

Optimization of the synthesis conditions of LiCoO_2 for lithium secondary battery by ultrasonic spray pyrolysis process

Kwan Young Choi^{a,b,1}, Ki Do Kim^{a,1}, Ji Won Yang^{b,*}

^a Nanonix Corp., Ochang Industrial Complex 102-23BL Cheongwon-gun, Chungbuk 363-883, Republic of Korea

^b Department of Chemical & Biomolecular Engineering, KAIST 373-1, Guseong-dong, Yuseong-gu, Daejeon 305-701, Republic of Korea

Received 2 March 2004; received in revised form 4 April 2005; accepted 17 June 2005

Abstract

LiCoO_2 powders for lithium secondary battery were successfully prepared by the ultrasonic spray pyrolysis process. In this work, the statistical experimental design method was used to compare the characteristics (particle size, standard deviation, surface area, tab density) of the LiCoO_2 particles according to the four parameters (synthesis temperature, sintering temperature, sintering time, sintering heating rate). The optimal synthesis conditions for the synthesis of LiCoO_2 particles in ultrasonic spray pyrolysis process were to be obtained. The above-mentioned optimal conditions were used to prepare the particles with particle size $4.7\text{ }\mu\text{m}$ (standard deviation: $\pm 1.3\%$) and the experimental results were in a good agreement with simulated values. The oxide powders were characterized by scanning electron microscopy, X-ray diffraction and electrochemical method including charge–discharge cycling. The characteristics as a cathode for lithium ion battery depended on the sintering temperature and sintering time. Consequently, LiCoO_2 powders made by the ultrasonic spray pyrolysis process displayed a good electrochemical performance and the experimental design method was well applied.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Experimental design method; LiCoO_2 ; Ultrasonic spray pyrolysis; Lithium secondary battery

1. Introduction

The increasing demand for portable and cordless electronic appliances is driving the development of compact batteries [1]. In particular, lithium ion batteries have attracted much attention because of the high output voltage, high specific energy, long cycle-life and no memory effect [2]. Lithium transition metal oxides, such as LiCoO_2 [3–5], LiMn_2O_4 [6,7] and LiNiO_2 [8,9] have been investigated in order to apply them as positive electrode (cathode) materials for lithium secondary batteries. In particular, research on LiCoO_2 has been most active on these materials because of not only the simple means of the materials preparation, but also its high potential for application. Recently, much attention also has been given to LiCoO_2 as the most promising

alternative cathode material for molten carbonate fuel cells [10].

These materials are traditionally prepared by a conventional ceramic method that is, firing solid reactants at high temperatures and grinding the product. Many advanced chemical processes, such as the sol–gel process [5], spray decomposition, precipitation method, the freeze drying method [11] and supercritical drying method, also have been evolved to prepare high-active materials of high purity and crystallinity. In this paper, the ultrasonic spray pyrolysis method [12–14] was used as a method to prepare sub-micrometer LiCoO_2 particles. Ultrasonic spray pyrolysis is very suitable for the formation of high-density ceramic particles, and is an effective production technique to lead to short production time, homogeneous particle composition and one-step production method. The droplets of the solution generated by ultrasonic waves can be transported by the carrier gases to a heated furnace, where several reactions such as solvent evaporation and atomic rearrangement take place successively.

* Corresponding author. Tel.: +82 42 869 3924; fax: +82 42 869 3910.
E-mail address: jwyang@kaist.ac.kr (J.W. Yang).

¹ Tel.: +82 43 217 8533; fax: +82 43 217 8538.

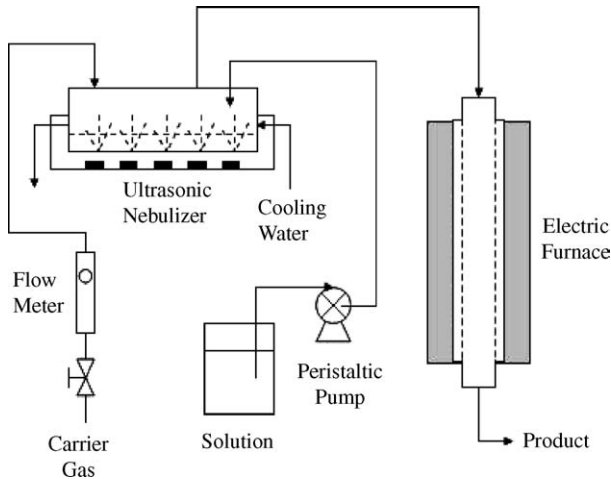


Fig. 1. Schematic diagram of experimental apparatus.

