Mechanochemical Synthesis

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Improved extraction of cobalt and lithium by reductive acid from spent lithium-ion batteries via mechanical activation process

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ABSTRACT

Cobalt (Co) and lithium (Li) were extracted from pure $LiCoO_2$ powders and actual cathode material powders from the spent lithium-ion batteries (LIBs) after L-ascorbic acid dissolution via a mechanical activation process. The influences of activation time and rotation speed on the leaching were discussed. The mechanism of the improved leaching yield was proposed based on the characterization analysis including X-ray diffraction, scanning electron microscope, BET-specific surface area and particle size analyzer. The reduced particle size, increased specific surface area of activated samples, destroyed crystal structure and amorphous state of $LiCoO_2$ contributed to the improved leaching efficiencies of Co and Li. With the activated process, about 99% Co and 100% Li were

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extracted from actual spent LIBs after 60-min grinding at 500 rpm with mild conditions. This effective process would be of great importance for recovering valuable metals from the spent LIBs at room temperature.

Introduction

Lithium-ion batteries (LIBs) are widely used in a multitude of portable electronics, especially mobile phones, personal computers, cameras, etc. [1]. With the features of small size, high power density, no memory effect, long cycle life, high voltage, low self-discharge, etc. [2, 3], it is evident that an ocean of spent LIBs will be produced. The quantity and weight of LIBs in 2020 can surpass 25 billion units and 500 thousand tons, respectively [4]. The higher number of LIBs utilization means that a huge amount of spent LIBs have been generated worldwide [5]. If the spent LIBs are simply disposed into the landfill, a serious environmental concern of soil contamination would be caused [6]. Furthermore, the spent LIBs are composed of cathode, anode, electrolyte and separator. The most widely used cathode material is lithium cobalt oxide ($LiCoO_2$), which is characterized by high specific energy density and durability [7]. The contained valuable metals, organic chemicals and plastics in the following proportions are 5–20% of Co, 5–10% of Ni, 5–7% of Li, approximately 15% of organic chemicals and 7% of plastics, in which the contents of valuable metals are higher than those found in natural ores [8–10]. Therefore, the recovery of the valuable metals, especially Co and Li from the spent LIBs, is considered to be highly desirable, as it will largely help to alleviate the potential environmental pressures and solve the crisis of cobalt and lithium shortages.

Recently, many researches have been reported for the recycling of Co and Li from the spent LIBs, focusing on pyrometallurgy, hydrometallurgy or bio-hydrometallurgy processes [11–14]. In contrast, hydrometallurgical processes, involving higher metal recovery with good purity and minimal gas emission, attracted worldwide attention. The leaching of $LiCoO_2$ from spent LIBs is usually carried out by using inorganic acids (such as sulfuric, hydrochloric and nitric acids) [15–20] and organic acids (such as organic oxalate, organic citric acid and succinic acid) [21–25] as the leaching agents. Compared with these

mild organic acids, the strong inorganic acids have the demerits of high cost, difficulty to be handled in large scale and environment unfriendliness as they usually emit toxic gases. Furthermore, for both the inorganic and organic acid leaching media, temperature higher than 70°C is always needed to be inputted [15–25], which is regarded as promoting or activating processes for acid extraction, and may result in a higher average cost, serious corrosion and operational environmental risk, instead. Therefore, an economic and environmentally friendly recovery process of Co and Li from waste LIBs is urgently desired.

The mechanochemical approach has attracted more attention to recover metal based on the triggered physicochemical changes, including phase transformations, structural defects, strain, amorphization and even direct reaction under normal temperature and pressure [26, 27]. This approach can also eco-friendly recycle metals from some specific wastes, such as cathode ray tube funnel glass [28], tin-doped indium oxide containing waste [29–32] and waste fluorescent lamps [33], significantly improving the recycling efficiency. Compared with traditional hydrometallurgical processes, these methods can simplify and enhance the metal leaching. With the solid–solid reaction, the extraction of valuable metals can be obtained at room temperature without the addition of other enhanced solvents. Therefore, with the aforementioned traditional organic acid leaching of spent LIBs, a mechanochemical process to pretreat the spent LIBs might be a promoting or activating method for the extraction of valuable metals Co and Li.

