Journal of the Korean Ceramic Society
Vol. 41, No. 11, pp. 793~796, 2004.

Electrochemical Performance of Spherical $LiCoO_2$ Powders Synthesized Using Ultrasonic Spray Pyrolysis Method (I): Effect of Pyrolysis Conditions on Powder Characteristics

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(Received September 24, 2004; Accepted October 25, 2004)

ABSTRACT

Process parameters were studied in synthesis of $LiCoO_2$ powder by ultrasonic spray pyrolysis. Concentration of the mixed solution influenced the size, shape, and yield of the synthesized powder. The yield was affected primarily by the height of the solution, and then by the flow rate of a carrier gas. The temperature of the reactor governed the crystallinity and morphology of the powder. $LiCoO_2$ powders were synthesized as a layered high temperature phase above 800°C. The synthesized powders were sphere and secondary particles consisted of primary particles of 55–70 nm. The secondary particles became bigger from 0.28 to 1.43 μm as the concentration of the solution was increased from 0.05 to 2.0 M. The 2.0 M solution provided the highest production rate.

Key words : Ultrasonic spray pyrolysis, Process parameter, Production rate

1. Introduction

Spray pyrolysis has a merit of continuous process which is considered to be more economic than a batch process. It can employ various starting materials as long as they are soluble in water or organic solvents. Furthermore it produces spherical particles which are desirable for advanced ceramic process.[1-3] The process comprises 4 steps : 1) generation of drops from a precursor solution, 2) shrinkage of drop due to evaporation of the solvent, 3) formation of spherical oxide composite by decomposition, 4) crystallization.[4] Ultrasonic spray pyrolysis is a process to produce drops of a precursor by ultrasonication. The production rate is low comparing to that of drops produced by high speed gas blowing but the drops are more homogeneous. Submicron size drops can be produced when a high frequency is employed, which results in homogeneous spherical submicron particles.[5,6] But the relationship between drops and produced particles are not clear yet, therefore researches have been undergoing. Milosevic *et al.*[4] reported that they were able to synthesize $BaTiO_3$ of 0.53 μm by producing drops of 2.2 μm. Choa *et al.*[7] synthesized Fe_2O_3/MgO of 0.41 μm by producing drops of 2.89 μm. The drop sizes were not measured but calculated from Lang's equation derived from Kelvin's and they have a tendency to be come out smaller.[8] Tsai *et al.*[9] measured drops of the zirconia precursor solution by a laser diffraction. Drops of 6.8 μm produced at 1.67 MHz became particles of 0.65 μm, but unexpectedly drops of 37 μm produced by ultrasound two-fluid atomization resulted in 0.35 μm. This confliction comes from incomplete understanding of the processing condition. Moreover, the optimization of the processing conditions is essential for higher production rate as well as morphology control. Therefore, it is the objective of this study to optimize the processing parameters in ultrasonic spray pyrolysis method for higher production rate and better particle size control.

2. Experimental Procedure

The precursor solutions were prepared by mixing $LiNO_3$ (Kanto Chemical, 99.95%) and $Co(NO_3)_2 \cdot 6H_2O$ (Junsei Chemical, 97%) at a mole ratio of 1 : 1 in deionized water. The concentrations were varied from 0.05, 0.5, 1.0 to 2.0 M. Ultrasonic spray pyrolysis was performed with an equipment shown schematically in Fig. 1. It consists of a ultrasonicator which generates drops, a vertical furnace with a quartz tube (70×1200 mm) where thermal decomposition and reaction take place, and a collector where the produced powder are collected. The precursor solution was placed in a polypropylene bottle and the height of the solution was maintained constant using a peristaltic pump. Drops generated by a sonicator operated at 1.67 MHz were moved to the 2 zone furnace by a carrier gas and transformed to powder.

