ELSEVIER

Journal of Materials Processing Technology 171 (2006) 118–124

Journal of Materials Processing Technology

www.elsevier.com/locate/jmatprotec

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 Cheongweon-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 μm (standard deviation: ±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.

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 submicrometer $LiCoO_2$ 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.

0924-0136/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jmatprotec.2005.06.060

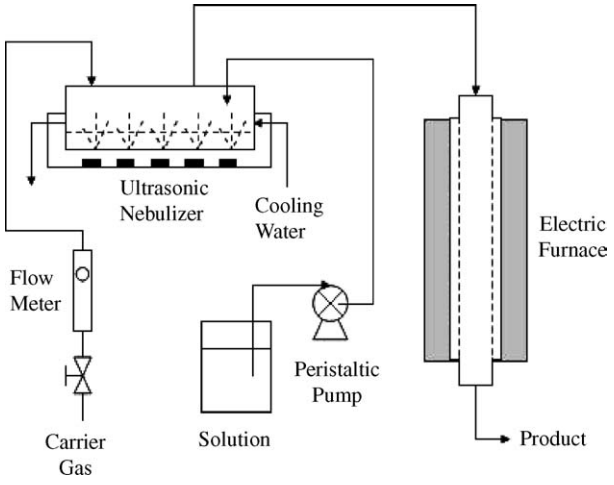

Fig. 1. Schematic diagram of experimental apparatus.

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

Properties of $LiCoO_2$ 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 $LiCoO_2$ particles, (2) to establish the optimal conditions by using a statistical experimental design method and (3) to characterize the $LiCoO_2$ particles obtained by optimal conditions in ultrasonic spray pyrolysis process.

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