Table 1
Experimental parameters and desirable properties

Parameter	Property
Synthesis temperature (°C): 800–900	Particle size (μm): 4–5
Sintering temperature (°C): 700–900	Standard deviation (%): minimize
Sintering time (h): 1–12	Surface area (m ² /g): 0.3–0.4
Sintering heating rate (°C/h): 200–700	Tab density (g/cm ³): 2–3

Table 2
Orthogonal arrays for experimental design and test results

Experiment no.	Synthesis conditions				Results			
	Synthesis temperature (°C)	Sintering temperature (°C)	Sintering time (h)	Heating rate (°C/h)	Particle size (μm)	Standard deviation (%)	Surface area (m ² /g)	Tab density (g/cm ³)
1	800	700	1	200	1.7	4.5	1.3	1.026
2	800	900	12	200	4.7	1.6	0.5	1.784
3	800	700	12	700	1.9	3.9	1.2	0.986
4	800	900	1	700	3.4	2.9	0.7	1.393
5	900	700	12	200	1.8	4.1	2.8	0.997
6	900	900	1	200	3.2	2.2	0.7	1.707
7	900	700	1	700	1.5	6.4	4.1	1.133
8	900	900	12	700	4.7	1.6	0.5	2.090
9	850	800	6.5	450	2.4	3.6	1.8	1.232
10	850	800	6.5	450	2.4	3.0	1.9	1.245
11	850	800	6.5	450	2.7	3.4	1.8	1.399
12	850	800	6.5	450	2.6	3.2	1.9	1.529

Table 3
Correlation coefficient of each parameter and confidence level of properties

	Coefficients								R^2
	Constant	Sintering temperature	Heating rate	Synthesis temperature	Sintering time	Sintering temperature × heating rate	Sintering temperature × sintering time	Heating rate × sintering time	
Particle size	−2.443	0.00731	−0.0012	−0.00127	−0.34527	1.4×10^{-6}	0.000511	0.00002	0.97
Standard deviation	9.909	−0.01208	0.0070	0.00305	−0.13854	-5.1×10^{-6}	0.000177	−0.00025	0.93
Surface area	−2.647	−0.00764	0.0077	0.01088	−0.04588	-5.7×10^{-6}	0.000225	−0.00039	0.97
Tab density	−2.063	0.00237	0.0002	0.00185	−0.17967	-5.2×10^{-7}	0.000215	0.00005	0.95

Properties of LiCoO₂ particles prepared by ultrasonic spray pyrolysis method are affected by various parameters such as the molar ratio (Li:Co) of starting materials, synthesis temperature, sintering temperature, sintering time, sintering heating rate and so on. The interrelationships between the above parameters are complex, and the analysis of this system to optimize the factors is a time and labor consuming work. The current main experimental approach to investigate the effects of the parameters and to obtain the optimal conditions is the classical method of varying one parameter at a time while keeping the other entire factors constant, thus measuring the influence of each parameter separately. The major disadvantage of the one factor at a time strategy is that it fails to consider any possible interaction between the factors and thus might miss the real optimum. Hence, the analyses using conventional experimental methods are inefficient. Therefore, a statistical experimental design method [15–18] to find the optimal conditions for satisfying the properties simultaneously was used. In this work, optimization program was utilized and took three levels for each factor (four parameters, three levels).

The objectives of this work are: (1) to examine the effects of synthesis temperature, sintering temperature, sintering time and sintering heating rate on the formation of LiCoO₂ particles, (2) to establish the optimal conditions by using a statistical experimental design method and (3) to characterize the LiCoO₂ particles obtained by optimal conditions in ultrasonic spray pyrolysis process.

2. Experimental method and data treatment

2.1. Starting solutions and experimental apparatus

LiCoO₂ particles were prepared by using LiNO₃ (Kanto, 99%) and Co(NO₃)₂·6H₂O (Kanto, 98%) as starting materials for the ultrasonic spray pyrolysis method. An aqueous solution was prepared by dissolving LiNO₃ and Co(NO₃)₂·6H₂O in distilled water at the molar ratio of Li:Co=1.05:1, and stirred for 1 h. The schematic diagram of the experimental apparatus is shown in Fig. 1. This apparatus is divided into three parts, such as droplet generator, electrical furnace and particle collector. The droplet generator consists of an ultrasonic nebulizer (frequency: 1.67 MHz), a peristaltic pump and thermostat circulation parts. A pump delivers lithium nitrate and cobalt nitrate aqueous solutions to an ultrasonic nebulizer at constant feed rate. Subsequently, a carrier gas takes them into a furnace (length: 1.2 m) while the nebulizer sprays them out. Then, they are dried or, if necessary, sintered at a desired temperature.

