

Preparation of LiCoO_2 from spent lithium-ion batteries

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Abstract

A recycling process involving mechanical, thermal, hydrometallurgical and sol–gel steps 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 can be concentrated with a two-step thermal and mechanical treatment. The leaching behavior of lithium and cobalt in nitric acid media is investigated in terms of reaction variables. Hydrogen peroxide in 1 M HNO_3 solution is found to be an effective reducing agent by enhancing the leaching efficiency. Of the 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 to Co in the leach liquor is adjusted to 1.1 by adding a fresh LiNO_3 solution. Then, 1 M citric acid solution at a 100% stoichiometry is added to prepare a gelatinous precursor. When the precursor is calcined at 950 °C for 24 h, purely crystalline LiCoO_2 is successfully obtained. The particle size and specific surface-area of the resulting crystalline powders are 20 μm and 30 $\text{cm}^2 \text{g}^{-1}$, respectively. The LiCoO_2 powder is found to have good characteristics as a cathode active material in terms of charge–discharge capacity and cycling performance. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Lithium-ion battery; Cathode active material; Recycling; Cobalt; Spent batteries

1. Introduction

Recycling of lithium batteries is interesting because lithium batteries can replace other types of batteries due to their light weight and good performance [1,2]. In 1998, the world-wide production of lithium-ion secondary batteries (LIBs) was about 250 million of which 10% of the market share is in Korea. The annual production of LIB waste which contains 5–15 wt.% Co and 2–7 wt.% Li was estimated to be 200–500 t.

Spent lithium primary batteries cannot be disposed safely unless metallic lithium is properly removed from them due to its explosive nature. In the case of LIBs with lithium cobalt oxide as the cathodic active mineral, heavier, valuable metals such as cobalt and lithium have to be recycled [3–7]. Thus, there are two problems to be solved during recycling LIB waste, namely, disposal of harmful waste and prevention of explosion. 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 LIBs, safety in mechanical treatment and waste minimization are considered to be the most important issues.

In this study, a recycling process which involves mechanical, hydrometallurgical treatment and a amorphous citrate precursor process (ACP) [8] has been applied to prepare LiCoO_2 from spent LIBs. A flowchart for the recovery of valuable metals and synthesis of cathodic active material is shown in Fig. 1. Thermal pre-treatment is necessary to liberate the unit cell from the battery package, but it causes the plastic casing to harden and the metallic lithium to be partially oxidized. The thermally treated batteries are then shredded to liberate the electrode materials. A shredder has been designed and fabricated in terms of the selectivity of electrode active materials as well as cost. Reductive nitric acid leaching is employed to improve the dissolution of cobalt and lithium. ACP is applied to synthesize powders with a large specific surface-area and an exact stoichiometry.

2. Experimental

A LIB consists of an IC chip, a plastic casing, and several unit cells (Fig. 2). The unit cell is composed of a cathode, an anode, an organic separator, an organic electrolyte, and a Ni-coated steel casing. The cathode is fabricated by pasting LiCoO_2 active materials, carbon-conducting additives, and a

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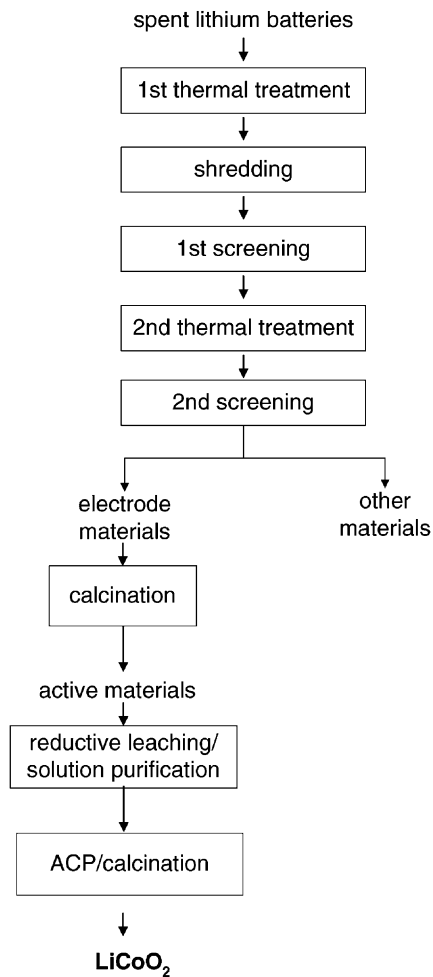


