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Preparation and electrochemical properties of re-synthesized $LiCoO_2$ from spent lithium-ion batteries

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A new idea for reuse of the cathode materials of lithium-ion batteries (LIBs) is investigated to develop an environmentally friendly process for recycling spent batteries. $LiCoO_2$ is re-synthesized from spent LIBs by leaching and a sol-gel method calcined at high temperature. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) are employed to study the reactions occurring calcination that are responsible for the weight losses. X-ray diffraction (XRD) and scanning electron microscopy (SEM) are used to determine the structures of the $LiCoO_2$ powders. It was found that a pure phase of $LiCoO_2$ can be obtained by the re-synthesis process. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) are used to evaluate the electrochemical properties of the $LiCoO_2$ powders. The discharge capacity of re-synthesized $LiCoO_2$ is 137 mAh g^{-1} at the 0.1 C rate, and the capacity retention of the re-synthesized $LiCoO_2$ is 97.98% after 20 cycles at the 0.1 C rate, and 88.14% after 40 cycles. The results indicate that the re-synthesized $LiCoO_2$ displays good charge/discharge performance and cycling behavior.

spent lithium-ion batteries, lithium cobalt oxide, sol-gel, recycling

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Secondary rechargeable LIBs are the batteries of choice for many applications because of their favorable characteristics including high energy density, long cycle life, low self-discharge and safe handling, and LIBs represent about 28% of the rechargeable batteries in the consumer electronics market. Schneider et al. [1] revealed that at the end of the assessment process, a considerable number of these cells still had reuse potential, with approximately 37% of all discarded and tested cells being approved for reuse. Fergus [2] has stated a lithium-ion secondary battery comprises a cathode, anode, organic electrolyte, and a separator. $LiCoO_2$, $LiMn_2O_4$, $LiNiO_2$ or related oxides are used as cathode materials for almost all commercialized LIBs, and $LiCoO_2$ is the most common positive electrode material for commercial LIBs because of its high energy density, high operating voltage and good electrochemical performance. Consequently, $LiCoO_2$ currently dominates the cathode materials market. However, it has been shown by Zhang et al. [3] and Hayashi et al. [4], that $LiCoO_2$ material has several disadvantages such as high cost, limited cobalt resources and toxicity.

The market for LIBs is growing significantly, and the world consumption of LIBs is increasing year by year. Zhang et al. [5] studied the electrode materials in an LIB have expanded or contracted after about 1 charge/discharge cycles. Watanabe et al. [6] have reported the crystalline phase of the cathode material has been transformed from hexagonal with R3m space group to spinel with Fd3m space group, and lithium ion is not embedded and prolapsed effectively, which leads to increased resistance and reduced capacity of the LIB. The total worldwide rechargeable battery demand is predicted to reach 4.6 billion cells by 2010, and it is expected that a massive amount of waste generated during LIB manufacturing will cause a serious environmen-

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*Corresponding authors (email: chenrj@bit.edu.cn; wufeng863@vip.sina.com) tal problem. Swain et al. [7] have stated the increasing waste generated, ever increasing energy demand, rapid decrease in primary resources and strict environmental regulations make it essential to improve waste recycling.

Paulino et al. [8] and Lain [9] have stated that spent LIBs are discarded as domestic waste, which may have a cumulative effect on the environment as metal oxides are converted into their metallic forms during incineration of garbage, and may thus pollute water resources. Ferreira et al. [10] and Freitas et al. [11] studied the recovery of valuable metals from the waste cathodic active material by pyro-metallurgical and hydrometallurgical processes. Commonly used methods include crushing, physical separation, acid leaching, and precipitation or solvent extraction to recover the cobalt and lithium from the battery waste. Lupi et al. [12] investigated the recovery process of Ni metal by electrowinning after preventive separation by solvent extraction of Co from Ni. Wang et al. [13] studied a novel process which separated and recovered metal values such as Co, Mn, Ni and Li from the cathode active materials of the lithium-ion secondary batteries. Grimes et al. [14] studied a combined photolytic-electrochemical system using an activated carbon concentrator cathode that achieved the rapid simultaneous pH independent destruction of phthalic acid and recovery of cobalt. Some recovery technologies for the spent LIBs are shown in Table 1. However, these processes have inherent problems such as solid-liquid separation, high cost, low purity and slow reactions.

