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# Ultrasound-assisted Hydrothermal Renovation of $LiCoO_2$ from the Cathode of Spent Lithium-ion Batteries

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$LiCoO_2$ powders are separated from aluminum sheet of spent $LiCoO_2$ electrodes and renovated by ultrasound radiation. $LiCoO_2$ was obtained from electrode materials by burning off carbon and binder of the spent $LiCoO_2$ electrodes at 500 ºC for 1 h. Used $LiCoO_2$ material was renovated by means of hydrothermal ultrasound radiation in a concentrated LiOH solution at 80ºC, ultrasonic power 600W and ultrasonic radiation time for 6h. The experimental results show that the ultrasonic shearing effects produced hydroxyl radical which could help achieve the removing of Polyvinylidene fluoride (PVDF)，the renovated $LiCoO_2$ had high degree of crystallinity, fine layered structure, good dispersion of particles and improved electrochemical cycle performance. The renovated $LiCoO_2$ phase exhibits the first discharge capacity of 133.5mAh/g and the discharge capacity retention of 99.5 After 40 cycles which can reach electrochemical properties of commercial batteries.

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**Keywords:** spent lithium-ion batteries; $LiCoO_2$; ultrasound radiation; Polyvinylidene fluoride;

## 1. INTRODUCTION

$LiCoO_2$ 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. Therefore, the production of lithium rechargeable batteries as those power sources is exponentially increased. The tremendous growth in the use of rechargeable lithium ion batteries has stimulated efforts to recycle valuable components from spent batteries [1,2]. Since recycling of spent batteries may bring economic benefits[3-8]. Recovery of cobalt and lithium is one of primary objectives in recycling of spent LIBs, since cobalt is a rare and precious metal, and is a relatively expensive material compared with the other constituents of LIBs, and lithium is also vitally important in many industrial applications[9]. However, Acid/alkali wastewater, which produced in hydrometallurgical recycling process of spent lithium-ion battery, will cause serious pollution to the environment[10,11]. Furthermore, because the $LiCoO_2$ electrodes in the lithium rechargeable batteries do not have only $LiCoO_2$ but also electron-conducting carbon, binder and Al current collector, the recycling of spent $LiCoO_2$ electrodes using the conventional method should be more sophisticated[12-17]. A single recycling process can only achieve the destination of recovering a part of components or can only be one step of a whole procedure for recycling spent LIBs[18]. Therefore, combination of several single recycling processes is necessary to recover the $LiCoO_2$ from spent LIBs.

It is reported that renovated $LiCoO_2$ may indeed provide high quality grade recycled materials[19-26]. For instance, Ra et al. reported that depleted $LiCoO_2$ cathode material was recovered and renovated in a single synthetic step using electrochemical and hydrothermal reaction, called as Etoile-Rebatt technology [27,28]. S.G Zhu et al. studied a laboratory process, in which the spent $LiCoO_2$ active material was separated from spent cathodic material by scraping and renovated using hydrothermal method [29]. Therefore, in the course of trying to develop such a novel synthetic approach to achieve both the separation of $LiCoO_2$ from spent electrodes and the renovation of $LiCoO_2$ can be accomplished simultaneously. During the recycling procedure, the ultrasonic has been applied to effectively separate electrode materials, and control the particle shape and size of both the recycled cobalt compound and the prepared lithium cobalt oxide.

The focus of this work is to present the results of an attempt to separate $LiCoO_2$ from the anode plates without any scraping procedures and the renovation of the ideal layered $LiCoO_2$ using the ultrasound technology. In the study, TG、SEM、XRD and Raman analysis were utilized to analyze the crystal structure of $LiCoO_2$. The renovation mechanism of $LiCoO_2$ crystal structure was discussed.

## 2. EXPERIMENTAL

### *2.1. Material*

The experiment used recycled waste lithium-ion batteries from electronic waste recycling factories. First, the batteries were fully discharged and then split into isolate-positive aluminum foil. Lithium hydroxide (AR) and chemical reagents including hydrochloric acid and nitric acid were purchased from Sinopharm Chemical Reagent; the battery housing (CR2025, containing the spring plate and the spacer) and commercial diaphragm were purchased from American Celgard[30].

