

## Synthesis of LiCoO<sub>2</sub> Nanoparticles From Leach Liquor of Lithium Ion Battery Wastes by Flame Spray Pyrolysis<sup>†</sup>

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### Abstract

LiCoO<sub>2</sub> nanoparticles were synthesized from leach liquor of lithium ion battery waste using flame spray pyrolysis. Electrode materials containing lithium and cobalt could be concentrated with thermal and mechanical treatment. After dissolution of used cathode materials of the lithium battery with nitric acid, the molar ratio of Li/Co in the leach liquor was adjusted at 1.0 by adding a fresh LiNO<sub>3</sub> solution. The nanoparticles synthesized by the flame spray pyrolysis showed clear crystallinity and were nearly spherical, and their average primary particle diameters ranged from 11 to 35 nm. The average particle diameter increased with an increase in the molar concentration of the precursor. Raising the maximum flame temperature by controlling the gas flow rates also led to an increase in the average diameter of the particles. The LiCoO<sub>2</sub> powder was proved to have good characteristics as cathode active materials in charge/discharge capacity and cyclic performance.

**Key words :** LiCoO<sub>2</sub> nanoparticle, Flame spray pyrolysis, Spent lithium ion battery, Recycling

### 요 약

폐리튬이온전지로부터 회수된 코발트와 리튬 침출액으로부터 화염분무열분해법에 의하여 LiCoO<sub>2</sub> 나노분말을 제조하였다. 리튬 및 코발트 성분을 함유하는 전극물질은 열처리 및 기계적 처리에 의해 그 농도를 증가 시켰다. 리튬이온전지 양극물질을 질산으로 용해한 다음 침출액중 Li와 Co의 당량비가 1.0 되도록 LiNO<sub>3</sub>로 조절하여 화염분무열분해용 전구체를 제조하였다. 화염분무열분해법에 의해 제조된 LiCoO<sub>2</sub> 분말의 평균입자크기는 전구체의 몰 농도가 증가하면서 증가되었으며, 화염온도 역시 입자의 크기를 증가시켰다. 변수실험 결과 11~35 nm 크기의 결정형 LiCoO<sub>2</sub> 나노분말을 제조할 수 있었다. 또한 나노 LiCoO<sub>2</sub>의 전극재료로서의 가능성을 확인하기 위하여 충방전 특성 평가와 같은 전기화학적 분석을 수행하였다.

**주제어 :** LiCoO<sub>2</sub> 나노 입자, 화염열분해, 폐리튬이온전지, 재활용

## 1. INTRODUCTION

Lithium batteries are of interest because those can substitute other type of batteries due to their lightness characteristics and good performance. In 2004, the worldwide production of lithium ion secondary batteries (LIBs) was about 400 millions of which 20% market share in Korea. The annual production of LIB waste containing 5~15wt% Co and 2~7wt% Li was estimated in the range 200~500 metric tons<sup>1-2</sup>.

Spent lithium primary batteries cannot be disposed

unless metallic lithium is properly removed from them due to its explosive nature. However, in the case of LIB adopted lithium cobalt oxide as cathodic active materials, valuable metals such as cobalt and lithium have to be recycled<sup>3-7</sup>). Thus, there are two problems to solve-disposal of harmful waste and prevention of explosion during recycling LIB waste. Metallic lithium in the used LIB can be formed on graphite anode by overcharging and abnormal deposition. Vigorous oxidation of metallic lithium with moisture can be dangerous during the mechanical treatment of LIB. For successful recovery of cobalt and lithium from spent LIB, safety in mechanical treatment and waste minimization are considered most importance.

