

Preparation of LiCoO_2 from Used Lithium Ion Battery by Hydrometallurgical Processes

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Recycling process involving mechanical, thermal, hydrometallurgical, and sol-gel step has been applied to recover cobalt and lithium from spent lithium ion batteries and to synthesize LiCoO_2 from leach liquor as cathodic active materials. Electrode materials containing lithium and cobalt could be concentrated with 2-step thermal and mechanical treatment. Leaching behaviors of the lithium and cobalt in nitric acid media was investigated in terms of reaction variables. Hydrogen peroxide in 1 M HNO_3 solution turned out to be an effective reducing agent by enhancing the leaching efficiency. Of many possible processes to produce LiCoO_2 , the amorphous citrate precursor process (ACP) has been applied to synthesize powders with a large specific surface area and an exact stoichiometry. After leaching used LiCoO_2 with nitric acid, the molar ratio of Li/Co in the leach liquor was adjusted at 1.1 by adding a fresh LiNO_3 solution. Then, 1 M citric acid solution at a 100% stoichiometry was also added to prepare a gelatinous precursor. When the precursor was calcined at 950°C for 24 hr, purely crystalline LiCoO_2 was successfully obtained. The particle size and specific surface area of the resulting crystalline powders were 20 μm and 30 cm^2/g , respectively. The LiCoO_2 powder was proved to have good characteristics as cathode active materials in charge/discharge capacity and cyclic performance.

Keywords: Lithium ion battery, Recycling, Cathode active materials

Introduction

A recycling of lithium batteries is interesting because lithium batteries can substitute other type of batteries due to their lightness characteristics and good performance [1~2]. In 1998, the worldwide production of lithium ion secondary batteries (LIBs) was about 250 millions of which 10% 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.

Spent lithium primary batteries can not 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 [3~7]. 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.

In this study, recycling process involving mechanical, hydrometallurgical treatment and amorphous citrate precursor process (ACP)[8] has been applied to prepare LiCoO_2 from the spent LIBs. Fig. 1 shows a flowchart to recover valuable metals and to synthesize cathodic active materials.

Thermal pre-treatment was necessary to liberate unit cell from battery package, however, it caused plastic casing to be hardened and metallic lithium to be partially oxidized.

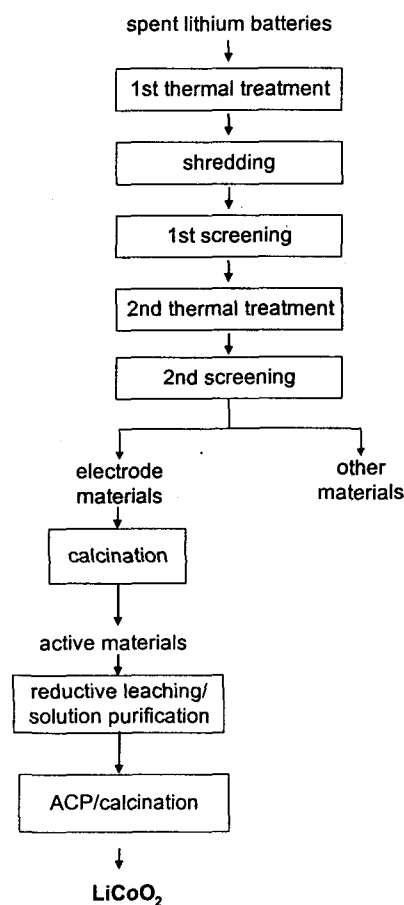


Fig. 1. A flowsheet proposed to recycle spent lithium ion batteries.

Then, the thermally treated batteries were shredded to liberated electrode materials. A shredder has been designed and fabricated, considering the selectivity of electrode active materials as well as the reduction of cost. Reductive nitric acid leaching was employed to improve the dissolution of cobalt and lithium. ACP was applied to synthesize powders with a large specific surface area and an exact stoichiometry.

Experimental

A LIB consists of an IC chip, a plastic casing, and several unit cells (Fig. 2). The unit cell had each of cathode, anode, organic separator, organic electrolyte, and Ni-coated steel casing. The cathode was fabricated by pasting 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. Table 1 shows the chemical composition of a typical LIB.

