

Simultaneous separation and renovation of lithium cobalt oxide from the cathode of spent lithium ion rechargeable batteries

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Abstract

LiCoO₂ cathode material is renovated and simultaneously separated from spent LiCoO₂ electrodes containing LiCoO₂, electron-conducting carbon, binder, Al current collector, and separator in a single synthetic step using hydrothermal method in a concentrated LiOH solution at 200 °C without any scraping procedures. It is found that the renovated LiCoO₂ phase crystallizes in the rhombohedral system with the space group *R-3m*. Although the obtained material has some electrochemically inactive impurities, the renovated LiCoO₂ phase exhibits the first discharge capacity of 144.0 mAh/g and the discharge capacity retention of 92.2% after 40 cycles.

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1. Introduction

LiCoO₂ is used as the cathode material for almost all commercialized lithium rechargeable batteries due to its suitable performances such as high energy density, longevity, ease of manufacture, etc. However, it also has several unfavorable points such as high cost, limited cobalt resources, toxicity, etc. As the mobile electronic devices are extensively used, the production of lithium rechargeable batteries as those power sources is exponentially increased. In the parallel way, the consumption of LiCoO₂ is also increased. Considering the unfavorable points of LiCoO₂, the recycling of spent LiCoO₂ electrodes has many advantages such as an alternative cobalt resource, mitigation of environmental pollution, etc. Although all of the spent LiCoO₂ electrodes will have to be recycled in the near future, the technology for the recycling of spent LiCoO₂ electrodes is not well considered, far from being established. It is

mainly ascribed to the inferiority of the economical efficiency in the recycling of spent LiCoO₂ electrodes 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. Furthermore, because the LiCoO₂ electrodes in the lithium rechargeable batteries do not have only LiCoO₂ but also electron-conducting carbon, binder and Al current collector, the recycling of spent LiCoO₂ electrodes using the conventional method should be more sophisticated. Therefore, the development of an economical and simple synthetic route for the recycling of spent LiCoO₂ electrodes is quite worthy to be considered. In the course of trying to develop such a novel synthetic approach, the hydrothermal method seems to fit these criteria [1–6]. It is reported that LiCoO₂ phase can be obtained by the hydrothermal reaction [1–6]. In addition, the reaction mechanism is fully based on “dissolution–precipitation” mechanism [3–6]. Therefore, if we can control the hydrothermal conditions for the selective dissolution of spent LiCoO₂ phase and the optimal precipitation of renovated LiCoO₂ phase, both the separation of LiCoO₂ phase from spent electrodes and the renovation of

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LiCoO₂ phase can be simultaneously accomplished without any scraping procedures.

In this work, we present the results of an attempt to implement the hydrothermal method for the simultaneous separation and renovation of LiCoO₂ cathode material from spent LiCoO₂ electrodes.

2. Experimental

2.1. Materials

Spent LiCoO₂ electrodes containing LiCoO₂, electron-conducting carbon, binder, Al current collector, and separator were separated from spent lithium ion batteries. The simultaneous separation and renovation of LiCoO₂ cathode material was carried out in a laboratory-made stainless steel autoclave with two polytetrafluoroethylene (PTFE) vessels. One of the PTFE vessels is adapted to the pressure vessel of the autoclave. The other is a small PTFE vessel with a lid. The spent LiCoO₂ electrodes were located in the small PTFE vessel. During the hydrothermal reaction, the small PTFE vessel was immersed in 5.0 M LiOH solution. The lid of the small PTFE vessel has a lot of holes 1 mm in diameter in order to make the possible exchange of the inside and outside solutions. Five molar LiOH solution was prepared from reagent grade lithium hydroxide monohydrate (Junsei Chemical Co.) and doubly distilled water. The temperature in the reaction vessel was regulated using an external heating system, a Chromel–Alumel thermocouple and an automatic controller. The hydrothermal experiment was carried out at 200 °C for 20 h. The heating processed to 200 °C with an approximate heating rate of 3.0 °C/min and the subsequent isothermal process followed by the cooling process. No external pressure and gas injection were added during the hydrothermal reaction. The pressure in the autoclave is just ascribed to water evaporation at 200 °C.