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Lithium cobalt oxide,  $\text{LiCoO}_2$ , has been considered one of the most suitable cathode materials in Li-ion secondary batteries<sup>8)</sup>. Commercial  $\text{LiCoO}_2$  has been synthesized by solid-state reactions. Other methods such as sol-gel process, reflux reaction, spray-drying synthesis, and combustion synthesis have been used to synthesize  $\text{LiCoO}_2$ . Oh *et al.*<sup>9)</sup> have synthesized  $\text{LiCoO}_2$  nanoparticles with an average particle diameter of 30 to 60 nm by a sol-gel method consisting of several steps including calcination at temperatures of 500–600°C for 1 h. Chang *et al.*<sup>10)</sup> have synthesized the particles with a uniform size distribution around 100 nm by reflux reactions at 130–200°C for 6–48 h. Li *et al.*<sup>11)</sup> have synthesized  $\text{LiCoO}_2$  powders with a grain size in the order of hundreds of nanometers by a spray-drying followed by sintering. The whole synthesizing process have been completed within 8 h. Santiago *et al.*<sup>12)</sup> have produced  $\text{LiCoO}_2$  powders with a mean particle size of 98–243 nm by combustion synthesis followed by a post heat treatment at 400–700°C for 12 h. A single phase was observed after the thermal treatment at 600°C. So far, many attempts have been undertaken to reduce the operating temperature, to shorten the processing time and steps, and to obtain smaller particles with a good crystallinity.

The flame spray pyrolysis (FSP), a flame-assisted liquid droplet-to-particle conversion process, has been of interest to produce multi component nanoparticle with an advantage of starting with solution of precursors<sup>13–16)</sup>. A typical experimental setup for the FSP consists of an aerosol generator, a burner, and a collector. A few studies have been reported on the synthesis of multi-component metal oxide nanoparticle by the FSP. Zachariah and Huzarewicz<sup>17)</sup> synthesized  $\text{YBaCuO}$  nanoparticle for preparation of superconducting materials from mixed nitrate salts. Bickmore *et al.*<sup>18)</sup> produced spinel particles of 28 nm in average diameter from magnesium aluminum double alkoxides. The nanoparticle generated by the FSP have shown high purity, controlled stoichiometry and crystallinity because the flame could be maintained at temperatures high enough to complete thermal decompositions through intense oxidation.

Given its characteristics and potential demonstrated by previous researchers, the FSP can be adopted to synthesize the  $\text{LiCoO}_2$  nanoparticles from the dis-

solution solution of LIB cathode material. In the present study, our goal was to generate crystalline  $\text{LiCoO}_2$  nanoparticles from aqueous precursor solution of nitrate compounds by the FSP.

In this study, recycling process involving mechanical<sup>19)</sup>, hydrometallurgical treatment<sup>20)</sup> and flame spray pyrolysis (FSP)<sup>10)</sup> has been applied to prepare  $\text{LiCoO}_2$  nanoparticles from the spent LIBs.

## 2. Experiments

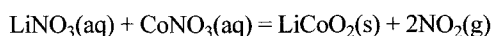
A LIB consists of an IC chip, a plastic casing, and several unit cells. The unit cell had each of cathode, anode, organic separator, organic electrolyte, and Ni-coated steel casing. The cathode was fabricated by pasting  $\text{LiCoO}_2$  active materials, carbon-conducting additives, and a binder on aluminum foil. In similar manner, the anode was made by same process with graphite active materials, carbon-conducting additives, and a binder pasted on copper foil.

First, LIB samples were thermally treated in a muffle furnace at 100–150°C for 1 hr. The samples were disassembled with a high-speed shredder, which was newly designed for this study. Separated segments were simultaneously classified into the range 1 to 50 mm in size. This shredding and liberation system was considered very effective to save the size reduction cost and increase the selectivity.

Second, the two-step thermal treatment was performed in a furnace, and electrode materials was liberated from the current collectors by vibrating screening. And then, cathodic active materials,  $\text{LiCoO}_2$  was obtained by burning off carbon and binder in the temperature range 500–900°C for 0.5–2 hr.

Third,  $\text{LiCoO}_2$  in a nitric acid solution was leached in a reactor, which was placed in a constant-temperature water bath.

Fourth, the flame spray pyrolysis method was selected so as to produce nanoparticles with a higher surface area that resulted in a higher performance. The formation of  $\text{LiCoO}_2$  particles from aerosol precursors by the FSP can be expressed as the following overall chemical reaction:



A schematic diagram of the experimental apparatus

for the preparation of  $\text{LiCoO}_2$  nanoparticles is shown in Fig. 1. The experimental apparatus consists of an ultrasonic atomizer for aerosol precursor, a diffusion flame burner, and a particle collector. The aqueous precursor solution of the metal nitrates was first atomized with an ultrasonic vibrator, and the atomized droplets of  $10\ \mu\text{m}$  in average diameter were subsequently carried into the central tube of the burner by flowing Ar gas.  $\text{H}_2$  was used as a fuel while  $\text{O}_2$  and air were used as oxidants. Mean value of three temperature measurements in the absence of the precursor was considered as the flame temperature. The temperature profile was obtained by moving the thermocouple in both axial and radial directions.

