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Enhancement of leaching of cobalt and lithium from spent lithium-ion batteries by mechanochemical process

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Abstract: A mechanochemical method with SiO_2 as the grinding aid was used to enhance the leaching efficiencies of Co and Li from spent lithium batteries (LIBs). Experiment results show that the optimal leaching efficiencies of 94.91% for Co and 97.22% for Li were obtained under the parameters of $SiO_2/LiCoO_2$ mass ratio of 1:1, grinding speed of 500 r/min and grinding time of 30 min in citric acid. Characterization results indicate that the surficial properties of $LiCoO_2$ were changed after mechanochemical grinding treatment due to the newly generated surfaces on $LiCoO_2$. Meanwhile, the incompletely coordinated atomic structure and defective lattice structure lead to the activation of $LiCoO_2$. The reduction effect of carbon black on Co^{3+} under the action of mechanical forces increases its leaching efficiencies in the citric acid solution. The proposed process was found efficiently to recover Co and Li from $LiCoO_2$.
Key words: mechanochemical grinding; leaching; spent lithium-ion batteries; surficial properties; reaction mechanism

1 Introduction

Lithium-ion batteries (LIBs) are widely used in electronic devices and new energy vehicle storage due to their high energy density, low self-discharge rate, and environmental protection. Their market capacity has increased and the output has been continuously improved in these years [1−5]. There has been a large increase of LIBs due to the gradual upgrading of electronic products and new energy automobile. LIBs are made of heavy metals, organic chemicals, and plastics and generally contain (5−20) wt.% cobalt, (5−7) wt.% lithium, 15 wt.% organic chemicals, and 7 wt.% plastics [6,7]. The improper disposal of spent LIBs will pose a major threat to ecosystems and human health.

Many researchers developed processes that combined physical and chemical methods to recycle valuable components from spent LIBs. Physical methods including crushing [8], sieving [3], and mechanical activation [9] are normally used in the pretreatment process. The hydrometallurgical method is one of the most widely used chemical processes [10−12]. Organic acids such as succinic acid [13], formic acid [14], oxalic acid [15], and citric acid [16] are commonly used as leaching agents. The organic acid can be easily degraded and recycled, but its long reaction time and high price restrict its commercial applications. Therefore, the recovery of the valuable metals especially Co and Li from the spent LIBs is considered to be highly desirable.

Recently, mechanochemical process has been widely applied to chemical engineering, materials engineering, mineral processing, and extractive metallurgy fields [17,18]. The lattice structure of solid waste was changed through high-energy ball milling mechanochemical treatment. Physical and

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chemical changes will occur compared to untreated materials, and the recovery efficiency of subsequent valuable metals could be strengthened [19−24]. Mechanical energy, rather than thermal energy, will provide the power for mechanochemical reaction. WANG et al [23] co-milled the $LiCoO_2$ and EDTA to form stable water-soluble compounds Li−EDTA and Co−EDTA. The efficiencies of 98% for Co and 99% for Li were obtained under $LiCoO_2$/EDTA mass ratio of 1:4 and the grinding time of 4 h as well as grinding speed of 600 r/min. However, Co and Li cannot be selectively separated. GUAN et al [24] developed a process that applied planetary ball mill to mix Fe and $LiCoO_2$ and then leached with nitric acid. The leaching rate of $LiCoO_2$ was enhanced because Co was reduced during the grinding process. However, strong and corrosive acid employed in this method could produce harmful gases and easily lead to environmental pollution.

Therefore, the cathode material was pretreated in this study by the mechanochemical method to enhance the leaching efficiencies of Co and Li. Quartz was employed as a grinding aid to co-grind with $LiCoO_2$ particles. The effect of co-grinding on the leaching efficiencies of Co and Li was investigated by changing grinding parameters such as grinding time, grinding speed, and SiO_2/$LiCoO_2$ mass ratio. Citric acid was used as the leaching agent to leach valuable metals from cathode material after mechanochemical grinding. Scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), X-ray diffractometry (XRD), and transmission electron microscopy (TEM) were used to analyze the surface morphology, particle size, phase change, and surface element change of $LiCoO_2$ before and after grinding. Based on measurement results, mechanochemical modification and strengthening mechanisms of valuable metal leaching were discussed.

2 Experimental

2.1 Materials and reagents

Mobile phone batteries collected from recycling companies were used as untreated materials in this study. After discharge treatment, batteries were manually disassembled to obtain the cathode material. The cathode foils were crushed to obtain the active materials with fraction (<0.074 mm) accounting for 94.37% of untreated material, and they were used for the subsequent study. 1 g material was dissolved in the aqua regia solution ($V(HNO_3)/V(HCl)$=1:3), the compositions of different metals in solution were then determined by ICP-MS and shown in Table 1. Citric acid ($C_6H_8O_7$) purchased from Chemical Reagent Company was employed as the leaching agent; quartz (SiO_2, ≥98% in purity) was employed as the additive. Deionized water was used for the preparation and dilution of chemical solutions.

Table 1 Chemical compositions of untreated cathode material (wt.%)

Mn	Co	Ni	Li	Al	Others
0.59	55.84	4.48	7.2	1.16	Bal.

