

초임계 수를 이용한 리튬코발트 옥사이드 나노입자 합성

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Preparation of Lithium Cobalt Oxide Nano Particles by a Continuous Hydrothermal Process using Supercritical Water

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Introduction

Intercalation compounds of the layered rock salt structure such as LiCoO_2 and LiNiO_2 , and spinels such as LiMn_2O_4 , are widely studied and used as electrodes in advanced lithium batteries[1]. The composition, structure, and cation ordering of these compounds determine the intercalation voltage and theoretical charge capacity, whereas extrinsic factors such as particle size and microstructure have important influence on characteristics such as cycle life and power capacity. Of these, the research on LiCoO_2 has been more active than that on the other oxides because of the simplicity of preparing the material. Also, LiCoO_2 has been widely used in commercial applications due to its advantages including easy preparation and high theoretical specific capacity of 274mAh/g. Many advanced chemical processes, such as the sol-gel process, spray decomposition, precipitation and freeze-drying rotary evaporation, supercritical drying, mechanical alloying and supercritical water synthesis, have been evolved to prepare high-active materials of high purity and crystallinity [2-4]. Supercritical water synthesis (SCWS) is a kind of hydrothermal crystallization in supercritical state.[5-8] In the SCWS, the morphology of produced particles can be controlled to some extent with pressure and temperature, and homogeneous reducing or oxidizing atmospheres can be provided by introducing gases or additional components (O_2 , H_2O_2).

In this paper, LiCoO_2 was prepared using SCWS method, in order to obtain single crystal transition metal oxide fine particles as cathode materials for Li-ion batteries.

Experimental

Figure 1 shows an apparatus for preparing lithium-cobalt oxide (LiCoO_2) using by supercritical water synthesis. The apparatus used in LiCoO_2 fine particles synthesis is consisted of feeding of reactants, preheating, reaction, and particle collecting part. Reactants were injected into reactor by diaphragm metering pumps (Pulsa Feeder Co., USA). $\text{LiOH}\cdot\text{H}_2\text{O}$ (Junsei, Japan 95+%) and $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (Junsei, Japan 97+%) were used as precursors without any further purification. Hydrogen peroxide (H_2O_2) was used as an oxidant. At room temperature, these precursors were mixed at a mixing point (MP1) just before the entrance of

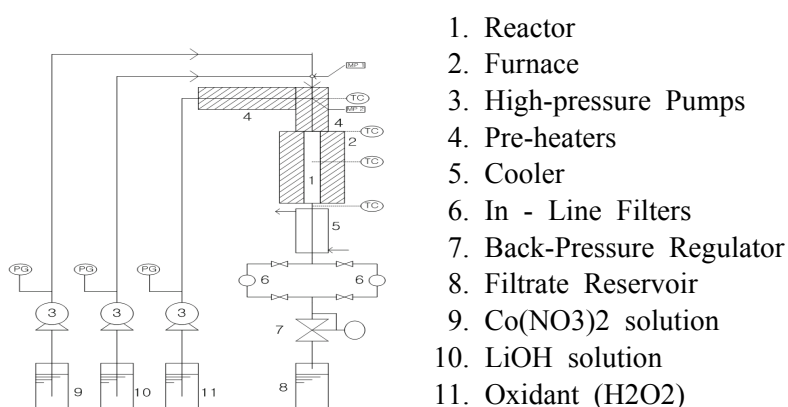


Figure 1. A flow type hydrothermal reaction apparatus for synthesis of LiCoO_2 .

the electric furnace. These solutions were then introduced into another mixing point (MP2) where supercritical water prepared by a pre-heater and a high-pressure metering pump was flowing. The resulting solution was fed into reactor that was made of stainless steel tube (16.5mm ID x 340mm L). The temperature and pressure in the reactor were maintained at 400°C and 300 bar. The effluent from the reactor was cooled to room temperature by a heat exchanger. The formed particles were collected by a tee-type filter (pore diameter: 0.5mm, TF series, Swagelok Co., U.S.A) disposed in front of the back-pressure regulator (P/N: 26-1721-24, Tescom Co., U.S.A), which was used to control the system pressure. The experimental was used to pressure gauge (MILLIPORE, max: 6000psi) for checking the pressure and used to K-TYPE thermocouple wrapping inconel for checking the temperature. Morphology and size of the particles obtained were observed using scanning electron microscope (SEM). The crystal structure of reaction product was analyzed by X-ray diffraction (XRD) with Cu K α radiation.