Table 1 Summary of recovery technologies for spent LIBs

Reference	Cathode material separated process	Leaching conditions	Treating process	Methods and reagents	Disadvantages
Contestabile et al. [15]	Thermal treatment to remove binder and organic additive C	4 mol/L HCl for 1 h at about 80°C	4 mol/L NaOH solution was added to recover cobalt as $Co(OH)_2$.	$Co(OH)_2$ was mixed with Li_2CO_3, heated in a muffle and homogenizing in a mortar, annealed at 700°C for about 20 h to produce $LiCoO_2$.	Li in leaching solution was not recovered [15].
Fouad et al. [16]	Thermal treatment to remove binder and organic additive C	–	$LiAlO_2$ material was prepared by thermal treatment of $LiCoO_2$ over its Al foil at 800–900°C for 1 h.	–	Co_3O_4 and CoO is contained in $LiAlO_2$ material, and Li/Al was hard to control [16].
Dorella et al. [17]	Dismantled using a manual procedure	H_2SO_4 (2%–8%, v/v), (1/10 to 1/50 g mL^{-1}), temperature (20–80°C)	NH_4OH was added to make the precipitation pH range from 4 to 9.	Extraction tests, Cyanex 272 was added to extract the different metals.	The separate process is complicated, and Cyanex 272 will make a secondary pollution. [17].
Swain et al. [7]	$LiCoO_2$ generated during the manufacturing process.	2.0 mol/L H_2SO_4 solution and H_2O_2 at 75°C	1.5 mol/L Cyanex 272, pH 5, O/A ratio of 1.6	0.1 mol/L Na_2CO_3, O/A ratio of 3.8, stripped using 0.5 mol/L H_2SO_4, extraction of cobalt with 99.99% purity as $CoSO_4$	Li in leaching solution was not recovered, Cyanex 272 will make a secondary pollution [7].
Lee et al. [18]	Samples were disassembled with a high-speed shredder	1 mol/L HNO_3, 20 g L^{-1}, initial S:L ratio, 75°C, 1.7 vol.%, H_2O_2 and 1 h.	Leach liquor and additional citric acid was used to prepare a gel, $LiNO_3$ was added to adjust Li:Co to 1.1.	Gel was placed with crucible and calcined into powder in air for 2 h in the temperature range 500–1000°C.	Strong acid after leaching is a threat to the environment [18].
Bahgat et al. [19]	$LiCoO_2$ was separated from the anode materials by calcining at 500°C to remove the binder and additives.	–	$LiCoO_2$ including residual carbon powder and was ground into fine powder.	The fine powder was fired at 900–1100°C to synthesize $Li_{0.5}Fe_2O_4$/$CoFe_2O_4$ [19].	–
Liu et al. [20]	$LiCoO_2$ was separated from Al foil with DMAC, and PVDF and carbon, powders in active material were eliminated by high temperature calcining.	–	Li_2CO_3 was added in recycled powder to adjust molar ratio of Li to Co, $LiCoO_2$ was obtained by calcining the mixture at 850°C for 12 h in air	–	Co_3O_4 present in the power, and the ratio of Li and Co is difficult to adjust [20].
Myoung et al. [21]	$LiCoO_2$ powder was separated from waste Li-ion batteries.	Dissolved in hot nitric acid HNO_3	Cobalt ions were potentiostatically transformed into cobalt hydroxide on a titanium electrode and cobalt oxide was then obtained via a dehydration procedure.	–	Strong acid after leaching is a threat to the environment [21].