2.2 Experimental procedures

The schematic diagram for recovering valuable metals from spent LIBs is shown in Fig. 1. Firstly, the spent LIBs were discharged in 5 g/L NaCl solution for 48 h. Then, they were dried in a dry box to prevent short-circuiting and self-ignition during the dismantling process [25]. The cathode sheet was manually separated and placed in a universal pulverizer for crushing. Then, $LiCoO_2$ powders with size <0.074 mm were sieved out.

In the mechanochemical experiment, a planetary ball mill (DM−4L, China) was used for material grinding. The ball mill was stopped every 15 min to avoid overheating. The effects of grinding conditions such as speed (0, 200, 300, 400, and 500 r/min), time (10, 15, 20, 25, and 30 min) and mass ratio (quartz to lithium cobalt oxide) (0:1, 0.25:1, 0.5:1, 1:1, and 1.5:1) on leaching efficiencies of Co and Li were studied.

The leaching conditions of 1.25 mol/L acid concentration, 20 g/L solid/liquid (S/L, 20:1) ratio, 30 min leaching time, and 80 °C were used in this study. The concentration of H^+ plays a key role in the leaching efficiencies of Co and Li. The citric acid (H_3Cit) used in the leaching test is a weak organic acid that contains three carboxyls and releases H^+ during hydrolysis. The main dissociation and the leaching reaction are shown as following reactions [26]:

$$H_3Cit=H_2Cit^-+H^+,\ K_{a1}=7.4\times10^{-4} \quad (1)$$

$$2H_3Cit+2LiCoO_2= 2Li^++2Co^{2+}+2Cit^{3-}+ 3H_2O+1/2O_2\uparrow \quad (2)$$

Fig. 1 Flowsheet for recovering valuable metals from spent LIBs

All leaching experiments were carried out in a 250 mL three-necked round-bottomed thermostatic Pyrex reactor, which was placed in a water bath to keep temperature stable. The reactor was assembled with an impeller stirrer and a reflux condenser to reduce the loss of liquid via evaporation at a high temperature. Products were added to the citric acid solution and leached for 30 min. The residue was obtained by filtration and the leachate was diluted 10000 times for the accurate determination of Co and Li contents by ICP-MS.

2.3 Analytical methods

The phase of $LiCoO_2$ particles before and after milling treatment was characterized by X-ray diffraction (XRD, D8 Advance, Bruker). XRD spectrum analysis was carried out using the MDI Jade 6.5 software. The morphology and the elemental composition were analyzed by scanning electron microscope (SEM, Quanta250, FEI) with energy dispersive spectrometer (EDS). The characterization of crystal structure changes of samples before and after grinding was carried out by transmission electron microscope (TEM, Tecnai G2 F20, FEI). Besides, laser particle size analysis was used to compare the particle size of the samples with the mechanochemical treatment before and after leaching. X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, USA) was used to analyze the distribution of surface elements of samples. Li and Co concentrations in solution were determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, 7900, Agilent). The calculation formula of the leaching efficiency is represented as follows:

$$E=\frac{C_a}{C_o}\times 100\% \tag{3}$$

where E is the leaching efficiency (%), C_a is the concentration of lithium or cobalt ions in solution after leaching (mg/L), and C_o is the concentration of lithium or cobalt ions before leaching (mg/L, the calculation equation is $C_o=m/V$, where m is the quality of the corresponding metals in cathode powders, and V is the volume of solution).

3 Results and discussion

3.1 Characterization of $LiCoO_2$ particles

Raw materials and the ground products at various speeds were analyzed by XRD, as shown in Fig. 2. It can be determined that the crystalline phase of cathode material is $LiCoO_2$ by comparing with the standard phase data. Figures 2(b−e) show that the peak intensity of $LiCoO_2$ decreased obviously with the increase of grinding speed. This indicates that the crystal structure of $LiCoO_2$ was destroyed by friction and impact during mechanochemical grinding, and gradually changes to an amorphous state as the grinding speed increases. Moreover, no new phase characteristic peak was found during the grinding process.

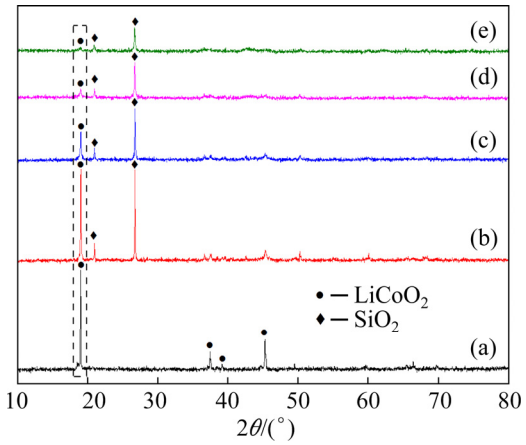

Fig. 2 XRD patterns of $LiCoO_2$ under different grinding speeds with grinding time of 30 min and SiO_2/$LiCoO_2$ mass ratio of 1:1: (a) 0 r/min; (b) 200 r/min; (c) 300 r/min; (d) 400 r/min; (e) 500 r/min

The size distribution of $LiCoO_2$ particles at different grinding speeds is shown in Fig. 3. It is indicated that the particle size of $LiCoO_2$ particles is decreased under the effect of grinding. The average particle size of $LiCoO_2$ particles is different in the grinding speed range of 200−500 r/min, and the relative content of fine $LiCoO_2$ particles is the highest at 500 r/min. The results show that the crushing effect of mechanochemical grinding on the cathode material of the spent LIBs is the most obvious in the relatively low grinding speed range. When the grinding speed continues to increase, the breakage degree change of $LiCoO_2$ particles is not significant. However, the internal energy obtained is greater with a continuous increase of grinding speed, which may cause internal changes in the crystal structure of $LiCoO_2$ during the grinding process.

