

Properties of lithium cobaltate powders prepared by FEAG and ultrasonic spray pyrolysis process

Hee Chan JANG, Seo Hee JU and Yun Chan KANG[†]

Department of Chemical Engineering, Konkuk University, 1 Hwayang-dong, Gwangjin-gu, Seoul 143-701, Korea

LiCoO₂ cathode powders were prepared by the two different spray pyrolysis processes. The mean size of the post-treated LiCoO₂ powders prepared by the FEAG process was 1.6 μ m when the excess amount of lithium component was 10 mol% of the stoichiometric value. The post-treated LiCoO₂ powders obtained by ultrasonic spray pyrolysis were finer than those prepared by the FEAG process. The initial discharge capacities of the LiCoO₂ powders prepared by the FEAG process changed from 119 to 156 mAh/g when the excess amounts of lithium component were changed from 3 to 20 mol% of the stoichiometric value. The maximum initial discharge capacity of the LiCoO₂ powders prepared by the ultrasonic spray pyrolysis was 151 mAh/g obtained from the excess amount of lithium component of 3 mol% of the stoichiometric value.

©2009 The Ceramic Society of Japan. All rights reserved.

Key-words : Cathode material, Spray pyrolysis, Lithium cobaltate

[Received September 4, 2008; Accepted February 19, 2009]

1. Introduction

Lithium ion batteries are currently widely used in modern portable electronic devices because of their high output voltage and specific energy, long life cycle, and the absence of memory effect.^{1,2)} Lithium transition metal oxides, such as LiCoO₂, LiMn₂O₄ and LiNiO₂ have been investigated in order to apply them as positive electrode (cathode) materials for lithium ion batteries.³⁻⁷⁾ Though LiCoO₂ cathode material has widely used in lithium ion batteries, there are still a lot of publications reporting new method to further improve the materials performance.^{8,9)} Various type of chemical process, such as sol-gel, coprecipitation, emulsion, spray drying, supercritical drying, were applied to prepare the LiCoO₂ cathode powders with good morphological and electrochemical properties.^{4,10,11)}

Spray pyrolysis, which is one of the gas phase reaction methods, was also applied to prepare the LiCoO₂ cathode powders. Fine-sized LiCoO₂ powders with high discharge capacities and good cycle properties were prepared by spray pyrolysis from a spray solution with citric acid and ethylene glycol.¹²⁾ The effect of synthesis factors on powder morphology, powder size and distribution, and crystallinity was also investigated.¹³⁾ The characteristics of the powders prepared by spray pyrolysis were affected by the types of spray generator. Different sizes of droplets generated by spray generators affected the characteristics of the powders prepared by spray pyrolysis. Ultrasonic spray generator was mainly applied to prepare the LiCoO₂ powders by spray pyrolysis. Kang and Park proposed the use of a new spray generator, the filter expansion aerosol generator (FEAG), in the preparation of powders and thin films under reduced pressure.¹⁴⁻¹⁶⁾ In recent, a new capability for spray generation through the FEAG process has been found.¹⁶⁾ The mean sizes of droplets generated by the FEAG process were able to be controlled from 1.7 μ m to 25 μ m. Surface tension and the viscosity of spray solutions controlled by adding polyethylene glycol (PEG) affected the mean sizes of droplets generated by the FEAG process.

The cathode materials with lithium excess compositions have been investigated to improve electrochemical performances of lithium rechargeable batteries.^{17,18)} However, the optimum excess amount of lithium was affected by the types of cathode material and the preparation conditions of cathode powders. In this study, LiCoO₂ powders were prepared by spray pyrolysis under low pressure using the FEAG process. The effects of excess amount of Li component on the characteristics of LiCoO₂ cathode powders prepared by the FEAG process were investigated. The characteristics of cathode powders prepared by the FEAG process were also compared to those of the powders prepared by the ultrasonic spray pyrolysis.