The nanoparticles generated by the FSP were collected on the surface of a cold glass tube. The cold tube was located 200 mm above the burner exit and maintained at  $12^\circ\text{C}$  by flowing cooling water inside.

The cathodes were prepared with a mixture of the  $\text{LiCoO}_2$  powders of  $30\ \text{m}^2/\text{g}$  surface area, 15 wt% acetylene black and 5 wt% binder pasted on an aluminum foil current collector. The  $\text{LiCoO}_2$  cathodes were tested in a sealed and half-cell typed Teflon cell.

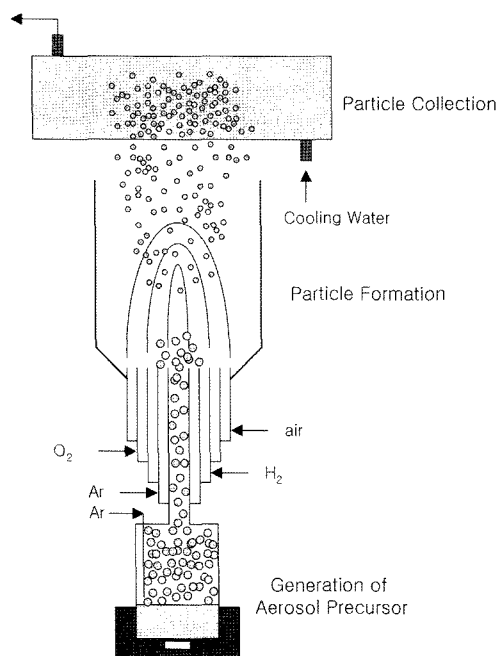


Fig. 1. A schematic diagram of experimental apparatus for the synthesis of  $\text{LiCoO}_2$  nanoparticles by FSP.

An EC-DMC contained  $\text{LiPF}_6$  was used as an electrolyte. Charge/discharge characteristics were analyzed with a Maccor 4000.

### 3. RESULTS AND DISCUSSION

#### 1. Preparation of $\text{LiCoO}_2$ precursor solution

Mechanical and thermal treatment was applied to concentrate the electrode active materials in a powder form. The following procedures were adopted for the mechanical and thermal steps, resulting in cost reduction and safety in shredding<sup>19</sup>.

- 1st thermal treatment at  $100\text{--}150^\circ\text{C}$  for 30 min
- high-speed shredding into the  $5\text{--}20\ \text{mm}$
- 2nd thermal treatment at  $300\text{--}500^\circ\text{C}$  for 1 hr
- vibrating screening
- calcination at  $700\text{--}900^\circ\text{C}$  for 1 hr

In order to dissolve Co and Li from cathodic active materials, acid dissolution was employed[20]. Prior to dissolution, the active material was ground in a ball mill and dried in an oven at  $60^\circ\text{C}$  for 48 hr. The mean particle size was about  $2.5\ \mu\text{m}$ . Fig. 2 shows the dissolution behavior of  $\text{LiCoO}_2$  in 1 M nitric acid solution at fixed  $20\ \text{g/L}$  pulp density and  $75^\circ\text{C}$ . In the absence of a reducing agent, the dissolution efficiencies of the cobalt and lithium were leveled off within 30 min with low extractions of 40% Co and 75% Li. To increase the efficiency, 0.8 vol% hydrogen peroxide