Hence, the aim of the present study is to put forward a novel mechanical activation process to enhance the acid leaching of Co and Li from spent LIBs at room temperature with low energy consumption and high efficiency. Herein, L-ascorbic acid, a typical and effective organic acid to leach Co and Li from spent LIBs [34], was tentatively selected as reagents to react with $LiCoO_2$ powders. Pure $LiCoO_2$

powders were selected to study the influences of mechanical activation parameters, such as rotational speed and mechanical activation time, on the Co and Li extraction. The physicochemical changes established by X-ray diffraction (XRD), scanning electron microscope (SEM), BET-specific surface area and Microtrac particle size analyzer give insights into the mechanism of the improved metals leachability from $LiCoO_2$ samples activated by mechanochemical process. Ultimately, the actual scrap sample separated and concentrated from the cathode materials in the spent LIBs was examined to verify the behavior of the improved process.

Experimental

Materials

Lithium cobalt oxide ($LiCoO_2$, 99.8% metals basis) powders were purchased from Aladdin Industrial Co. Ltd, Shanghai, China. L-ascorbic acid (AR, ≥ 99.7%) was obtained from Sinopharm Chemical Reagent Co., Ltd, Shanghai, China. Ultrapure water (18.2 MΩ·cm) was used for all the experiments. The spent mobile phone LIBs (model: AB463446BC, the capacity: 800 mAh) were collected from Samsung Electronics Co. Ltd.

Methods

A planetary ball mill (QM-QX04L, Nanjing University instrument plant, China) was used for the experiments. Stainless steel pots with a volume of 100 mL and balls with a diameter of 10 mm were used as grinding bodies for the ball milling experiments. In each pot, 180 g steel balls and 4 g $LiCoO_2$ samples were milled. Prior to each experiment, certain aliquots were transferred to the reactor vessel to obtain the desired amounts. The rotation speed of the planetary disk was set as a certain value. After the milling, all the samples were collected for characterization as well as acid leaching. To avoid the interference of other substances and exactly elucidate the mechanical activation mechanism, pure $LiCoO_2$ powders were firstly selected to study the influences of mechanical activation parameters on the Co and Li extraction, and physicochemical changes established by XRD, SEM, BET-specific surface areas and Microtrac particle size analyzer. Ultimately, the

leaching of Co and Li in the waste cathode materials from spent LIBs after mechanical activation was also examined. Prior to mechanical activation treatment, the spent LIBs were pretreated by discharging, dismantling and separating of cathode materials, followed by heat treatment to realize the separation of the cathode materials and the aluminum foil, and the removal of the polyvinylidene fluoride (PVDF) binder and acetylene black conductive agent. The detailed pretreatment was presented in the Supporting Information (SI).

All the batch leaching experiments were performed in 100 mL L-ascorbic acid solution (1 mol/L) in a 200-mL conical flask immersed in a constant temperature bath at $25 \pm 2°C$ under magnetic stirring. Briefly, 1 g grounded samples was added into 1 mol/L L-ascorbic acid solution to be immersed for 20 min except for the evaluation of improved leaching performance by mechanical activation process (Fig. 1) and then were centrifuged. 1 mL supernatant liquor was diluted to 50 mL with ultrapure water in a colorimetric tube. After that, the sample solutions were detected with an inductively coupled plasma atomic emission spectrometry (ICP-AES) instrument (iCAP-6300, THERMO, USA). The detection limits of Co and Li were 0.005 and 0.002 µg/mL, respectively. Most of the batch experiments were conducted, and the error bars were less than 3%.

The metal leaching efficiency was calculated according to Eq. (1).

$$R = \frac{C_0 \times V_0}{m \times w\%} \times 100\% \tag{1}$$

where R is the metal leaching efficiency; C_0 is the mass concentration of metal ions in the leachate; V_0 is the volume of leachate; m is the mass of samples; and $w\%$ is the metal mass fraction.