2. Experimental procedure

The schematic diagram of the FEAG process used in this study was shown in Fig. 1. The FEAG process consists of a porous glass filter, an ultrasonic spray generator, a vacuum pump and a bag filter.¹⁴⁻¹⁶⁾ In the FEAG process, spray solution was supplied through an ultrasonic spray generator using carrier gas on to a glass filter surface where it forms a thin liquid film. This liquid film is passed through the filter pores by the carrier gas and expanded into a low pressure chamber. Metal salt solution is atomized into droplets with fine size and delivered into hot-wall reactor of 8000 Pa. As the aerosol stream passes through the reactor, solvent evaporates and metal salt decomposes to form

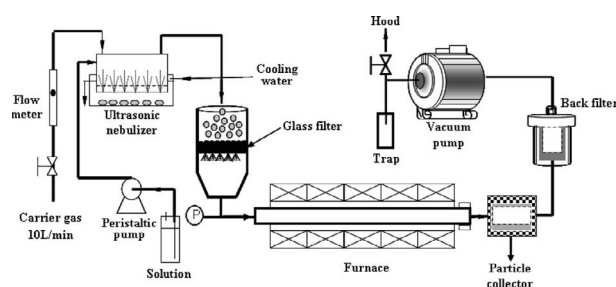


Fig. 1. Schematic diagram of the FEAG process.

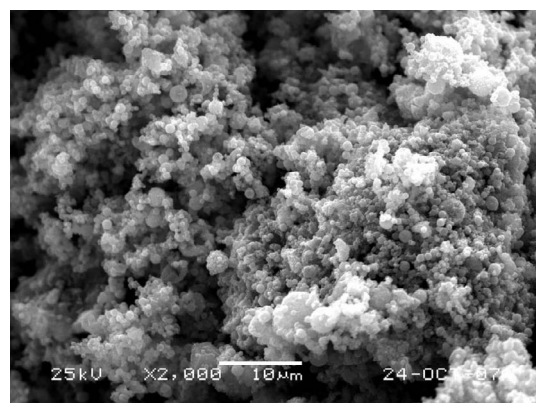
[†] Corresponding author: Y. C. Kang; E-mail: yckang@konkuk.ac.kr

product powders. At the end of the reactor, powder collection filter and vacuum pump of 600 L/min are connected in series. The length and diameter of the quartz reactor were 1200 and 50 mm, respectively. The reactor temperature was fixed at 800°C. In the ultrasonic spray pyrolysis process, droplets formed by ultrasonic spray generator were directly supplied into the hot wall reactor. Lithium carbonate (Li_2CO_3) and cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) with the cationic ratio $\text{Li}:\text{Co} = 1 + x : 1$ ($0.03 \leq x \leq 0.2$) were dissolved in distilled water. The overall solution concentration of lithium and cobalt components was 0.5 M. The precursor powders obtained by spray pyrolysis were post-treated at a temperature of 800°C for 2 h.

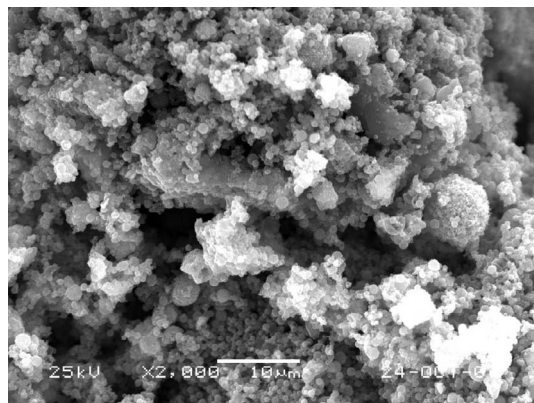
The crystal structures of the powders were investigated by X-ray diffractometry (XRD; RIGAKU Co., DMAX-33). The morphological characteristics of the powders were investigated by scanning electron microscopy (SEM; JEOL Ltd., JSM-6060). The cathode electrode was made of 12 mg of LiCoO_2 compounds mixed with 4 mg of conductive binder (3.2 mg of teflonized acetylene black and 0.8 mg of graphite). The lithium metal and polypropylene film were used as the anode electrode and the separator, respectively. The electrolyte was 1 M LiPF_6 in a 1:1 mixture by volume of EC/DMC. The entire cell was assembled in the glove box under argon atmosphere. The electrochemical performances of the various LiCoO_2 samples were measured by charge/discharge curves of Li/LiCoO_2 cell cycled in 3.0 – 4.3 V at various current densities.