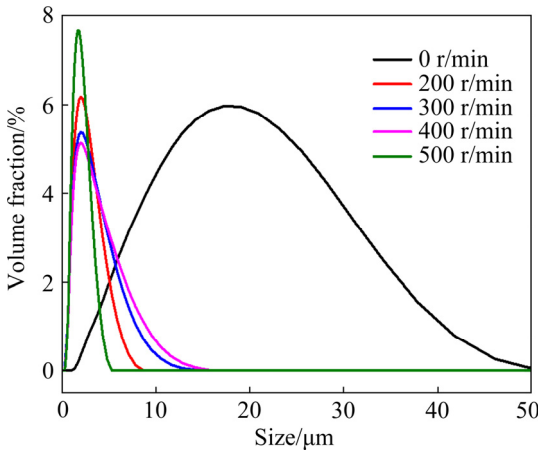

Fig. 3 Particle size distribution of $LiCoO_2$ at grinding time of 30 min and different grinding speeds

Morphologies of $LiCoO_2$ samples before and after different grinding treatments were investigated via SEM. Figures 4(a) and (b) show that part of the raw cathode materials (<0.074 mm) are agglomerated with organic binder. The liberated particles are of smooth surface and irregular shape, and the binder and tiny particles are still attached to their surfaces. Therefore, it makes the metal more difficult to dissolve in the citric acid solution. Figures 4(c) and (d) show the morphologies of $LiCoO_2$ samples after direct grinding and mechanochemical grinding. Compared with the untreated sample, the particle surface becomes rough and the size is significantly reduced, which leads to more new surfaces and larger specific surface area. In Fig. 4(d), some particles become floccules and no clear boundaries are observed among particles. For the mixture grinding of $LiCoO_2$ and SiO_2, SiO_2 plays the role of grinding media, which increases the fineness of $LiCoO_2$ compared with the direct grinding. It is helpful to improve the subsequent leaching of Co and Li from $LiCoO_2$ particles.

3.2 Crystal structure of $LiCoO_2$ particles

The crystal structures of $LiCoO_2$ samples were investigated by TEM. As shown in Figs. 5(a) and (b), the lattice fringes of the untreated particles are arranged regularly, and $LiCoO_2$ is of a long-range ordered crystal structure with a high preferred orientation [27]. Figure 5(c) shows that the inter-planar spacing of 0.198 nm is mainly derived from the (104) interplanar spacing of $LiCoO_2$. The compared analysis between Figs. 5(b) and (e) shows that the surface of $LiCoO_2$ particles changes from smooth to flocculent after mechanochemical grinding, which is consistent with SEM results. As seen from Figs. 5(c) and (f), HRTEM results further prove the damage of $LiCoO_2$ crystal structure after mechanochemical grinding treatment. The unclear and defective lattice fringes show the incomplete coordination of atomic arrangement in the crystal structure of $LiCoO_2$ in Fig. 5(f). Figure 5(c) shows that the particles have rough surface with a flocculent, which is consistent with SEM results. The HRTEM further proves the damage of the $LiCoO_2$ crystal structure after mechanochemical grinding treatment. The selected region in Fig. 5(d) shows incomplete coordination of atomic arrangement

