

Short communication

Used lithium ion rechargeable battery recycling using Etoile-Rebatt technology

Dong-il Ra^a, Kyoo-Seung Han^{a,b,*}

^a Division of Advanced Materials Engineering, Chungnam National University, Daeduk Science Town, Taejeon 305-764, South Korea

^b REBATT Corp., Daeduk Science Town, Taejeon 305-764, South Korea

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Abstract

Depleted LiCoO₂ cathode material in spent lithium ion rechargeable batteries was recovered and renovated in a single synthetic step using Etoile-Rebatt technology. The structural and compositional purities of the recovered and renovated LiCoO₂ were confirmed by elemental analyses, X-ray diffraction pattern analyses, and Raman spectroscopy. In spite of the simple and economical recycling, the recovered and renovated LiCoO₂ exhibits a prospective electrochemical activity; an initial discharge capacity of 134.8 mAh g⁻¹ and the discharge capacity retention of 95.9% after 50 cycles.

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1. Introduction

A lithium ion rechargeable battery having many suitable performances such as high energy density, longevity, and lightweight becomes the major power source for most small portable electrical equipment. Recently, the usage of lithium ion rechargeable batteries has rapidly increased. In the parallel way, the consumption of electrode materials has also increased.

A lithium ion rechargeable battery comprises a cathode, an anode, organic electrolyte, and a separator. The lamination of a cathode, an anode, and a separator by a pressing makes those electric contacts. The anode is a copper plate coated with a mixture of carbon graphite, conductor, binder, and additives. Similarly, the cathode is an aluminum plate coated with a mixture of active cathode material, electric conductor, binder, and additives. Here, LiCoO₂ is used as the cathode material for almost all commercialized lithium ion rechargeable batteries due to its suitable performances such as high energy density, ease of manufacture, etc. However, it also has several unfavorable points such as high cost, limited cobalt resources, toxicity, etc.

A lithium ion rechargeable battery has the capability of charging and discharging with a relatively longer life span. However, it has a limited life span of about 500 cycles. Therefore, the number of disposed batteries increases as the consumption of batteries increases. Considering the unfavorable points of LiCoO₂, the recycling of the depleted LiCoO₂ has many advantages such as alternative cobalt resources, mitigation of environmental pollution, etc. Although all of the depleted LiCoO₂ will have to be recycled in the near future, the technology for the recycling is not well considered, far from being established. It is mainly ascribed to the inferiority of the economical efficiency in the recycling of the depleted LiCoO₂ using the conventional method. The conventional method for the recycling of industrial waste bound in cobalt consists of complicated multi-step procedures such as dissolution in mixed acid solution, neutralization and precipitation, filtering, various extraction procedures using different organic solvents, etc. As mentioned above, because the lithium ion rechargeable batteries do not only have LiCoO₂ but also carbon graphite, electric conductor, binder, several additives, as well as Al and Cu current collectors, the recycling of the depleted LiCoO₂ using the conventional method should be more sophisticated. Therefore, the development of an economical and simple synthetic route for the recycling of the depleted LiCoO₂ is quite worthy to be considered. In the course of trying to develop such a novel synthetic approach, we succeeded recovery and reno-

* Corresponding author. Tel.: +82 42 821 5897; fax: +82 42 822 6637.
E-mail address: kshan@cnu.ac.kr (K.-S. Han).

vation of LiCoO_2 in single synthetic step from used lithium ion rechargeable batteries using Etoile-Rebatt technology. Since recycling using the Etoile-Rebatt technology is performed in an open system, its upper limit in capability depends on just voluminal scale of recycling instrument.

In this paper, we present the results of the recovery and renovation of LiCoO_2 from the spent lithium ion rechargeable batteries using the Etoile-Rebatt technology.