### *2.2 Experimental procedure*

The experimental procedure was schematized in Figure.1 Li-ion batteries were manually dismantled and physically separated into their different parts: anode plates, cathode plates, steel, separators. the anode plates were put into muffle and heated at 400 ºC for 60 min. Then used $LiCoO_2$ powder can be obtained by separated with aluminum sheet. 10.0g used $LiCoO_2$ powder was placed in a beaker and then 2.0 mol/L of LiOH solution was added to fmake 600 mL of mixed solution, and was renovated by means of ultrasound radiation under hydrothermal method in a concentrated LiOH solution at 80 ºC, ultrasonic power 600W, ultrasonic method “work 5s-stop 2s”, ultrasonic radiation for 6 h and then cooled to room temperature. The residue was washed several times with deionized water and dried at 80 ºC until constant weight. The obtained sample was collected for subsequent testing and battery production.

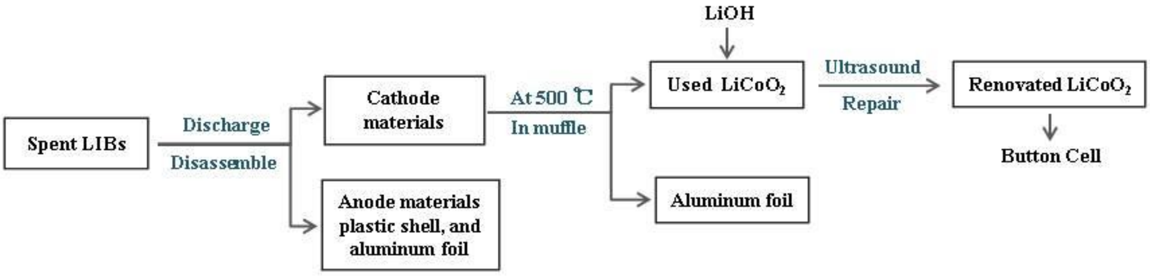

**Figure 1.** Schematization of renovated $LiCoO_2$ cathode material using the ultrasound technology

### 2.3. Material characterization

The thermal analyses were carried out on a Discovery TGA thermal analyzer. The X-ray diffraction (XRD) analysis was carried out using a D8 advance X-ray diffractometer with Cu Kα radiation ($\lambda$ = 1.5406 Å) operated at 30 mA and 30 kV. The diffractograms were recorded in the 2θ range of 10° to 80° with 0.02° resolution and scanning rate of 2°/min. scanning electron microscope (SEM) images were obtained using a Japan Hitachi S-4800 microscope. To determine the contents of lithium and cobalt, elemental analysis was carried out by using ICPs-Optima 2100 DV ICP spectrometer. Electrochemical tests were carried out at room temperature using coin cells. The renovated $LiCoO_2$ powders were mixed with 10 wt.% acetylene black (AB) and 10 wt.% PVDF binder dissolved in N-methyl-2-pyrrolidone (NMP) until a slurry was obtained. The slurry was laminated on an Al foil using a blade. The electrolyte was a 1M solution of $LiPF_6$ in ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1, in wt.%) obtained from Zhangjiagang Guotai-Huarong new chemical material Co., Ltd. The anode was a lithium foil. CR2025-type coin cells were assembled in an Ar-filled glove box. Charge/discharge cycle tests were performed using BTS-5V1A (Neware Co., Ltd, China) at a constant current density and at the C/5, 1C and 5C rate between 2.7V and 4.3V.

## 3. RESULTS AND DISCUSSION

The used cathode of Li-ion battery which includes $LiCoO_2$, the aluminum foil, Polyvinylidene fluoride (PVDF) and carbon powders must be separated to get $LiCoO_2$. Due to PVDF is the binder which used to glue the $LiCoO_2$ powders to the aluminum foil and mainly composed of organic material, so calcination is an excellent way to eliminate PVDF and removing carbon powders [31]. The volatilization temperature of PVDF is 500ºC but low temperature is suitable for other organic compounds. So the cathode active material was heated at 500 ºC for 1 h, $LiCoO_2$ powders can be easily gained by separated from the aluminum foil, the next step is to repair the structure of used $LiCoO_2$ by means of ultrasound radiation under hydrothermal method in a concentrated LiOH solution.