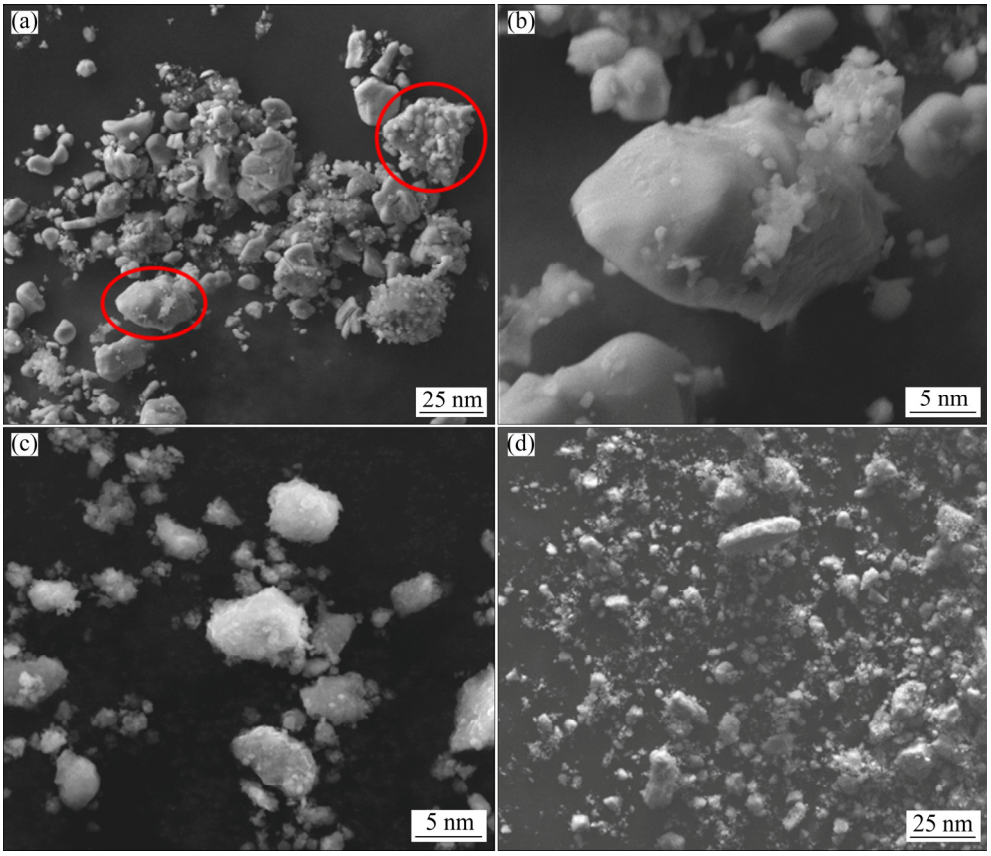

Fig. 4 SEM images of $LiCoO_2$ particles under different conditions: (a, b) Untreated; (c) Direct grinding (Grinding time: 30 min; grinding speed: 500 r/min; $SiO_2/LiCoO_2$ mass ratio: 0:1); (d) Mechanochemical grinding (Grinding time: 30 min; grinding speed: 500 r/min; $SiO_2/LiCoO_2$ mass ratio: 1:1)

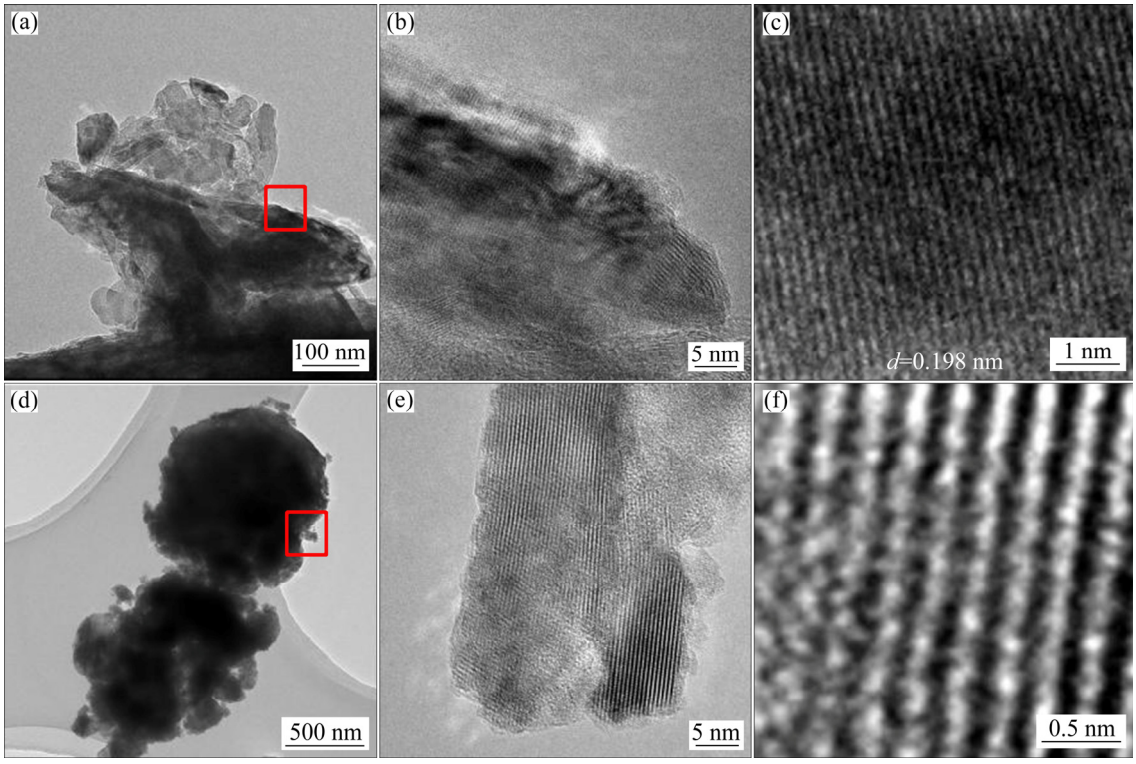

Fig. 5 TEM and HRTEM images: (a−c) $LiCoO_2$ particles; (d−f) Mechanochemically grinding products

and defect state of a lattice fringe. There are many defects in the crystal structure at various locations on the edge, which indicates that the crystal structure of $LiCoO_2$ has been changed by grinding. It is fully demonstrated that physical and physicochemical properties of $LiCoO_2$ are changed using a high energy planetary with mechanochemical grinding method during the grinding process. Its change in crystal structure enhances subsequent leaching efficiency.

