

# Short-term and High-performance Recycling of Cathode Material from Spent Lithium Ion Batteries

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**Abstract.** In the industrial practice of spent lithium-ion battery recycling, mechanical separation, pyrometallurgy and chemical dissolution technologies are often used to achieve the separation and recovery of cathode materials, but there are problems such as low material dissociation rate, low recovery rate, high energy consumption, serious lithium loss, and impurity ion embedding. In this paper, supercritical CO<sub>2</sub> fluid was used to strengthen the separation of the cathode active material from the aluminum foil in the spent lithium-ion battery to achieve direct and efficient recovery of the active substance. The analysis of charge and discharge, AC impedance and differential capacitance curves show that the electrode of supercritical recovered material has higher ion diffusion coefficient and better redox reversibility, so it has higher charge and discharge capacity and better cycle stability than the traditional high-temperature calcined recovered material.

**Keywords:** Recycling; cathode material; spent lithium-ion batteries; short-term.

## 1. Introduction

In current recovery methods, the cathode material is mainly recovered by pyrometallurgy, which is dissolved with acid and then chemically precipitated. The use of large amounts of acid and alkali solutions creates additional waste while complicating the recycling process. What's more, in such a destructive recycling process, the usable energy in the active material particles is lost<sup>[1]</sup>. Recently, there has been increasing interest in the direct recycling of cathode materials, which is relatively a green recycling idea that simplifies the recycling process and preserves the embedded energy<sup>[2]</sup>. Sloop found that there was no need for calcination by fire method, and there was no damage or radical change to the material structure caused by wet treatment<sup>[3]</sup>. Hydrometallurgy can complete the direct restoration of the waste cathode material.

The key technology of direct regeneration of cathode materials is to ensure the stoichiometric ratio of various metal elements, repair broken or collapsed crystal structures, and ensure the smooth flow of lithium ion channels. Yang Shi studied the direct restoration and recovery of waste LiCoO<sub>2</sub> materials through a simple high-temperature sintering method<sup>[4,5]</sup>, which eliminated a series of processes such as "acid leaching - precipitation - precursor preparation - re-synthesis materials" in traditional recycling methods, and directly added the corresponding stoichiometric Li<sub>2</sub>CO<sub>3</sub> through calculation.

## 2. Experimental Section

### 2.1 Recycling Process

The cathode electrode plate of the LiCoO<sub>2</sub>(LCO) battery was transferred to the supercritical fluid extraction(SFE) device, and after being sealed, CO<sub>2</sub> was pumped into the device. According to the capacity of the extraction reactor and the specific characteristics of the extracted material, the temperature was set at 38°C and the pressure was 10 MPa. Due to the high pressure, the supercritical fluid was fully in contact with the material inside the battery electrode and carried out material exchange. Static extraction and dynamic extraction were carried out alternately, static extraction was 30 min, dynamic extraction was 15 min, and the gas flow was 1.5 L/min. Then the

pressure was reduced and the temperature was lowered, so the electrolyte and the organic binder entered the collection kettle with the gas  $\text{CO}_2$ , and the gas-liquid separation was completed. Through mechanical shaking, the cathode active substance on the surface of the aluminum foil was completely shed, the aluminum foil was recovered, the flake active substance was cleaned and dried, and the cathode active substance powder was recovered. As the control group, materials recovered by high-temperature calcination were recovered by air calcination at  $500\text{ }^\circ\text{C}$ .

## 2.2 Material Characterization

The microstructure and particle morphology of all materials were analyzed with scanning electron microscopy (SEM, Hitachi). Inductively coupled plasma-optical emission spectroscopy (ICP-OES) (iCAP 7400, Thermo Scientific, USA) was used to determine the metal content. Carbon content test was analyzed by the means of a carbon sulfur meter TOC-VCPN-(SSM-5000A) of Shimadzu Company, Japan.

## 2.3 Electrochemical Test

The electrochemical performances of recovered  $\text{LiCoO}_2$  materials by calcination and supercritical carbon dioxide, noted as C-LCO and S-LCO respectively, were evaluated using a coin, which was assembled with a lithium anode electrode and a cathode electrode sheet. The recovered electrode was prepared with cathode material, acetylene black and PVDF dissolved in NMP solvent, and then covered to the Al foil to obtain the cathode electrode with about 20 mg active materials. The electrolyte consisted of  $\text{LiPF}_6$  dissolved in EC, DMC and DEC at the volume ratio of 1:1:1. The assembled cells were left for 10 h, then the batteries were tested with BTS-5 V/5 mA test system. The charge and discharge performance were tested in the range of 3.0 to 4.2 V. CV tests and EIS tests from 0.01 Hz to 100 kHz were conducted with electrochemical workstation (CHI660E, China).