Fig. 1. A flowsheet of proposed process for recycling spent lithium-ion batteries.

binder on aluminum foil. The anode is made by same process with graphite active materials, carbon-conducting additives, and a binder pasted on copper foil. The chemical composition of a typical LIB is shown in Table 1. The recycling process for spend LIBs consisted of the following stages.

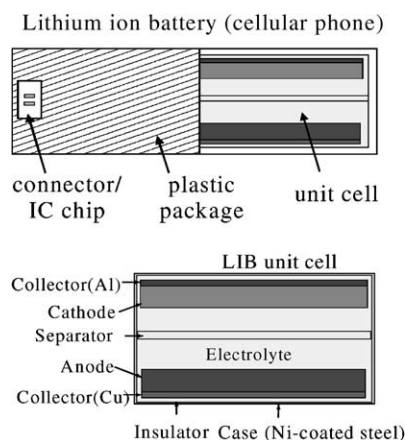


Fig. 2. Schematic diagram of lithium-ion battery.

Table 1
Chemical composition of lithium-ion battery

Component	wt. %
LiCoO ₂	27.5
Steel/Ni	24.5
Cu/Al	14.5
Carbon	16
Electrolyte	3.5
Polymer	14

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

Second, a two-step thermal treatment was performed in a furnace, and electrode materials were liberated from the current-collectors by a vibrating screening. Next, the cathodic active material, LiCoO₂, was obtained by burning off carbon and binder in the temperature range 500–900 °C for 0.5–2 h.

Third, LiCoO₂ in a nitric acid solution was leached in a reactor (Fig. 3), which was placed in a constant-temperature water bath. The leaching conditions were optimized by varying HNO₃ concentration, solid liquid (S:L) ratio, temperature and added amount of H₂O₂. To increase leaching efficiency, reductive leaching was carried out in the presence of a reducing agent.

Fourth, an amorphous precursor method with citric acid was selected to produce powder with a higher surface-area that gave a higher performance. A mixture of leach liquor in nitrate form and additional citric acid was used to prepare an amorphous gel precursor in a rotary vacuum dryer (Büchi Rotavapor R-114) at 65 °C for 2 h. The molar ratio of Li:Co in the leach liquor was adjusted to 1.1 by adding LiNO₃

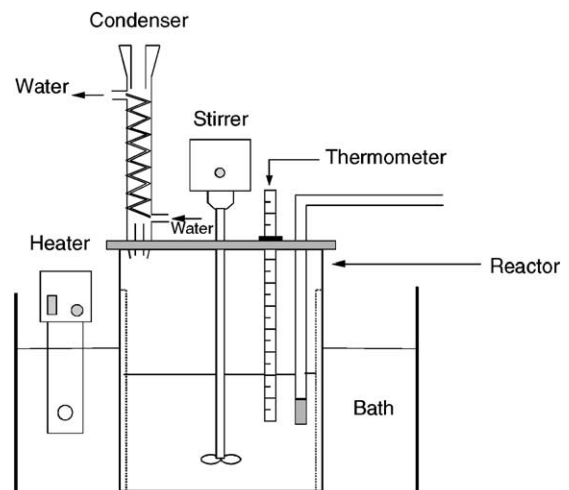


Fig. 3. Schematic diagram of leach cell.

solution. The gel was placed inside a stainless-steel crucible and calcined into powder in air for 2 h in the temperature range 500–1000 °C.

The concentrations of various metallic ions were measured with an atomic absorption spectrometer (Perkin-Elmer M3100) and an inductively coupled plasma atomic emission spectrometer (JY-38). Phase analysis of the solids was determined with an X-ray diffractometer (Rigaku, Cu K α). The surface-area and the particle-size distribution were obtained with BET (Quantasorb) and Malvern Instruments, respectively.