It is important to develop an environmentally acceptable recycling process to recover as much of the valuable metals as possible; at the same time recycling of waste materials must be as simple and as low cost as possible. The objective of this work was to develop an effective process for recovery of a pure and marketable form of $LiCoO_2$ from the LIB industry waste. Re-synthesized $LiCoO_2$ from spent LIBs should be reusable as LIB cathode material, have excellent chemical stability, and lead the LIB industry to achieve the internal loop. In this paper, we report a process that consists of acid leaching and a sol-gel step and produces cathode material upon calcination. Citric acid was first used as leaching agent to leach Co and Li as their respective citrates, then the remaining citric acid was utilized as a chelating agent for a sol-gel process. The processes that were developed are environmental friendly; only CO_2 and H_2O are released to the atmosphere. The process allows reduction of the amount of cobalt mining needed for portable applications, thus reducing costs and helping to reduce environmentally harmful electrochemical waste.

1 Experimental

1.1 Materials

The spent LIBs used in our study were kindly donated by students of the Beijing Institute of Technology. Citric acid, $C_2H_3LiO_2$, $NH_3 \cdot H_2O$ and ethylene glycol were used in the experimental process. All of the reagents were utilized as received without any further purification. Other chemicals were reagent grade materials.

1.2 Experimental

A flow sheet of the re-synthesis process is shown in Figure 1. The spent LIBs were dismantled, $LiCoO_2$ was separated from aluminum foil, and the polyvinylidene fluoride (PVDF) and carbon in the active material were eliminated by calcining at 700°C for 5 h. The leaching process is described by our previous work [22]. The concentration of Co and Li in the leaching solution was determined by inductively coupled plasma (ICP) analysis. Ding et al. [23] studied $C_2H_3LiO_2$ was added to the leaching solution to adjust the Li:Co molar ratio to 1.05. Two drops of ethylene glycol was added to the solution as dispersant to make the size of the re-synthesized material particles more homogeneous. $NH_3 \cdot H_2O$ was added dropwise to the solution to adjust the pH to 6.5. The solution was then heated at 80°C to evaporate water until a transparent gel was obtained, and the gel precursor was decomposed at 120°C in a vacuum oven to remove the organic contents. The resulting solid was ground to a fine powder and calcined at different temperatures in air for 8 h to obtain re-synthesized $LiCoO_2$.

1.3 Analytical methods

To determine the chemical changes during heat treatment of the gels, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of the gel were conducted at heating rate 10°C min^{-1} from 30 to 1000°C using a combined