Characterization

Besides the above-mentioned ICP determinations, the chemical composition changes of the solid samples during the mechanical activation process were also characterized. The SEM observations were carried out on a JSM 6400, JEOL, Japan. The particle sizes of $LiCoO_2$ powders before and after mechanical activation treatment were measured by a Microtrac particle size analyzer (MT3300; Tokyo, Japan) in liquid mode with deionized water as a dispersing agent. In the present research, median particle size (d_{50}) was used.
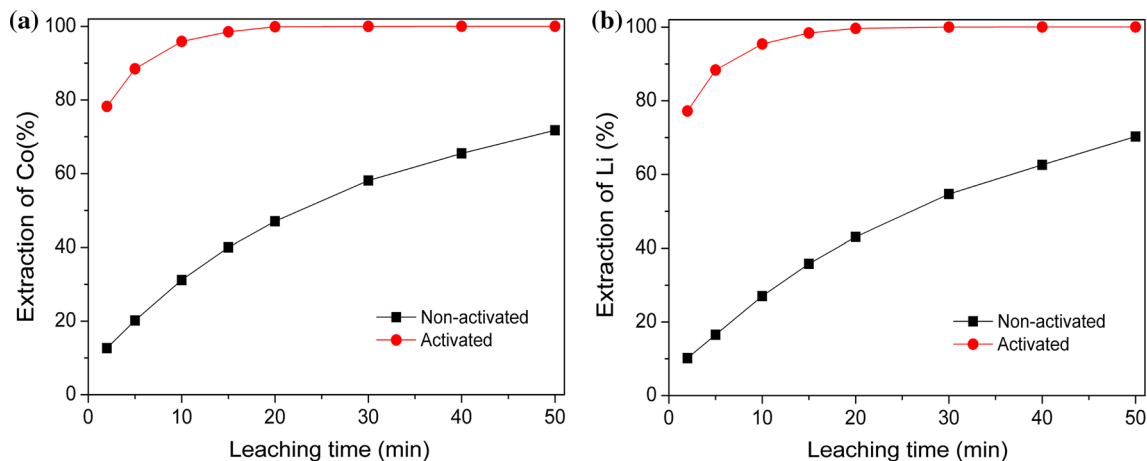
Figure 1 Extraction of Co and Li from non-activated sample (pure $LiCoO_2$) and activated sample (pure $LiCoO_2$ after ground for 60 min at 500 rpm) at room temperature.

The specific surface areas of the raw and activated samples are calculated applying the BET method by N_2 adsorption at liquid N_2 temperature in a fully automatic specific surface area and porosity analyzer (TriStar II 3020 V1.04, Micromeritics Instrument Corporation, USA) [35]. XRD was conducted using an X-ray diffractometer (D8 Advance, Bruker AXS Corporation, Germany) with Cu K_α radiation at a scan speed of 8° (2θ) per minute ranging from of $2\theta = 10°$–80°. The degree of disorder developed during milling process was obtained from Eq. (2) [36].

$$\eta = 1 - \frac{\sum I_{activated}}{\sum I_{raw}} \qquad (2)$$

where η is the degree of disorder, I_{raw} is the intensity of each crystal plane diffraction peak for raw sample, and $I_{activated}$ is the intensity of each crystal plane diffraction peak for activated samples. The values of $\sum I_{activated}$ and $\sum I_{raw}$ were obtained from XRD patterns analysis using JADE 5.0 software.

Results and discussion

Improved leaching performance by mechanical activation process

The leaching of valuable metals of Co and Li from activated and non-activated $LiCoO_2$ powders was both examined (Fig. 1). The results show that the mechanical activation can significantly increase the leaching yield at room temperature. Compared with non-activated samples, it appears that more than 99% of Co and Li can be extracted from the activated

samples after leaching for 20 min. In comparison, the leaching efficiency was increased by around 50% after ground by the mechanical process, showing a good performance for extraction of Co and Li.