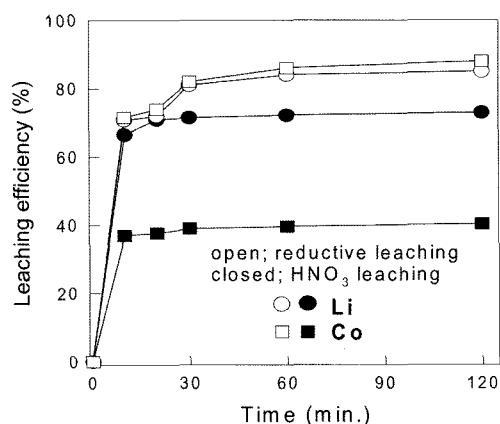


Fig. 2. Dissolution behaviors of  $\text{LiCoO}_2$  in nitric acid solution. ( $20\ \text{g/L}$ ,  $75^\circ\text{C}$ , 400 rpm, 1 M  $\text{HNO}_3$ ,  $\text{H}_2\text{O}_2$  0.8 vol%).

was added as a reducing agent. The extractions of both metals were improved to about 85% by the reductive dissolution as shown in the figure.

Fig. 3 shows the effects of  $\text{HNO}_3$  concentration in

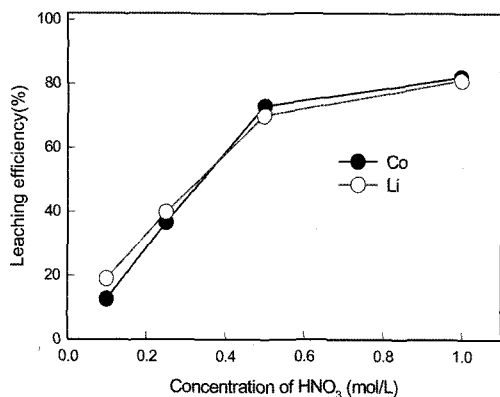


Fig. 3. Effect of  $\text{HNO}_3$  concentration on the dissolution. (20 g/L, 75°C, 400 rpm, 30 min, 0.8 vol%  $\text{H}_2\text{O}_2$ ).

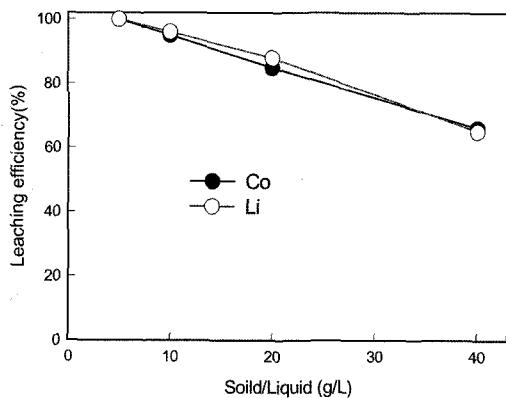


Fig. 4. Effect of pulp density on the dissolution. (1 M  $\text{HNO}_3$ , 75°C, 400 rpm, 30 min, 0.8 vol%  $\text{H}_2\text{O}_2$ ).

the presence of 0.8 vol.%  $\text{H}_2\text{O}_2$  on the dissolution of  $\text{LiCoO}_2$  at 20 g/L pulp density and 75°C for 30 min. The efficiencies of both Co and Li were increasing with increasing  $\text{HNO}_3$  concentration. Over 80% Co and Li each were readily extracted within 30 min at 1 M  $\text{HNO}_3$  concentration. The dissolution behaviors with different pulp densities are presented in Fig. 4 in the constant conditions of 1 M  $\text{HNO}_3$  concentration, 75°C, 0.8 vol%  $\text{H}_2\text{O}_2$ , and 30 min. The extractions of Co and Li were decreased with increasing the pulp density. Over 95% Co and Li each were readily extracted in 30 min at 10 g/L pulp density.

## 2. Preparation of $\text{LiCoO}_2$ nanoparticles

Characteristics of the diffusion flame were measured in the absence of the aqueous precursor droplets. It shows parabolic temperature profile having a maximum at 1610°C while the height of that flame was about 10cm. Table 1 shows flow rates in the concentric tubes and the rates were kept constant during the experiment except otherwise mentioned.