2.2. Synthesis and characterization of LiCoO₂ particles

The concentration of the lithium nitrate and cobalt nitrate were 1.575 and 1.5 M, respectively. The fog of aqueous metal

nitrate solution was generated by an ultrasonic nebulizer, and then the fog was introduced into the electrical furnace to possess a drying and pyrolysis process. The feed rate of carrier gas for carrying the fog was 0.38 m³/min. The fog was remained inside the electrical furnace for approximately 1.5 s and pyrolyzed at variable temperatures (800–900 °C). The decomposed powders were further heated to 700–900 °C at the heating rate of 200–700 °C/h for 1–12 h to obtain single phase polycrystalline LiCoO₂ powders.

The particle size, standard deviation, morphology and microstructure of particles were determined using a scanning electron microscopy (SEM, JEOL, JSM-6330F) and Laser Particle Size Analyzer (Otsuka electronics, LPA-3000, 3100). The phase identification of the particles was carried out by X-ray diffraction (XRD, Rigaku, Rint-2000) using Cu K α radiation. The specific surface area of the material was also determined by the liquid nitrogen physisorption method (Micromeritics, GEMINI-2375).

The electrochemical cells were assembled, each with the prepared LiCoO₂ as a positive electrode, lithium foil (Cyprus, Foote Mineral, purity 99.9%) as a negative electrode, and an electrolyte of 1 M LiPF₆ in a 1:1 (volume ratio) mixture of ethylene carbonate (EC) and diethylcarbonate (DEC). A glass filter (Wattman GF/A) was used as the separator. The cells were assembled in an argon filled dry box. All electrochem-

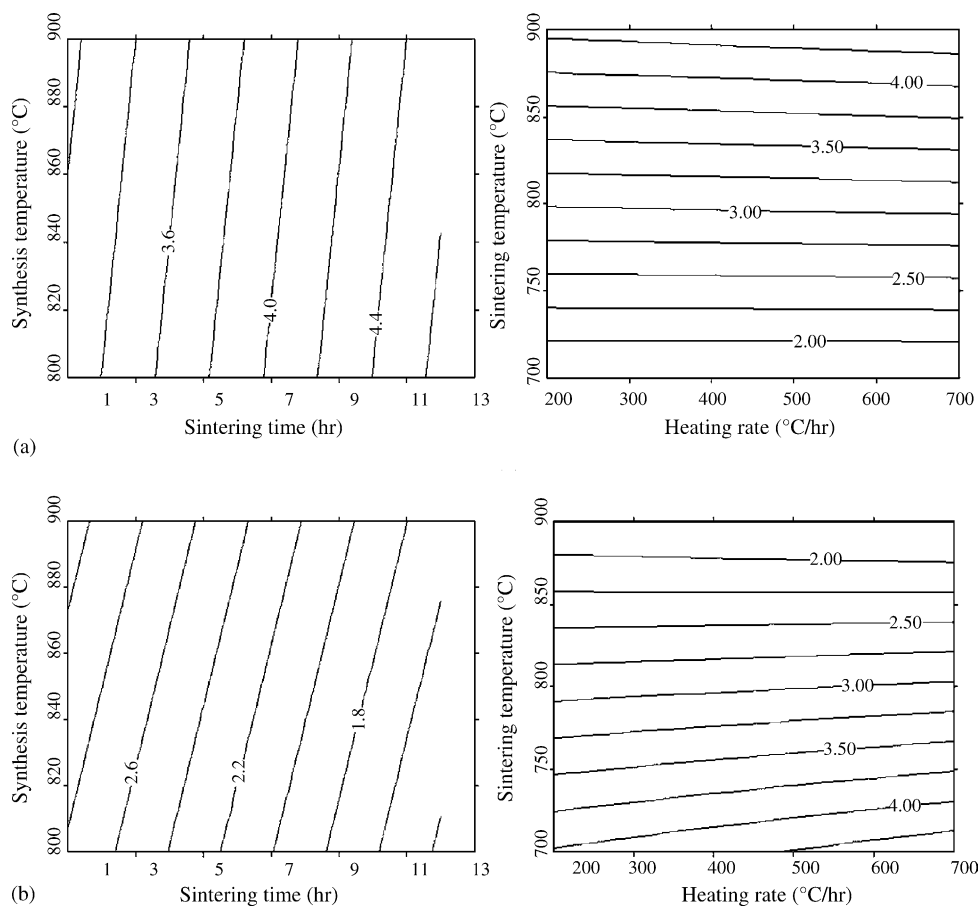


Fig. 2. Simulated results of parameters effect on (a) particle size (μm) and (b) standard deviation (%).

ical tests were performed at room temperature with a battery charge–discharge cycle tester (WBCS3000, WonATech).