The dark gray colored powder was precipitated on both of the bottom of two PTFE vessels. The precipitate in the large PTFE vessel was washed several times using doubly distilled water and ultrasonic cleaner to eliminate residual LiOH solution, and then dried at 80 °C for 10 h.

2.2. Characterization

The X-ray diffraction (XRD) pattern analyses were performed using a Rigaku RTP 300 RC diffractometer and Cu K α radiation ($\lambda = 1.5405 \text{ \AA}$) operated at 30 mA and 30 kV. The diffractograms were recorded in the 2θ range of 10–80° with 0.02° resolution and scanning rate of 2°/min. Scanning electron microscope (SEM) images were obtained using a Philips XL 30S FEG microscope. To determine the contents of lithium, cobalt and aluminum, elemental analysis was carried out by using ICPS-5000 (SHIMAZU) ICP spectrometer. Room-temperature Raman measurements were performed using a Jobin Yvon/Atago Bussan T64000 triple spectrom-

eter with a liquid nitrogen cooled CCD detector for 300–600 s. The laser beam ($\lambda = 514.5 \text{ nm}$) was focused to a $\sim 3 \mu\text{m}$ diameter spot by a 90 \times microscope objective. The spectral resolution was 2–3 cm^{-1} . Co K-edge X-ray absorption near edge structure spectroscopy (XANES) was obtained using beam line 10 B in Photon Factory, the National Laboratory for High Energy Physics (Tsukuba, Japan). Synchrotron radiation from the electron storage ring (2.5 GeV with about 250–350 mA of stored current) was monochromatized with a channel-cut Si(3 1 1) monochromator. The Co K-edge absorption data were collected in transmission mode at room temperature. Absorbance was measured with the ionization chamber filled with N₂ (25%) plus Ar (75%), and N₂ (100%) for incident and transmitted beams, respectively. Energy of each spectrum was calibrated from the energy scale of Co metal spectrum. The absorbance $\mu(E)$ was normalized to an edge jump of unity for comparing the XANES features directly with one another. The ⁷Li NMR measurements were carried out at room temperature on Bruker DSX 400 with a 9.4 T magnet. For magic angle spinning (MAS) NMR experiments, a 4 mm CP-MAS probe was used with zirconia rotor at 155.6 MHz as ⁷Li resonance frequency. The sample spinning speed of 14 kHz was employed. Spectra were acquired with single-pulse and echo pulses. Both quadrupolar echoes and spin-echoes were used to acquire spectra of all samples. However, the spectra were subsequently acquired with echo pulse sequences to ensure that no resonances were missed with single-pulse sequence. All spectra were referenced to external 1 M LiCl solution. The 90° pulse length of 4.3 μs , repetition delay of 0.1 s, and spectral width of 0.7 MHz were used. For enhancement of spectral resolution, from 256 to 20,000 acquisitions were acquired to get a spectrum. Electrochemical tests were carried out at room temperature using coin cells. The renovated LiCoO₂ powders were mixed with 10 wt.% super-P carbon black and 10 wt.% poly-vinylidene fluoride (PVDF) binder dissolved in *N*-methyl-2-pyrrolidone (NMP) until a slurry was obtained. The slurry was laminated on an Al foil using a hot roller presser. The electrolyte was a 1 M solution of LiPF₆ in ethylene carbonate (EC) and ethyl methyl carbonate (EMC) (1:2). The anode was a lithium foil. The cell assembly was performed in an Ar-filled glove box. The cells were charged and discharged at the C/5 rate between 3.0 and 4.3 V.