2. Experimental

2.1. Materials

The recycling procedure, as schematized in the flow chart of Fig. 1, consists of five steps: dismantling, discharging, separation, detachment, and recycling treatment. Used lithium ion rechargeable batteries, which have already been depleted of their performances, were dismantled to eliminate package, protection circuit module, positive temperature coefficient element, safety vent, etc. Unit cells were soaked in brine and completely discharged for security. Then, anode, separator, electrolyte, and cathode in the unit cell were separated. As shown in Fig. 2, 16.678 kg of black pastes separated from cathode were electrochemically and thermally treated in a laboratory-made recycling instrument. The separated pastes were immersed in the ER-MRT-13 solution containing 4 M LiOH and KOH , and located on the bottom of the reaction vessel and at a dis-

tance of 70 cm from the platinum electrodes located in another vessel for product collecting. The recycling reaction was carried out at a fixed temperature between 40 and 100 °C. During the recycling reaction, the platinum working electrode was galvanostatically charged at a fixed current density between 0.001 and 1.00 mA cm^{-2} . In detail, the recycling reaction simultaneously consists of the dissolution of the depleted LiCoO_2 , the deposition of the dissolved LiCoO_2 on the platinum working electrode, the formation of the recovered and renovated LiCoO_2 film, as well as the precipitation of the recovered and renovated LiCoO_2 powder from the surface of the LiCoO_2 film. The recycled LiCoO_2 was filtered and washed with doubly distilled water, and then dried at 80 °C for 10 h. 12.564 kg of LiCoO_2 was recovered from 16.678 kg of black pastes separated from cathode.

2.2. Film characterization

The X-ray diffraction (XRD) pattern analysis of the recovered and renovated LiCoO_2 was achieved by using a Mac Science M03XHF22 diffractometer and $\text{Cu K}\alpha$ radiation ($\lambda = 1.5405 \text{ \AA}$). Elemental analysis of the recycled LiCoO_2 was carried out by ICP-AES (Jobin Yvon, JY38S) and Carlo Erba EA 1108 CHN analyzer. Room-temperature Raman measurements were performed using a Jobin Yvon/Atago Bussan T64000 triple spectrometer. The scanning electron microscope (SEM) image of the recycled LiCoO_2 was obtained using an Hitachi SEM