3. Results and discussion

3.1. Design of statistical experiment

The operational parameters and desirable properties for the formation of LiCoO_2 particles are summarized in Table 1. As shown in Table 1, four parameters are controllable factors at the synthesis and sintering of LiCoO_2 particles, and they have a great influence on the properties of powders. In case of properties, four characteristics were selected and the values are very similar to those of commercial product. And it is necessary to control the four parameters affecting the four properties. Therefore, a statistical experimental design method was used to find the optimal conditions for satisfying the four properties. A design of the orthogonal arrays and its experimental results are shown in Table 2. We carried out 12 experiments and took three levels for each factor. As shown in Table 2, four experiments (Nos. 9–12) with same conditions were performed to confirm the reproducibility of the test.

3.2. Determination of the optimal conditions to find the desirable properties

The correlation coefficients of each parameter from the results of Table 2 were obtained by a statistical experimental design method. In addition, the values of confidence level (R^2) were calculated from regression analysis. These results are shown in Table 3. Table 3 indicates that the correlation function ($R^2 = 0.97$) of particle size and surface area is more reliable than that of standard deviation and tab density. From the data of each property in Table 3, the graphs of four properties about each parameter were obtained.

Figs. 2 and 3 are the simulated results obtained by a statistical experimental design method. Fig. 2 shows the simulated results about the effect of four parameters on particle size and standard deviation. Fig. 2(a) illustrates that the particle size increase while increasing the sintering time and sintering temperature. It was also found that, however, the synthesis temperature and heating rate were not seriously influence on particle size. In case of standard deviation, low synthesis temperature, long sintering time and high sintering temperature were required to obtain the monodispersed LiCoO_2 particles (Fig. 2(b)). Fig. 3 represents the effect of parameters on surface area and tab density. The surface area

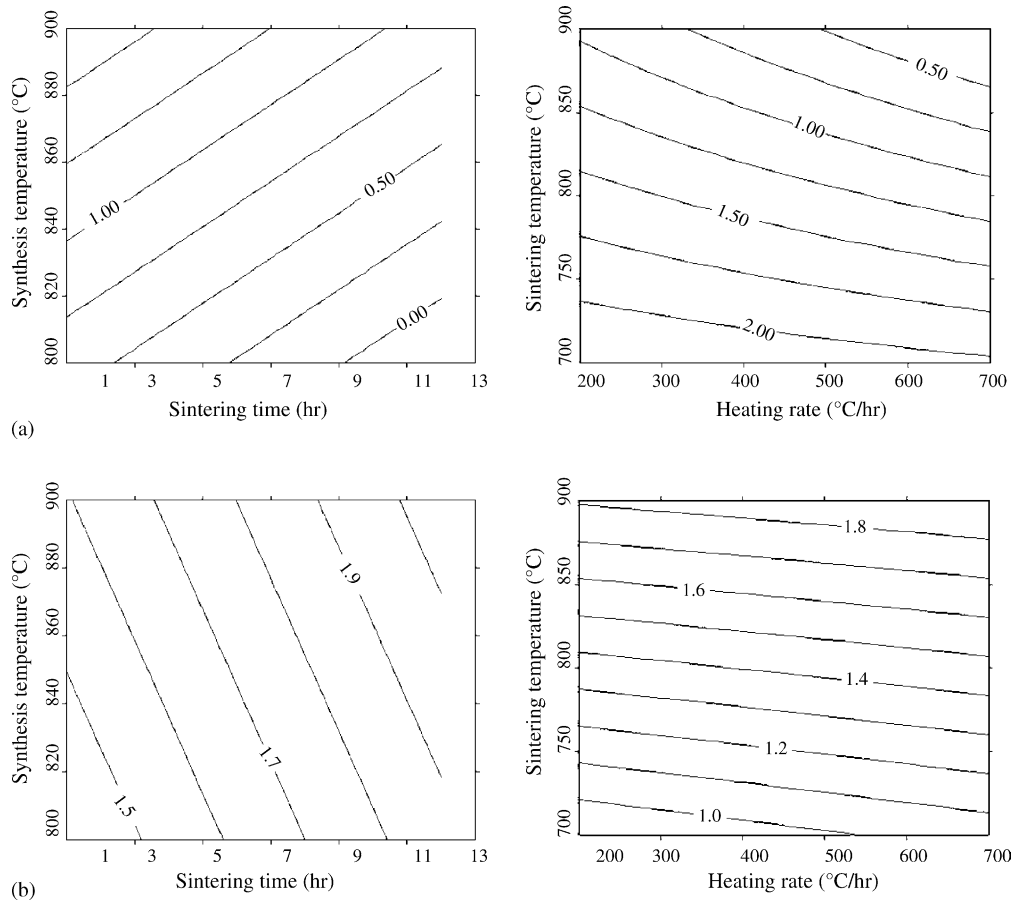


Fig. 3. Simulated results of parameters effect on (a) surface area (m^2/g) and (b) tab density (g/cm^3).