## 3. Results and Discussion

### 3.1 Physicochemical Structure of the Recovered Materials

The SEM image of the recovered lithium cobaltate cathode material is shown in Fig.1. Fig. 1(a, b) shows the SEM images of recovered materials with different magnifications under supercritical conditions. Fig. 1 (c, d) shows the SEM images of recovered materials with different magnifications under calcination conditions.

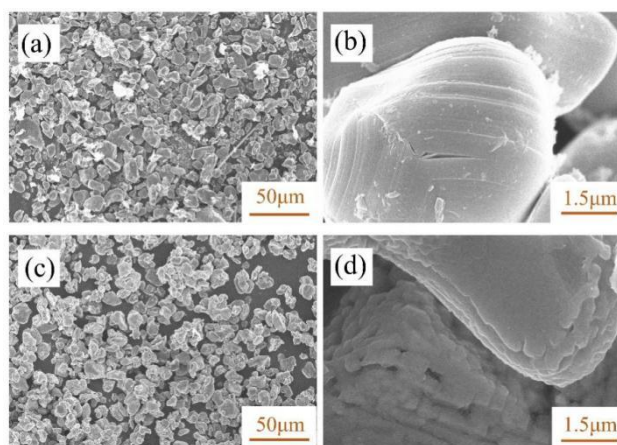


Fig. 1 SEM image of recovered LCO material under different magnifications:  
(a, b) recovered by SFE, (c, d) recovered by calcination

The surface of the cathode material after supercritical  $\text{CO}_2$  recovery treatment is flat and uniform and the color is dark. Under the condition of high magnification, the particle shape is ellipsoid, the

particle size is about 5  $\mu\text{m}$ , the particles are uniformly dispersed, and there is no agglomeration on the surface of the electrode plate. However, the morphology of recovered materials calcined at 500°C has undergone great changes, with layered distribution on the surface of the original uniform structure, accompanied by small pores, large differences in particle morphology, and further expansion of particle size distribution. For large particle size particles, the path of lithium ion migration from the interior to the surface is longer, which directly affects the reaction kinetic rate of lithium ion removal and embedding, and decreases the magnification performance of the material. In addition, the surface cavity caused by high temperature is a sign of lithium ion loss, and high temperature conditions are not conducive to the stability and recovery of lithium ions.

Table 1 shows the effects of different separation methods on the recovery efficiency of recovered materials and the content of aluminum impurities. From the table, it can be found that the separation method of supercritical CO<sub>2</sub> has significant advantages from the perspective of recovery efficiency and impurity content, and introduces a very small amount of aluminum impurities. Lithium depletion is one of the main reasons for the structural collapse of cathode materials and the deterioration of electrochemical performance during the battery cycle. It can also be found from the change in the proportion of lithium cobalt in the recovered material that the calcination method leads to the further deterioration of the lithium deficiency phenomenon. The ratio of lithium to cobalt for commercial use is 0.986 [6], the ratio of lithium to cobalt for the material obtained by supercritical CO<sub>2</sub> separation is 0.90, and the ratio of lithium to cobalt for the LCO material obtained by calcining is 0.87. From the carbon content measurement results, calcination can effectively remove conductive carbon, and the carbon content is only 0.79, while the supercritical extraction process does not lose C, which is basically the same as the carbon content of commercial batteries.

Table 1. Effects of SFE and calcination on the composition of recovered materials

Sample	Recovery efficiency (g/g)	Al impurities (wt.%)	Li/Co molar ratio	C content (%)
Recovered LCO by SFE	0.98	0.14	0.90	2.21
Recovered LCO by calcination	0.62	3.31	0.87	0.79

### 3.2 Charge and Discharge Performance of the Recovered Materials

Fig 2 shows the charge and discharge curve of recovered LCO materials at 3.0-4.2 V. It can be seen that for the cathode material obtained by high-temperature calcination, its initial specific discharge capacity is 63.3  $\text{mAh}\cdot\text{g}^{-1}$ , which is the highest among the same test samples. Compared with the cathode electrode sheet from the same spent lithium-ion battery after supercritical CO<sub>2</sub> stripping treatment, the specific discharge capacity of the cathode electrode material is above 80  $\text{mAh}\cdot\text{g}^{-1}$ . In the figure, the specific discharge capacity of the sample is 85.1  $\text{mAh}\cdot\text{g}^{-1}$ . No obvious discharge platform can be seen from the figure, which is the characteristic of lithium cobaltate material. Generally, the average value of the discharge smooth stage is the discharge platform, and it can be seen from the figure that the discharge voltage platform changes around 3.9 V.