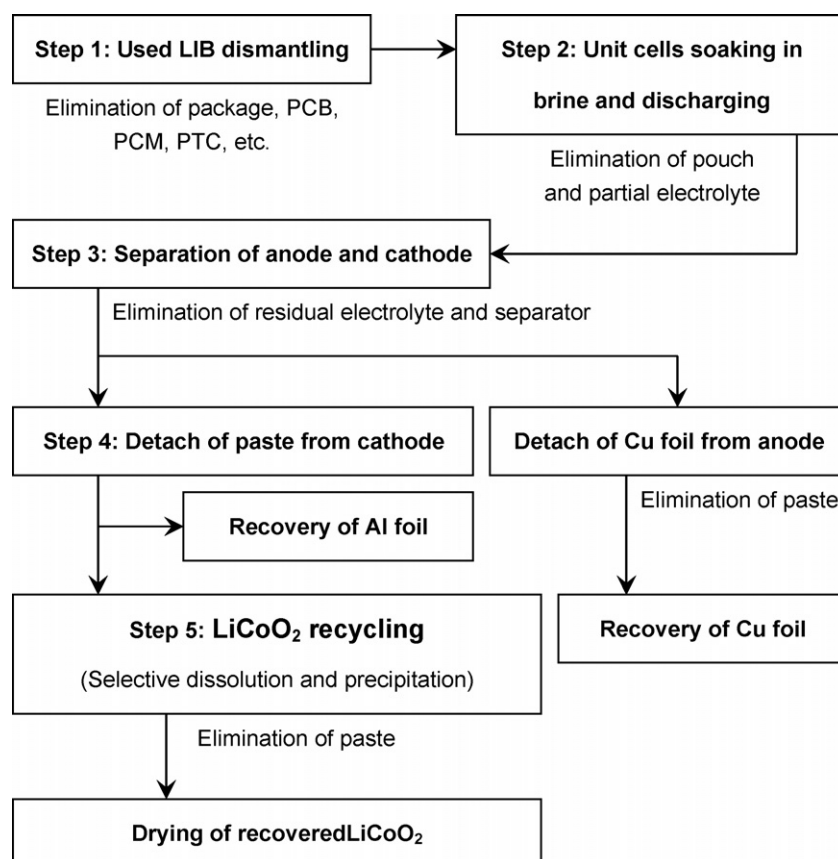


Fig. 1. Schematization of used lithium ion rechargeable battery (LIB) recycling steps using the Etoile-Rebatt technology.

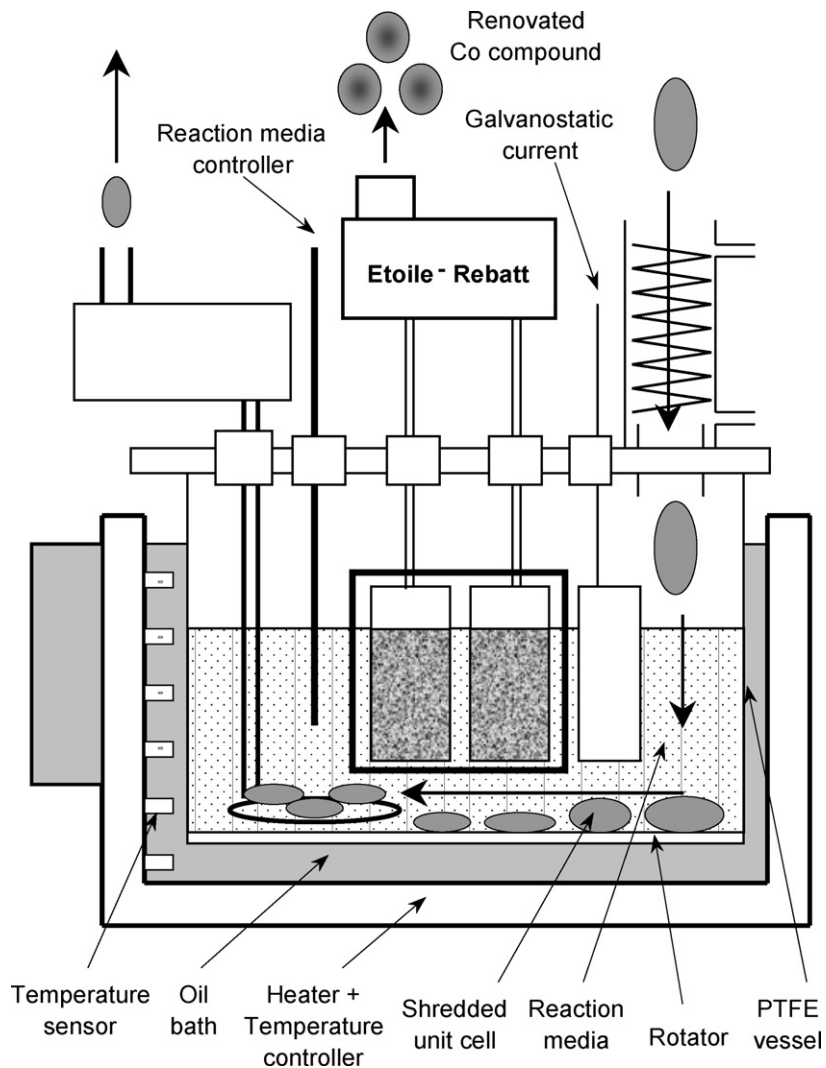
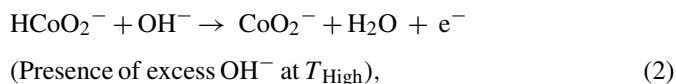
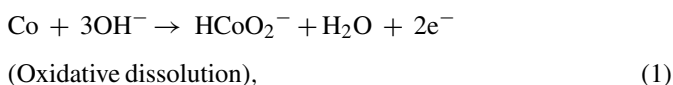


Fig. 2. Schematization of the recycling instrument using the Etoile-Rebatt technology.