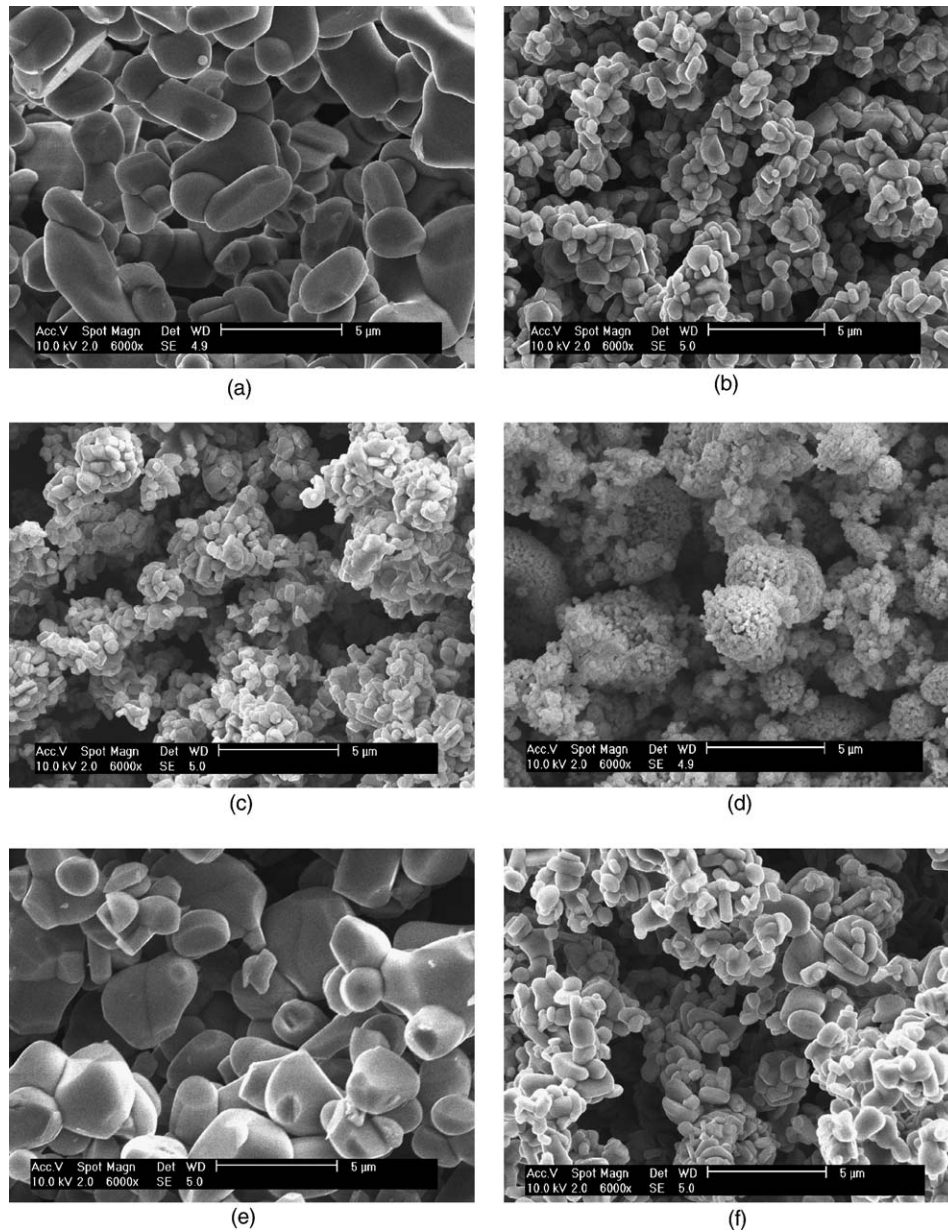


Fig. 4. SEM images of LiCoO₂ particles prepared by a design of the statistical experiment.

of LiCoO₂ particles decreases with increasing the sintering time, sintering temperature and heating rate except the synthesis temperature (Fig. 3(a)). Fig. 3(b) shows that the tab density of LiCoO₂ particles increases with increasing of all parameters. Fig. 4 is the SEM images of LiCoO₂ particles prepared by a design of the statistical experiment (Table 2). The SEM photographs of LiCoO₂ particles with the largest particle size and surface area were shown in Fig. 4 (a, e, c and d), respectively. These results are in a good agreement with the Table 2.