3. Results and discussion

Figure 2 show the SEM images of the $\text{Li}_{1+x}\text{CoO}_2$ ($0.03 \leq x \leq 0.2$) powders prepared by the FEAG process. An excess of lithium



(a) 3 mol% excess



(b) 15 mol% excess

Fig. 2. SEM images of the LiCoO_2 powders obtained from FEAG process with different concentration of lithium component.

component was used to compensate for lithium loss during the preparation and post-treatment processes. The LiCoO_2 powders had a spherical shape and submicron size regardless of the excess amount of lithium component. Assuming that one dense powder is derived from one droplet, the mean size of the powders prepared by spray pyrolysis can be calculated using the following equation:

$$d_{\text{powder}} = d_{\text{drop}} \times \left(\frac{M_x \cdot C \cdot 10^{-3}}{\rho_x} \right)^{1/3} \quad (1)$$

where d_{drop} and d_{powder} are the mean diameters of the droplets and the powders, respectively; ρ_x and M_x are the density and molecular weight, respectively, of the oxide or dried salt powders; and C is the molar concentration of the spray solution. Therefore, the mean size and size distribution of the powders were affected by the mean size and size distribution of the droplets that were formed by the spray generator used. The morphology of the $\text{Li}_{1.03}\text{CoO}_2$ powders directly prepared by ultrasonic spray pyrolysis was shown in Fig. 3. The powders prepared by ultrasonic spray pyrolysis had a spherical shape and several micron sizes. The size distributions of the powders prepared by the FEAG and ultrasonic spray pyrolysis processes were shown in Fig. 4. The mean sizes of the as-prepared LiCoO_2 powders obtained by the filter expansion aerosol generator (FEAG) and ultrasonic spray pyrolysis processes were 0.7 and 1.2 μm . In the FEAG and ultrasonic spray pyrolysis processes, one LiCoO_2 powder was formed from one droplet. Therefore, the mean size and size distribution of the LiCoO_2 powders was affected by the characteristics of the drop-

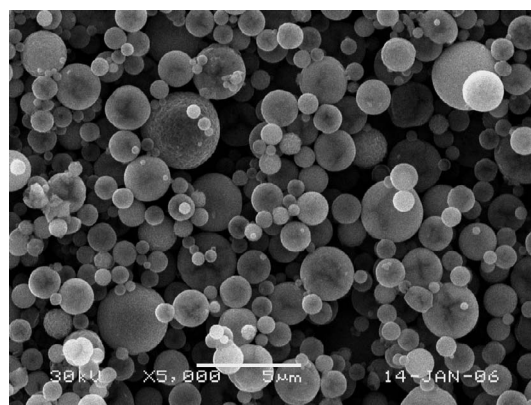


Fig. 3. SEM image of the as-prepared LiCoO_2 powders obtained by ultrasonic spray pyrolysis.

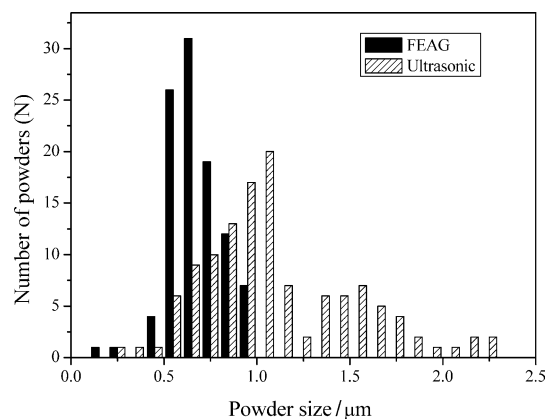
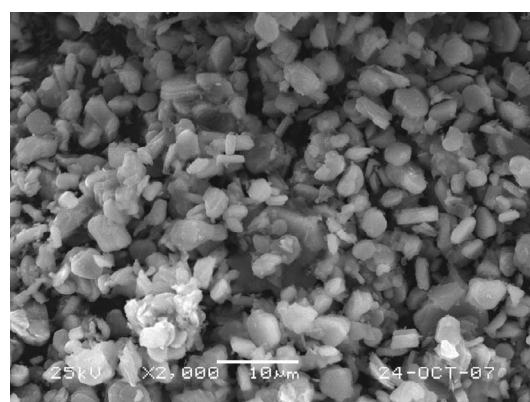