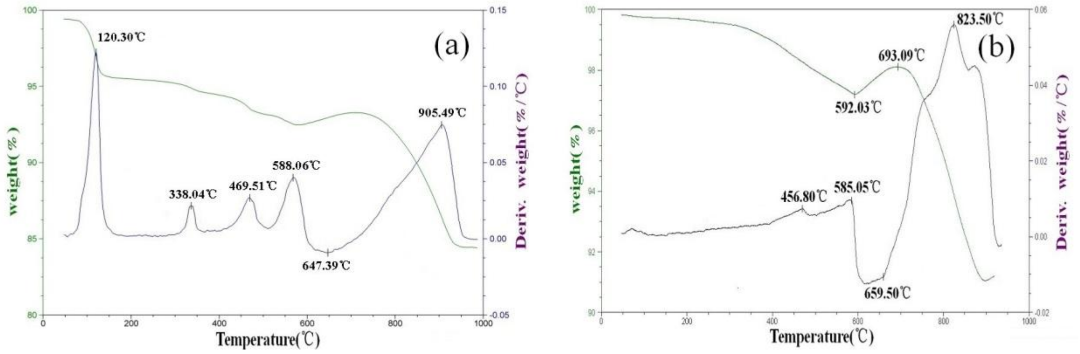

**Figure 2.** TGA plot of the thermal decomposition of $LiCoO_2$ before (a) and after (b) calcination

The untreated $LiCoO_2$ and the calcined $LiCoO_2$ samples were characterized by TGA. Figure.2 (a) and Figure.2 (b) are untreated $LiCoO_2$ and the calcined $LiCoO_2$ TGA curves, respectively.

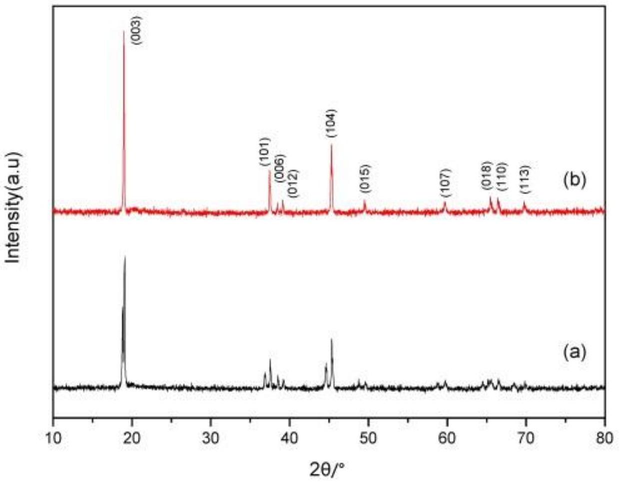

**Figure 3.** X-ray diffraction patterns for (a) the used $LiCoO_2$ powder and (b) the renovated $LiCoO_2$ powder

According the substances that may exist in samples and their physicochemical properties[32-35], compare with the weight-loss temperature, We can get the weight-loss zone, there is the residual electrolyte which contains $LiPF_6$ and Ethylene carbonate on the surface of $LiCoO_2$ powders, the decomposition temperature of $LiPF_6$ is 107 ºC to 133ºC, the decomposition temperature of Ethylene carbonate is 326ºC to 350ºC, the decomposition temperature of PVDF is 430 ºC to 492ºC, The decomposition temperature of $LiCoO_2$ is 570ºC to 614 ºC and break up into $Co_3O_4$ and $Li_2CO_3$. At last, about 790 ºC to 915 ºC, $Co_3O_4$ are converted into CoO. In Figure.2 (a) the organic compound can be found at the temperature of 120.3℃, 338.04 ºC, and 469.51 ºC obviously, but in In Figure.2 (b), there is no organic compound exits before 456.80 ºC. The main reason is that $LiPF_6$ and Ethylene carbonate are decomposed in the calcined process and most of PVDF are decomposed. Residues of PVDF can be decomposed in the process of ultrasound radiation under hydrothermal method in a concentrated LiOH solution. The organic matter on the surface of $LiCoO_2$ was removed effectively which helps to get the $LiCoO_2$ powders easily and reduce the particles gathered.