So far, the effect of parameters on properties was discussed to find the optimal conditions. However, it is necessary to find the overall optimal conditions that can synthesize the LiCoO₂ particles satisfying the four properties presented in

the Table 1. In this work, therefore, the overall optimal conditions were obtained by experimental design method program and were represented in Table 4. Simulated values obtained from the optimal conditions of Table 4 were compared with the experimental values. Table 5 shows that experimental values of properties were in a good agreement with simulated

Table 4
Optimal synthesis conditions

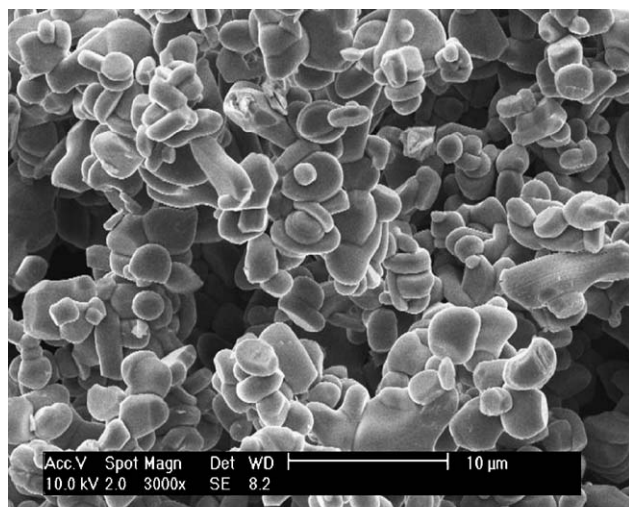
Parameter	Range
Synthesis temperature (°C)	835–840
Sintering temperature (°C)	890–900
Sintering time (h)	10–11
Sintering heating rate (°C/h)	580–590

Table 5

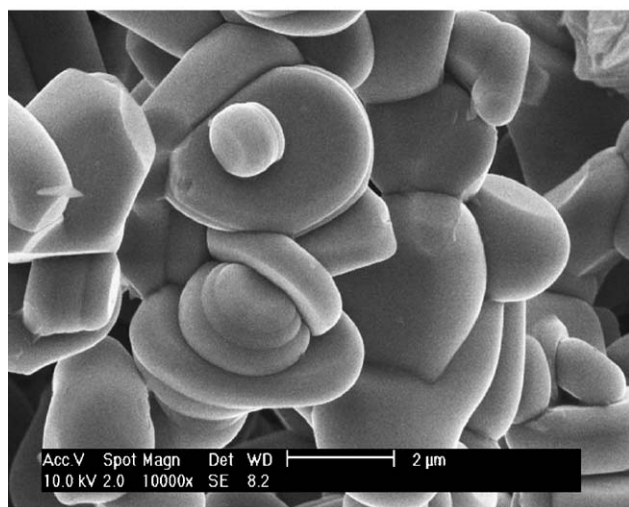
Comparison of the properties between simulated and experimental value

	Simulated value	Experimental value
Particle size (μm)	4.4	4.7
Standard deviation (%)	± 1.7	± 1.3
Surface area (m^2/g)	0.34	0.30
Tab density (g/cm^3)	1.88	1.92

value. The particle size and surface area were in better agreement with the simulated value than standard deviation and tab density. These good agreements between two values can also be predicted from the confidence level (R^2) as shown in Table 3. Figs. 5 and 6 are, respectively, SEM image and particle size distribution of LiCoO_2 particles, which was prepared under the conditions of Table 4. The morphology of particles is very smooth and flat as shown in Fig. 5(b), and these characteristics are demanded for commercial product.



(a)



(b)

Fig. 5. SEM images of LiCoO_2 particles prepared by optimal experimental conditions of Table 4.

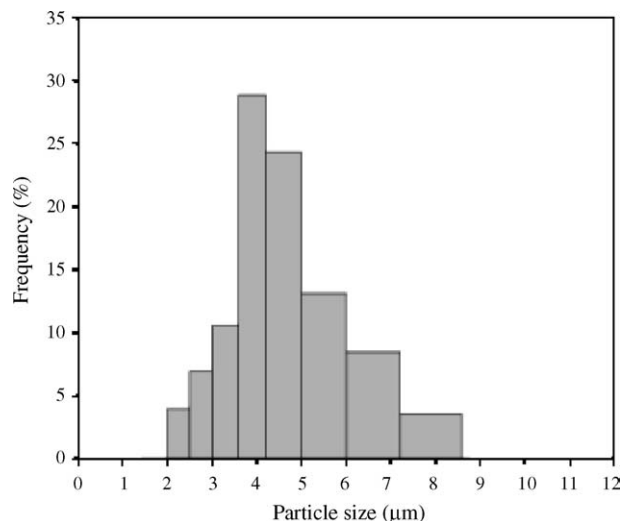


Fig. 6. Particle size distribution of LiCoO_2 particles prepared by optimal experimental conditions of Table 4.