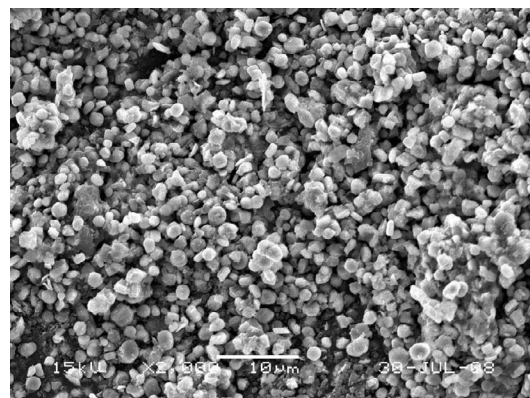
Fig. 4. Size distributions of the as-prepared LiCoO_2 powders obtained by FEAG and ultrasonic spray pyrolysis processes.

lets generated by the spray generators. The characteristics of the droplets generated by the FEAG process were changed by the characteristics of spray solution.¹⁶⁾ The mean sizes of droplets were changed from $1.7\mu\text{m}$ to $25\mu\text{m}$ according to the viscosities and surface tensions of the spray solutions. On the other hand, the characteristics of the droplets generated by the ultrasonic spray generator were not changed by the characteristics of spray solution. The droplets generated by the FEAG process were finer than those generated by the ultrasonic spray generator. Therefore, LiCoO_2 powders prepared by the FEAG process were finer than those prepared by the ultrasonic spray pyrolysis.

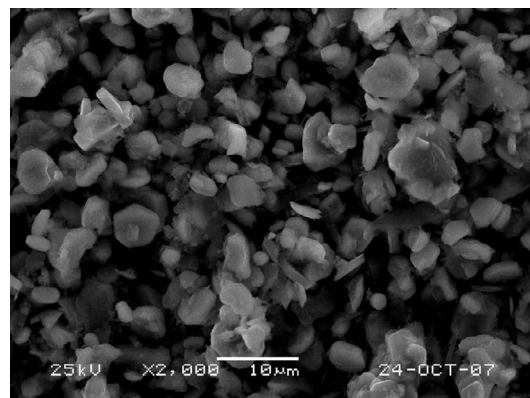
Figure 5 shows the morphologies of the post-treated LiCoO_2 powders. The as-prepared powders obtained by spray pyrolysis at 800°C had poor crystallinity of the LiCoO_2 because of short residence time of the powders inside hot wall reactor. Therefore,



(a) 3 mol% excess



(b) 10 mol% excess



(c) 15 mol% excess

Fig. 5. SEM images of the post-treated LiCoO_2 powders obtained from FEAG process with different concentration of lithium component.

the as-prepared powders obtained by the FEAG process were post-treated at a temperature of 800°C . The spherical shape of the as-prepared powders disappeared after post-treatment by crystallization process. The post-treated LiCoO_2 powders had plate-like shapes and several micron sizes. The mean sizes of the LiCoO_2 powders were affected by an excess amount of lithium component added to the spray solutions. The mean sizes of the powders were 3.1 , 1.6 and $3.8\mu\text{m}$ when the excess amounts of lithium component were 3, 10 and 15 mol% of the stoichiometric value. **Figure 6** shows the SEM image of the post-treated LiCoO_2 powders obtained by ultrasonic spray pyrolysis. The sizes of the primary LiCoO_2 powders prepared by ultrasonic spray pyrolysis were finer than those prepared by the FEAG process. The different mean sizes and morphologies of the as-prepared powders obtained by the two different spray pyrolysis processes affected the morphologies of the post-treated LiCoO_2 powders. The fine size powders had high reactivity at a high post-treatment temperature. Therefore, submicron size LiCoO_2 powders obtained by the FEAG process had high reactivity during the post-treatment process. On the other hand, the as-prepared powders obtained by the ultrasonic spray pyrolysis had large size, hollow and porous morphology. Therefore, the crystal growth of the powders was restricted because of their morphological characteristics.