3. Results and discussion

The application of the hydrothermal treatment at the spent cathode electrode having LiCoO₂, electron-conducting carbon, binder, Al current collector, and separator is expected to lead to the simultaneous separation and renovation of LiCoO₂ cathode material. After the hydrothermal treatment, the dark gray colored powder that precipitated on the bottom of the reaction vessel was subsequently analyzed with respect to its structure, composition, and electrochemical activity. The X-ray diffraction patterns of the renovated powder

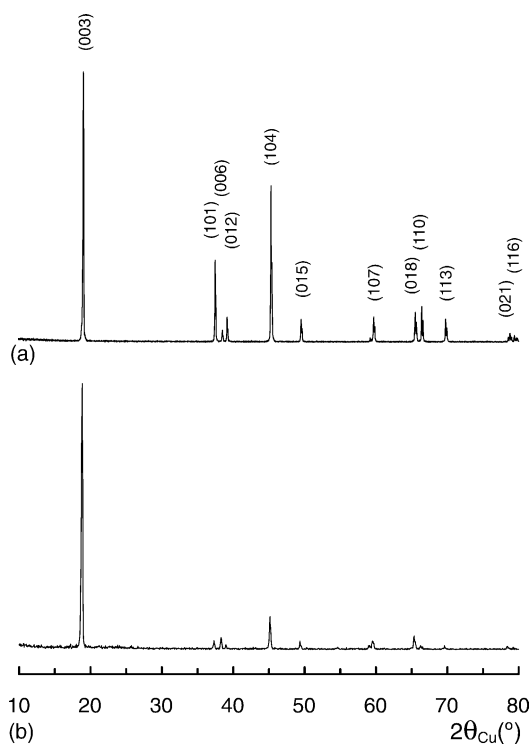


Fig. 1. X-ray diffraction patterns for (a) the layered LiCoO_2 reference powder and (b) the renovated LiCoO_2 powder.

and the pristine LiCoO_2 phase are shown in Fig. 1. Considering the behavior of our system under hydrothermal conditions, we can anticipate either Co(OH)_2 or LiCoO_2 as the most probable products. Co(OH)_2 crystallizes in the hexagonal system with the space group $P-3m1$ ($a = 3.183 \text{ \AA}$, $c = 4.652 \text{ \AA}$) [7], and on the other hand LiCoO_2 crystallizes in the rhombohedral system with the space group $R-3m$ ($a = 2.816 \text{ \AA}$, $c = 14.04 \text{ \AA}$) [8]. Although the peak intensity of all reflection except [003] reflection is feeble in the case of the renovated powder, the XRD peaks characteristic for the space group $R-3m$ as shown in the layered LiCoO_2 phase such as (101), (104), (015), (107), and (018) peaks are observed. However, the exact structural characterization of the prepared material is restrained by the feeble peak intensities.

As shown in Fig. 2, the prepared material consists of well crystallized particles as well as nano-sized and aggregated grains. When the crystallized particles should be the renovated LiCoO_2 phase, the evolution of morphology upon the hydrothermal treatment can be easily found. The different morphologies between the crystallized particle in Fig. 2(a) and the pristine LiCoO_2 powder in Fig. 2(b) means that the renovation mechanism proposed for the hydrothermal treatment is based on “dissolution–precipitation” mechanism. Because the SEM images have been obtained without Au coating procedure, the bright image of nano-sized and aggregated grains suggests that those are conducting materials. Therefore, nano-sized and aggregated grains might be electron-conducting carbon such as KS-6 and Super-P.