3.3 Surface properties of $LiCoO_2$ powders

After being treated by direct and mechanochemical grinding, the $LiCoO_2$ particles were characterized by XPS to study their chemical state of the surficial elements. It can be seen from Fig. 6(a) that the main elements were found to be Co, O, C, F, and Li on the $LiCoO_2$ surface. Figure 6(a) shows that the presence of 3.7 at.% Co, 44.25 at.% C, and 20.69 at.% F. In Figs. 6(b) and (c), the element contents of C and F were significantly reduced whereas the content of Co was increased after grinding, and the content of Co reached 13.25 at.% after mechanochemical grinding. This indicates that the organic film composed of PVDF binder containing F element, has been

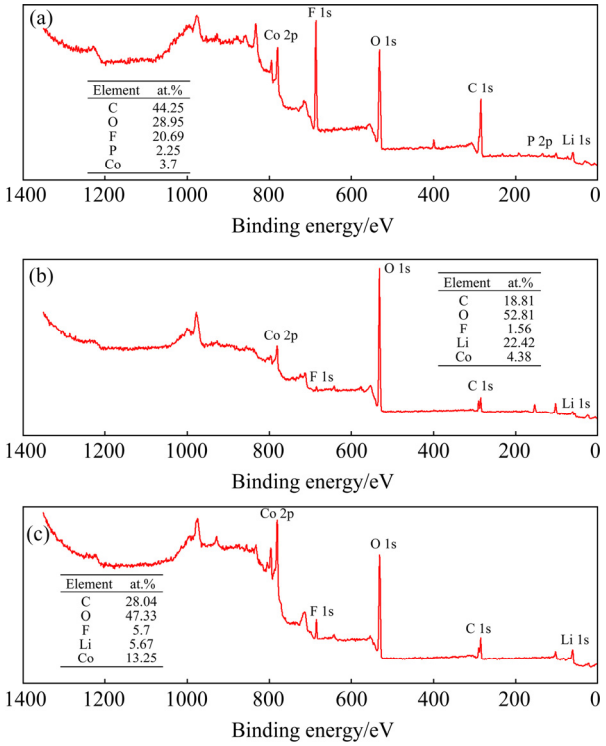

Fig. 6 XPS wide energy spectra of $LiCoO_2$ particles before (a) and after (b) direct and mechanochemical (c) grinding

significantly removed from the particle surface, and the surface of $LiCoO_2$ is partially exposed.

To understand the chemical states of C and Co on the $LiCoO_2$ surface, C 1s and Co 2p XPS spectra of the samples were analyzed, as shown in Fig. 7, Table 2, and Table 3. For C 1s, peaks at binding energies of 284.3, 284.8, 286.05, and 290.55 eV are corresponding to the following groups: carbon black, C—C/C—H, —$(CF_2CH_2)_n$— and —$(CF_2CH_2)_n$—, respectively [28−30]. After mechanochemical grinding, the fluorinated functional groups, such as —$(CF_2CH_2)_n$—, are greatly reduced from 46.88% to 17.60% (Table 2). This indicates that the content of PVDF on the particle surface decreases after grinding. Besides, the Co 2p spectrum of samples was analyzed. In Table 3, it can be seen that the energy difference ΔE between Co $2p_{3/2}$ and Co $2p_{1/2}$ splitting is approximately 15 eV, which indicates the presence of Co^{2+} and Co^{3+} in the sample. Peaks at 779.9 and 794.6 eV are mainly attributed to Co^{3+} in $LiCoO_2$, and peaks of 781.3 and 796.4 eV are mainly attributed to Co^{2+} [31]. Compared with the untreated sample, the $I(Co^{3+})/I(Co^{2+})$ values of samples after mechanochemical grinding decreased, indicating that the Co^{3+} proportion declined during mechanochemical grinding, while the Co^{2+} proportion increased, due to the reduction effect of carbon black on Co^{3+} under the action of mechanical forces. Co^{2+} is more easily leached than Co^{3+} in organic acids, so the use of reducing agents can be avoided [32,33]. The main reactions are shown as follows:

$$4LiCoO_2+C\rightarrow 4CoO+2Li_2O+CO_2\uparrow \quad (4)$$

$$Li_2O+CO_2\rightarrow Li_2CO_3 \quad (5)$$

The analysis mentioned above demonstrates obvious changes in physical and chemical properties of $LiCoO_2$ particles treated by mechanochemical grinding, such as the reduction of particle size and the increasement of the specific surface area. Moreover, the crystal structure of $LiCoO_2$ is gradually transformed into amorphous state. The atomic arrangement is incomplete and lattice fringes are dislocated and distorted. The analysis of surface elements shows that Co^{3+} was reduced to Co^{2+} due to the reduction of carbon black in the grinding process. All these changes in physical and chemical properties will conduce to improve the leaching rate of citric acid cathode material.