Influences of activation conditions on leaching

Figure 2a shows the activation time ranging from 0 to 180 min. The extraction of Co and Li was increased from 47 to 98% and from 43 to 97%, respectively, when the milling time was extended from 0 to 60 min, and the recovery ratio of Co and Li was stable at a high level when the activation time was over 60 min. Figure 2b represents the leaching yields of the Co and Li dissolved from the powder ground at different rotational speeds. It can be seen that the rates increased with the increase in rotational speed ranging from 0 to 600 rpm. At a rotational speed of 200 rpm, the rates for activated samples were found to be only slightly different from those for raw material, but the rates of activated samples at 500 and 600 rpm were very high. The above obtained results indicate that the activation time and rotation speed are critical factors for the recovery of Co and Li from the spent LIBs. Compared with raw materials, the corresponding changes of physicochemical properties introduced by the mechanical activation may be the reason for the change of leaching yields of Co and Li. The mechanism of mechanical activation will be elucidated and investigated following by some characterization analysis.
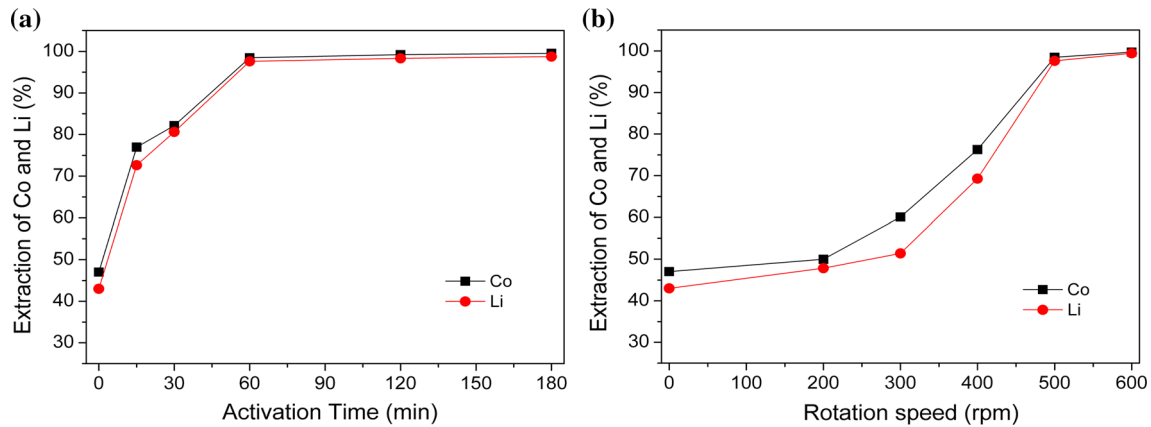
Figure 2 Influences of activation time (a) and rotation speed (b) on Co and Li leaching. Conditions: **a** rotation speed = 500 rpm; **b** activation time = 60 min.
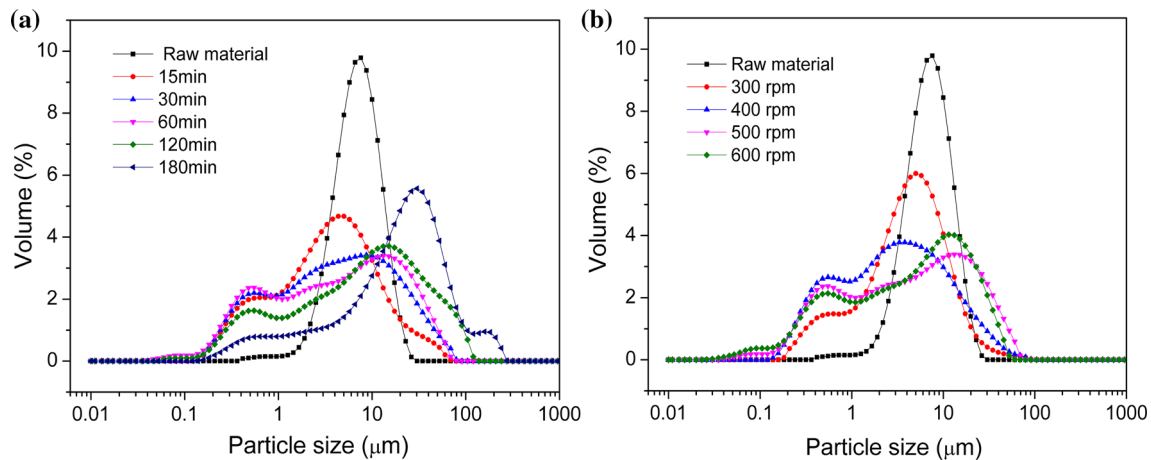
Figure 3 Particle size distributions of mechanical activation under different activation times (a) and rotation speeds (b). Conditions: **a** rotation speed = 500 rpm; **b** activation time = 60 min.

Characterization and mechanism discussion

As shown in Fig. 3a, the particle size distribution became wide with the increase in the activation time. There were two significant peaks in the particle size distributions, and the average particle size decreased after 15-min milling. Increasing activation time over 15 min produced a significantly upward trend in particle size. Namely, the particle size decreased significantly with the ball milling time prolonged from 0 and 60 min. However, with the milling time gradually extended to 180 min, the fraction of smaller particles in the samples was reduced, and that of large particle size showed an upward trend. Furthermore, it is evident from Table 1 that the milling time greatly influences the BET surface area of the

Table 1 The specific surface area of different samples

Samples numbers	1# Non-activated	2# Activated for 15 min at 500 rpm	3# Activated for 60 min at 500 rpm	4# Activated for 180 min at 500 rpm	5# Activated for 60 min at 300 rpm
Specific surface area (m²/g)	0.61	10.25	24.14	33.75	3.29

activated materials. For example, the BET surface area was increased from 0.61 to 34 m^2/g with the activation time ranging from 0 to 180 min. This indicates that the mechanical activation time could result in a decrease in the particle sizes and an increase in the BET surface area, leading to an improved extraction of Co and Li (Fig. 2a). Similarly, with the increase in the rotation speed, the percentage of small particle size was obviously increased (Fig. 3b). The decrease in particle size during the mechanical activation can be attributed to the fact that the kinetic energy generated by the series of collisions among balls was transferred to the samples. Meanwhile, the BET surface area was also increased from 0.62 to 3.29 and then to 24.14 m^2/g with the rotation speed increasing from 0 to 300 and then to 500 rpm (Table 1). The particle size reduction and BET surface area augment resulted from the accelerated rotation speed might contribute to the enhanced leaching of Co and Li (Fig. 2b).