The effects of excess amount of lithium component on the initial charge/discharge capacities of the LiCoO_2 powders prepared by the FEAG process were shown in **Fig. 7**. The initial discharge

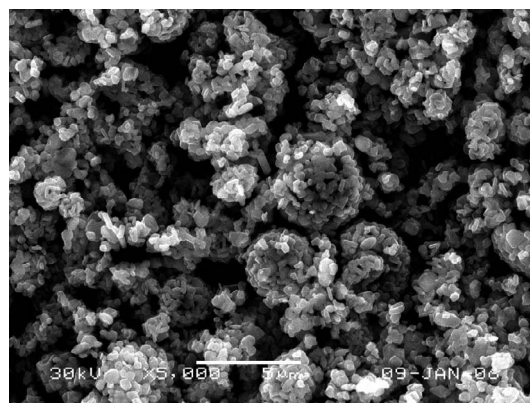


Fig. 6. SEM image of the post-treated LiCoO_2 powders obtained by ultrasonic spray pyrolysis.

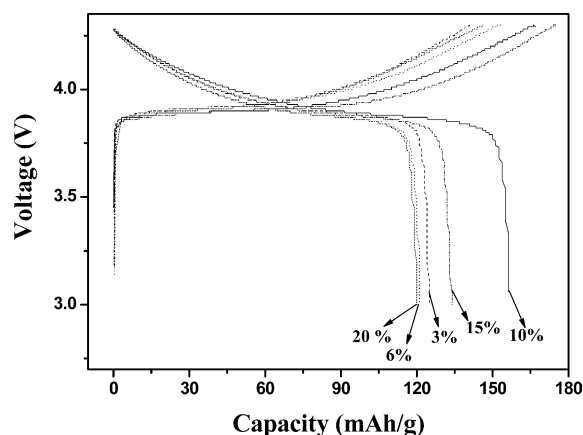


Fig. 7. Initial charge/discharge capacities of LiCoO_2 powders obtained from FEAG process with different concentration of lithium component.

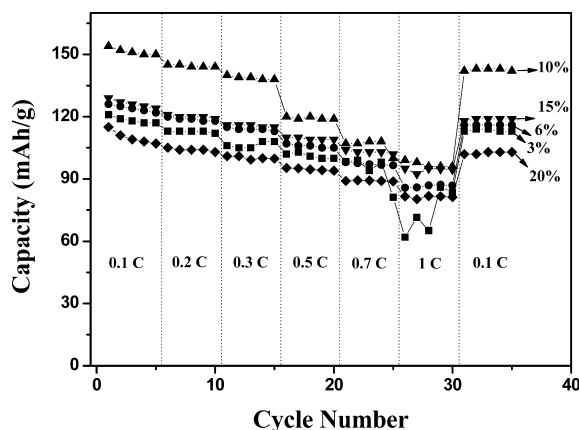


Fig. 8. Cycle properties of LiCoO_2 powders obtained from FEAG process with different concentration of lithium component.

capacities of the LiCoO_2 powders changed from 119 to 156 mAh/g when the excess amounts of lithium component were changed from 3 to 20 mol% of the stoichiometric value. The LiCoO_2 powders obtained from the excess amount of lithium component of 10 mol% of the stoichiometric value had the maximum initial discharge capacity. The maximum initial discharge capacity of the LiCoO_2 powders prepared by the ultrasonic spray pyrolysis was 151 mAh/g obtained from the excess amount of lithium component of 3 mol% of the stoichiometric value. The optimum excess amounts of lithium component showing the maximum initial discharge capacities were different in the FEAG and ultrasonic spray pyrolysis processes. Loss of lithium component by evaporation was too high in the FEAG process because of low pressure operation.