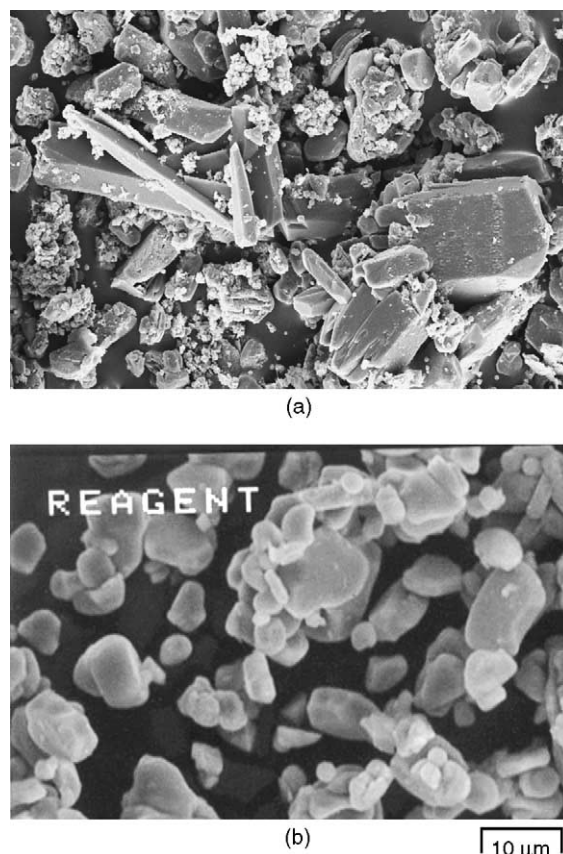


Fig. 2. SEM images for the morphology of (a) the renovated LiCoO_2 phase and (b) the pristine layered LiCoO_2 reference powder.

In order to evaluate the impurity content, the weight percentages of Li, Co, and Al in the prepared material were determined as 6.2, 51.9, and 0.8%, respectively. Assuming the chemical formula of the prepared material as LiCoO_2 , the weight percentage of impurities is 13.7%. The usual weight percentage of LiCoO_2 in the pristine cathode is about 45%, and on the other hand the sum of the weight percentages of electron-conducting carbon, binder, and Al current collector is about 55%. Especially, the weight percentage of Al current collector in the pristine cathode is predicted to be about 35%. It means that Al takes up the largest percentage of the impurity phases before any separation procedure. Unless LiCoO_2 phase is separated from the spent cathode electrode, the anticipated impurity weight percentage should be about 55%. According to the results of the chemical analyses, the real impurity weight percentage of 13.7% as well as the calculated atomic ratios of Li/Co and Al/Co, are 1.01 and 0.03, respectively, suggesting successful renovation and separation of LiCoO_2 phase despite of the single synthetic step. In addition, the Al weight percentage of 0.8% indicates that the major impurity of the prepared material is either electron-conducting carbon or binder. Because the binder also contains abundant carbons, the carbon elemental analysis is not performed.

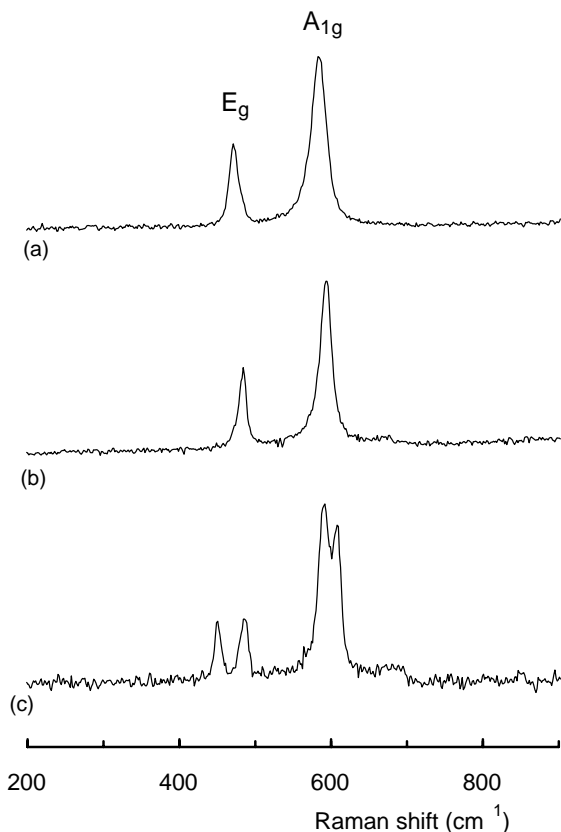


Fig. 3. Raman spectra of (a) the layered LiCoO_2 reference powder, (b) the renovated LiCoO_2 phase, and (c) the spinel $\text{Li}_{1-x}\text{CoO}_2$ reference powder.

