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Short Communication

Renovation of Lithium Cobalt Oxide from Spent Lithium Ion Batteries by an Aqueous Pulsed Discharge Plasma

Shuguang Zhu[1,2,*], *Ying Qin*[1], *Jin Zhang*[1]

[1] Anhui Advanced Technology Research Institute of Green Building, Anhui Jianzhu University, Hefei 230601, China
[2] Shanghai Cooperative Centre for WEEE Recycling, Shanghai Second Polytechnic University, Shanghai 201209, China
[*]E-mail: 286537056@qq.com

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Used $LiCoO_2$ cathode material in spent lithium ion batteries was renovate in 0.1 M LiOH solution using aqueous pulsed discharge plasma for 30 min, in which aqueous pulsed discharge plasma was used for the first time as an alternative process to renovate its electrochemical characteristics. After treatment, the microstructure of spent and renovated $LiCoO_2$ has been studied by Raman spectroscopy, and the results obtained were compared with those by XRD and SEM, respectively. Experimental results showed that electrohydraulic cavitation could be effectively used to remove organic substance stuck on $LiCoO_2$ surface and facilitate the ordered crystalline layer compound processes. The validity of the process has been evaluated by electrochemical test. Its charge capacity was 132.9 mAh g^{-1} in the first cycle and the discharge capacity was 126.7 mAh g^{-1}, which was retained 97.2 % after 50 cycles.

Keywords: Spent lithium-ion batteries; $LiCoO_2$; aqueous pulsed discharge plasma; renovation

1. INTRODUCTION

Lithium-ion batteries (LIBs) are used extensively in various areas as rechargeable energy supplier. The usage amount of LIBs has increased sharply in recent years because of their updating function and decreasing cost. However, a lithium-ion battery has a limited life span of about 500 cycles [1]. In consequence, the spent LIBs have been generated in astonishing quantities, which has stimulated efforts to recycle valuable components from them. Lithium cobalt oxide ($LiCoO_2$) is commonly used as an active cathodic material for almost all commercialized LIBs [2]. In order to efficiently recover Li and Co, various hydrometallurgical and pyrometallurgical processes have been reported [3-19].

Many efforts have made to try to separate and renovate $LiCoO_2$ from spent LIBs by simple procedures, such as electrochemical-hydrothermal reaction [1], hydrothermal treatment [20] and ultrasound radiation[21, 22]. It is reported that renovated $LiCoO_2$ may indeed provide high-quality-grade recycled materials [1, 20-22]. For instance, Ra et al. [1] 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. Zhang et al. studied a laboratory process, in which the spent $LiCoO_2$ active material was renovated and simultaneously separated from spent cathodic material in a single synthetic step using ultrasound radiation [22]. 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.

However, the above methods are batch processing spent LIBs, which can not achieve continuous operation. In the course of trying to develop a novel approach for renovation of $LiCoO_2$, the aqueous pulsed discharge plasma process seems to be a good choice. The aqueous pulsed discharge plasma process is pulsed high-voltage discharge in the time scale of microseconds or nanoseconds in an aqueous solution, which favors non-thermal plasma, to produce chemically active species, i.e. high-energy electrons, ·OH, ·H, O·, O_3, H_2O_2, and ionic species. Simultaneously various physicochemical phenomena occur, whose effects are similar to electro-hydraulic cavitation, UV-radiation, shock waves and supercritical water conditions [23, 24]. The aqueous pulsed discharge plasma process can provide a source of energy which can be used to enhance a wide range of chemical processes [25-29]. For instance, cavitation refers to the rapid growth and implosive collapse of bubbles in a liquid resulting in an unusual reaction environment within and in the vicinity of bubbles [29]. The concentration of energy upon collapse results in extreme localized conditions including high temperatures and pressures inside the cavity. Under such conditions, the renovated $LiCoO_2$ is simply obtaineda from spent LIBs using a relatively simple reactor.

In this work, we present the results of the removal of the organic component and the renovation of the ideal layered $LiCoO_2$ from spent $LiCoO_2$ electrodes by an aqueous pulsed discharge plasma.

2. MATERIALS AND METHODS

2.1 Materials

The spent LIBs used in this study was supplied by TES-AMM (Shanghai) Co., Ltd. A LIB comprises an anode, a cathode, organic electrolyte, and a separator. Carbon graphite and $LiCoO_2$ powders were fixed on Cu and Al foils as anode and cathodes, respectively. After discharging, the $LiCoO_2$ powder used in this work was obtained from the cathode by mechanical separation. LiOH used for experiment was analytical grade (A.R.) reagent.