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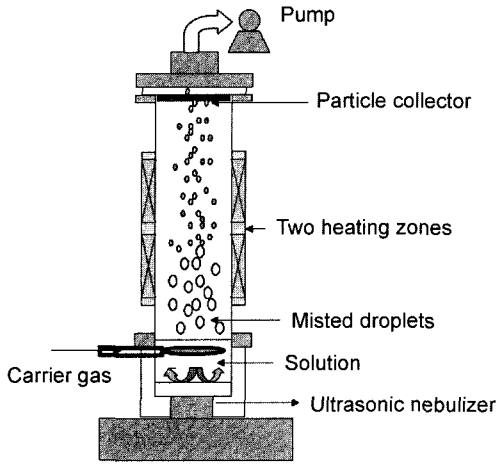

Fig. 1. Schematic diagram of ultrasonic spray pyrolysis apparatus.

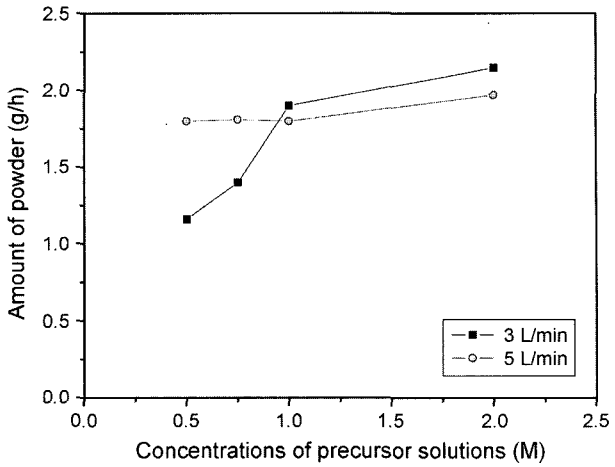

Fig. 3. The amount of powders obtained versus various concentrations of the precursor solution.

Such produced powder were collected by a filter paper (pore size 1 μm, 5C, Adavantic) under 90 kPa. The heights of the precursor solution were 20, 40, or 50 mm. Oxygen was used as a carrier gas at a rate of 3 *l*/min or 5 *l*/min. The furnace was maintained at 400°C for the 1st zone where the drops passed first and set the temperature of the 2nd zone at 700, 800, or 900°C. The yield was calculated from the difference in weights of the filter paper before and after collection. The collected powder were subjected to XRD analysis with a scanning rate of 2 degree/min using XRD (Model D/Max-3A, Rigaku, Japan) and observed by SEM (Model L-240, Hitachi, Japan) and TEM (JEM-200FX2, Jeol, Japan).

3. Results and Discussion

The amount of synthesized powder was influenced by the height of the precursor solution as shown in Fig. 2. The powder obtained from the bath of 20 mm high amounted twice of those from 40 and 50 mm baths. The flow rate of 5 *l*/min produced more powder than 3 *l*/min when the bath height

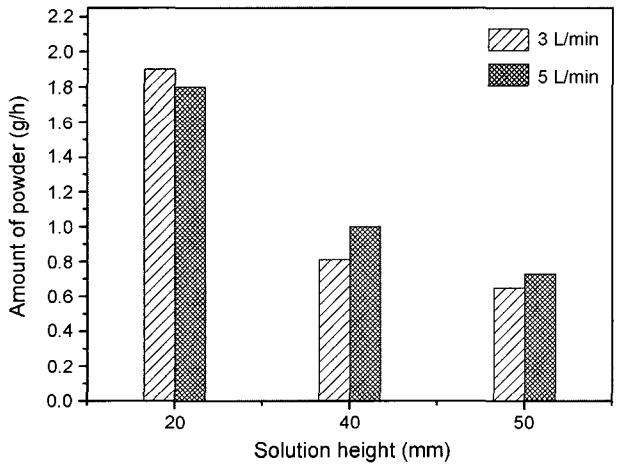

Fig. 2. The amount of powders obtained versus various heights of the precursor solution of 1.0 M.