It is worth noting that with increasing both the milling time and intensity, the particles size of samples showed an upward trend (Fig. 3), which might be due to the agglomeration of the small particles, a common phenomenon during dry grinding, usually explained by agglomeration of the structurally modified particles following the initial reduction in particle size [37]. The d_{50} changes with varying the activation time and rotation speed might also account for this (Fig. S1). This phenomenon of structurally modified particles agglomeration is mainly owing to the tendency of the activated materials to reduce its surface free energy [38]. However, the slight agglomeration of the particles during grinding hardly has an influence on the extraction of Co and Li in the present examined conditions (Fig. 2), probably due to related higher specific surface area (Sample No. 4# in Table 1), the rougher particle surface (Figs. 4, 5) and the destroyed crystal structure of LiCoO$_2$ (Figs. 6, 7).

Figure 4 shows the SEM photographs of the grounded samples for different grinding times. A significant reduction in the particle sizes could be observed after the grinding process, which explains the wider particle size distribution. The slight agglomeration of small primary particles in the nanosize scale can be observed after 120 min, which also supports the results of the particle size distribution. Moreover, the particle surfaces became much rougher with increasing the grinding time for mechanical activated samples. Both of the

aforementioned were probably conducive to the promoted leaching of Co and Li (Fig. 2a).

Figure 5 represents the morphology image of LiCoO$_2$ powders after mechanical activation for 60 min at different rotation speeds. With the increase in rotation speeds, the damaged particles and much rougher particle surfaces increased, due to that a higher rotation speed can increase the intensity of friction, shear and impact in the milling process. During the mechanical activation process, huge energy was generated and transferred to the samples, and the energy storage might improve the leaching reactivity.

Figure 6 demonstrates the dramatic change of crystal structure of grounded sample powders. The diffraction peak of crystal plane of 003 represents the layer structure of LiCoO$_2$, and the basic unit Co-O-Co of the aforementioned layer structure can be reflected by the diffraction peak of 104 crystal plane [39]. In addition, a higher I_{006}/I_{003} ratio indicates a longer cycle life of LiCoO$_2$. There is no new phase formation in the samples during the ball milling, and it is obviously found that the intensities of XRD diffraction peaks decreased with the increase in both the activation time and the rotation speed (Fig. 6 and Tables S1 and S2). This indicates that the basic unit Co-O-Co and the layer structure of LiCoO$_2$ suffered from destruction. Moreover, the I_{006}/I_{003} ratio declined gradually whether increasing the activation time or the rotation speeds (Tables S1 and S2), which indicates the cycle life of LiCoO$_2$ greatly was decreased due to the destruction of crystalline layer structures. Furthermore, the line widths of diffraction peaks widened with both the increase in activation time and rotation speed (Fig. 6). These might indicate that the crystalline structures changed from crystalline to amorphous due to the friction and impact during the grinding process [40, 41].