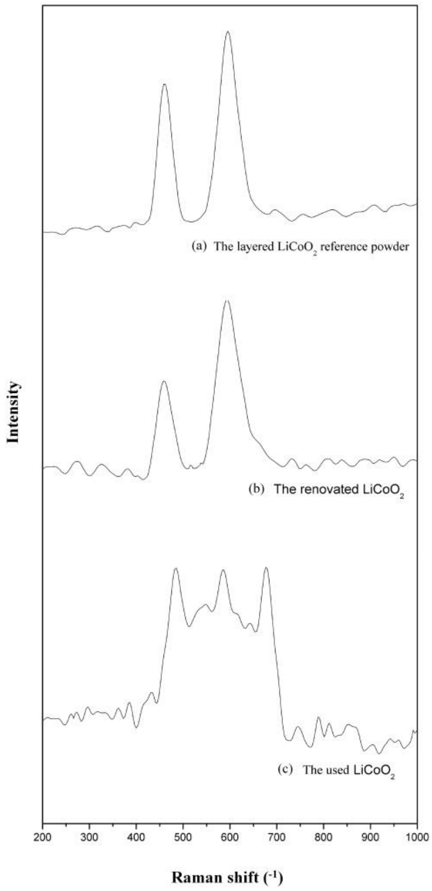

**Figure 4.** Raman spectra for (a) the layered $LiCoO_2$ reference powder, (b) the renovated $LiCoO_2$ powder, and (c) the used $LiCoO_2$ powder

The XRD patterns of the used $LiCoO_2$ powder, as well as the renovated $LiCoO_2$ powders bulk phase are shown in Figure.3. It can be observed from Figure.3 that all the patterns can be indexed to the α-$NaFeO_2$ structure (JCPDS No. 50-0653) as all the fingerprint peaks, viz., 003, 101, 006, 012, 104, 015, 018, 110, and 113, are clearly assignable. All XRD peaks are characteristic for the space group R-3m as layered $LiCoO_2$ phase. Both of the $LiCoO_2$ phases crystallize in the hexagonal system ( a=2.816A, c=14.04A). No XRD peaks of possible impurities, such as $Co(OH)_2$ and $Co_3O_4$ phases, are detected.

The intensity ratio of the (003) to (104) lines can indicate the cation mixing of the layered structure, which has strong influences on the electrochemical properties[36,37]. Cation disordering occurs into the structure via exchange of Li and Co ions between 3a and 3b sites, and increased cation disordering can be identified by the decreasing intensity ratio of (003) to (104) peaks. The intensity ratio between the (003) and (104) reflections vary significantly during lithium insertion/extraction in $LiCoO_2$. It is convenient to use the I(003)/I(104) value as an indicator of repeated Li-insertion and extraction capacities, the higher the I(003)/I(104) value, the better the Li-insertion and extraction capacities. The I(003)/I(104) value of the renovated $LiCoO_2$ is larger than that of the used $LiCoO_2$, indicating that the renovated $LiCoO_2$ sample has a good prerequisite for achieving reasonable Li insertion and extraction capacities.

Raman spectra can provide information on both structural changes of the polymer in the membrane and interactions between ionic liquid and the membrane. The Raman spectra for the layered $LiCoO_2$ reference phase, the renovated $LiCoO_2$ phase, the used $LiCoO_2$ phase are compared in Figure.4. It is clear that the intensity of Raman band at 485cm$^{-1}$ and 605cm$^{-1}$ has significantly increased in the spectra of the membranes in favor of the repair of the $LiCoO_2$. It indicates that the degree of crystallinity of the $LiCoO_2$ was increased. As shown in Figure.4, it appears that the recycled $LiCoO_2$ powder consists of just the layered $LiCoO_2$ phase without any impurities.