was high, such as 40 or 50 mm. For the bath height of 20 mm, 1.9 g/h was collected at the flow rate of 5 *l*/min and 1.8 g/h at 3 *l*/min. From Fig. 3, almost same amount of powder, 1.8 g/h was obtained from the solutions of 0.5 M through 2.0 M at the flow rate of 5 *l*/min, but when the flow rate of 3 *l*/min was used, more powder was obtained as the concentration was increased. For example 1.2 g/h was obtained for the solution of 0.5 M, but 2.2 g/h for the solution of 2.0 M. Consumed amounts of the 0.5 M solution of 20 mm high for 1 h at the flow rate of 3 and 5 *l*/min were measured as 48 and 50 m*l*, but 36 and 32 m*l* for the 1.0 M solution, 35 and 34 m*l* for the 2.0 M solution, respectively. This phenomena can be explained by this way: the carrier gas ejected to the surface suppresses the generation of mist more from higher concentrated solution. The yield efficiency calculated from dividing collected powder by calculated amount of the consumed precursor was 81% at the flow rate of 5 *l*/min for the 0.5 M solution, 62~66% for the 1.0 M solution, and 41~43% for 2.0 M solution. The yield efficiency decreased as the concentration was increased.

Fig. 4 shows the SEM pictures of the powders obtained from the solutions of 0.05, 0.5, 1.0, and 2.0 M at the flow rate of 3 *l*/min and two zone furnace temperatures of 400 and 900°C, respectively. The left side pictures are at low magnification for secondary particles and the right ones are at high magnification for primary particles. As the concentration became lower, the powders became more agglomerate due to high surface area. It is noticeable primary particles are 55–70 nm for all the concentrations. It may be explained by heterogeneous nucleation of supersaturated particles due to evaporation of water in the drop, which is not much affected by drop size or concentration. But secondary particles became big as the concentration was increased: 0.28 μm for 0.05 M solution and 1.43 μm for 2.0 M solution. It could be explained by one particle per drop mechanism. The secondary particles were observed at higher magnification by TEM and shown in Fig. 5. As the concentration was increased, center of some particle was

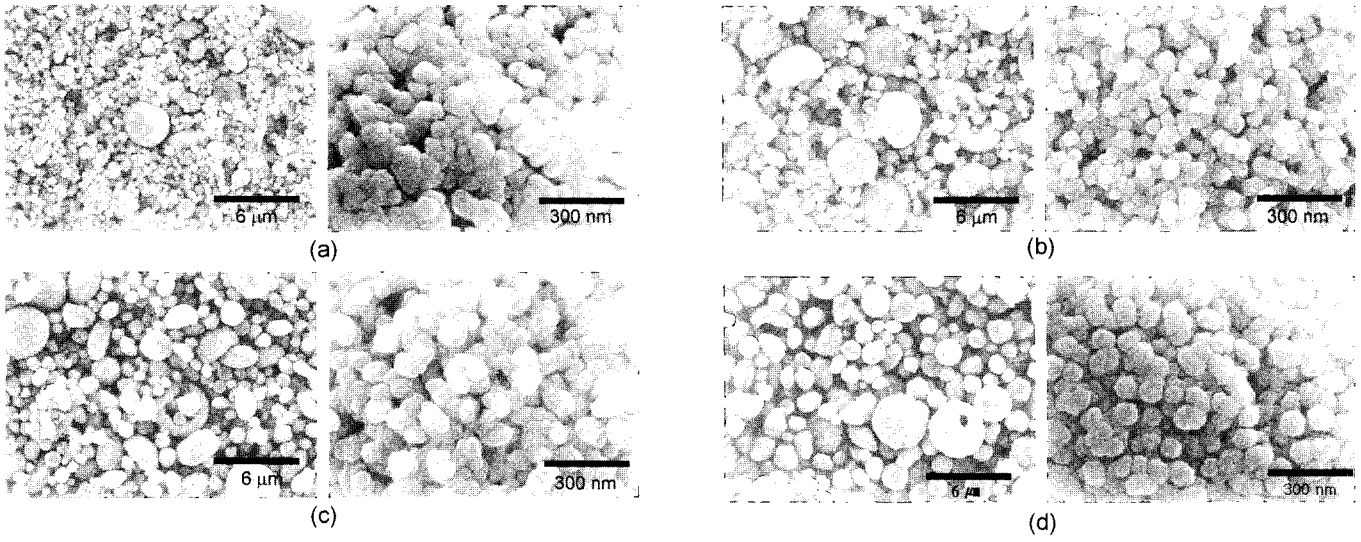

Fig. 4. SEM micrographs of $LiCoO_2$ powders obtained from various concentrations of the precursor solution of (a) 0.05, (b) 0.5, (c) 1.0, and (d) 2.0 M. Temperatures of the reactor at zone I and II were 400 and 900°C, respectively, and the flow rate of carrier gas was 5 *l*/min.