3.3. Electrochemical characteristics

The XRD patterns of the LiCoO_2 powder synthesized by sintering the precursor at optimal conditions shown in Table 4 were shown in Fig. 7. There are three strong peaks at 18.90° , 37.40° and 45.24° . No peaks attributed to other phases are observed [19]. This XRD pattern is well coincident with the JCPDS card #16-0427 [20]. It was also found that it is not agreement with JCPDS card #44-0145 [21] indicating the XRD pattern of imperfectly sintered LiCoO_2 powder. Therefore, it is concluded that LiCoO_2 powders synthesized in this work were well sintered.

Fig. 8 shows the charge/discharge curves for $\text{Li}/1\text{M LiPF}_6$ in EC-DEC/ LiCoO_2 calcined at optimal conditions in an argon atmosphere. The test condition was a current density of $0.3 \text{ mA}/\text{cm}^2$ between 3.0 and 4.4 V. The test coin cells were fabricated by using lithium foil as the anode and

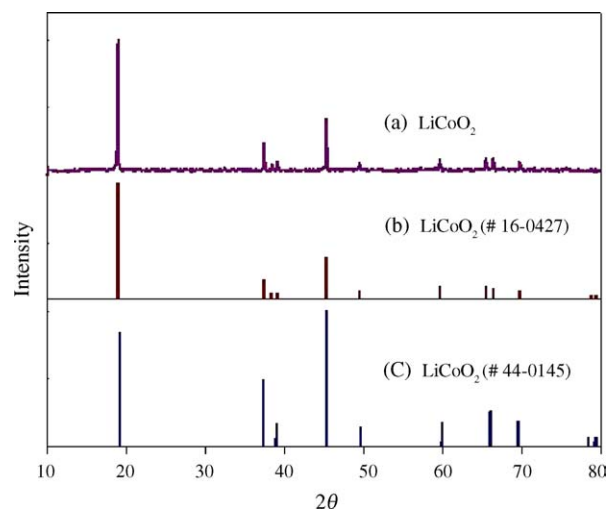


Fig. 7. XRD patterns of LiCoO_2 powders sintered at optimal conditions.

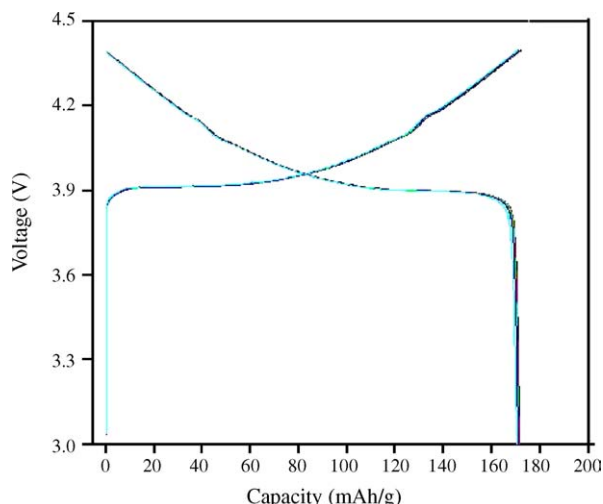


Fig. 8. The first charge/discharge curves for the Li/1M LiPF₆ in EC-DEC (1:1)/LiCoO₂ calcined at optimal conditions.

EC-DEC/LiPF₆ as the electrolyte. The cell voltage quickly increases from the end charge potential (3.0 V) to about 3.9 V and then it grows with an exponential fashion. During the discharge, the voltage drops quickly down to 4.0 V. The plateau region in the 3.9 V regions was detected and the specific capacity was 171 mA/hg, which was one of the previously reported largest values.

The plot of differential capacity is given in Fig. 9 for the LiCoO₂ electrode prepared by optimal conditions and it confirms the curve region presented in Fig. 8. The curve region means that the purity of active cathode materials (LiCoO₂) is very high. Fig. 9 shows the three couples of oxidation peaks at 3.91, 4.09 and 4.18 V, respectively. The reduction peaks are also observed at 3.90, 4.07 and 4.15 V. It was known that the main oxidation peaks during the first charge correspond to transitions in structure of hexagonal to monoclinic structure and monoclinic to hexagonal [22,23]. It means that the phase transition result from high purity. Consequently, the LiCoO₂ powders prepared in this work were single phase of high purity.