The full width at half-maximum (FWHM), a crystal lattice parameter [42, 43], became broadened with the increase in the activation time and the rotation speed (Fig. S2). The FWHM changes of the two main crystal planes of 003 and 104 become wider with the increase in activation time and rotation speed, indicating that the crystal structure of LiCoO$_2$ was destroyed seriously. Moreover, the XRD pattern of the crystal of the mechanical activated samples under the same conditions could not be observed by XRD analysis, due to the crystal lattice distortion after mechanically activated. However, the disorder degree of the
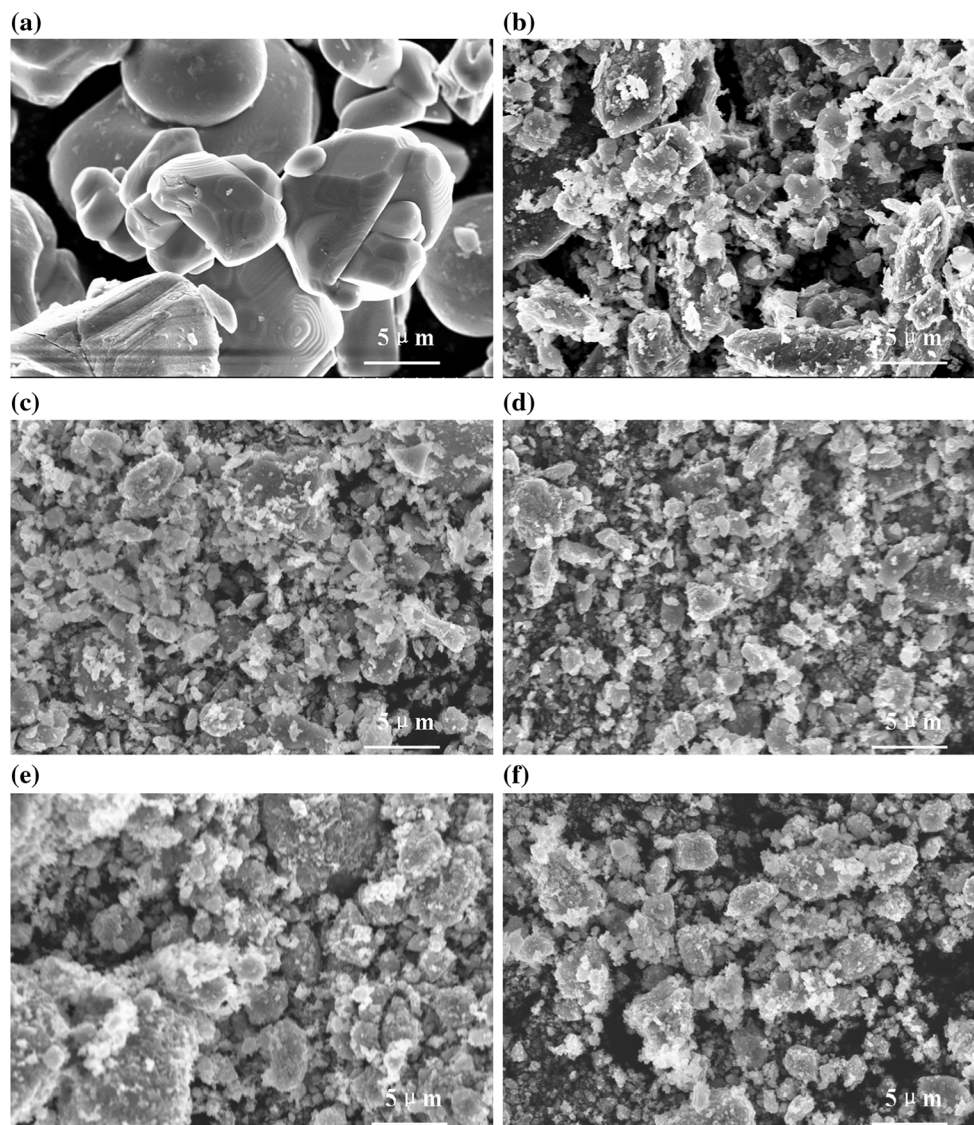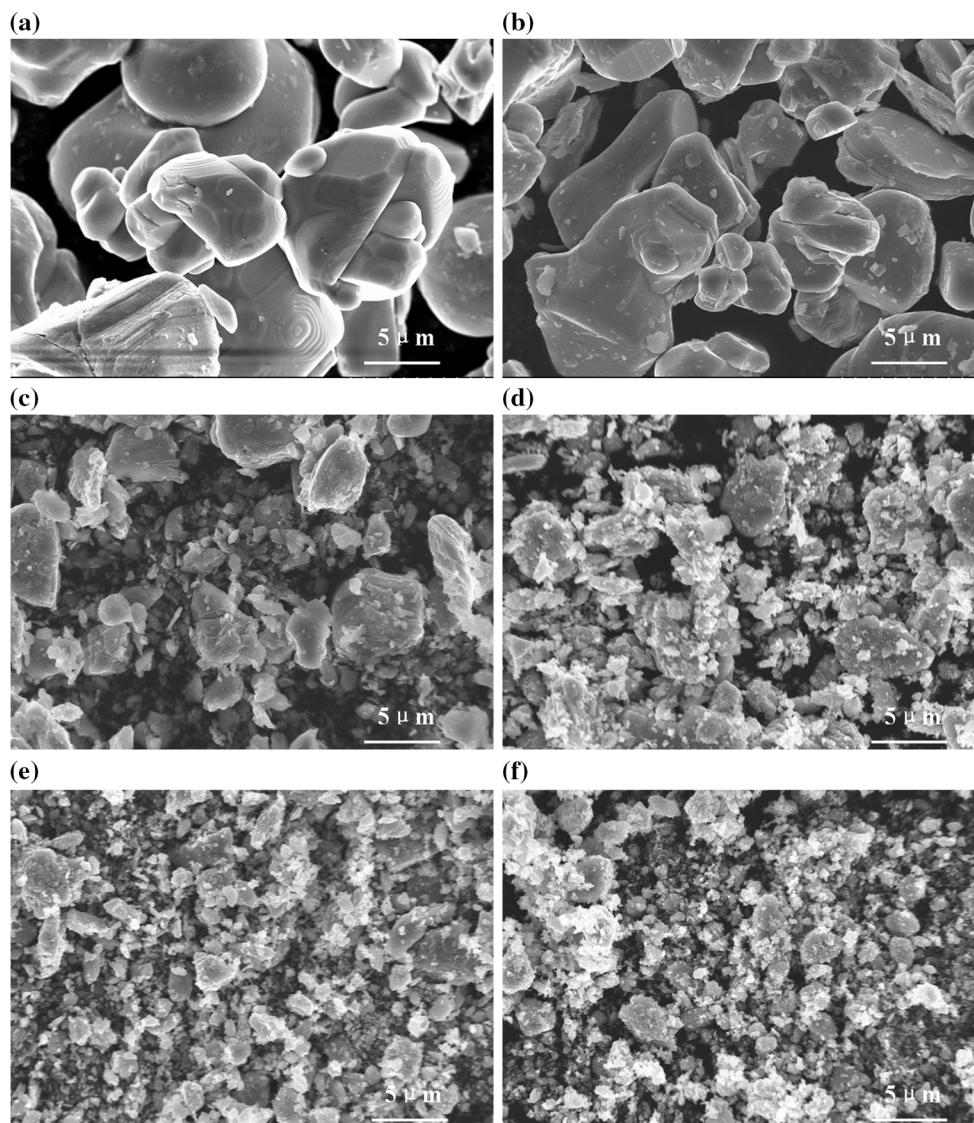
Figure 4 SEM images of LiCoO$_2$ powders after mechanical activation at 500 rpm for different times: **a** raw materials, **b** 15, **c** 30, **d** 60, **e** 120 and **f** 180 min.