The effect of precursor concentration on crystal structure and primary particle size was investigated by varying molar concentration in the aqueous solution. The particles generated were first collected on the glass tube and then analyzed by TEM, XRD, and BET method. The amount of particles collected on the cold glass tube by thermophoresis was 85% of theoretical estimation. As molar concentration of the precursor in the solution increased from 0.5 to 1.4 mol at a fixed molar ratio 1.0 of Li to Co, average diameter of primary particles increased from 11 to 28 nm while keeping their shape nearly spherical (Fig. 5). The size distributions of the nanoparticles were, however, quite

Table 1. Flow rates for the synthesis of  $\text{LiCoO}_2$  nanoparticles.

Controlled gas	Flow rates (l/min)				
	Ar (center) <sup>a</sup>	Ar (2nd) <sup>b</sup>	$\text{H}_2$ (3rd) <sup>b</sup>	$\text{O}_2$ (4th) <sup>b</sup>	Air (5th) <sup>b</sup>
None	2	1	6	6	15
$\text{H}_2$	2	1	48	6	15
$\text{O}_2$	2	1	6	26	15
Air	2	1	6	6	9.5~19.5

<sup>a</sup>Center corresponds to injection tube for bubbling precursor solution through the central tube of the burner.

<sup>b</sup>Number in parenthesis successively corresponds to the injection tubes next to the central tube.

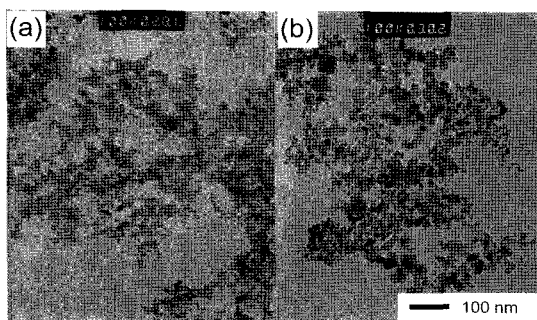


Fig. 5. TEM micrographs of  $\text{LiCoO}_2$  (a) 0.5 mol and (b) 1.4 mol.

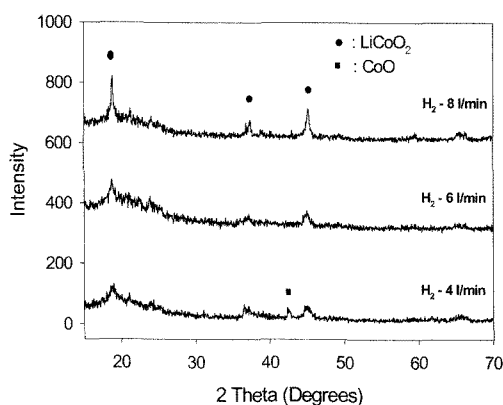


Fig. 6. XRD pattern of the particle at various  $\text{H}_2$  flow rate.

uniform according to small geometric standard deviation. Fig. 6 shows crystal structures of the nanoparticles produced at various precursor concentrations. The peak patterns of all the particles corresponded to those of  $\text{LiCoO}_2$ , and the peak intensities increased with an increase in the precursor concentration.

The effects of the hydrogen gas flow rate on the particle size were also investigated by varying the flow rate from 4 to 8 l/min (Table 1) while keeping the precursor concentration in the solution at 1.0 M. As the hydrogen flow rate increased, the maximum flame temperature increased from 1450 up to over 1700°C, which was beyond the measuring limit of the employed thermocouple. Higher flame temperature led to an increase in the average particle diameter from 16 to 35 nm (Fig. 7), exhibiting coagulation and coalescence played a dominant role in the particle growth. It is also observed that a crystalline peak of CoO appeared at  $\text{H}_2$  flow rate of 4 l/min and disappeared at higher flow

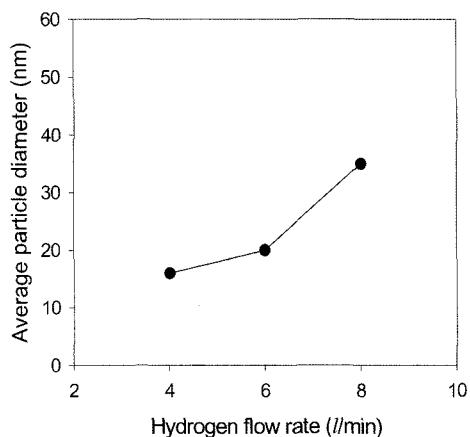


Fig. 7. Effect of  $\text{H}_2$  flow rate on the average diameter.

rates while the intensity of major crystalline peak of  $\text{LiCoO}_2$  increased with an increase in the flow rate (Fig. 6).