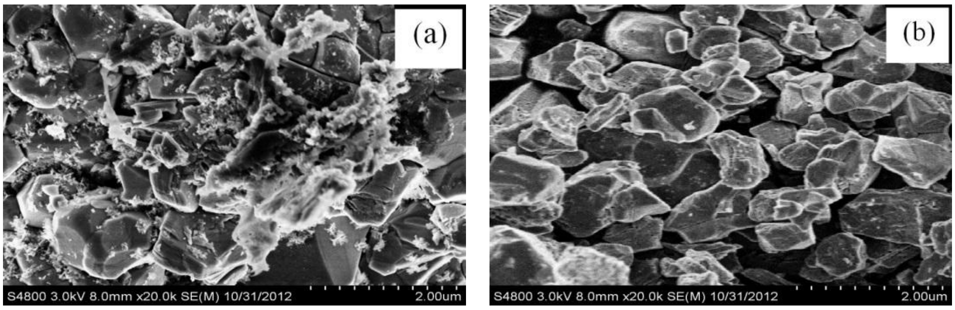

**Figure 5.** SEM images for the morphology of (a) the used $LiCoO_2$ powder and (b) the renovated $LiCoO_2$ powder

Figure.5 shows the SEM images of used and renovated $LiCoO_2$ samples obtained. In Figure.5 (a)**,** it was found that floccules appear in the SEM image of used $LiCoO_2$. They attached over the surface of $LiCoO_2$, which may be caused by oxidation and decomposed of organic substances in the electrolyte. From Figure.5 (b), we can see the size of the recovered $LiCoO_2$ with homogenous distribution and the floccules over the surface of the $LiCoO_2$ has significantly reduced after ultrasound radiation. It can be considered that the ultrasonic treatment enables floccules to be separated from the $LiCoO_2$ particles and to achieve degradation.

The morphology difference between the used and the renovated $LiCoO_2$ was mainly caused by the ultrasonic radiation. Cavitation cannot only lead to the production of free radicals but also the occurrence of microstreaming. The former can promote organic degradation, and the latter is able to accelerate the heat and mass transfer process accompanying the renovation process. Shock waves from cavitation in liquid-solid slurries produce high-velocity inter-particle collisions. Therefore, the agglomerates on the surface of the $LiCoO_2$ can easily be broken.

The flow field analysis of $LiCoO_2$ particles and PVDF is shown in Figure 6.

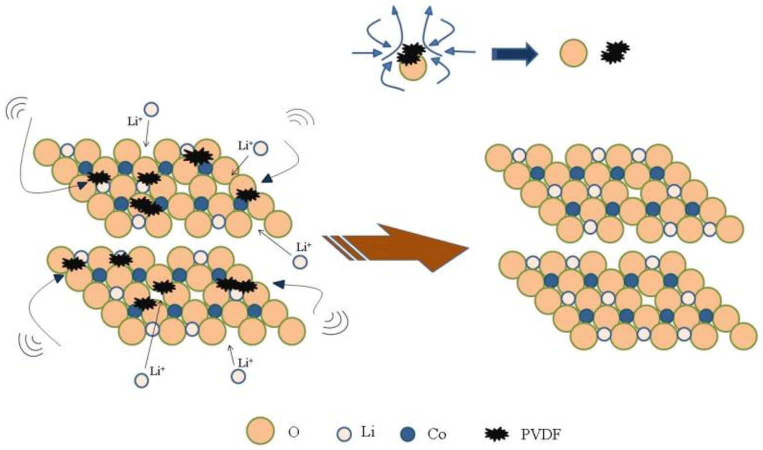

**Figure 6.** The flow field analysis of $LiCoO_2$ particles and PVDF

Ultrasonic wave can produce cavitation effect and acceleration effect in liquid, and appear lots of cavitation bubbles[38]. The force situation of PVDF from the surface of $LiCoO_2$ can be analyzed by a single particle and particles. Cavitation effect will produce sparse effect and compression effect for the liquid medium, and to a certain extent, it will destroy the liquid form. The stresses produced include shear stress and normal stress. Shear stress is related to the flow field which appeared near the surface of the $LiCoO_2$ particles when cavitation bubble was collapsing. Shear stress is related to the velocity components of the flow field which Parallel to the surface from the surface of $LiCoO_2$ particles. This can be expressed as flow:

$$\bar{\tau} = \eta_{sh} \frac{dv}{dx}$$

$\bar{\tau}$ represent shear stress in the formula, $\eta_{sh}$ represent shear viscosity, $d\upsilon/dx$ represent velocity gradient which is perpendicular to the surface. For PVDF on the surface of $LiCoO_2$, it protruded out of the surface of $LiCoO_2$ and velocity gradient of the flow field related to the cavitation has a high spatiotemporal efficiency. Therefore, the shear forces on PVDF will be more intense than on the surface of $LiCoO_2$, and speeded up $LiCoO_2$ and PVDF separate.