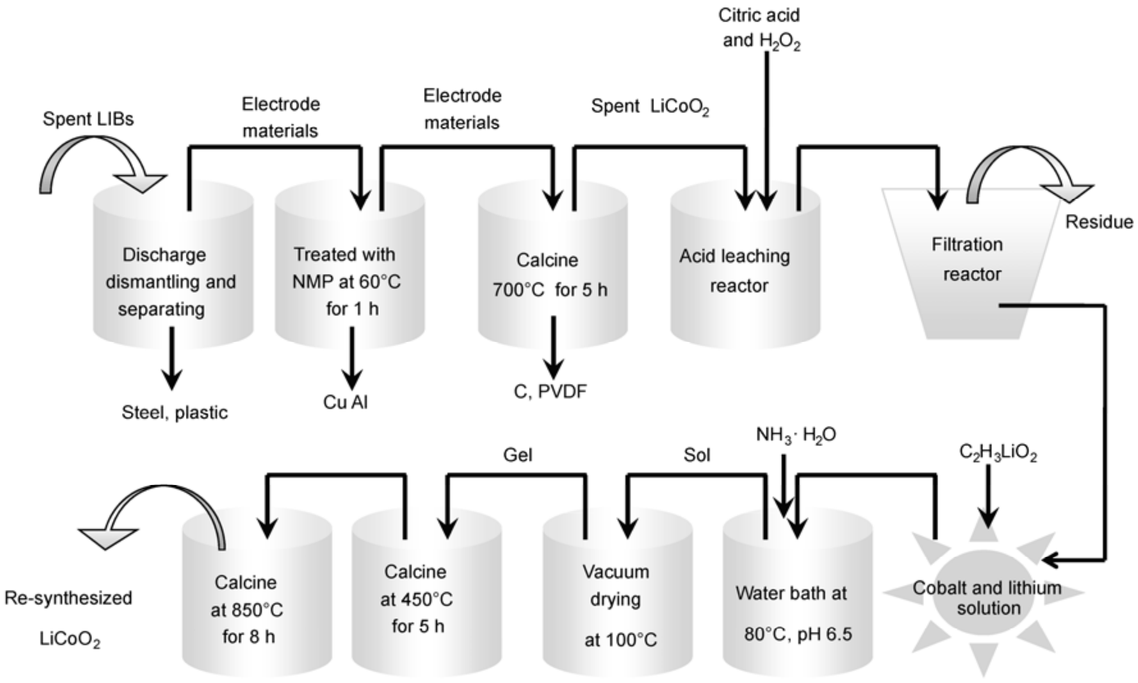

Figure 1 Flow sheet for re-synthesis of $LiCoO_2$ from spent LIBs.

TGA/DSC analyzer (Shimadzu STA449C). The crystalline structure of the samples was determined with an X-ray diffractometer (Rigaku, Cu Kα, λ=1.5405 Å) operated at 30 mA and 30 kV. The particle morphologies of the materials were observed by scanning electron microscopy (SEM, Hitachi X-650).

The electrochemical properties of re-synthesized $LiCoO_2$ powders were examined in CR2032 coin type cells. The cathodes were prepared by pasting a mixture of 85.0 wt.% $LiCoO_2$, 10 wt.% acetylene black and 5.0 wt.% PVDF binder onto an aluminum foil current collector. The anode was metallic lithium and the electrolyte was a 1 mol/L solution of lithium hexafluorophosphate ($LiPF_6$) in a 1:1 (v/v) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC). The cells were assembled in an argon-filled glove box, then aged for 12 h before being electrochemically cycled between 2.5 and 4.2 V (versus Li/Li^+) using a CT2001A Land instrument. Cyclic voltammograms (CV) were recorded at 0.1 mV s^{-1} between 2.5 and 4.2 V. Electrochemical impedance spectroscopy (EIS) was carried out using a CHI660a impedance analyzer, at amplitude voltage 5 mV and frequency range 0.001 Hz–0.1 MHz.

2 Results and discussion

2.1 TGA/DSC analysis

TGA/DSC scans of the sol-gel samples are shown in Figure 2. At least four regions of weight loss can be distinguished, and the results are given in Table 2. The data indicate that a number of complicated physicochemical processes occur during heating. From 20 to 113.82°C the weight loss was 10.01%, absorbed water was lost, and the chemical reaction began to occur. From 113.82 to 300°C, the weight loss was 29.83%, structural water began to be lost, and organic constituents begin to decompose: lithium and cobalt citrates decomposed into corresponding oxides. The exothermic DSC peak at 238°C corresponds to loss of H_2O and release of CO_2. From 300 to 530°C, the weight loss was 43.19%. The carbonates began to decompose, the significant exothermic DSC peak at 495°C indicates that $LiCoO_2$ was formed by solid-state reaction of oxides as described by Myoung et al. [21], and the organic component burned out. Finally, in the high temperature range from 530 to 1000°C, only 0.57% weight loss occurred, without any significant exothermic DSC peaks. The corresponding process is the $LiCoO_2$ structure change from spinel to layer. The overall reaction can be represented by