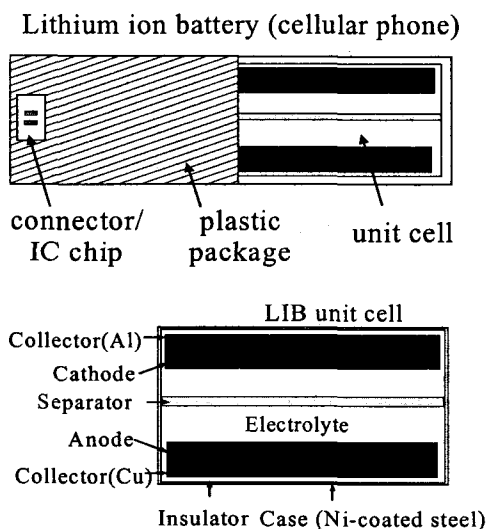


Fig. 2. Schematic diagram of a lithium ion battery.

Table 1. Chemical composition of a lithium ion battery.

component	LiCoO_2	steel/Ni	Cu/Al
wt%	27.5	24.5	14.5
component	carbon	electrolyte	polymer
wt%	16	3.5	14

First, LIB samples were thermally treated in a muffle furnace at $100\text{--}150^\circ\text{C}$ for 1hr. 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 50mm 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, LiCoO_2 was obtained by burning off carbon and binder in the temperature range $500\text{--}900^\circ\text{C}$ for 0.5~2 hr.

Third, LiCoO_2 in a nitric acid solution was leached in a reactor (Fig. 3), which was placed in a constant-temperature water bath. Leaching conditions were optimized, varying HNO_3 concentration, pulp density temperature, and H_2O_2 amount added. To increase leaching efficiency, reductive leaching was carried out in the presence of a reducing agent.

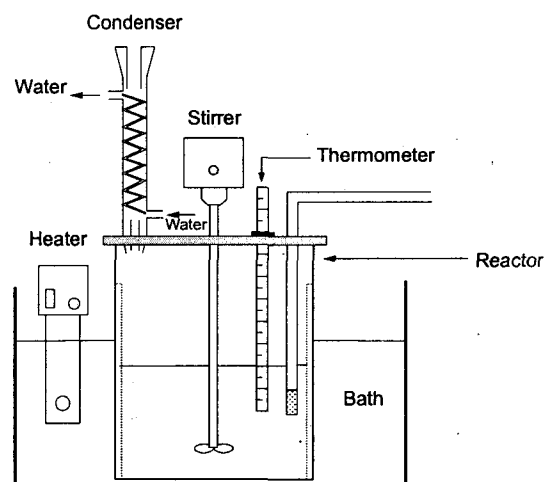


Fig. 3. Schematic diagram of leach cell.

Fourth, the amorphous precursor method with citric acid was selected so as to produce powder with a higher surface area that resulted in a higher performance. A mixture of the leach liquor in nitrate form and additional citric acid was used to prepare amorphous gel precursor in a rotary vacuum dryer (Büchi Rotavapor R-114) at 65°C for 2 hr. The molar ratio of Li/Co in the leach liquor was adjusted at 1.1 by adding an additional LiNO_3 solution. The gels was placed inside a stainless steel crucible and calcined into powder in air for 2 hr in the temperature range 500°C to $1,000^\circ\text{C}$.

The concentration of various metallic ions was measured using an atomic absorption spectrometer (Perkin-Elmer M3100) and inductively coupled plasma atomic emission spectrometer (JY-38). The phase of solids was analyzed by X-ray diffractometer (Rigaku, Cu-K α). The surface area and the particle size distribution was observed with BET (Quantasorb) and Malvern Instruments, respectively. The cathodes were prepared with a mixture of the 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 LiCoO_2 cathodes were tested in a sealed and half-cell typed Teflon cell. An EC-DMC contained LiPF_6 was used as an electrolyte. Charge/discharge characteristics were analyzed with a Maccor 4000.

Results and Discussion

Mechanical and Thermal Separation

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.

- ξ 1st thermal treatment at 100~150°C for 30 min
- ξ high-speed shredding into the 5-20mm
- ξ 2nd thermal treatment at 300~500°C for 1 hr
- ξ vibrating screening
- ξ calcination at 700~900°C for 1 hr

Fig. 4 shows XRD patterns of cathodic active materials calcined at temperature of 700~900°C. It indicated that the carbon and binder was burnt off by calcining above 800°C.