### 3. Electrochemical characterization of $\text{LiCoO}_2$ nanoparticles

Fig. 8 shows the charge/discharge characteristics of the  $\text{LiCoO}_2$  nanoparticles prepared from spent LIB. The charge and discharge capacities were 165 mAh/g and 154 mAh/g at 1st cycle, respectively. The capacities were over 90% of the values of  $\text{LiCoO}_2$  used in the battery industry.

Fig. 9 shows cyclic behaviors of the  $\text{LiCoO}_2$  electrode. A slow decrease in charge and discharge capacities was observed as the cycle number increased.

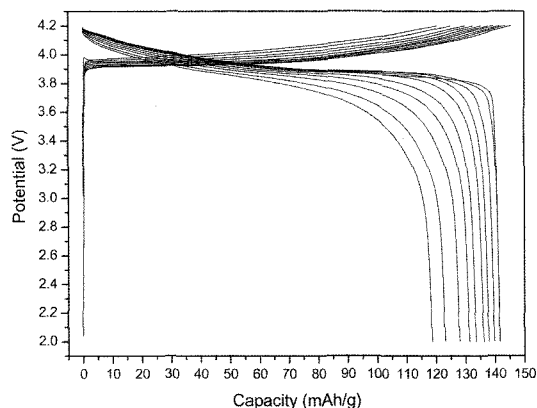


Fig. 8. Charge/discharge characteristics of the  $\text{LiCoO}_2$  powder prepared by FSP.

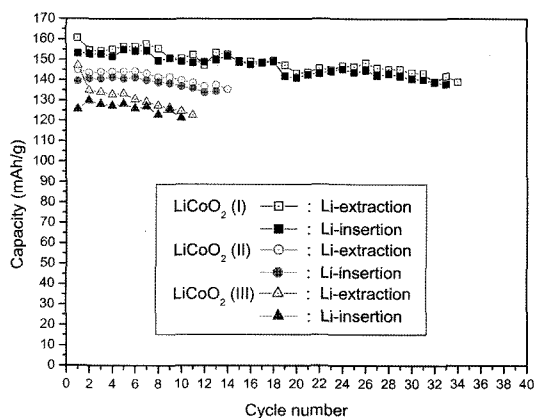


Fig. 9. Cyclic performance of the  $\text{LiCoO}_2$  powder prepared by FSP.

After 30 cycles, the both capacities decreased by less than 10% compared to the value of 1st cycle.

#### 4. CONCLUSION

A series of thermal treatment, high-speed shredding, calcination, reductive leaching, and a flame spray pyrolysis technique was applied to recycle spent lithium ion secondary batteries. Electrode material in a 0.5–20 mm fraction was liberated from other constituents like plastics and steel casing segments by high-speed shredding. By addition of hydrogen peroxide in the nitric acid leaching, the Co extraction was increased from 40% to 85% and the Li extraction from 75% to 85%. The extractions of Co and Li were increased with increasing  $\text{HNO}_3$  concentration and temperature, and amount of hydrogen peroxide and with decreasing of S/L ratio. The spherical, crystalline  $\text{LiCoO}_2$  nanoparticles ranged from 11 to 35 nm in the average particle diameter were synthesized by the flame spray pyrolysis from the leach liquor of cathode materials of lithium ion battery. It was possible to increase the particle size by raising the molar concentration of the precursor in the aqueous solution while keeping the gas flow rates constant. The particle size and crystalline phase can be controlled by the gas flow rates, too. The 1st charge and discharge capacities of the  $\text{LiCoO}_2$  powder were 165 mAh/g and 154 mAh/g at 1st cycle, respectively. The capacities were over 90% of the value of  $\text{LiCoO}_2$  used in the battery

industry. The cathode active material prepared from the spent LIB has good charge/discharge capacities and cyclic performance.

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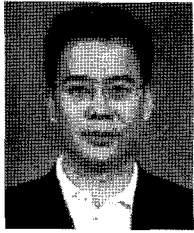
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