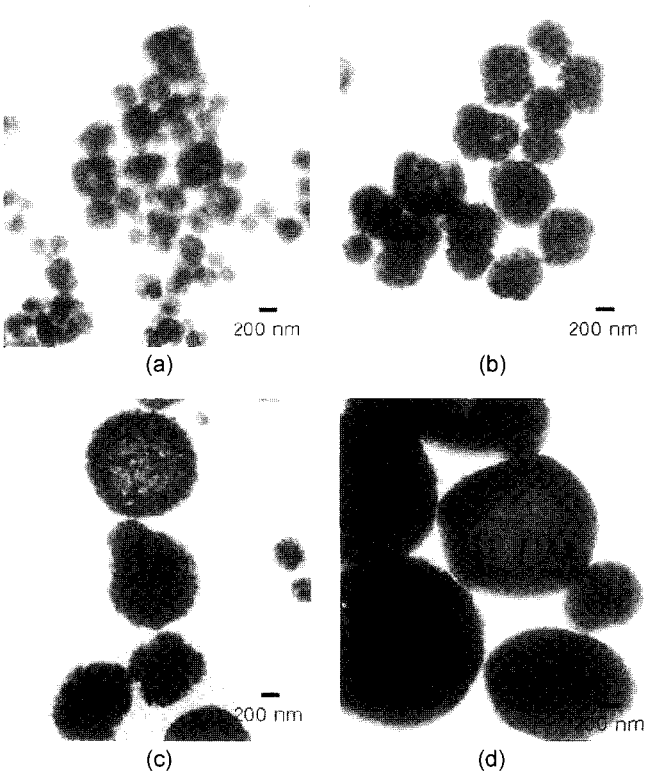

Fig. 5. TEM micrographs of $LiCoO_2$ powders obtained from various concentrations of the precursor solution of (a) 0.05, (b) 0.5, (c) 1.0, and (d) 2.0 mol/*l*. Temperatures of the reactor at zone I and II were 400 and 900°C, respectively, and the flow rate of carrier gas was 5 *l*/min.

transparent which implies it was a sphere with a hole. It can be explained in the following: as the solvent evaporates, viscous layer developed on the surface of the drop and then explosion of the drop caused by the increased inner pressure

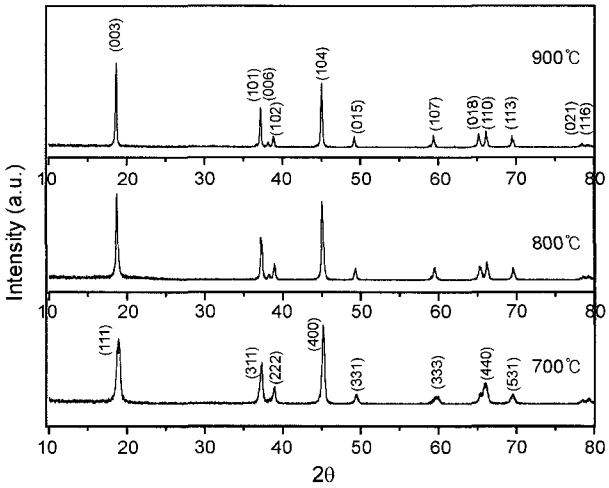

Fig. 6. X-ray diffraction patterns of $LiCoO_2$ synthesized at various temperatures.

gives rise to a sphere with a hole.