samples after mechanical activated could be analyzed by the intensity of diffraction peak. The disorder degree, an important characteristic of crystal defects, represents the degree of amorphous crystals, which is reflected by the intensity change of all peaks of different crystal planes [36, 44]. Figure S3 shows that the disorder degree becomes higher with the increase in activation time and rotation speed, which is consistent well with the changes of FWHM and the SEM images. The LiCoO$_2$ crystal became completely amorphous after the mechanical activation process for more than 60 min at a rotation speed no less than 500 rpm.

Based on the aforementioned observations, the reduction in particle size, the destroyed crystal structure and amorphous state of LiCoO$_2$ induced by mechanical activation process are the main reasons to improve the leaching efficiency of Co and Li with L-ascorbic acid.

Cobalt and lithium extraction from spent LIBs

To verify the effectiveness of this enhanced process for the pretreatment of valuable metals' leaching from the spent LIBs in the reductive L-ascorbic acid solution, the actual cathode materials disassembled

Figure 5 SEM images of LiCoO₂ powders after mechanical activation for 60 min at different rotation speeds: **a** raw materials, **b** 200 rpm, **c** 300 rpm, **d** 400 rpm, **e** 500 rpm and **f** 600 rpm.

from spent LIBs were also studied at the same conditions. The Co and Li contents of the cathode materials are shown in Table S1. The SEM images and XRD patterns of the actual pretreatment sample and activated sample are also shown in Figs. S4 and S5. Compared with the actual materials, a significant size reduction could be observed (Fig. S4), and the XRD pattern intensity was also decreased after the mechanical activation process for 60 min at a rotation speed of 500 rpm. Furthermore, the extractions of Co and Li were both significantly increased from 32.69 to 99.13 and from 47.68 to 100%, respectively, after the mechanical activation process for 60 min at a rotation speed of 500 rpm (Fig. 7), which were in good agreement with the aforementioned results obtained from pure LiCoO₂ powders. Herein, the results of actual samples from the spent LIBs further illustrates that mechanical activation process is an effective pretreatment approach for the improved leaching of valuable metals, and 99% Co and 100% Li can be favorably recycled from the L-ascorbic acid solutions at room temperature.
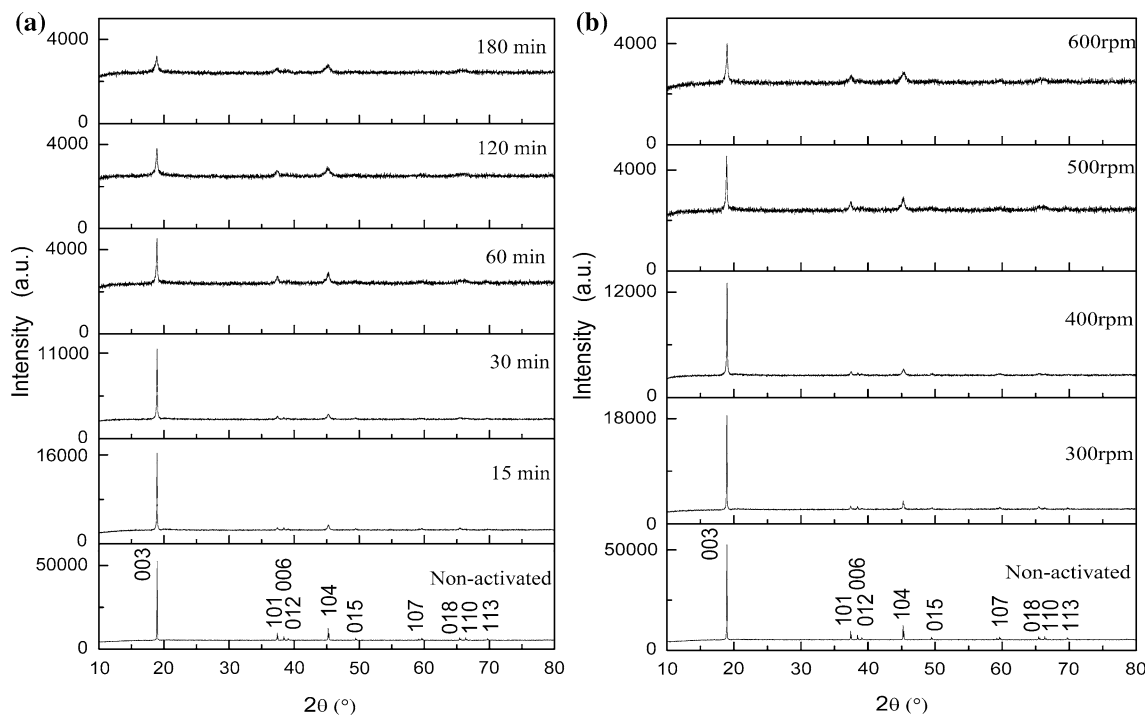
Figure 6 XRD patterns of raw material sample and samples activated at different **a** activation times and **b** rotation speeds.
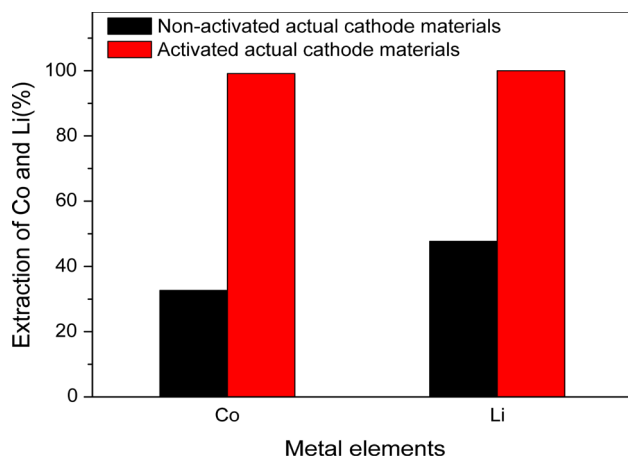
Figure 7 Extraction of Co and Li from different samples. Conditions: grinding time = 60 min, rotation speed = 500 rpm.

Conclusions

A mechanical activation process was applied to enhance the leaching of Co and Li in reductive L-ascorbic acid solution. The influences of activation conditions, such as the milling time and rotational speed, on leaching was discussed, both had positive effects on the extraction of Co and Li. Based on the characterization analysis conducted by XRD, SEM, BET-specific surface area and Microtrac particle size

analyzer, the mechanism of the improved extraction was proposed that the reduced particle size, increased specific surface area, destroyed crystal structure and amorphous state of $LiCoO_2$ were the main reasons for the enhanced leaching of Co and Li. Ultimately, around 99% Co and 100% Li were extracted in the reductive L-ascorbic acid solution from actual spent LIBs pretreated by this mechanical activation process with mild conditions. It is worth mentioning that the reductive L-ascorbic acid was just used as a representative in the present study. Other enhanced extraction of Co and Li with reductive acids induced by mechanochemical process can raise more concerns for recycling Co and Li from waste LIBs afterward.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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