Figure 8 shows the cycle properties of the LiCoO_2 powders prepared by the FEAG process. Several current densities were applied progressively on cycling in this experiment. The LiCoO_2 powders prepared by the FEAG process had good cycle properties irrespective of the excess amount of lithium component added to the spray solutions. The discharge capacities of the LiCoO_2 powders prepared from the spray solutions with too low and too high excess amounts compared to the optimum excess amount of lithium component were slightly affected by the current densities. However, the discharge capacities of the LiCoO_2 powders prepared from the spray solution with excess amount of lithium component of 10 mol% of the stoichiometric value were strongly affected by the current densities. The discharge capacities of the powders decreased with increasing the current density. When the current density was lowered to 0.1 C, the discharge capacity increased to the original value at this rate, irrespective of the excess amount of lithium component added to the spray solutions.

4. Conclusion

The characteristics of the as-prepared and post-treated LiCoO_2 cathode powders prepared by two different spray pyrolysis processes were investigated. The droplets generated by the FEAG process were finer than those generated by the ultrasonic spray generator. Therefore, the as-prepared and post-treated LiCoO_2 powders prepared by the FEAG and ultrasonic spray pyrolysis processes had different mean sizes and morphologies. The optimum excess amounts of lithium component showing the maximum initial discharge capacities were different in the FEAG and ultrasonic spray pyrolysis processes. Loss of lithium component by evaporation was too high in the FEAG process because of low pressure operation.

References

- 1) K. Mizushima, P. C. Jones, P. J. Wiseman and J. B. Goodenough, *Mater. Res. Bull.*, **15**, 783–789 (1980).
- 2) B. Scrosati, *Nature*, **373**, 557–558 (1995).
- 3) H. Zhao, L. Gao, W. Qui and X. Zhang, *J. Power Sources*, **132**, 195–200 (2004).
- 4) Z. Wang, X. Huang and L. Chen, *J. Electrochem. Soc.*, **151**, A1641–A1652 (2004).
- 5) S. Ma, H. Nouchi and M. Yoshio, *J. Power Sources*, **125**, 228–235 (2004).
- 6) S. H. Ju, D. Y. Kim, E. B. Jo and Y. C. Kang, *J. Mater. Sci.*, **42**, 5369–5374 (2007).
- 7) H. Arai, M. Tsuda, K. Saito, M. Hayashi and Y. Sakurai, *Electrochem. Acta*, **47**, 2697–2705 (2002).
- 8) S. B. Tang, M. O. Lai and L. Lu, *J. Alloy. Compd.*, **449**, 300–303 (2008).
- 9) M. Matsui, K. Dokko and K. Kanamura, *J. Power Sources*, **177**, 184–193 (2008).
- 10) S. M. Park, T. H. Cho, Y. M. Kim and M. Yoshio, *Electrochem. Solid-State Lett.*, **8**, A299–A302 (2005).
- 11) C. H. Lu and P. Y. Yeh, *J. Europ. Ceram. Soc.*, **22**, 673–679 (2002).
- 12) D. Y. Kim, S. H. Ju and Y. C. Kang, *Mater. Res. Bull.*, **42**, 362–370 (2007).
- 13) T. Ogihara, Y. Saito, T. Yanagawa, N. Ogata, K. Yoshida, M. Takashima, S. Yonezawa, Y. Mizuno, N. Nagata and K. Ogawa, *J. Ceram. Soc. Japan*, **101**, 1159–1163 (1993).
- 14) Y. C. Kang and S. B. Park, *J. Aerosol Sci.*, **26**, 1131–1138 (1995).
- 15) S. H. Ju and Y. C. Kang, *Mater. Res. Bull.*, **43**, 590–600 (2008).
- 16) D. S. Jung and Y. C. Kang, *J. Eur. Ceram. Soc.*, **28**, 2617–2623 (2008).
- 17) J. M. Kim, N. Kumagai and S. Komaba, *Electrochim. Acta*, **52**, 1483–1490 (2006).
- 18) S. Levasseur, M. Menetrier, E. Suard and C. Delmas, *Solid State Ionics*, **128**, 11–24 (2000).