2.2 Experimental procedure

The recycling procedure was schematized in the flow chart of Fig. 1. The pulsed high-voltage power source consisted of a transformer, voltage rectifying circuit, rotating double spark gap, and storage capacitance (see Fig. 2). The experimental apparatus was applied to a storage capacitor (3 nF) to obtain an applied voltage of 0-50 kV with a frequency of 150 Hz through the rotating spark-gap switch, and the energy of one pulsed discharge with approximately 100 ns rise time and about 500 ns duration can be calculated from current and voltage waveforms via a digital oscilloscope (Lecroy LT264) with a high-voltage probe (INC P150-GL/5k) and a current transducer (Waring-3525)[29].

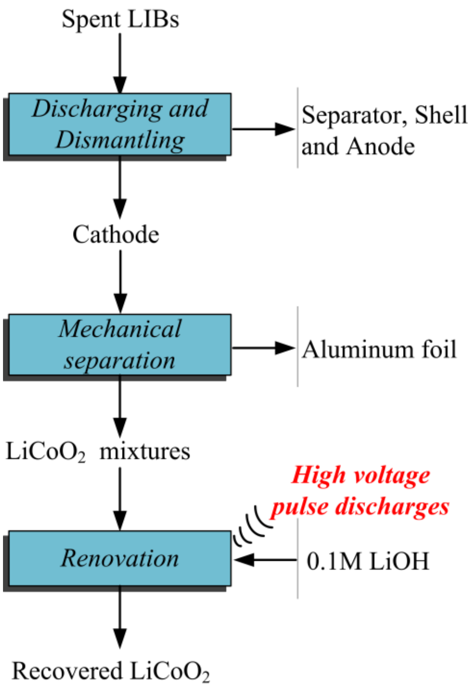

Figure 1. Schematization of renovated $LiCoO_2$ cathode material by an aqueous pulsed discharge plasma

The spent $LiCoO_2$ cathode material was conducted in a laboratory-made plexiglas cylinder. The reactor has dimensions of ϕ60 mm×130 mm and was fitted with an needle-plate reactor and a positive needle electrode (see Fig. 2). The positive needle electrode was composed of five stainless steel acupuncture needles (ϕ0.30 mm×75 mm, Hefei medical instruments Co., Ltd.), which were placed approximately 1.5 cm above the bottom of the reactor, and were connected with five microtubes. When the gas bubbled through the microtubes into the reactor, the gas surrounded the needle tip and formed gas bubbles to homogenize the solution with an ultrasonic effect from shock waves in a pulsed discharge to stabilize $LiCoO_2$ suspension. The spent $LiCoO_2$ cathode material was immersed in 0.1 M LiOH solution. After a treatment of 30 min, the renovated $LiCoO_2$ in the reactor was filtered and washed three times using doubly distilled water to remove residual LiOH solution, and then dried at 80 °C for 8h.

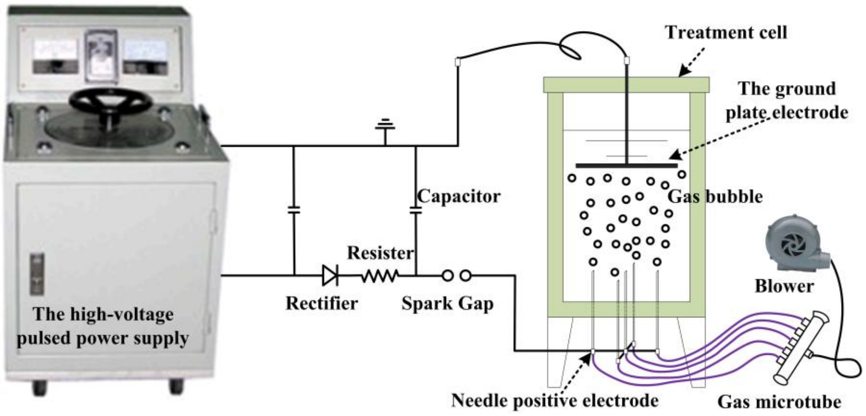

Figure 2. Schematic diagram of the experimental set-up

2.3 Analysis Methods

The structure of the renovated $LiCoO_2$ was characterized by X-ray diffraction pattern analyses (XRD, Bruker D8 Advance, GER). The diffractometer equipped with Cu Kα radiation (λ = 1.5406 Å), employing a scanning rate of 0.02° s^{-1} and 2θ ranges from 10° to 80°. The accelerating voltage was set at 40 kV with a 40 mA flux. Diffraction patterns were compared with reference data in the ICDD PDF-2 database. The Raman spectra was employed to identify the crystalline phase of the spent and renovated $LiCoO_2$ at room temperature using a Rainshaw Invia triple spectrometer. The wavelength of the Ar/Cr laser used for this experiment was 5145 Å. Surface aspects were observed with scanning electron microscope (SEM, Hitachi S-4800, Japan).