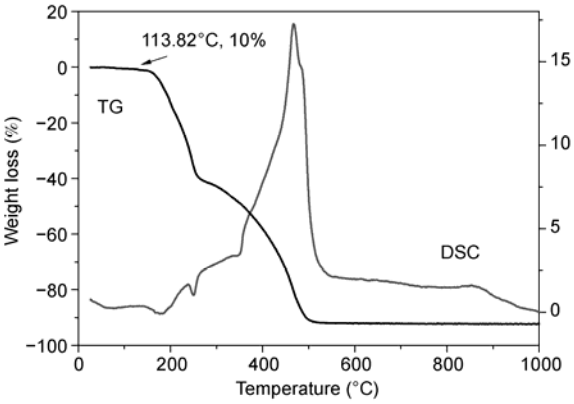

Figure 2 TGA/DSC curves of re-synthesized $LiCoO_2$ precursor gel.

$$\begin{aligned} &LiC_6H_7O_7 + CoC_6H_6O_7 + \frac{37}{4}O_2 \\ &\rightarrow LiCoO_2 + CO_2 + \frac{13}{2}H_2O \end{aligned} \tag{1}$$

2.2 Morphology

Figure 3 shows SEM images of the spent, commercial and re-synthesized $LiCoO_2$. There is an evident distinction in morphology and clearly a change in the dimensions of the particles. The particles of spent $LiCoO_2$ were small and inhomogeneous, and had irregular morphology. The particles were partially aggregated, restricting motion of Li^+ ions in the cathode material: the uniformity of particle size results from charge/discharge cycles. The commercial and re-synthesized $LiCoO_2$ powders were composed of more rounded and smooth particles, with average particle size more than 5 μm. The porous structure facilitates free movement of lithium ions in the intercalation process.

2.3 Phase identification

$LiCoO_2$ has a well-ordered layered α-$NaFeO_2$-type framework (space group R3m) in which Co and Li planes alternate in the AB CA BC packing of oxygen layers. XRD patterns of commercial, original individually separated cathode materials, and re-synthesized $LiCoO_2$ powders are shown in Figure 4. By comparison with Joint Committee on Powder Diffraction Standards (JCPDS), the main diffraction peaks of the cubic spinel phase, (003), (101) and (104), were well developed. The diffraction peaks of $LiCoO_2$, C and Co_3O_4 can be observed in Figure 4(b) compared with Figure 4(a),

Table 2 TGA data for the re-synthesized $LiCoO_2$ precursor gel

Temperature range (°C)	20–113.82	113.82–300	300–530	530–1000
Weight loss (%)	10.01	29.83	43.19	0.57
Assignment	adsorbed water	structural water, organic residue and citrates decomposition	carbonates begin to decomposed	$LiCoO_2$ formation