S-4500. Electrochemical tests were carried out at room temperature using coin cells. The recycled LiCoO_2 was mixed with 7 wt.% super-P carbon black and 8 wt.% poly-vinylidene fluoride (PVDF) binder dispersed in *N*-methyl-2-pyrrolidone (NMP) until a slurry was obtained. The slurry was laminated on an Al foil using a hot-roller press. The electrolyte was a 1.0 M solution of LiPF_6 in ethylene carbonate (EC) and ethyl methyl carbonate (EMC) with 1:2 volume ratio. Lithium foil was used as anode; cell assembly was performed in an Ar-filled glove box; and cells were charged and discharged at the *C*/5 rate using a Biologic Macpile II.

3. Results and discussion

Recently, we found that an aqueous solution reaction combined with electrochemical and hydrothermal reactions is capable of fabricating LiCoO_2 film. In addition, we have proposed the reaction pathway to obtain LiCoO_2 film as follows [1–4]:



It would be underscored LiCoO_2 was directly prepared without any intermediates of $\text{Co}(\text{OH})_2$ and CoOOH during the reaction [1–3]. Oppositely, on the same reaction condition, $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$ could be prepared with the following steps: oxidative dissolution to form nickelite, precipitation of $\text{Ni}(\text{OH})_2$, oxidation to form NiOOH , and cationic exchange between H^+ and Li^+ [1,4].

If we can control the reaction conditions for the selective dissolution of used LiCoO_2 and the optimal precipitation of renovated LiCoO_2 , both the separation of LiCoO_2 from spent lithium ion rechargeable battery and the renovation of LiCoO_2 can be simultaneously accomplished without any additional separation procedures and impurities. According to the above-given reaction pathway, hydroxyl groups play a key role in obtaining LiCoO_2 phase. Thus, if excess hydroxyl groups can be locally provided at the desired position, LiCoO_2 phase can

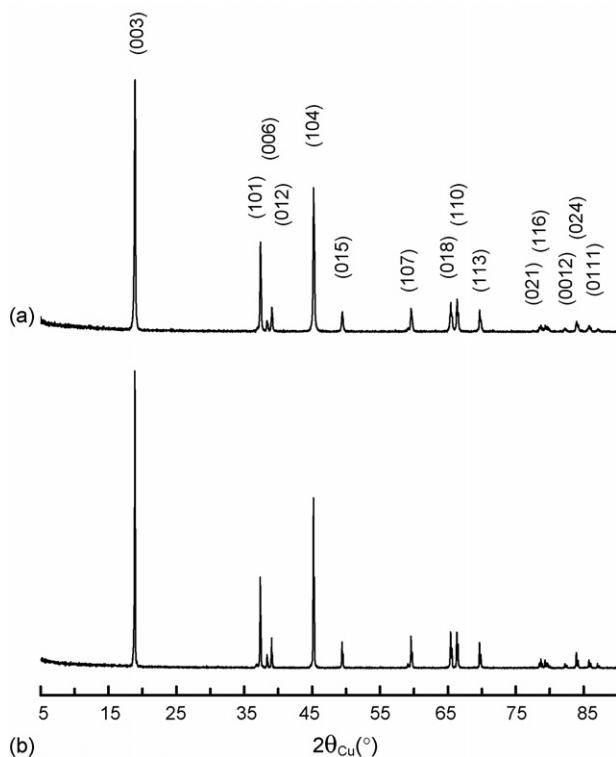


Fig. 3. X-ray diffraction patterns for (a) the LiCoO_2 bulk phase renovated using Etoile-Rebatt technology and (b) the layered LiCoO_2 reference bulk phase (space group: $R\text{-}3m$).

be obtained at the desired position. Actually, we can supply excess hydroxyl groups by electrolysis of water (cathode: $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^- + \text{H}_2$). In this way, we succeeded the simultaneous recovery and renovation of LiCoO_2 cathode material from spent lithium ion rechargeable battery in an aqueous solution by a local supply of galvanostatically generated hydroxyl groups, called as Etoile-Rebatt technology.