Electrochemical tests were performed at room temperature using coin-type cells. The renovated $LiCoO_2$ powders were mixed with 10 wt.% acetylene black (AB) and 10 wt.% poly-vinylidene fluoride (PVDF) binder dissolved in N-methyl-2-pyrrolidone (NMP) until a slurry was obtained. The mixture was pasted on aluminum foil to prepare the test electrode; pure lithium piece was used as auxiliary electrode. 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. CR2025-type coin cells were assembled in an Ar-filled glove box. The coin-type cells were charged and discharged at the C/5 rate between 2.8 and 4.2V using BTS-5V1A (Neware Co., Ltd, China).

3. RESULTS AND DISCUSSION

The active positive pole material of $LiCoO_2$ in LIBs commonly refers to the layered structure materials, which is conducive to the lithium ion migration. The changes of crystal structure of $LiCoO_2$ in the aqueous pulsed discharge plasma process was clearly identified by the XRD analysis as shown in the Fig. 3. It can be observed from Fig. 3 that the patterns of spent $LiCoO_2$ powder and renovated $LiCoO_2$ can be indexed to the α-$NaFeO_2$-type structure (JCPDS No. 50-0653) as all the fingerprint peaks, viz., (003), (101), (006), (012), (104), (108), (110), and (113), are clearly assignable. At the same time, the XRD data also displays that the renovated $LiCoO_2$ material has no new crystalline phase.

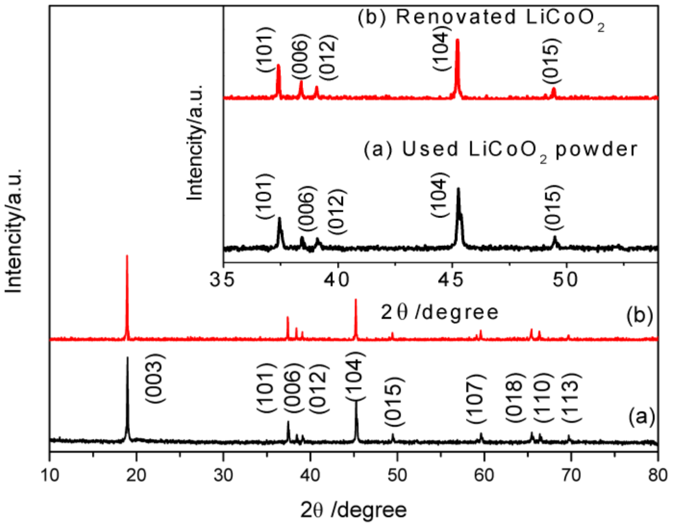

Figure 3. X-ray diffraction patterns for (a) the spent $LiCoO_2$ powder and (b) the renovated $LiCoO_2$ powder.

Previous researchers [30-32] used the changes in layer occupancy have a direct effect on the XRD patterns, viz., the integrated intensity ratio I(003)/I(104), and the split of the (006)/(102) or (108)/(110) lines, to indicate the cation mixing of the layered structure. Cation disordering occurs into the structure via exchange of Li and Co ions between 3a and 3b sites during Li^+ insertion/extraction in $LiCoO_2$. When the intensity ratio of I(003)/I(104) value was decreased, the cation mixing between Li and Co cations can seriously degrade electrochemical performance of the $LiCoO_2$ such as rechargeable capacity and cyclability. As shown in Fig. 3, the I(003)/I(104) value of the renovated $LiCoO_2$ is larger than that of the spent $LiCoO_2$, indicating that the renovated $LiCoO_2$ sample has a better the Li-insertion and extraction capacities.

It is convenient to use the doublet splitting of (006)/(102) and (108)/(110) as an indicator of ordered crystalline layer compound [33]. It is seen from the Fig. 3(b) that the lines of (102) and (006), and (108) and (110) are clearly split, and it is inferred that the renovated $LiCoO_2$ have perfect layering involving the metal ions and oxygen atoms [34].

It has been reported that the integrated intensity ratios I(006)/I(003) value is an important index to measure the cycle life of $LiCoO_2$. The I(006)/I(003) value of the renovated $LiCoO_2$ is larger than that of the spent $LiCoO_2$, indicating that cycle life of the renovated $LiCoO_2$ sample are superior to those of spent $LiCoO_2$ [35].