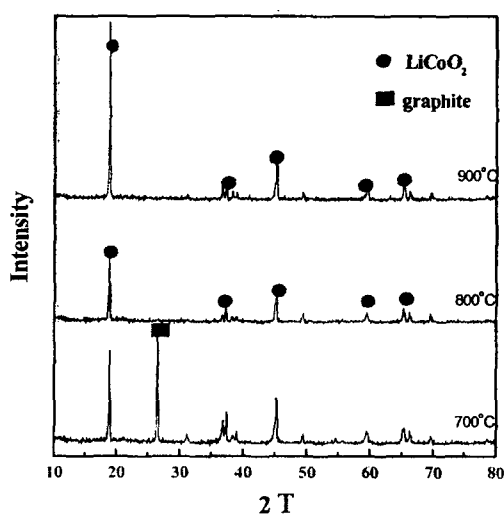


Fig. 4. XRD patterns of cathodic active materials calcined.

Reductive Leaching

In order to dissolve Co and Li from cathodic active materials, acid leaching was employed. Prior to leaching, the active material was ground in a ball mill and dried in an oven at 60°C for 48 hr. The mean particle size was about 2.5 μm.

Fig. 5 shows the leaching behavior of LiCoO₂ in 1 M nitric acid solution at fixed 20 g/L pulp density and 75°C. In the absence of a reducing agent, the leaching 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 was added as a reducing agent [7]. The extractions of both metals were improved to about 85% by the reductive leaching as shown

in the figure. It seems to be due to the reduction of Co³⁺ to Co²⁺ that can be readily dissolved.

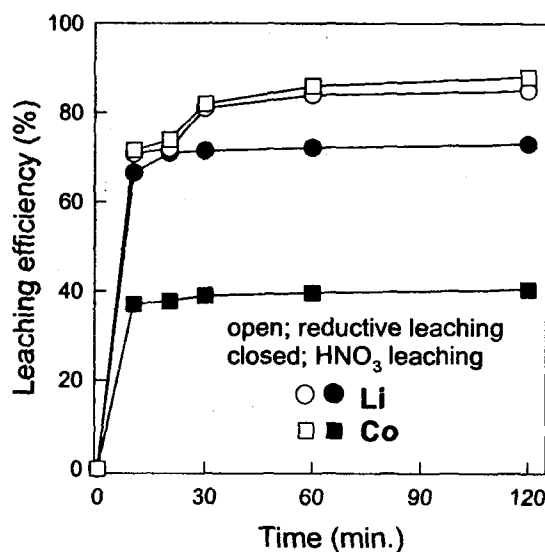


Fig. 5. Leaching behaviors of LiCoO₂ in nitric acid solution. (20 g/L, 75°C, 400 rpm, 1M HNO₃, H₂O₂ 0.8 vol%).

To obtain the optimum conditions for the reductive leaching of LiCoO₂, several sets of leaching experiment were tested under different conditions, i.e. various HNO₃ concentrations, pulp density, temperature, and H₂O₂ amount added.

Fig. 6 shows the effects of HNO₃ concentration in the presence of 0.8 vol.% H₂O₂ on the leaching of LiCoO₂ at 20 g/L pulp density and 75°C for 30 min. The efficiencies of both Co and Li were increasing with increasing HNO₃ concentration. Over 80% Co and Li each were readily extracted within 30 min at 1 M HNO₃ concentration.

The leaching behaviors with different pulp densities are presented in Fig. 7 in the constant conditions of 1 M HNO₃ concentration, 75°C, 0.8 vol% H₂O₂, 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.

Fig. 8 shows the effect of temperature on the leaching of LiCoO₂ under the constant conditions of 10 g/L pulp density, 1 M HNO₃ concentration, 0.8 vol% H₂O₂. The extraction of Co was increased from 30% to 75% and close to 99% as the temperature was raised from 25°C to 50°C and finally to 75°C. The Li extraction was found similar to that of Co.