The cathodes were prepared with a mixture of LiCoO₂ powder surface-area (30 m² g⁻¹), 15 wt.% acetylene black and 5 wt.% binder pasted on an aluminum foil current-collector.

The LiCoO₂ cathodes were tested in a sealed and half-cell type of Teflon cell. The electrolyte was ethylene carbonate and dimethyl carbonate. Charge–discharge characteristics were analyzed with a Maccor 4000 instrument.

3. Results and discussion

3.1. Mechanical and thermal separation

Mechanical and thermal treatment was applied to concentrate the electrode active materials in a powder form. The following procedure was adopted for the mechanical and thermal steps, and resulted in cost reduction and safety in shredding.

1. first thermal treatment at 100–500 °C for 30 min;
2. high-speed shredding to 5–20 mm;
3. second thermal treatment at 300–500 °C for 1 h;
4. vibrating screening;
5. calcination at 700–900 °C for 1 h.

Typical XRD patterns of cathodic active materials calcined at a temperature of 700–900 °C are shown in Fig. 4. The data indicates that the carbon and binder were burnt off by calcination above 800 °C.

3.2. 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 h. The mean particle size is about 15 μ m.

The leaching behavior of LiCoO₂ in 1 M HNO₃ solution at a fixed S:L ratio of 20 g l⁻¹ and 75 °C is shown in Fig. 5. In the absence of a reducing agent, the leaching efficiencies of cobalt and lithium leveled off within 30 min with a low extraction of Co (40%) and Li (75%). To increase the efficiency, 0.8 vol.% hydrogen peroxide was added as a reducing agent [7]. The extraction of both metal improved to about 85% by the reductive leaching as shown in Fig. 5.

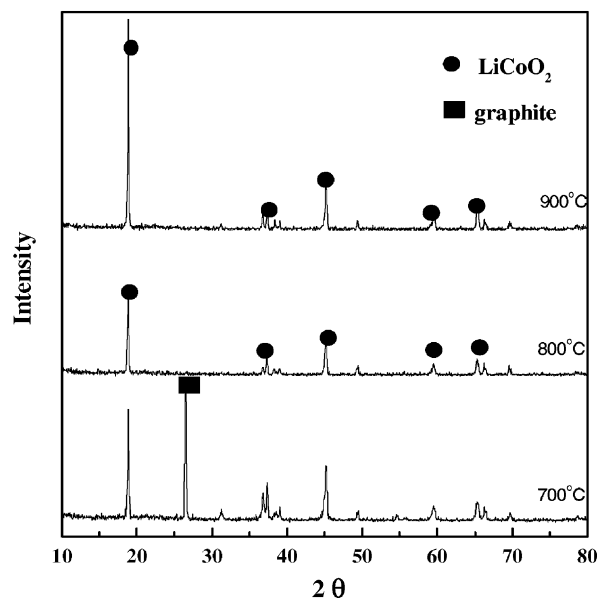


Fig. 4. XRD patterns for calcined cathodic active materials.

It seems to be due to the reduction of Co³⁺ to Co²⁺ that can be readily dissolved. To obtain the optimum conditions for the reductive leaching of LiCoO₂, several leaching experiments were performed under different conditions i.e., various HNO₃ concentrations, S:L ratio, temperature, and added amount of H₂O₂.

The effects of HNO₃ concentration in the presence of 0.8 vol.% H₂O₂ on the leaching of LiCoO₂ at a L:S ratio of 20 g l⁻¹ and 75 °C for 30 min are shown in Fig. 6. The efficiencies of both Co and Li increase with increasing HNO₃ concentration. Over 80% Co and 80% Li are readily extracted within 30 min at 1 M HNO₃.