SEM images of spent and renovated $LiCoO_2$ samples are given in Fig. 4. In Fig. 4(a), the floccules are organic electrolyte and PVDF adhere to the spent $LiCoO_2$ particle surfaces. From the Fig. 4(b), after treatment, the floc is significantly reduced. Furthermore, the surface of the renovated $LiCoO_2$ powder were relatively smooth and clean compared with spent $LiCoO_2$ powder. The analysis shows that the aqueous pulsed discharge plasma systems enables floc to be separated from the spent $LiCoO_2$ particles and to achieve degradation.

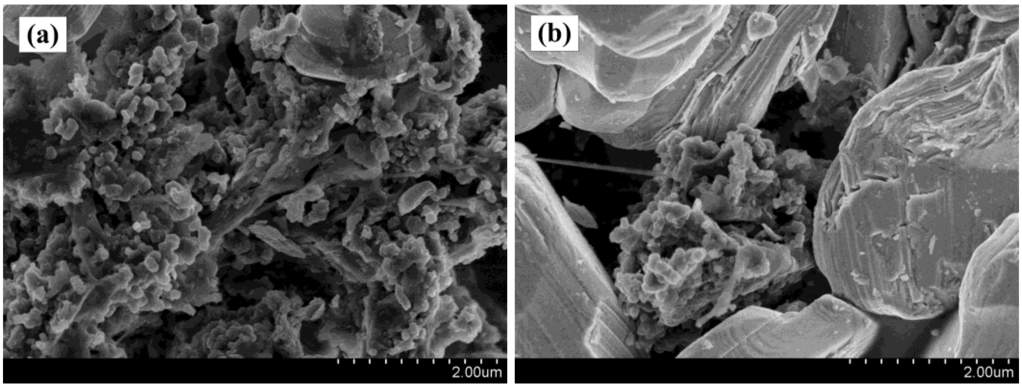

Figure 4. SEM images for the morphology of (a) the spent $LiCoO_2$ powder and (b) the renovated $LiCoO_2$ powder.

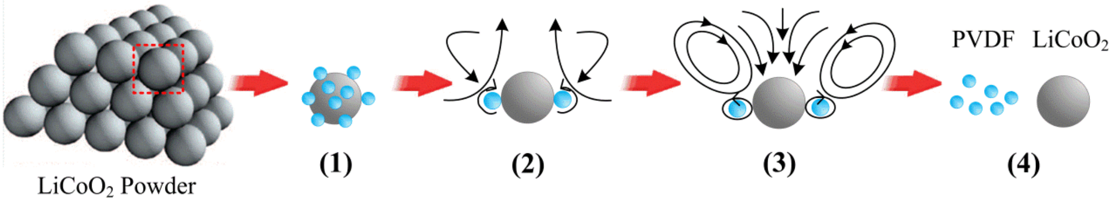

Figure 5. The flow field analysis of $LiCoO_2$ particles and PVDF

The morphology difference between the spent $LiCoO_2$ and the renovated $LiCoO_2$ was mainly caused by the aqueous pulsed discharge plasma systems treatment. The pulsed high voltage system helps transfer the electrohydraulic cavitation to the $LiCoO_2$ being treated in the liquid phase, which can not only lead to the production of freeradical but also the occurrence of cavitation bubble. The former can promote organic degradation (including PVDF and organic electrolyte) and the latter is able to accelerate the heat and mass transfer process accompanying the renovation process[22]. Shock waves from electrohydraulic cavitation in liquid-solid slurries produce high-velocity interparticle collisions (see Fig. 5). Hence, spent $LiCoO_2$ agglomerates can easily be broken when subjecting to rapidly alternating pressure.

After removal of organic residues by 1-methyl-2-pyrrolidinone (MNP) and methylene chloride, the structures of the spent and renovated $LiCoO_2$ powders were confirmed by Raman spectroscopy. The Raman spectra for the spent $LiCoO_2$ phase and the renovated $LiCoO_2$ phase are compared in Fig. 6. As shown in Fig. 6(b), the renovated $LiCoO_2$ phase exhibits two Raman active modes of E_g and A_{1g} at 483 and 590 cm^{-1}, respectively. Two Raman bands at 483 and 590 cm^{-1} for the renovated material agree with those of the layered $LiCoO_2$ phase (space group R-3m), which offer more active positions for lithium ion intercalating/deintercalating.