Fig. 3 shows the Raman spectra of the layered LiCoO_2 phase (space group $R\bar{3}m$), the prepared LiCoO_2 phase, and the spinel $\text{Li}_{1-x}\text{CoO}_2$ phase (space group $Fd\bar{3}m$). While the layered LiCoO_2 phase exhibits two Raman active modes of E_g and A_{1g} at 471 and 584 cm^{-1} , respectively, the spinel $\text{Li}_{1-x}\text{CoO}_2$ phase exhibits four Raman active modes of $2F_{2g}$, E_g , and A_{1g} at 450 , 485 , 590 and 607 cm^{-1} , respectively [9].

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Co K-edge XANES analyses of the prepared material and reference compounds containing various cobalt valencies were performed to evaluate the exact cobalt valency in the prepared material. As shown in Fig. 4, the photon energies of the pre-edge and the black line for the prepared material are a little inferior than those of the layered LiCoO_2 phase and superior than those of Co_3O_4 . Because the layered LiCoO_2

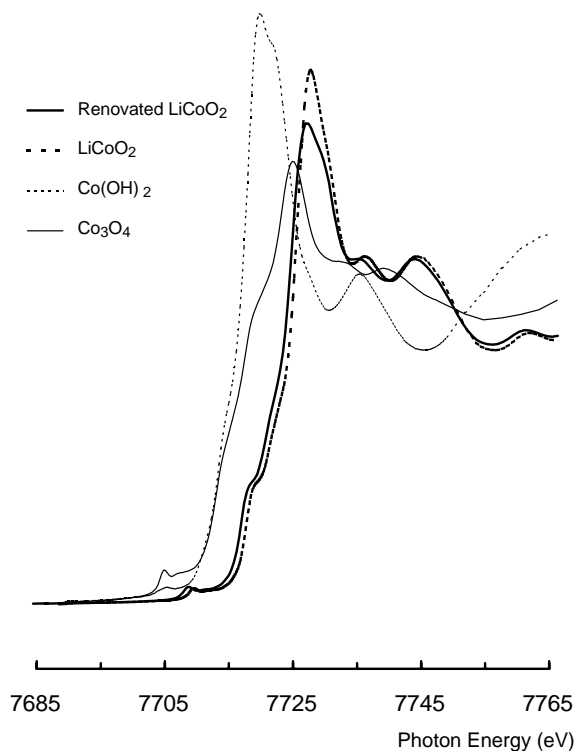


Fig. 4. Co K-edge X-ray absorption near edge structure (XANES) spectra for the renovated LiCoO_2 phase and reference compounds.

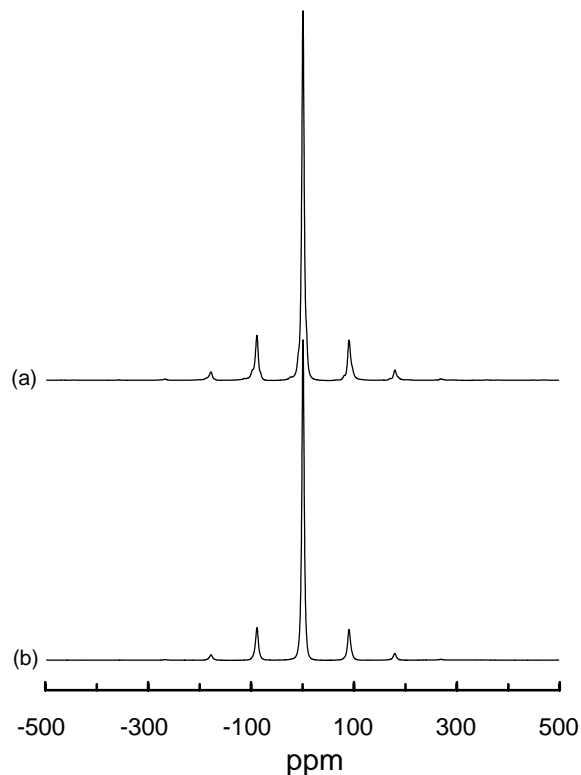


Fig. 5. ^7Li MAS NMR spectra of (a) the layered LiCoO_2 reference powder and (b) the renovated LiCoO_2 phase. All spectra were acquired at room temperature with sample spinning speed of 14 kHz .