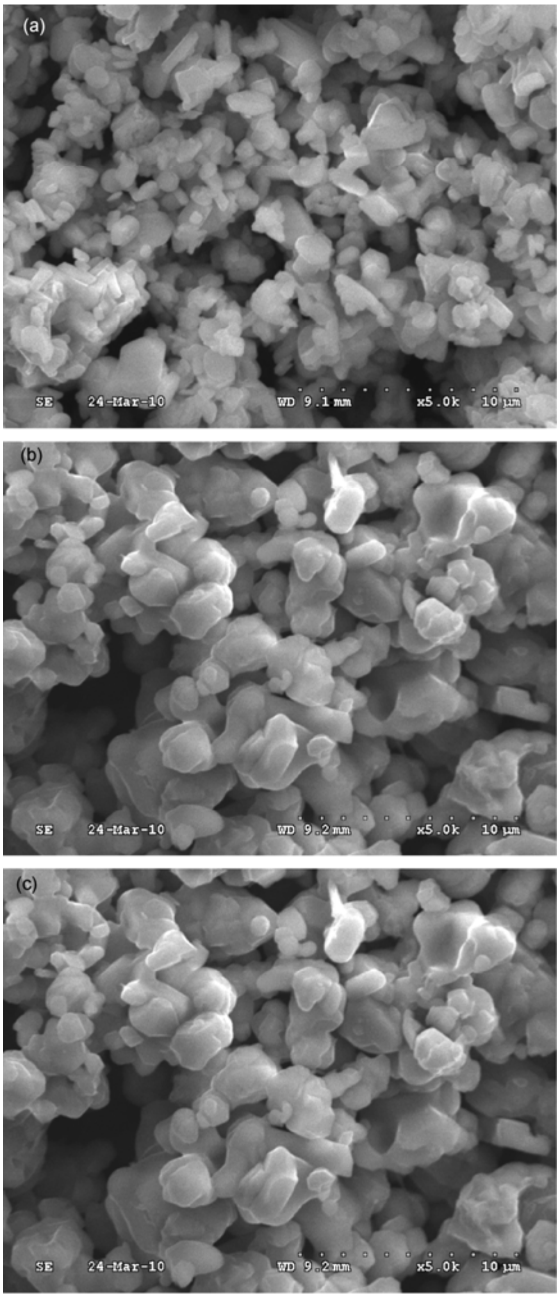

Figure 3 SEM images of (a) spent $LiCoO_2$; (b) re-synthesized $LiCoO_2$; (c) commercial $LiCoO_2$.

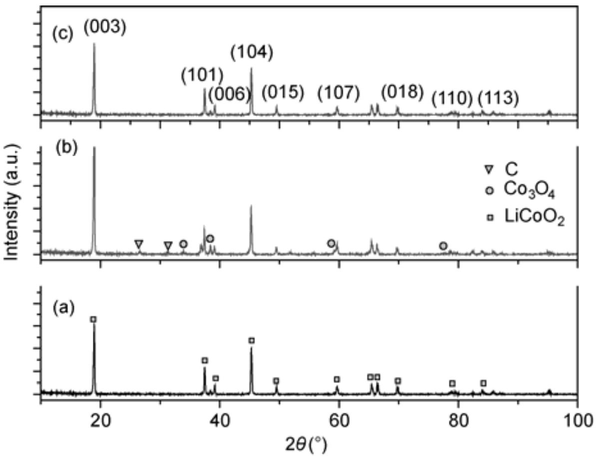

Figure 4 XRD patterns of (a) commercial $LiCoO_2$; (b) spent cathodic material; (c) re-synthesized $LiCoO_2$.

Table 3 Comparison of lattice parameters of $LiCoO_2$ powders

	a (Å)	*c* (Å)	*c*/*a*	I(003)I(104)
Commercial	2.8149	14.0679	4.9976	1.2409
Spent	2.8179	14.0535	4.9871	2.87
Re-synthesize	2.8117	14.0673	5.0031	1.2456

and the diffraction peaks of Co_3O_4 at 31.3° and 36.8°, for HF reacts with $LiCoO_2$ to produce Co_3O_4 and LiF when calcined at 700°C. Moreover, the diffraction peaks of C and Co_3O_4 are absent from Figure 4(c). This indicates that the structure of the recycled synthesized $LiCoO_2$ was similar to that of the commercial $LiCoO_2$. The lattice constants of $LiCoO_2$ powder were calculated from the diffraction data; the results and values of *c/a* are listed in Table 3. The lattice constant *a* represents the distance between Co atoms. When *a* is less than 2.82 Å, $LiCoO_2$ shows metallic conductivity, and with decrease of *a* the conductivity of Li^+ in the materials increases. The value of the lattice constant *a* for the re-synthesized $LiCoO_2$ was 2.8117 Å, indicating that the sample shows better structural stability compared with the spent $LiCoO_2$. The *c/a* ratio also reflects the structural stability of the $LiCoO_2$ layered framework. The *c/a* values of spent, commercial and re-synthesized $LiCoO_2$ were 4.9871, 4.9976 and 5.0031, respectively, and significantly greater than the ideal *c/a* ratio of 4.899 for a cubic close packed structure. Thus the re-synthesized $LiCoO_2$ appears to be high crystalline.