Fig. 9 shows the effect of H₂O₂ addition on the leaching at the constant conditions of 20 g/L pulp density, 1 M HNO₃ concentration, 75°C and 30 min. Although the Co and Li extractions were increased with increasing the amount of H₂O₂ added, sufficient extractions of over 95% Co and Li could be obtained at 1.7 vol% H₂O₂ addition.

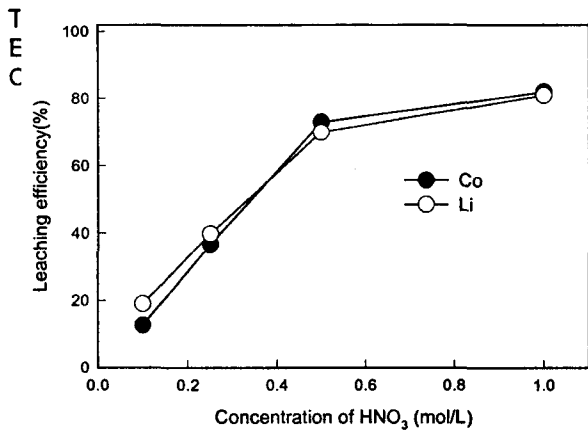


Fig. 6. Effect of HNO₃ concentration on LiCoO₂ leaching. (20 g/L, 75°C, 400 rpm, 30 min, 0.8 vol% H₂O₂).

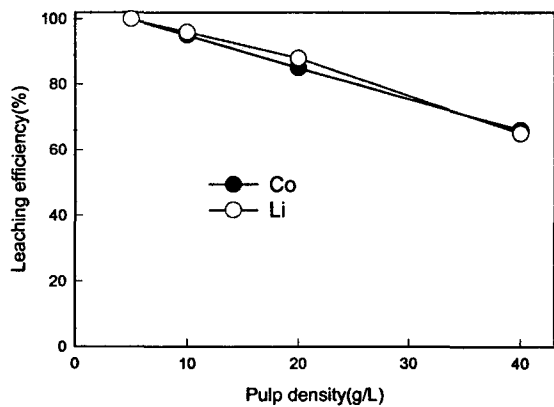


Fig. 7. Effect of pulp density on LiCoO₂ leaching. (1M HNO₃, 75°C, 400 rpm, 30 min, 0.8 vol% H₂O₂)

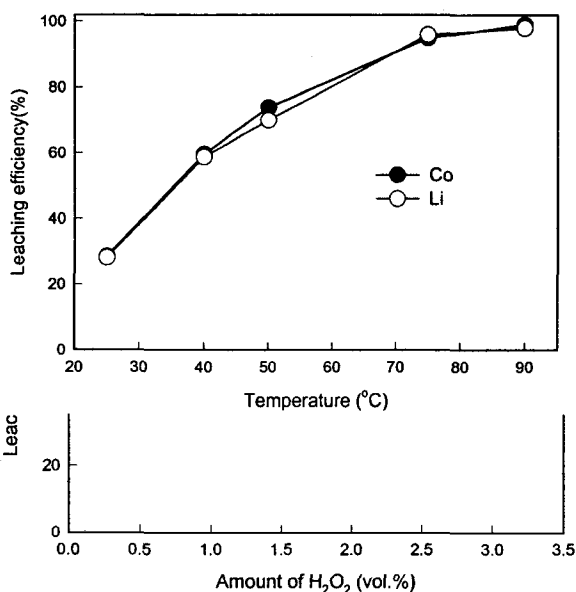


Fig. 8. Effect of temperature on LiCoO₂ leaching. (1M HNO₃, 20 g/L, 400 rpm, 30 min, 0.8 vol% H₂O₂)

Fig. 9. Effect of H₂O₂ amount on LiCoO₂ leaching. (1M HNO₃, 75°C, 20 g/L, 400 rpm, 30 min)

Based on the leaching results, the optimum conditions were determined at 1 M HNO₃ concentration, 75°C operating temperature, 20 g/L initial pulp density, 1.7 vol% H₂O₂ addition, and 1 hr.

Preparation of LiCoO₂ powder and characterization

Various processes are considered to produce LiCoO₂, known as cathodic active materials, from the leach liquor. Of many possible processes, the amorphous citrate precursor process has been applied to synthesize powders with a large specific surface area and an exact stoichiometry.