Results and Discussion

It is found that defect free single phased LiCoO_2 particles (< 500 nm) can be produced by supercritical water synthesis (SCWS) with a large excess of LiOH at a short residence time as shown in Figure 2. However, in subcritical condition (350°C or below, 300bar), LiCoO_2 was prepared with side products like CoO or Co_3O_4 , as shown in Figure 3. As it can be seen in Figure 4, there are two routes starting from $\text{Co}(\text{NO}_3)_2$: Supercritical route and subcritical route. In supercritical route, hydrolysis of $\text{Co}(\text{NO}_3)_2$ yields $\text{Co}(\text{OH})_3$ with reaction with H_2O_2 . Dehydration of $\text{Co}(\text{OH})_3$ gives Co_2O_3 in supercritical water. If the concentration of LiOH is high enough, then $\text{Co}(\text{OH})_3$ has a lot of chance to react with LiOH producing LiCoO_2 as shown in Figure 5. At least, Li/Co should be maintained at 10 or larger to produce LiCoO_2 . Below $\text{Li}/\text{Co} = 5$, the particles of Co_3O_4 were formed as a main product. In this supercritical route, it is crucial to have Co^{+3} because the oxidation state should be +3 for matching with the oxidation state of cobalt in LiCoO_2 . In supercritical water, there is no

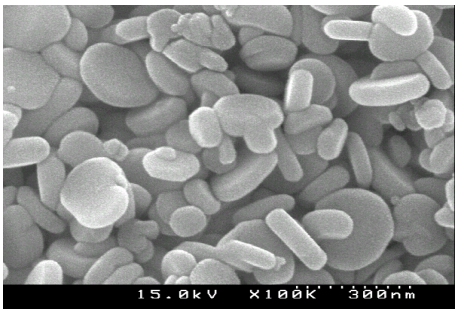


Figure 2. SEM of LiCoO₂ prepared by SCWS.

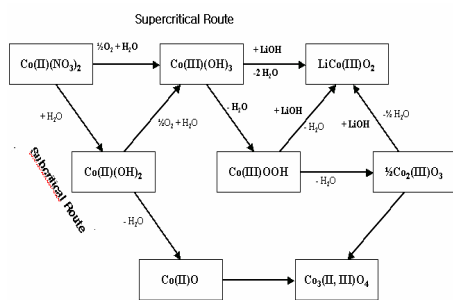


Figure 4. Synthesis route for Lithium cobalt oxide.

vapor phase in the reactor so that O₂ exist in a single phase together with Co(NO₃)₂ or Co(OH)₂. As a result, oxidation of Co+2 is very efficient under supercritical conditions. In subcritical route, on the other hands, Co(NO₃)₂ becomes Co(OH)₂ by hydrolysis since most O₂ exist in vapor phase and then this is turned into CoO by dehydration.

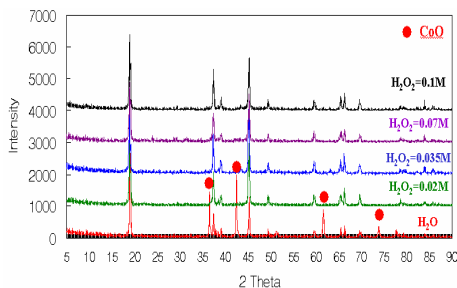


Figure 6. XRD patterns for LiCoO₂ @ T=400°C, P=300bar, t=40sec, LiOH=0.4M, Co(NO₃)₂=0.02M.

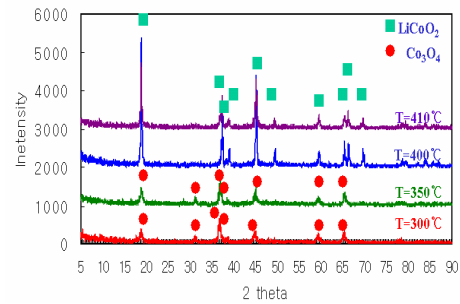


Figure 3. XRD patterns for LiCoO₂ @ P=300bar, t=40sec, LiOH=0.4M, Co(NO₃)₂=0.02M, H₂O₂=0.02M.

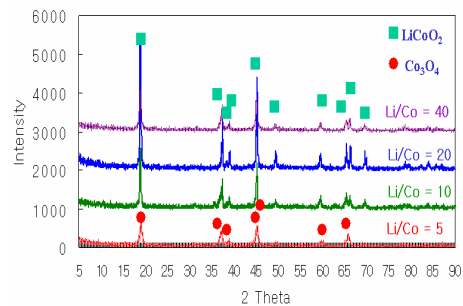


Figure 5. XRD patterns for LiCoO₂ @ T=400°C, P=300bar, t=40sec, Co(NO₃)₂=0.02M, H₂O₂=0.02M.