The leaching behavior with different pulp densities are presented in Fig. 7 for the constant conditions of 1 M HNO₃,

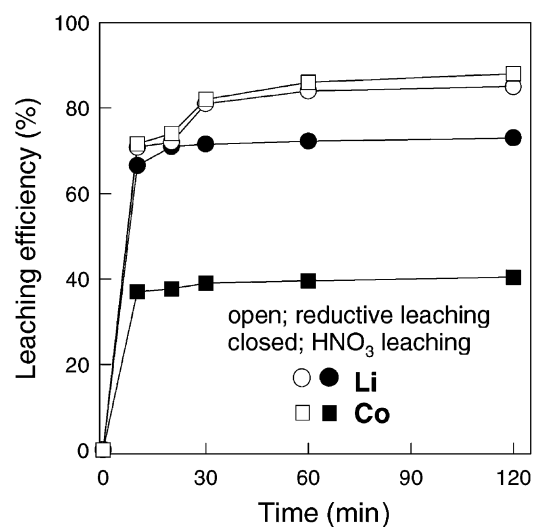


Fig. 5. Leaching behavior of LiCoO₂ in nitric acid solution (20 g l⁻¹, 75 °C, 400 rpm, 1 M HNO₃, 0.8 vol.% H₂O₂).

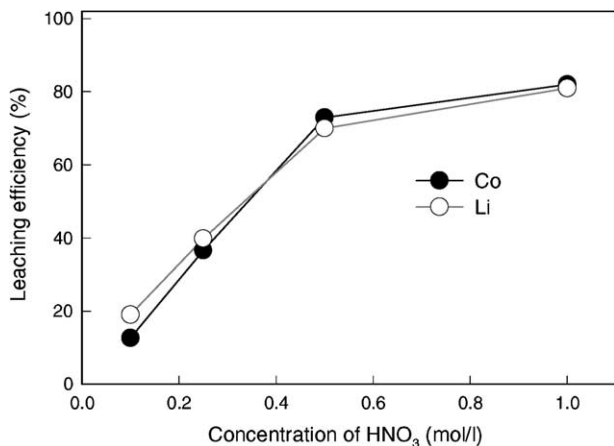


Fig. 6. Effect of HNO₃ concentration on LiCoO₂ leaching (20 g l⁻¹, 75 °C, 400 rpm, 30 min, 0.8 vol.% H₂O₂).

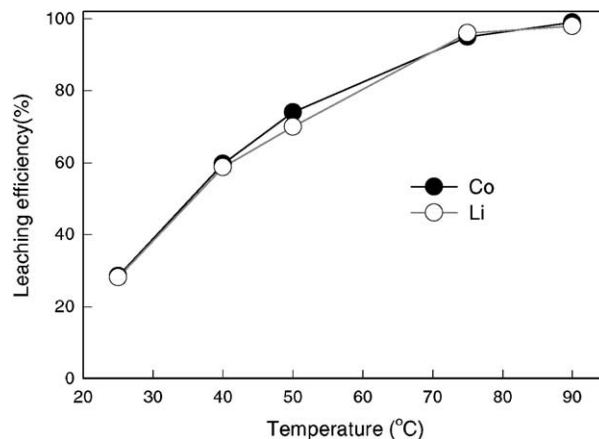


Fig. 8. Effect of temperature on LiCoO₂ leaching (1 M HNO₃, 20 g l⁻¹, 400 rpm, 30 min, 0.8 vol.% H₂O₂).

75 °C, 0.8 vol.% H₂O₂, and 30 min. The extraction of both Co and Li were decreased with increasing S:L ratio. Over 95% Co and Li are readily extracted in 30 min at a S:L ratio of 10 g l⁻¹.

The effect of temperature on the leaching of LiCoO₂ under the constant conditions of a S:L ratio of 10 g l⁻¹, 1 M HNO₃, and 0.8 vol.% H₂O₂ is shown in Fig. 8. The extraction of Co increases from 30 to 75% and close to 99% as the temperature is raised from 25–50 °C and finally to 75 °C. The Li extraction is similar to that of Co.