During the recycling of the used LiCoO_2 , the formation of a dark-gray film from beginning to end was visually detected only on the platinum working electrode. Although the platinum working and counter electrodes were located at the same intervals from the separated pastes, no film was deposited on the counter electrode. This demonstrates the key role of excess hydroxyl groups in obtaining LiCoO_2 and the possible recovery and renovation of LiCoO_2 in a single synthetic step. The recovered and renovated LiCoO_2 phase was subsequently analyzed.

The XRD patterns of the recovered and renovated powder, as well as the LiCoO_2 reference bulk phase are shown in Fig. 3. The X-ray diffractogram of the recovered and renovated powder is one with that of the LiCoO_2 reference phase. All XRD peaks are characteristic for the space group $R\text{-}3m$ as layered LiCoO_2 phase [5]. Both of the LiCoO_2 phases crystallize in the hexagonal system ($a = 2.816 \text{ \AA}$, $c = 14.04 \text{ \AA}$). No XRD peaks of possible impurities, such as Co(OH)_2 , CoOOH , and Co_3O_4 phases, are detected.

Additionally, an important evidence for the chemical composition of the recycled LiCoO_2 can be obtained by the ICP-AES results; the weight percentage of 7.08 for Li and the weight per-

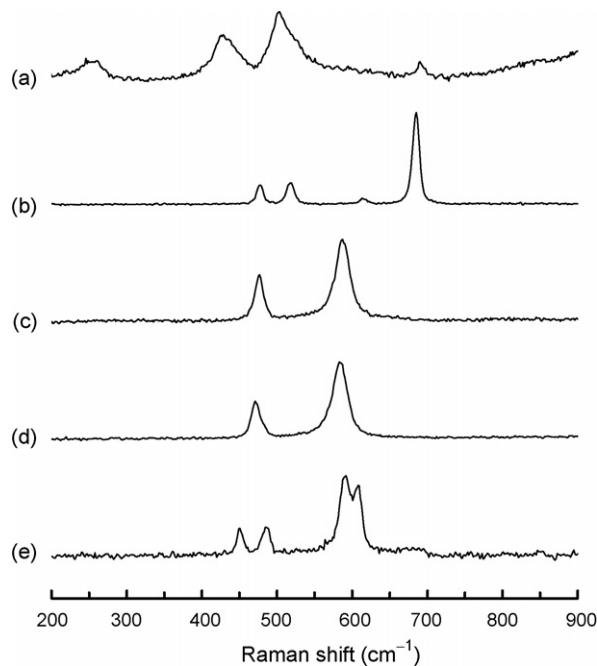


Fig. 4. Raman spectra for (a) Co(OH)_2 reference powder, (b) Co_3O_4 reference powder, (c) the renovated LiCoO_2 powder, (d) the layered LiCoO_2 reference powder, and (e) the spinel $\text{Li}_{1-x}\text{CoO}_2$ reference powder.

centage of 60.21 for Co. The Li/Co molar ratio in the recycled LiCoO_2 , calculated from the ICP-AES results, was close to 1.0, which is in accordance with expected stoichiometry.

The Raman spectra for the Co(OH)_2 reference phase, the Co_3O_4 reference phase, the recycled LiCoO_2 phase, the layered LiCoO_2 reference phase, and the spinel $\text{Li}_{1-x}\text{CoO}_2$ reference phase are compared in Fig. 4. As shown in Fig. 4, it appears that the recycled LiCoO_2 powder consists of just the layered LiCoO_2 phase without any impurities, such as Co(OH)_2 and Co_3O_4 phases (Fig. 5).