From the function angle of particles, ultrasonic wave and pressure field of collapsing of cavitation bubble act on $LiCoO_2$ particles together by the liquid, as make collides mutually and rubs, which increased the probability of stripping of PVDF from the surface of $LiCoO_2$.

$Li^+$ disaffiliated from the crystal of used $LiCoO_2$ lead to the lack of $Li^+$ in the structure of $LiCoO_2$. In the experiment of ultrasonic irradiation, the system provides $Li^+$ in LiOH solution. There is a differences exist of $Li^+$ in the crystal interface of $LiCoO_2$, the ion concentration of Lithium on solid-phase is far less than in liquid phase, which provide a new system environment in the mass transfer process. Ultrasonic wave was used for removing PVDF effectively which adhere to the surface of $LiCoO_2$, the "Channel" on the surface of $LiCoO_2$ was opened and $Li^+$ was re-embedded into the

$LiCoO_2$ layer, Under the partial high temperature and voltage of ultrasonic cavitation, spent $LiCoO_2$ fused and achieved in order cation rearrangement of $Co^+$ and $Li^+$ in LiOH., atoms were arranged in order and recovered its good layered structure.

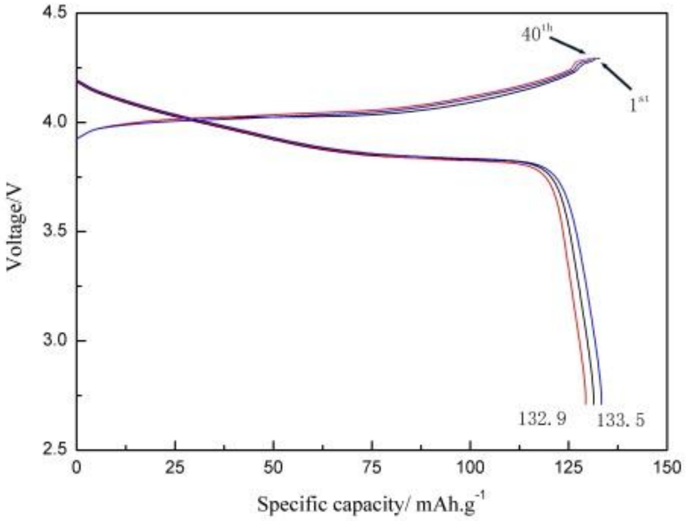

**Figure 7.** Charge–discharge curves of $LiCoO_2$ at 0.2C

Renovated $LiCoO_2$ was assembled into button battery for electrochemical performance tests. The coin-type cells were charge/discharged between 2.7 V and 4.3 V at 0.2C rate. The first charge-discharge curves for the renovated $LiCoO_2$ are shown in Figure.7. The charge capacity in the first cycle is 134.2mAh/g and the discharge capacity is 133.5mAh/g. The first-time charge and discharge efficiency was 99.5 %. The renovated $LiCoO_2$ exhibits the discharge capacity maintained 98.4 % after 40 cycles, the discharge capacity is still 132.9mAh/g.

## 4. CONCLUSIONS

In this paper, the technology of renovation of lithium cobalt oxide from the cathode of spent lithium-ion batteries by hydrothermal ultrasound radiation was studied. the main conclusions were

(1) $LiCoO_2$ powders can be easily gained by separated from the aluminum foil by heating at 500 ºC for 1 h and renovated by ultrasound radiation in a concentrated LiOH solution at 80 ºC for 6 h .

(2) The restoration of $LiCoO_2$ crystallization degree enhancement and the layered structure is more evident, that ultrasonic water dicating to used $LiCoO_2$ crystal structure repair has remarkable effect.

(3) Ultrasonic wave can produce cavitation effect and acceleration effect in liquid which increased the probability of stripping of PVDF from the surface of $LiCoO_2$. The ultrasonic shearing

effects also promoted the mass transfer process of $Li^+$. As a result, the average content of $Li^+$ from the spent $LiCoO_2$ was increased.

(4) The charge capacity in the first cycle is 134.2mAh/g and the discharge capacity is 133.5mAh/g. The first-time charge and discharge efficiency was 99.5 %. After 40 cycles, the discharge capacity is still 132.9mAh/g.

(5) Our technology can be expected to serve as an effective route for the recycling of spent lithium rechargeable batteries.

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