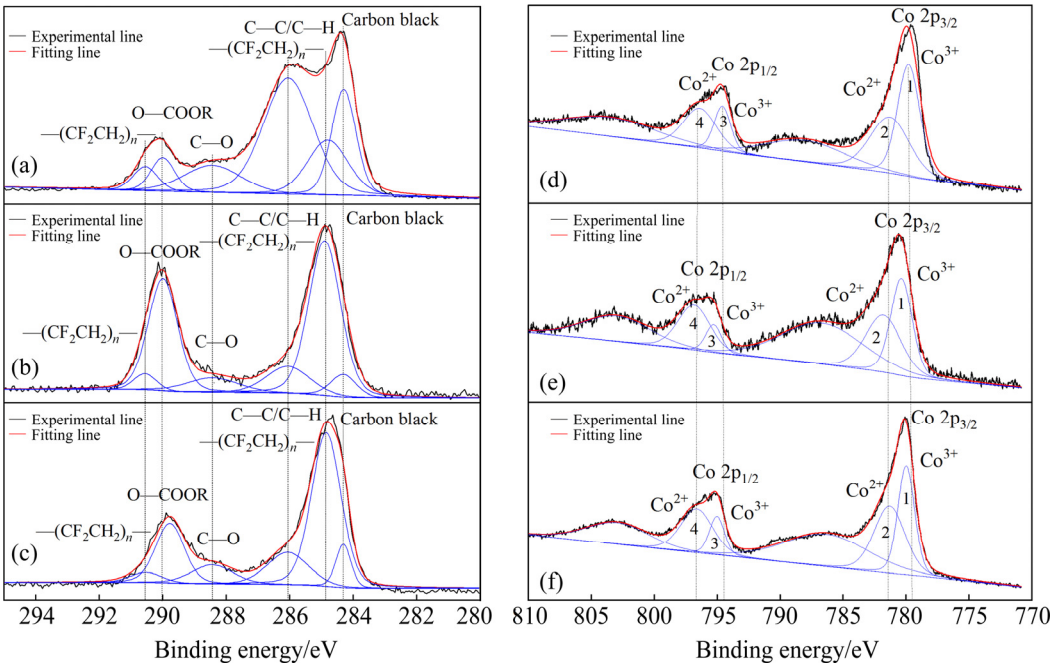

Fig. 7 C 1s (a−c) and Co 2p (d−f) XPS spectra: (a, d) Untreated sample; (b, e) Direct grinding sample; (c, f) Mechano-chemical grinding sample

Table 2 Chemical states of carbon on surface of $LiCoO_2$ particle under different grinding treatments

Name	Peak position/eV	Content/wt.%		
		Untreated sample	Direct grinding sample	Mechanochemical sample
Carbon black	284.3	19.08	5.14	6.96
C—C/C—H	284.8	16.49	44.38	48.63
—$(CH_2CF_2)_n$—	286.05	42.42	10.51	14.17
C—O	288.5	11.61	6.91	8.56
O—COOR	289.9	5.91	29.67	18.24
—$(CH_2CF_2)_n$—	290.55	4.46	3.33	3.43
—$(CH_2CF_2)_n$— total content/wt.%		46.88	13.84	17.60

Table 3 Fitting peaks of Co 2p XPS spectra of $LiCoO_2$ particles in Figs. 7(d−f) under different conditions

Sample	Co^{3+}					Co^{2+}					$I(Co^{3+})/I(Co^{2+})$
	w_1/wt.%	w_3/wt.%	E_1/eV	E_3/eV	ΔE_1/eV	w_2/wt.%	w_4/wt.%	E_2/eV	E_4/eV	ΔE_2/eV	
Untreated	24.56	7.34	779.80	794.60	14.80	21.36	12.81	781.30	796.4	15.10	0.93
Direct grinding	18.91	3.99	780.37	795.29	14.92	18.43	12.96	781.81	796.85	15.04	0.73
Mechanochemical grinding	22.43	7.12	779.99	795.03	15.04	25.52	17.31	781.31	796.63	15.32	0.69

w_1−w_4 and E_1−E_4 stand for contents and binding energies at Positions 1, 2, 3 and 4 in Figs. 7(d−f), respectively; $\Delta E_1=E_3-E_1$, $\Delta E_2=E_4-E_2$; I stand for peak intensity of Co^{3+} or Co^{2+}

3.4 Influence of grinding conditions on leaching results

Leaching experiments of $LiCoO_2$ were conducted to investigate the effect of mechano-chemical pretreatment on the leaching efficiencies of Co and Li after grinding. The optimal leaching efficiencies of valuable metals in $LiCoO_2$ were obtained under the optimal grinding conditions such

as $SiO_2/LiCoO_2$ mass ratio, grinding speed, and grinding time.

3.4.1 Influence of $SiO_2/LiCoO_2$ mass ratio

The effect of $SiO_2/LiCoO_2$ mass ratio on the leaching efficiencies of Li and Co was examined under the conditions of 80 °C, pulp density 20 g/L, grinding speed 400 r/min, and grinding time 30 min. As shown in Fig. 8(a), the leaching efficiencies of Co and Li increased with the increase of the $SiO_2/LiCoO_2$ mass ratio. When $SiO_2/LiCoO_2$ mass ratio increased from 0 to 1:1, the leaching efficiency of Co increased from 75.21% to 98.05%, and that of Li increased from 62.50% to 83.33%. The leaching efficiency is not changed significantly as the mass ratio continuously increased. To reduce the consumption of reagents and ensure a high leaching efficiency, $SiO_2/LiCoO_2$ mass ratio of 1:1 was selected.

3.4.2 Influence of grinding speed

Figure 8(b) shows the effect of grinding speed on leaching efficiencies of Co and Li derived from $LiCoO_2$ at $SiO_2/LiCoO_2$ mass ratio of 1:1 and grinding time of 30 min. It can be seen that the leaching efficiencies of Co and Li show an increasing trend with the increase of grinding speed. For the direct leaching, the leaching efficiencies of Co and Li are not remarkable because Co^{3+} is arduous to dissolve from the layered structure of $LiCoO_2$. Furthermore, citric acid is a kind of weak acid that is insufficient to extract valuable elements from LIBs in the absence of a reducing agent. Leaching efficiencies of Co and Li increased rapidly at a grinding speed of 200 r/min, which manifests that the mechanochemical pretreatment is effective to improve the leaching efficiency. The leaching efficiency of Co decreased slightly to 94.91% whereas Li still rose to 97.22% with the grinding speed increasing to 500 r/min. Therefore, the grinding speed of 500 r/min was selected.