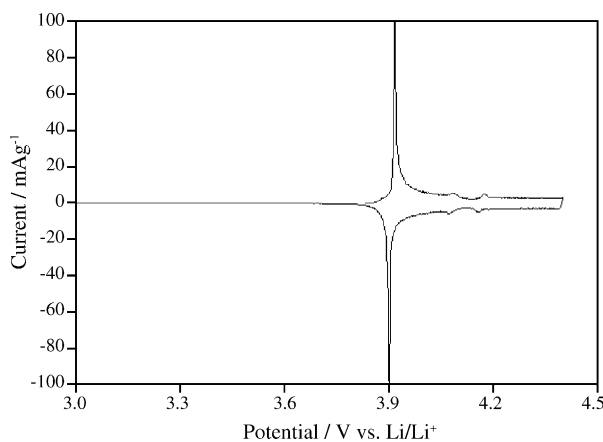


Fig. 9. Differential capacity plot (3.0–4.4 V, first cycle).

4. Conclusions

LiCoO₂ particles for lithium secondary battery were synthesized by using an ultrasonic spray pyrolysis process. The properties of LiCoO₂ particles were controlled by varying the synthesis temperature, sintering temperature, sintering time and sintering heating rate. The interrelationships between the above parameters are complex and the analysis of this system to optimize the factors is a time and labor consuming work. Therefore, statistical experimental design method was used. As a result, the main factors affecting the electrochemical properties of LiCoO₂ particles were sintering temperature and sintering time. In addition, the optimal synthesis conditions obtained by the experimental design method were as follows: synthesis temperature, 835–840 °C; sintering temperature, 890–900 °C; sintering time, 10–11 h; sintering heating rate, 580–590 °C/h. By using the above optimal synthesis conditions, LiCoO₂ powders with mean diameters of 4.7 μm (standard deviation: ±1.3%) were obtained and the properties of experimental results were in a good agreement with the simulated data.

References

- [1] B. Scrosati, *Nature* 373 (1995) 557.
- [2] S. Megahed, W. Ebner, *J. Power Sources* 54 (1995) 155.
- [3] Z.S. Peng, C.R. Wan, C.Y. Jiang, *J. Power Sources* 72 (1998) 215.
- [4] S.T. Myung, N. Kumagai, S. Komaba, H.T. Chung, *J. Appl. Electrochem.* 30 (2000) 1081.
- [5] G.T.K. Fey, K.S. Chen, B.J. Hwang, Y.L. Lin, *J. Power Sources* 68 (1997) 519.
- [6] T. Ohzuku, M. Kitagawa, T. Hirai, *J. Electrochem. Soc.* 137 (1990) 1221.
- [7] J.M. Tarascon, E. Wang, F.K. Shokoohi, W.R. Mckinnon, S. Colson, *J. Electrochem. Soc.* 138 (1991) 2859.
- [8] J.P. Dahn, U. von Sacken, C.A. Michal, *Solid State Ionics* 44 (1990) 87.
- [9] W. Ebner, D. Fouchard, L. Xie, *Solid State Ionics* 69 (1994) 238.
- [10] L. Plomp, E.F. Sitters, C. Vessies, F.C. Eckes, *J. Electrochem. Soc.* 138 (1991) 629.
- [11] T.J. Boyle, D. Ingersoll, T.M. Alam, C.J. Tofoya, M.A. Rodriguez, K. Vanheusden, D.H. Doughty, *Chem. Mater.* 10 (1998) 2270.
- [12] S. Che, O. Sakurai, K. Shiozaki, N. Mizutai, *J. Aerosol Sci.* 29 (1998) 271.
- [13] P.S. Patil, *Mater. Chem. Phys.* 59 (1999) 185.
- [14] A.S. Gandhi, V. Jayaram, A.H. Chokshi, *Mater. Sci. Eng. A* 304 (2001) 785.
- [15] W.A. Talyor, *Optimization and Variation Reduction in Quality*, McGraw-Hill, Singapore, 1991.
- [16] T. Bendell, *Taguchi Methods*, Elsevier, New York, 1988.
- [17] K.D. Kim, H.T. Kim, *J. Ind. Eng. Chem.* 6 (2000) 212.
- [18] R. Roy, *A Primer on the Taguchi-Method*, Van Nostrand Reinhold, New York, 1990.
- [19] G.G. Amatucci, J.M. Tarascon, D. Larcher, L.C. Klein, *Solid State Ionics* 84 (1996) 169.
- [20] Joint Committee on powder Diffraction Standards, File no. 24-0743.
- [21] J.L. Martin de Vidales, E. Vila, R.M. Rojas, O. Gracia-Martinez, *Chem. Mater.* 7 (1995) 1716.
- [22] W. Li, J.N. Reimers, J.R. Dahn, *Solid State Ionics* 67 (1993) 123.
- [23] R. Alcantara, P. Lavela, J.L. Tirado, R. Stoyanova, M. Gorova, E. Kuzmanova, E. Zhecheva, *Electrochem. Soc. Proc.* 97 (18) (1997) 109.