The effect of H₂O₂ addition on the leaching at the constant conditions S:L ratio of 20 g l⁻¹, 1 M HNO₃, 75 °C and 30 min is shown in Fig. 9. Although the extraction of Co and Li increase with increasing amount of H₂O₂ added. Sufficient extractions of over 95% Co and 95% Li can be obtained at 1.7 vol.% H₂O₂ addition.

Based on the leaching results, the optimum conditions were determined to be 1 M HNO₃, 75 °C an operating temperature, and 20 g l⁻¹ initial S:L ratio, 1.7 vol.% H₂O₂ addition, and 1 h.

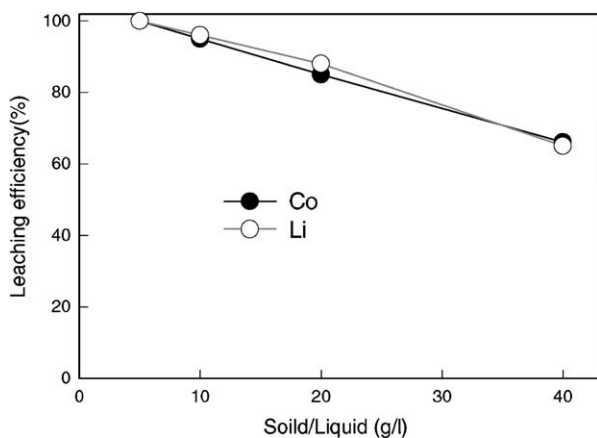


Fig. 7. Effect of S:L ratio on LiCoO₂ leaching (1 M HNO₃, 75 °C, 400 rpm, 30 min, 0.8 vol.% H₂O₂).

3.3. Preparation of LiCoO₂ powder and characterization

Various processes have been considered to produce LiCoO₂ from the leach liquor. Of the 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 to 1.1 by adding a fresh LiNO₃ solution. Then, a 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 h, a purely crystalline LiCoO₂ was successfully obtained (Fig. 10). The particle size and specific surface-area of the resulting crystalline powder were 20 μm and 30 cm² g⁻¹, respectively.

Charge–discharge characteristics of LiCoO₂ prepared from spent LIB are shown in Fig. 11. The charge and discharge capacities are 165 and 154 mAh g⁻¹, respectively. On the first cycle, the capacities were over 90% of those for LiCoO₂ which is used in the battery industry.

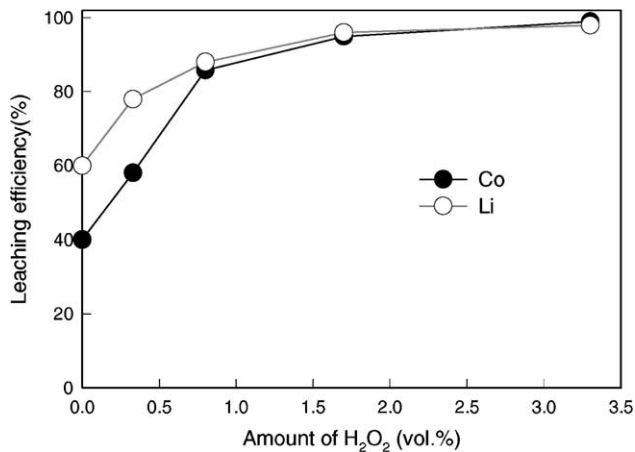


Fig. 9. Effect of H₂O₂ amount on LiCoO₂ leaching (1 M HNO₃, 75 °C, 20 g l⁻¹, 400 rpm, 30 min).

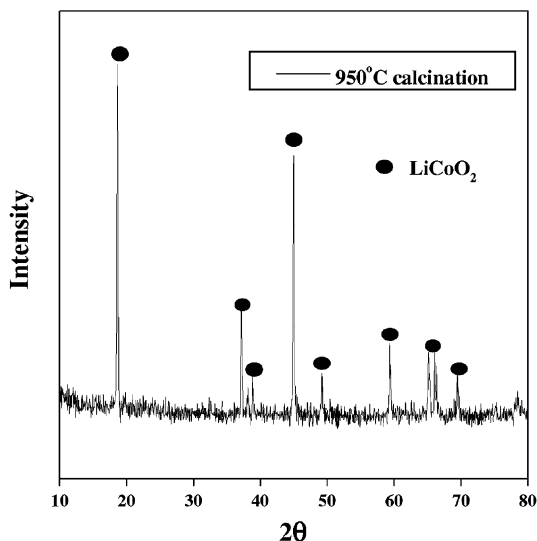


Fig. 10. XRD patterns for LiCoO₂ powder prepared by amorphous citrate precursor process.

