57 (MR-3), 9:1 (MR-4), and 0:1 (MR-5), respectively. XRD patterns of samples prepared at different molar ratios of lithium precursors with the molar ratio of Li/Co at 1.05 are shown in Figure 6. The peaks of the five samples can be assigned to a hexagonal α-NaFeO$_2$ structure with a space group of R 3m. The intensity ratios of the (003) and (104) peaks, full width at half maximum (FWHM) of the (003) peak and the lattice parameters, are listed in Table 1.

HT-LiCoO$_2$ with a well-ordered hexagonal layered structure is distinguished by well-resolved splitting between lines (006, 012) and (108, 110) in Figure 6 and the c/a ratio of 4.99 in Table 1. All samples have these features of HT-LiCoO$_2$. The intensity ratio of the (003) and (104) peaks is known to be closely related to the degree of cation disordering. A higher $I_{003}/I_{104}$ ratio corresponds to a lower degree of cation mixing [16]. The value of $I_{003}/I_{104}$ increases at first and then decreases as the molar ratio of LiOH·H$_2$O to Li$_2$CO$_3$ increases, as shown in Table 1. Sample MR-3 shows the highest value for 3.24. As the molar ratio of Li/Co increases, the Co$_3$O$_4$ can be surrounded by richer lithium precursors and the evaporation loss of Li ions can be compensated. The amount of unreacted Co$_3$O$_4$ decreases as a result compared with the molar ratio of Li/Co, as shown in Figure 1. In the case of samples of MR-3, although the intensity ratio between the (311) peak of Co$_3$O$_4$ and the (003) peak of LiCoO$_2$ decreases from 0.074 to 0.072 as the molar ratio of Li/Co increases.
from 1 to 1.05, Co$_3$O$_4$ still remains, which may be ascribed to the more serious evaporation loss of lithium ions in this composition of LiOH$\cdot$H$_2$O and Li$_2$CO$_3$.

Table 2. Lattice parameters and densities of LiCoO$_2$ powders prepared at 750°C/2 h with different molar ratios of lithium precursor.

| Molar ratios of LiOH$\cdot$H$_2$O:Li$_2$CO$_3$ | I$_{003}$/I$_{104}$ | FWHM (Å) | a (Å) | c (Å) | c/a | Density (g cm$^{-3}$) |
|---------------------------------------------|-------------------|----------|-------|-------|-----|-------------------|
| 0:1                                        | 2.11              | 0.23     | 2.8114| 14.0419| 4.995| 4.6758            |
| 5:5                                        | 1.91              | 0.22     | 2.8136| 14.0645| 4.992| 4.6562            |
| 8.43:1.57                                  | 1.91              | 0.22     | 2.8143| 14.0347| 4.987| 4.6766            |
| 9:1                                        | 1.89              | 0.22     | 2.8151| 14.0475| 4.990| 4.6667            |
| 1:0                                        | 1.97              | 0.23     | 2.8134| 14.0263| 4.986| 4.6875            |

SEM images of LiCoO$_2$ obtained at 650°C/2 h with different molar ratios of lithium precursors are presented in Figure 7. Regardless of the different molar ratios of lithium salts, all the samples are in the shape of hexagonal flakes. The powders are loosely aggregated particles with diameters of about 400 nm~600 nm.

3.3. Effect of the sintering temperature

Figure 8 shows XRD patterns of samples prepared with different molar ratios of lithium precursors at 750°C for 2 h. The intensity ratios of the (003) and (104) peaks, FWHM of the (003) peak, and unit cell parameters of these samples are given in Table 2. Compared with samples prepared at 650°C/2 h, samples prepared at 750°C/2 h have higher densities. The values for both I$_{003}$/I$_{104}$ and FWHM of the (003) peak are decreased, moreover, and the differences in these values depend on the samples becoming smaller. This is because that all

Figure 9. SEM images of the LiCoO$_2$ powders prepared from LiOH$\cdot$H$_2$O and Li$_2$CO$_3$ at different molar ratios at 750°C for 2 h. [(a) 0:1, (b) 5:5, (c) 8.43:1.57, (d) 9:1, (e) 1:0].
samples will finally obtain a melt of lithium precursors as the sintering temperature in raised and the higher temperatures enhance the diffusion rate of lithium ions into the cobalt precursor. The XRD peaks of all the samples become sharper, as shown in Figure 8. But Co₃O₄ still remains in samples MR-2 and MR-3. Although the reaction rate is increased at higher sintering temperatures, the amount of lithium ion evaporation also becomes larger.