The specific discharge capacity of supercritical recovered materials is shown in Fig 2 (b). The coulomb efficiency in the first 10 cycles is low, but that in the later cycles decreases slowly and can basically remain stable. After 100 cycles, the discharge capacity of S-LCO material decreases from 84.76  $\text{mAh}\cdot\text{g}^{-1}$  to 65.32  $\text{mAh}\cdot\text{g}^{-1}$ , and the corresponding capacity retention rate is 77.1%. Because the recovered material has not been replenished and repaired, the charge and discharge capacity is low, but from the comparison of the capacity retention rate of 100 cycles, the overall structural framework of the material is still stable, so the cyclic stability of the material is good.

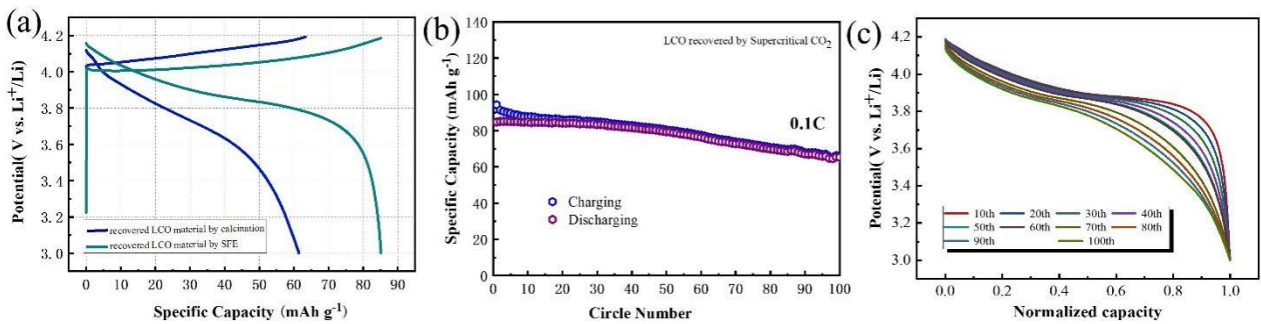


Fig. 2 Electrochemical performance of LCO electrodes recovered by supercritical fluid extraction and calcination: (a)Initial charge/discharge curves, (b)Cycling performances at 0.1 C rate and (c)Normalized discharge curves of S-LCO

The voltage drop of the recovered material is relatively slow as seen from Fig 2(c), which indicates that it has a good capacity retention rate or a more stable structure, and the crystal structure and original electrochemical properties of the material can be better maintained through supercritical treatment, which is of great significance for direct repair. It is worth noting that, compared with high-temperature calcined recovered materials from the same source, supercritical recovered materials have a higher specific discharge capacity, and the first coulomb efficiency is also higher than that of same-origin calcined materials. On the one hand, supercritical CO<sub>2</sub> extraction maintains the original energy of LCO, and does not adversely affect the composition and crystal structure of the recovered materials. On the other hand, studies have also shown that supercritical CO<sub>2</sub> treatment can assist the formation of oxygen vacancies, and these oxygen vacancies have the effect of activating the activity of the materials, thus improving the electrochemical performance of the recovered materials.

### 3.3 Analysis of AC Impedance of the Recovered Materials

Fig. 3 shows the AC impedance spectra of calcined recovered materials and supercritical recovered materials measured at 0.1 C cycle charging to 4.2 V. The whole AC impedance spectrum is composed of two parts: the semi-arc of the high frequency region and the inclined straight line of the low frequency region. *R<sub>s</sub>* is reflected at the intersection of the semi-arc and the real axis, representing the ohmic resistance, and *R<sub>ct</sub>* is the charge transfer resistance, which is related to the semicircle of the high frequency region, and can reflect the charge transfer speed at the interface. The fitted resistance values are listed in Table 2. The *R<sub>s</sub>* resistance of S-LCO electrode and C-LCO electrode has a small difference of 3.23 Ω and 3.13 Ω, respectively, while the *R<sub>ct</sub>* of S-LCO electrode and C-LCO electrode has a significant difference of 116.4 Ω and 216.7 Ω, respectively.

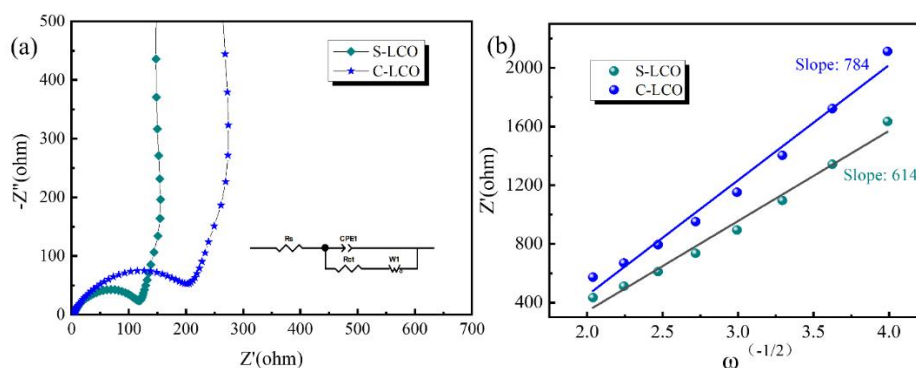


Fig. 3 Nyquist plots and  $w^{-1/2}$  relationship in the low frequency region for recovered LCO electrodes: (a) Nyquist plots of LCO electrodes reclaimed by SFE and calcination (Inset shows the equivalent circuit), (b)  $w^{-1/2}$  relationship in the low frequency region