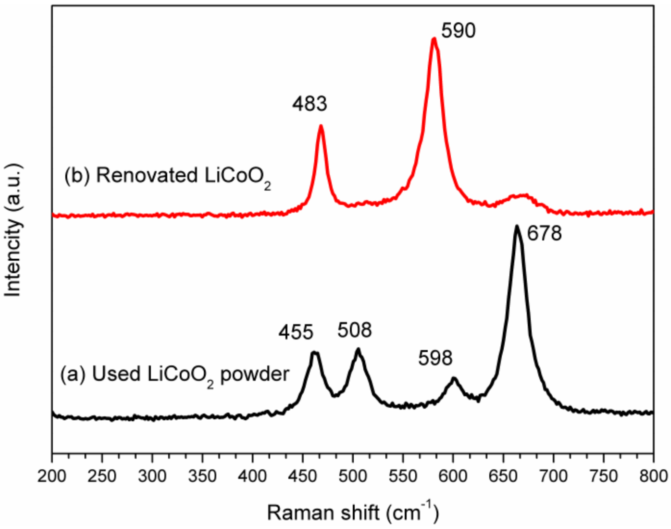

Figure 6. Raman spectra for (a) the spent $LiCoO_2$ powder and (b) the renovated $LiCoO_2$ powder.

Of particular interest observed in Fig. 6(a) and (b) is a remarkable spectral variation of the film by aqueous pulsed discharge plasma. This apparent change is due to a cation rearrangement in the $LiCoO_2$. The order-disorder transition for the hexagonal phase is predicted to occur at ~4850 °C [35-37], quite well above the melting point of this material. Electrohydraulic cavitation causes high-energy chemistry. During cavitation, these localized hot spots have temperatures of roughly 5000 °C, pressures of about 500 atmospheres, and lifetimes of a few microseconds [36]. Electrohydraulic cavitation was able to instantaneously heat the sample as high as ~4850 °C, which is sufficient to melt $LiCoO_2$ and lead to cation rearrangement.

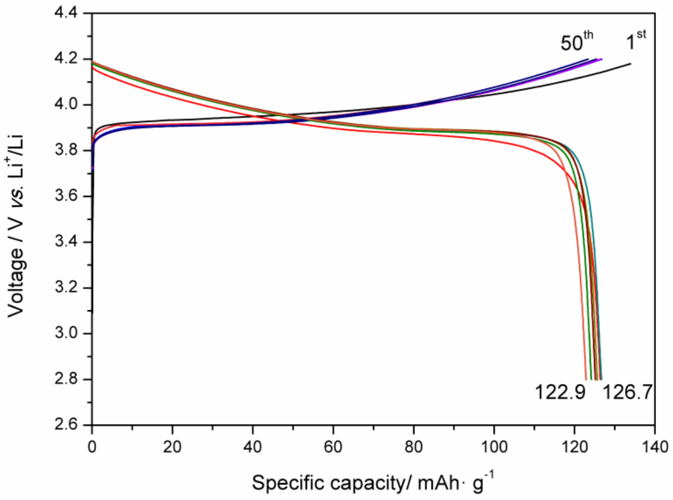

Figure 7. Charge-discharge characteristics of the renovated $LiCoO_2$ powder at C/5.

The 1st, 10th, 20th, 30th, 40th and 50th first charge-discharge curves for the renovated $LiCoO_2$ at C/5 rate were shown in Fig.7. The coin-type cells were charge/discharged between 2.8 and 4.2 V, which is well compatible with the voltage cut-off in the current commercial lithium ion batteries. From the data given in Fig. 7, it can be seen that the charge capacity in the first cycle is 132.9 mAh g^{-1}, and the discharge capacity is 126.7 mAh g^{-1}. The discharge efficiency is nearly 95.4 %. The efficiency did not reach 100 %, probably due to the oxidation of the solvent. The renovated $LiCoO_2$ exhibits a prospective electrochemical activity and the cell performance: an initial discharge capacity of 122.9 mAh g^{-1} and the discharge capacity retention of 97.2% after 50 cycles. The chemical properties of renovated $LiCoO_2$ were similar to the commercial batteries under different rate charge and discharge test.

4. CONCLUSIONS

We develop a simple method for the renovation of spent $LiCoO_2$ electrodes from the spent LIBs based on the characteristics of aqueous pulsed discharge plasma. The spent $LiCoO_2$ cathode material was successfully renovated using aqueous pulsed discharge plasma technology in 0.1 M LiOH solution at room temperature for 30 min. The renovated $LiCoO_2$ is an ordered crystalline layer compound which is the most widely used cathode material in commercial LIBs. The cycling test (at 5/C rate) showed that the initial discharge capacity of renovated samples and capacity retention after 50 cycles are 131.9 mAh g^{-1} and 97.2 %, respectively.

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