SEM images of samples prepared at 750°C/2 h are presented in Figure 9. As the synthetic temperature increases, crystallization of the samples is observed accompanied by increased particle size. The particles in Figure 9(a) and (e) seem to be more agglomerated than other samples prepared with a composition of LiOH·H₂O and Li₂CO₃ as lithium precursors. The appearance of the melt of lithium precursors at low sintering temperatures may contribute to finer, more isolated particles because the liquid phase can hinder agglomeration in solid-state sintering.

Figure 10 shows the charge and discharge profiles of the first cycle of samples at a constant current of 0.2 C. The initial discharge capacities (a) at 0.2 C of MR-2, MR-3, and MR-4 samples sintered at 650°C were 87.9, 83.0, and 83.9 mAhg⁻¹, respectively. Their initial discharge capacities rose to 100.5, 86.9, and 98.3 mAhg⁻¹, respectively, with an increase in the sintering temperature to 750°C. The cycle performances of samples prepared at 750°C/2 h are displayed in Figure 11. The first five cycles were carried out at 0.2 C, and were followed by 50 cycles at 1 C. MR-4 samples prepared at 750°C/2 h have the highest discharge capacity (80.9 mAhg⁻¹) in the first cycle of 1 C. MR-3 samples exhibit the worst

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electrochemical properties at either sintering temperature, and it seems certain that the existence of impurities affects their performance. The capacity retentions of MR-2, MR-3, and MR-4 samples after 50 cycles at 1C were 77.3%, 78.5%, and 80.7%, respectively.

4. Conclusions

HT-LiCoO$_2$ powders were synthesized successfully via a solid-state reaction using LiOH·H$_2$O and Li$_2$CO$_3$ as lithium precursors at relatively low temperatures (650 and 750°C) and a short holding time (2h). The effects of the process parameters, such as the molar ratio of LiOH·H$_2$O to Li$_2$CO$_3$, the molar ratio of Li/Co, and the sintering temperatures were studied in this paper.

(1) Compared with using Li$_2$CO$_3$ as a single lithium starting material, the decomposition temperature of Co(OH)$_2$ could be reduced by using LiOH·H$_2$O or a mixture of LiOH·H$_2$O and Li$_2$CO$_3$ as lithium starting materials. The addition of eutectic of lithium salts enhanced the reaction between the cobalt precursor and lithium precursors. This was evidenced by the intensity ratios of the (311) peak of Co$_3$O$_4$ to the (003) peak of LiCoO$_2$ prepared as Li/Co = 1 and TG-DTA results. Since some LiOH·H$_2$O compounds turn into Li$_2$CO$_3$ during the sintering process in air, the molar ratio between lithium salts deviates from the initial ratio.

(2) All samples prepared at 650 and 750°C exhibit the features of HT-LiCoO$_2$. When the molar ratio of Li/Co was increased from 1.0 to 1.05, the Co$_3$O$_4$ residue decreased. It still remained in the MR-3 samples (molar ratio LiOH·H$_2$O: Li$_2$CO$_3$ = 8.43: 1.57); however, at both sintering temperatures, possibly as a result of serious evaporation loss of lithium ions.

(3) As the sintering temperature was raised from 650°C to 750°C, the values for $I_{003}/I_{104}$ and FWHM of the (003) peak decreased depending on the molar ratios of LiOH·H$_2$O to Li$_2$CO$_3$. On the other hand, the particle size and the density and capacity of the powder and capacity increased. When the sintering temperature was 750°C, the MR-4 samples (molar ratio of LiOH·H$_2$O: Li$_2$CO$_3$ = 9: 1) exhibited the best electrochemical properties.

Disclosure statement

No potential conflict of interest was reported by the authors.

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