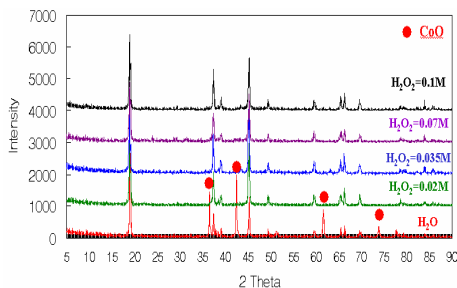


Figure 6. XRD patterns for LiCoO₂ @ T=400°C, P=300bar, t=40sec, LiOH=0.4M, Co(NO₃)₂=0.02M.

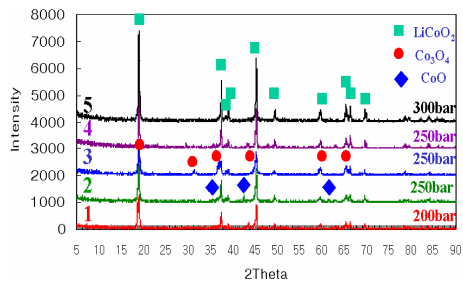


Figure 7. XRD patterns for LiCoO₂ @ T=400°C, t=40sec, LiOH=0.4M, Co(NO₃)₂=0.02M, H₂O₂=0.02M.

As shown in Figure 6, CoO was the main product when the experiment was carried out without H₂O₂ (or O₂). Therefore, it is desirable that the reaction should take place in supercritical water over 400°C in order to get LiCoO₂. It is also important to supply a large excess of LiOH which drives the reaction not to the side reaction (Co₂O₃) but to the main reaction (LiCoO₂). We have also carried out a series of experiments to demonstrate the effect of pressure on preparing LiCoO₂. In Figure 7, it can be seen that pressure should be maintained 300 bar or higher to get single phase LiCoO₂. At the pressure of 250 bar, Co₃O₄

or CoO, or sometimes LiCoO₂ was produced as a main product.

In general, the crystal structure of LiCoO₂ is divided into HT (high temperature) and LT (low temperature) types according to preparation methods.

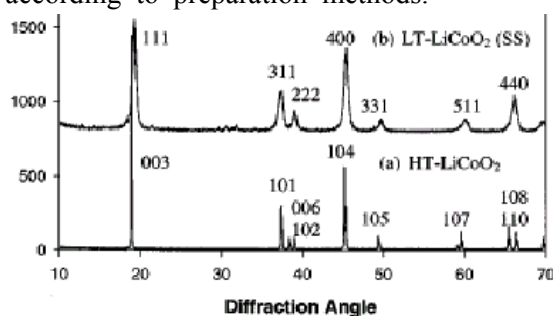


Figure 8. XRD patterns of (a) HT-LiCoO₂, (b) LT-LiCoO₂ [9]

As in Figure 8, when comparing XRD patterns, (222) peak and (440) peak of LT-LiCoO₂ are split into (006) peak and (012) peak, and (018) peak and (110) peak at HT type LiCoO₂, respectively. It is generally accepted that lithium ion battery cathode materials of layered hexagonal structure have shown better performance. Therefore, many researchers have been investigated on preparation methods to produce HT-type (layered hexagonal) LiCoO₂. Conventional solid phase method to uses Li₂CO₃ and CoCO₃ for production of HT structure need reaction time of 24hr at 900°C. In Sol-Gel method, HT structure can be obtained by performing calcination about 800°C after drying LiOH/NH₄OH/Co(CO₃)₂. In this study, LiCoO₂ particle obtained have shown single crystal and HT structures in spite of being prepared at low temperature of 400°C. In SCWS, it is possible to save energy to produce HT-type (layered hexagonal) LiCoO₂, since it is not necessary to have an additional heat treatment.

Conclusion

We are able to produce defect free single phased LiCoO₂ particles (< 500 nm) by supercritical water synthesis (SCWS) with a large excess of LiOH at a short residence time (< 1 min). Also, the high crystallinity LiCoO₂ was prepared without side products like CoO and Co₃O₄. Hydrothermal synthesis using supercritical water is energy-efficient, continuous, environmental friendly process in comparison with conventional solid phase method or sol-gel method. In addition, particle of HT-LiCoO₂ is produced high crystallinity without thermal post-treatment.

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