Peak splits in XRD at ~38° and ~66° are observed for the powders synthesized at 800 and 900°C, not for 700°C as shown in Fig. 6. It means that powders synthesized at above 800°C are high temperature phase, layered bidimensional α-$NaFeO_2$ structure ($R\bar{3}m$) and that at 700°C is low temperature phase, spinel like structure ($Fd3m$).[10,11] These two phases exist in $LiCoO_2$, in which the high temperature phase is preferred due to its excellent electrochemical properties for the cathode material.

4. Conclusions

Synthesis of $LiCoO_2$ powder by ultrasonic spray pyrolysis was studied in aspects of concentration of the precursor solution, flow rate of the carrier gas, temperature of the fur-

nace, and height of the solution. Particle size of the powder increased from 0.28 to 1.43 μm as the concentration of the solution increased from 0.05 to 2.0 M. It consisted of primary particles of 55–70 nm regardless of the concentration of the solution. Low temperature spinel like phase was obtained at the furnace temperature of 700°C, but high temperature layered structure at those of 800 and 900°C. The highest production rate was obtained from the concentration of the solution of 2.0 M, the flow rate of 3 *l*/min and the solution height of 20 mm, and the maximum yield efficiency from 0.5 M, 5 *l*/min and 20 mm.

REFERENCES

1. G. L. Messing, S.-C. Zhang, and G. V. Jayanthi, "Ceramic Powder Synthesis by Spray pyrolysis," *J. Am. Ceram. Soc.*, **76** [11] 2707-26 (1993).
2. K. Eguchi, T. Hatagishi, and H. Arai, "Power Generation and Steam Electrolysis Characteristics of an Electrochemical Cell with a Zirconia-or Ceria-Based Electrolyte," *Solid State Ionics*, **86-88** 1245-49 (1996).
3. S. C. Lee, H. F. Lin, C. Y. Tung, H. M. Lin, and S. L. Hsu, "Molecular Simulation of the Properties of Gas Absorption on the Surface of Nanocrystalline TiO_2," *Nanostruct. Mater.*, **9** 697-700 (1997).
4. O. B. Milosevic, M. J. Mirkovic, and D. P. Uskokovic, "Characteristics and Formation Mechanism of $BaTiO_3$ Powders Preparation by Twin-Fluid and Ultrasonic Spray-Pyrolysis Methods," *J. Am. Ceram. Soc.*, **79** 1720-22 (1996).
5. S. C. Tsai, P. Childs, and P. Luu, "Ultrasound-Modulated Two-Fluid Atomization of a Water Jet," *AIChE J.*, **42** 3340-50 (1996).
6. S. C. Tsai, P. Luu, P. Childs, A. Teshome, and C. S. Tsai, "The Role of Capillary Waves in Two-Fluid Atomization," *Phys. of Fluids*, **9** [10] 2909-18 (1997).
7. Y. H. Choa, J. K. Yang, W. J. Yang, and K. H. Auh, "Synthesis and Characterization of Isolated Iron Oxide Nanoparticle Dispersed in MgO Matrix," *J. Magn. Magn. Mater.*, **266** 20-7 (2003).
8. R. J. Lang, "Ultrasonic Atomization of Liquids," *J. Acoustic Soc. of Am.*, **34** [1] 6-8 (1962).
9. S. C. Tsai, Y. L. Song, C. S. Tsai, C. C. Yang, W. Y. Chiu, and H. M. Lin, "Ultrasonic Spray Pyrolysis for Nanoparticles Synthesis," *J. Mater. Sci.*, **266** [39] 3647-57 (2004).
10. E. Rossen, J. N. Reimers, and J. R. Dahn, "Synthesis and Electrochemistry of Spinel LT-$LiCoO_2$," *Solid State Ionics*, **62** 53-60 (1993).
11. S. G. Kang, S. Y. Kang, K. S. Rhy, and S. H. Chang, "Electrochemical and Structural Properties of HT-$LiCoO_2$ and LT-$LiCoO_2$ Prepared by the Sol-Gel Method," *Solid State Ionics*, **120** 155-61 (1999).