After the nitric acid leaching of used LiCoO₂, the molar ratio of Li/Co in the leach liquor was adjusted at 1.1 by adding a fresh LiNO₃ solution. Then, 1 M citric acid solution at 100% stoichiometry was also added to prepare a gelatinous precursor. When the precursor was treated at 950°C for 24 hr purely crystalline LiCoO₂ was successfully obtained (Fig. 10). The particle size and specific surface area of the resulting crystalline powders were 20 μm and 30 cm²/g, respectively.

Fig. 11 shows the charge/discharge characteristics of the LiCoO₂ 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 LiCoO₂ used in the battery industry.

Fig. 12 shows cyclic behaviors of the LiCoO₂ electrode. A slow decrease in charge and discharge capacities was observed as the cycle number increased. After 30 cycles, the both capacities decreased by less than 10 % compared to the value of 1st cycle.

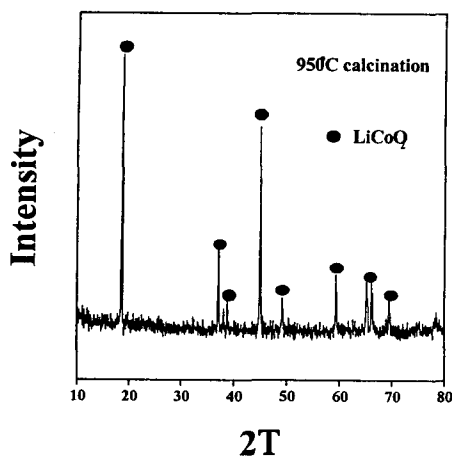


Fig. 10. XRD patterns of LiCoO_2 powder prepared by the amorphous citrate precursor process.

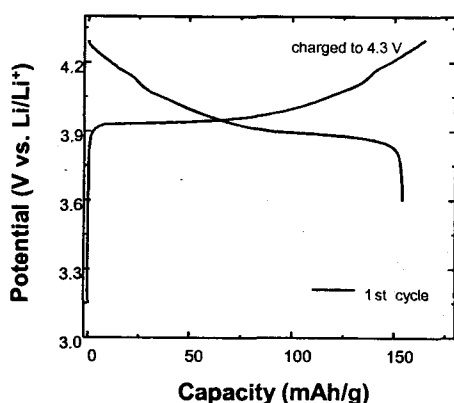


Fig. 11. Charge/discharge characteristics of the LiCoO_2 powder prepared by the amorphous citrate precursor process.

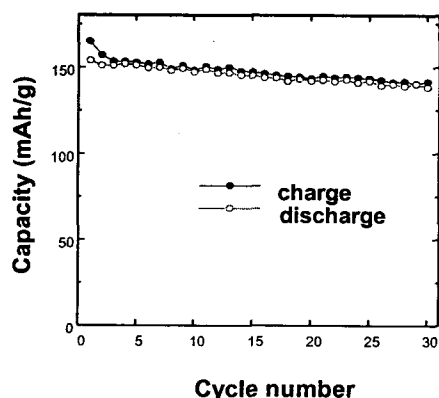


Fig. 12. Cyclic performance of the LiCoO_2 powder prepared by the amorphous citrate precursor process.

Conclusions

1. A series of thermal treatment, high-speed shredding, calcination, reductive leaching, and an amorphous citrate precursor technique was applied to recycle spent lithium ion secondary batteries.
2. Electrode material in a 0.5-20mm fraction was liberated from other constituents like plastics and steel casing segments by high-speed shredding. This step increased the selectivity of active materials as well as decreased comminution cost.
3. 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%. It seems to be due to the reduction of Co^{3+} to Co^{2+} that can be readily dissolved. The extractions of Co and Li were increased with increasing HNO_3 concentration and temperature, and amount of hydrogen peroxide and with decreasing of pulp density. The optimum leaching conditions were 1 M HNO_3 , 20 g/L initial pulp density, 75°C , and 1.7 vol% H_2O_2 and 1 hr.
4. LiCoO_2 crystalline powder of 20 μm size and 30 cm^2/g specific surface area could be synthesized from the leach liquor by the amorphous citrate precursor method.
5. The 1st charge and discharge capacities of the LiCoO_2 powder were 165 mAh/g and 154 mAh/g. at 1st cycle, respectively. The capacities were over 90% of the value of 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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