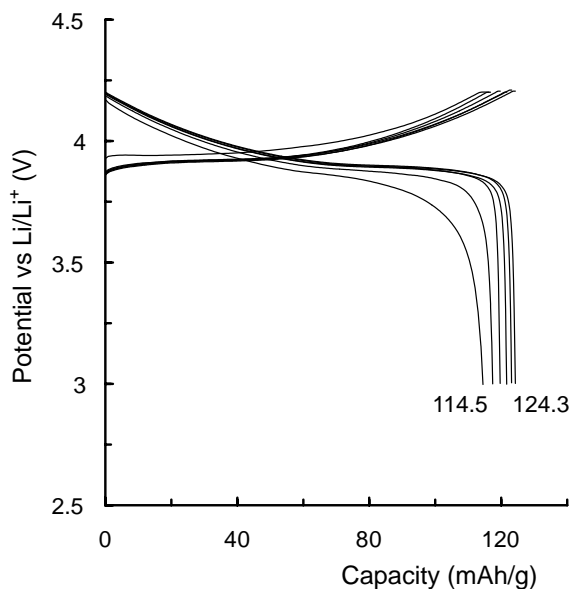


Fig. 6. Voltage vs. capacity profiles of 1st, 5th, 10th, 20th, 30th, and 40th cycles at the $C/5$ rate with Li metal anode and 1.0M $\text{LiPF}_6/\text{EC}/\text{EMC}$ electrolyte for the renovated LiCoO_2 phase.

phase and Co_3O_4 have Co^{3+} and $\text{Co}^{2.7+}$, respectively, the prepared material has the interposed cobalt valency between 2.7 and 3.0.

As shown in Fig. 5, the same appearance in ^7Li MAS NMR spectra between the layered LiCoO_2 phase and the renovated LiCoO_2 phase confirms again the preparation of layered LiCoO_2 phase upon the hydrothermal treatment of the spent cathode electrode.

Fig. 6 shows the 1st, 5th, 10th, 20th, 30th, and 40th charge–discharge curves of the renovated LiCoO_2 phase. A potential plateau around 3.9 V shown in both charge and discharge profiles is one of the typical properties for the layered LiCoO_2 phase, which corresponds to the reversible two-phase reactions for $0 < x < 1/4$ in $\text{Li}_{1-x}\text{CoO}_2$ in a topotactic manner [10–12]. Discharge capacities for the 1st and 40th cycles for the renovated LiCoO_2 phase display 114.5 and 124.3 mAh/g. It means that the renovated LiCoO_2 phase is simply obtained by the hydrothermal treatment of the spent cathode electrode in a single synthetic step, its battery performance is quite encouraging.

4. Conclusion

Simultaneous separation and renovation of LiCoO_2 cathode material are carried out in a single synthetic step by the hydrothermal treatment of spent LiCoO_2 electrodes. Because the mechanism proposed for the hydrothermal reaction is fully based on “dissolution–precipitation” mechanism, no scraping procedure is applied to divide spent LiCoO_2 electrodes into LiCoO_2 , electron-conducting carbon, binder, Al current collector, and separator. Although the separation of LiCoO_2 is not completely achieved, the estimated properties show the renovated LiCoO_2 phase to be encouraging as a cathode material for lithium rechargeable batteries. Therefore, our technology can be expected to serve as an effective route for the recycling of spent lithium rechargeable batteries.

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