Fig. 6 shows the voltage versus capacity profiles for the recovered and renovated LiCoO_2 . Open-circuit voltage of freshly

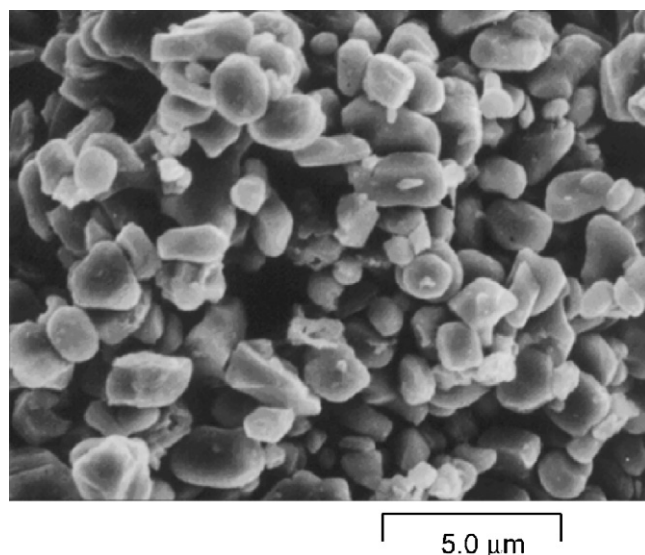


Fig. 5. SEM image of the LiCoO_2 recycled using the Etoile-Rebatt technology.

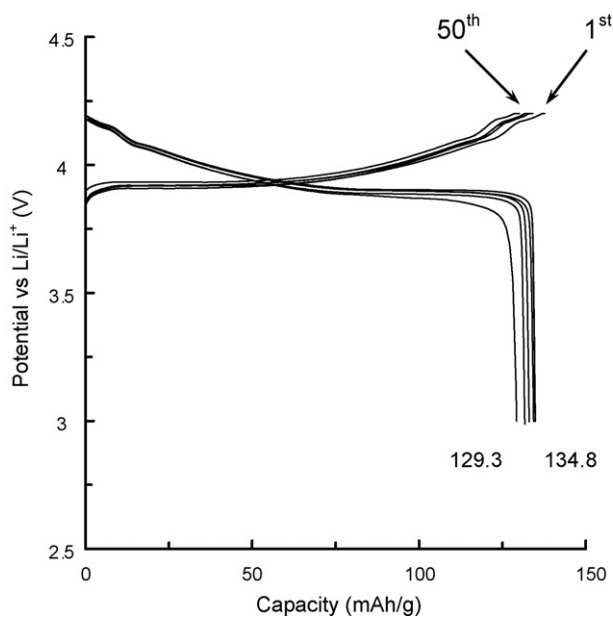


Fig. 6. Voltage vs. capacity profiles for the LiCoO_2 recycled using the Etoile-Rebatt technology.

prepared cell is 3.32 V, which is similar to that of layered LiCoO_2 phase [6–9]. In addition, both charge and discharge curves show a potential plateau at 3.8–3.9 V, that is one of the typical properties for the layered LiCoO_2 phase [6–8]. Thus, these two points are consistent with the results of Raman spectroscopy.

The recovered and renovated LiCoO_2 exhibits an initial discharge capacity of 134.8 mAh g^{-1} and the discharge capacity retention of 95.9% after 50 cycles.

4. Conclusion

Layered LiCoO_2 phase was simultaneously recovered and renovated from spent lithium ion rechargeable batteries using an economical Etoile-Rebatt technology in an aqueous solution. While the renovated LiCoO_2 phase is simply obtained from spent lithium ion rechargeable batteries using the Etoile-Rebatt technology in a single synthetic step, its battery performance is quite prospective.

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