3.4.3 Influence of grinding time

Figure 8(c) shows the effect of grinding time on the leaching efficiencies of Co and Li at $SiO_2/LiCoO_2$ mass ratio of 1:1 and grinding speed of 500 r/min. The results show that the increasing trend of Li and Co leaching efficiencies was not significant as the grinding time increased from 10

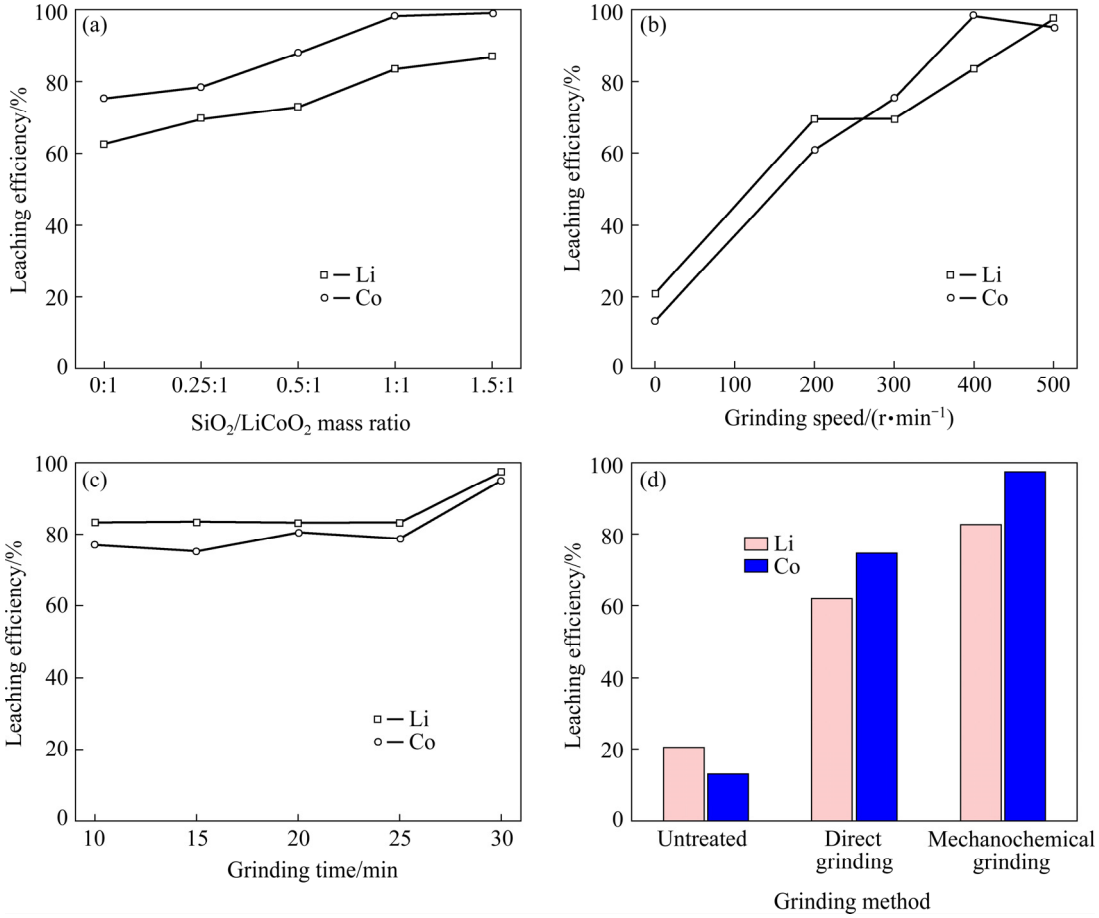

Fig. 8 Effects of $SiO_2/LiCoO_2$ mass ratio (a), grinding speed (b), grinding time (c), and grinding method (d) on leaching efficiencies of Li and Co

to 25 min. The leaching efficiencies of Co and Li increased to 94.91% and 97.22% at grinding time of 30 min, respectively. Therefore, on the premise of ensuring a high leaching efficiency and low energy consumption, grinding time of 30 min was selected.

Besides, different samples were leached in citric acid solution, and the leaching results were compared. As shown in Fig. 8(d) under conditions of $SiO_2/LiCoO_2$ mass ratio of 1:1, grinding speed of 400 r/min and grinding time of 30 min, only 20.83% of Li and 13.43% of Co in the untreated sample were leached. The leaching efficiencies of 62.50% Li and 75.21% Co were obtained after direct grinding, respectively, indicating that direct grinding is not an effective method for extracting Co and Li. Mixture grinding of SiO_2 and cathode particles results in the obvious increase of leaching efficiencies of two elements, which further proves that the mechanochemical method is feasible to improve the leaching efficiency of $LiCoO_2$.