2.4 Electrochemical properties

The electrochemical performance of re-synthesized $LiCoO_2$ was tested in coin cells, and compared with the performance of the commercial material and spent $LiCoO_2$, tested in the same way. The samples were cycled between 2.5 and 4.2 V at a constant current density and 0.1 C rate. The first discharge curves of the samples are given in Figure 5(a). The discharge capacities of samples of spent, commercial and re-synthesized $LiCoO_2$ were 80.5, 142.5 and 137 mAh g^{-1} at the 0.1 C rate, respectively. The discharge plateau was the same (3.8–4.0 V) for the three samples. Figure 5(b) shows the cycling data of $LiCoO_2$ powder. The test cells were cycled at different discharge rates between 2.5 and 4.2 V at room temperature. After 20 cycles, the capacity retention of the re-synthesized and commercial materials were 94.38% and 97.98% at the 0.1 C rate, respectively. After the next 10 cycles at the 0.2 C rate, the capacity retention of the re-synthesized and commercial materials were 87.36% and 92.04%, respectively; then from 31 to 40 cycles at the 0.5 C

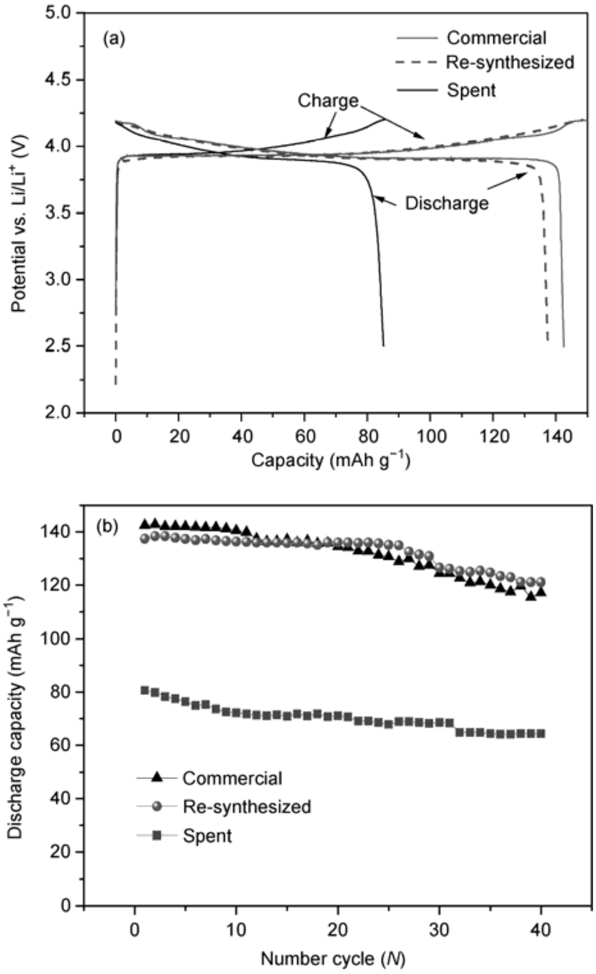

Figure 5 Charge-discharge characteristics of the re-synthesized $LiCoO_2$ powder. (a) Charge and discharge curves at 0.1 C rate in the first cycle; (b) cycle performance at different discharge rates (0.1 C for the first 20 cycles, 0.2 C for the next 10 cycles, then 0.5 C for the last 10 cycles).

rate, the capacity retention of the re-synthesized and commercial materials were 82.17% and 88.14%. Compared with the commercial $LiCoO_2$, these results indicate that the re-synthesized $LiCoO_2$ displayed good cycling behavior, and had even lower first discharge capacity.

Cycle voltammetry was used to compare the re-synthesized $LiCoO_2$ and the spent $LiCoO_2$. Figure 6 shows the CV curves. According to the relationship between cell capacity and the area under the cyclic voltammograms, the re-synthesized material seemed to have a larger capacity compared with the spent $LiCoO_2$ powder. There are two obvious and one inconspicuous peak in the oxidation process, and three corresponding peaks in the reduction process. The first peak at 4.045 V is related to the existence of a two-phase domain for $LiCoO_2$.