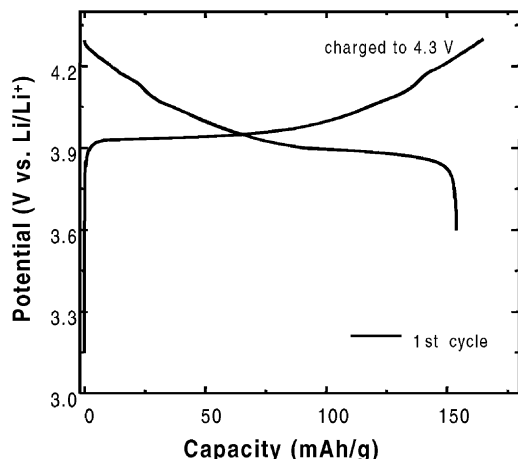


Fig. 11. Charge–discharge characteristics of the LiCoO₂ powder prepared by amorphous citrate precursor process.

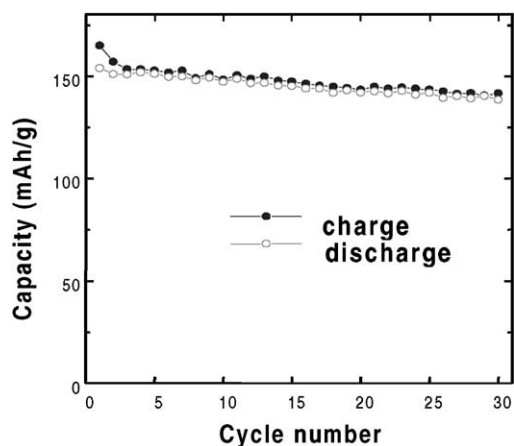


Fig. 12. Cycling performance of LiCoO₂ powder prepared by amorphous citrate precursor process.

The cycle behavior of the LiCoO₂ electrode is presented in Fig. 12. A slow decrease in the charge and discharge capacities is observed as the cycle number increases. After 30 cycles, both capacities have decreased by less than 10% compared to the values on the first cycle.

4. Conclusions

From the work presented here, the following conclusions can be drawn.

1. A sequential process, thermal treatment, high-speed shredding, calcination, reductive leaching, and an amorphous citrate precursor technique has been applied to recycle spent lithium-ion secondary batteries.
2. Electrode material in a 0.5–20 mm fraction is liberated from other constituents such as plastics and steel casing segments by high-speed shredding. This step increases the selectivity of active materials as well as decreases the comminution costs.
3. By addition of hydrogen peroxide to the nitric acid used for leaching, Co extraction is increased from 40–85% and the Li extraction from 75–85%. This appears to be due to the reduction of Co³⁺ to Co²⁺ which can be readily dissolved. The extraction of Co and Li is increased with increasing HNO₃ concentration, temperature and the amount of hydrogen peroxide and with decreasing S:L ratio. The optimum leaching conditions are 1 M HNO₃, 20 g l⁻¹ initial S:L ratio, 75 °C, 1.7 vol.% H₂O₂ and 1 h.
4. LiCoO₂ crystalline powder of 20 μm size and 30 cm² g⁻¹ specific surface-area can be synthesized from the leach liquor by the amorphous citrate precursor method.
5. The initial charge and discharge capacities of the LiCoO₂ powder are 165 and 154 mAh g⁻¹ respectively. The capacities are over 90% of that obtained from LiCoO₂ used by battery industry. The cathode active material prepared from spent LIBs has good charge–discharge capacities and cycling performance.

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