The lithium ion diffusion changes corresponding to Warburg impedance can be qualitatively analyzed by slashes in the low frequency region [7, 8]. The slope of the S-LCO electrode is significantly lower than that of the C-LCO electrode, corresponding to a smaller  $\sigma$  value. It can be seen that the diffusion coefficient of lithium ions of S-LCO electrode is higher than that of C-LCO electrode, and the supercritical CO<sub>2</sub> treatment is conducive to the rapid diffusion of lithium ions.

Table 2. The impedance values of recovered LCO electrodes

Sample	$R_s$ ( $\Omega$ )	$R_{ct}$ ( $\Omega$ )
Recovered LCO by SFE	3.23	116.4
Recovered LCO by calcination	3.13	216.7

### 3.4 Recycling Process and Differential Capacity Curve Analysis of the Recovered Materials

Through the charge and discharge test of the recovered material S-LCO electrode in 100 cycles, the cycle process of the charge and discharge stage was analyzed, as shown in Fig. 4. In the initial cycle, the oxidation peak of LCO material at 3.95 V shifts to low potential significantly, and it basically stabilizes from the 7th cycle, and no longer shifts to low potential, which corresponds to the rapid decay of charging capacity in the first ten cycles of the cycle curve. After 20 cycles, the peak of the oxidation reaction gradually shifts to the high-potential region, and returns to the original position at 100 cycles, but during this period, the peak strength is gradually weakened, and the peak site is gradually widened, indicating that the degree of polarization gradually increases.

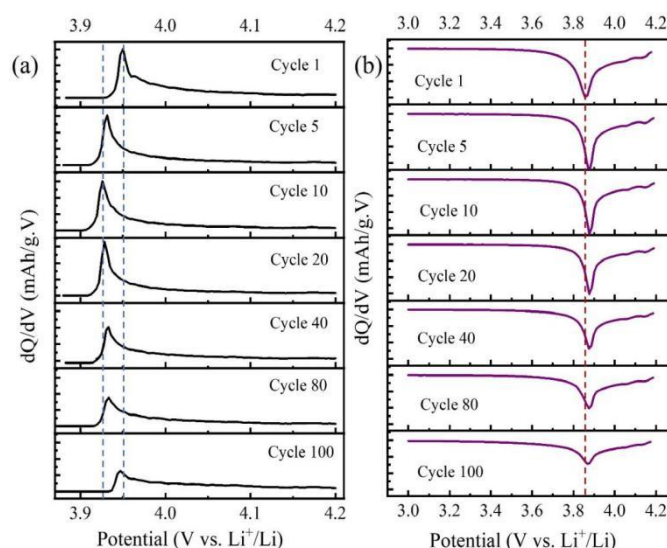


Fig. 4 Analysis of cycle process of S-LCO electrode in charge/discharging phase

Corresponding to the charging stage, the peak of the reduction reaction in the discharge process is located at 3.85 V, and the peak excursion experiences a slight change of first increasing and then decreasing. The overall excursion amplitude is very small, but after 40 cycles, the peak intensity decreases significantly and the peak excursion gradually widened. The oxidation peak and reduction peak of commercial LCO materials are 4.2 V and 3.7 V respectively. Compared with this, the oxidation peak of recycled materials has a lower potential and insufficient oxidation reaction, resulting in low charging capacity [6,9]. The difference between oxidation peak and reduction peak displacement is generally used to measure the reversibility of positive electrode materials. The redox peak displacement of supercritical recovered materials is only 0.1V, which has relatively good reversibility.

#### 4. Summary/Conclusion

In conclusion, the various testing results prove that we successfully recovered the LiCoO<sub>2</sub> from spent lithium ion battery by using supercritical CO<sub>2</sub> extraction and assistant mechanical oscillation. Compared with the LiCoO<sub>2</sub> recovered by calcination, the S-LCO cathode material performed much better in cycle stability and rate capacity. What's more, the recovered materials obtained from supercritical CO<sub>2</sub> treatment show certain advantages in crystal structure, composition and microstructure, maintaining the original energy of LCO, and supercritical CO<sub>2</sub> treatment is conducive to charge conduction and rapid diffusion of lithium ions, and the redox reaction polarization is small during the cycle, and the recovered materials have direct repair potential.

#### 5. Acknowledgements

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