Figure 7 compares the EIS profiles of the commercial, spent and re-synthesized $LiCoO_2$. It is apparent that a single semicircle appears at a high-frequency measured resistance of 38.6 Ω (calculated from the diameter of the first semicircle) for the commercially assembled cell, followed by an inclined straight line. In general, the high-frequency semicircle reflects the impedance (R_{SEI}) due to film formation on the surface of electrodes, i.e. the so-called solid electrolyte interface (SEI). The low-frequency tail is associated with the diffusion effects of Li ion at the interface between the active material particles and the electrolyte, which is referred to as Warburg diffusion. The R_{SEI} value for the spent electrode increased to 93.6 Ω, which means that an SEI film formed at the interface between electrode and electrolyte. The results showed that R_{SEI} and R_{ct} of the electrodes markedly decreased after re-synthesis. It is clear that the diffusion coefficient of lithium ion was greatly increased, suggesting that the intercalation characteristics of the cathode changed after re-synthesis.

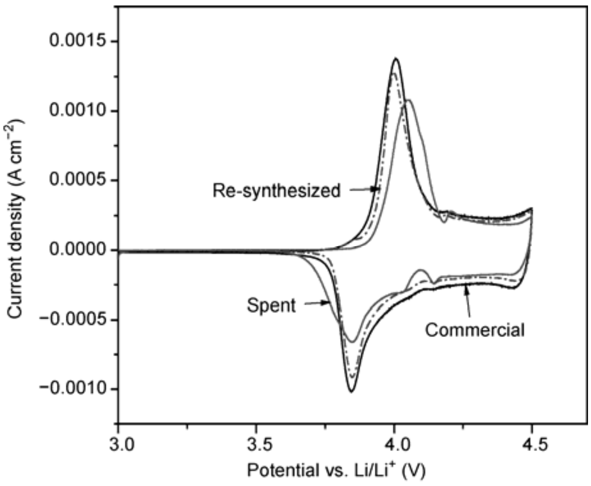

Figure 6 CV curves of the re-synthesized, commercial and spent $LiCoO_2$.

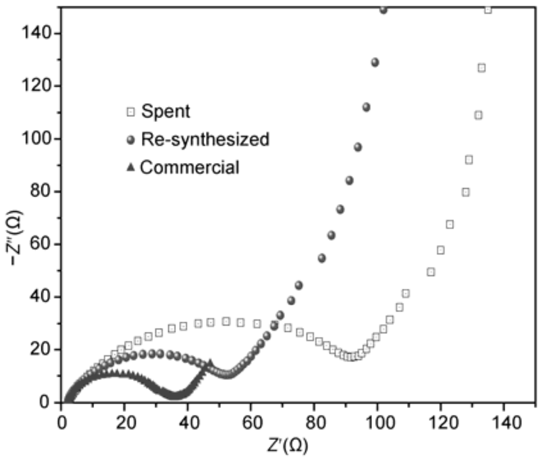

Figure 7 Nyquist plots for different $LiCoO_2$ samples in the frequency range 0.001 Hz–0.1 MHz.

3 Conclusions

The most important aspect of this work was carrying out an environmentally benign hydrometallurgical process to treat spent LIBs, and good quality $LiCoO_2$ cathode material was successfully re-synthesized by the citric acid sol-gel method from spent LIBs. The lattice parameter and the more uniform cubic structure of the material improved electrochemical performance, compared with spent $LiCoO_2$. The re-synthesized $LiCoO_2$ cathode had larger initial discharge capacity and much higher capacity retention rate. The discharge capacity of re-synthesized $LiCoO_2$ was 137 mAh g^{-1} at the 0.1 C rate, and the capacity retention of the re-synthesized material was 97.98% after 20 cycles, and 88.14% after 40 cycles. Compared with commercial $LiCoO_2$, the results indicate that the re-synthesized $LiCoO_2$ displayed good cycling behavior. This study may provide interesting direction for future research into regeneration of spent LIBs.

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