The leaching residue was also studied by SEM−EDS. It can be seen from the SEM image of Fig. 9(a) that the leaching residue partially appeared in the form of particles and partially in the form of flocs. EDS mapping images show that the main component of leaching residue is Si. The results indicate that the silica is functioned as a co-grinder during the mechanochemical process, which means that there is no obvious change in terms of the chemical content of $LiCoO_2$ powders.

4 Conclusions

(1) The mechanism of mechanochemical grinding indicates that with the increase of grinding speed, the particle size of $LiCoO_2$ is gradually reduced, and more new surfaces are exposed on the cathode material of the spent batteries.

(2) The diffraction peak of $LiCoO_2$ gradually decreases and finally disappears, which proves that the crystal structure of $LiCoO_2$ is destroyed and transformed into an amorphous state. TEM results show that the atomic arrangement of Li (Co) appears to be incomplete coordination and partial defects of lattice streaks after mechanochemical grinding, which causes Co^{3+} to transform into Co^{2+}, which is easier to be leached in acid solution than Co^{3+}. The presence of SiO_2 causes the particles to be ground completely and acts as the secondary grinding.

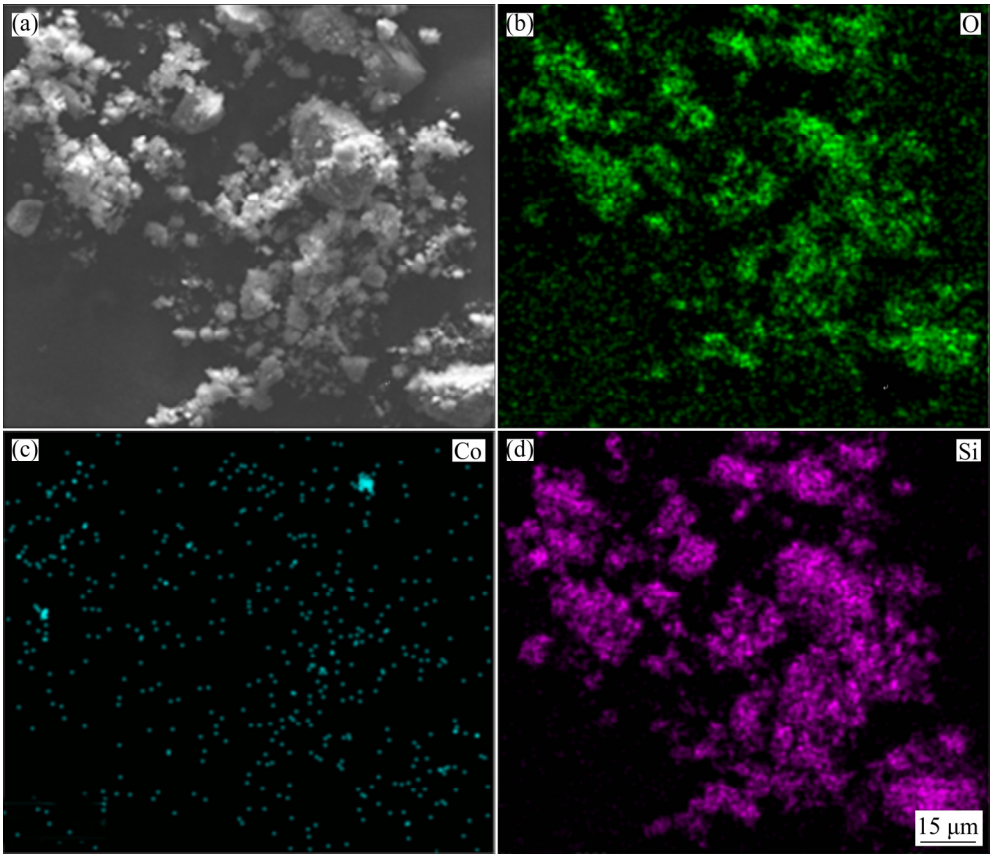

Fig. 9 SEM image of leaching residue (a), and its corresponding EDS mapping of O (b), Co (c), and Si (d)

(3) The grinding speed and the grinding time on the subsequent leaching efficiencies of Co and Li show that the optimal leaching efficiencies of 94.91% Co and 97.22% Li in $LiCoO_2$ are obtained at $SiO_2/LiCoO_2$ mass ratio of 1:1, grinding speed of 500 r/min, and grinding time of 30 min.

Acknowledgments

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机械化学法强化废弃锂离子电池中钴和锂的浸出

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摘　要：以 SiO_2 为助磨剂，采用机械化学法提高废弃锂离子电池中 Co 和 Li 的浸出率。实验结果表明，在 SiO_2 与 $LiCoO_2$ 质量比为 1:1、研磨转速为 500 r/min 及研磨时间为 30 min 的最优条件下，Co 和 Li 在柠檬酸中的浸出率分别达到 94.91%和 97.22%。表征结果表明，通过机械化学研磨，$LiCoO_2$ 形成新的活性表面，表面性质发生变化。同时，$LiCoO_2$ 晶格结构发生缺陷，原子配位不全使反应活性增强。在机械作用下，炭黑的还原作用提高了 Co^{3+}的浸出效率。结果表明，该工艺能有效地从 $LiCoO_2$ 中回收 Co 和 Li。

关键词：机械化学研磨；浸出；废弃锂离子电池；表面性质；反应机理

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