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Preferentially selective extraction of lithium from spent $LiCoO_2$ cathodes by medium-temperature carbon reduction roasting

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Abstract: Lithium recovery from spent lithium-ion batteries (LIBs) have attracted extensive attention due to the skyrocketing price of lithium. The medium-temperature carbon reduction roasting was proposed to preferential selective extraction of lithium from spent $LiCoO_2$ (LCO) cathodes to overcome the incomplete recovery and loss of lithium during the recycling process. The LCO layered structure was destroyed and lithium was completely converted into water-soluble Li_2CO_3 under a suitable temperature to control the reduced state of the cobalt oxide. The Co metal agglomerates generated during medium-temperature carbon reduction roasting were broken by wet grinding and ultrasonic crushing to release the entrained lithium. The results showed that 99.10% of the whole lithium could be recovered as Li_2CO_3 with a purity of 99.55%. This work provided a new perspective on the preferentially selective extraction of lithium from spent lithium batteries.

Keywords: spent $LiCoO_2$ cathodes; medium-temperature carbon reduction; lithium extraction priority; crystal transformation; macroscopic transport resistance

1. Introduction

Lithium cobalt oxide ($LiCoO_2$, LCO) with high voltage, high energy density, and long cycle life dominates lithium-ion batteries (LIBs) cathodes materials for portable electronic devices [1–5]. With an average lifespan of 5–10 years, a large number of LIBs will be retired in the next several years [6]. It is predicted that the volume of portable LIBs reaching their end-of-life will reach 180000 $t\cdot a^{-1}$ by 2023 [7]. The recycling of spent LCO has attracted extensive attention [8]. Conventionally, cobalt and nickel are of priority in the LIBs recycling process due to their metal prices, leaving lithium the last one to be concerned [9–11]. In recent years, the price of lithium element hiked up to be the most precious element in LIBs [12–13]. The drastically enlarged profit margin of lithium makes preferentially selective recycling of lithium from spent lithium batteries lucrative, ensuring the recovery of lithium maximal.

Traditional pyrometallurgical recovery of spent LCO is usually prepared by sintering at high temperature of approximately 1000°C. In this process, Cu and Co form an alloy, while lithium is often lost as a by-product in the slag phase [14], which requires further extraction and separation [15]. Although pyrometallurgical methods are simple, low recovery of lithium and high energy consumption need to be considered [16]. Hydrometallurgy methods are employed to recover valuable metals from spent LIBs [17]. All metals are first dissolved into the solution and then all metals except lithium are precipitated or extracted [18–20] with a lithium recovery rate of more than 95%. The leaching process is usually carried out in a reducing agent and organic/inorganic acid solution [21–23]. However, these reducing agents are either expensive or pollutants. In recent years, reduction roasting has been extensively investigated by researchers [24–27], which is to convert all metallic elements into water-insoluble forms except lithium, in which lithium is water-leached solely [28–30]. Zhou *et al.* [31] reported a biomass carbon thermal reduction method for recovering Li from spent $LiCoO_2$ by vacuum pyrolysis of pine sawdust. Dai *et al.* [16] proposed an enhanced strategy for the efficient selective recovery of Li from spent Li-ion batteries based on the pyrolysis of bean dregs (BDs). High-efficiency and simple recovery operations have drawn much attention [32–35]. Yin *et al.* [36] converted the Co_3O_4 and Li into CoO and Li_2CO_3 by carbon thermal reduction, respectively [37] and produced battery-grade Li_2CO_3 directly after the water leaching, with a

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lithium recovery rate of 93%. However, there is still a chasm in the recovery of preferential lithium extraction in contrast to the traditional process, which is imperative to be solved.

Currently, the incompleteness of Li recovery can be attributed to the complex layered structure of the LCO [38], which is associated with Li being encapsulated by the octahedral structure of the transition metal oxide. If the degree of reduction of cobalt oxide is controlled, then it is possible that the Li is completely released. Xu *et al.* [39] reported that the Co–O octahedral structure may be disrupted and cobalt metal was observed by reduction roasting at appropriate temperatures (800 and 1000°C). Petránikova *et al.* [40] converted Co_3O_4 to CoO by carbon reduction roasting at 600°C. The partial CoO structure was disrupted and Co was observed in the products with temperatures above 700°C, which was reported by Hu *et al.* [41]. Therefore, the structure of cobalt oxide octahedral opened by carbon reduction roasting, which will release the trapped lithium and enhance the leaching recovery.

This work proposed a preferential selection of lithium from spent LCO cathodes through the design of a medium-temperature carbon reduction roasting process in which lithium is completely converted into water-soluble Li_2CO_3. The cobalt oxide octahedral structure is destroyed and transformed into cobalt metal, which is further partially transformed into cobalt metal agglomerates under medium-temperature conditions. The aqueous leaching process is going to be intensified through wet grinding coupled with ultrasonic crushing and Li_2CO_3 is crystallized directly.

2. Experimental

2.1. Materials

LCO were provided by Anhui Chaoyue Environmental Protection Technology Co., Ltd., China. The relevant chemical composition details of the LCO were shown in Table S1. Hydrochloric acid (HCl, AR) and nitric acid (HNO_3, AR) were purchased from the Beijing Chemical Factory, China. Carbon black (99wt%, 200 mesh) was purchased from Sinopharm Chemical Reagent Co., Ltd., China. The deionized water was produced in the Laboratory Center of the University of Science and Technology Beijing, China.

2.2. Preparation of Li_2CO_3

The changes in the standard Gibbs free energy ($\Delta G^{\ominus}$) of the reactions were estimated by the HSC software (HSC chemistry 6.0). The LCO cathode powder and carbon black with the mass ratio of (1:0.05, 1:0.10, 1:0.15, 1:0.20, and 1:0.25) were mixed with a vortex mixer (HY-1, Shanghai Yidian Scientific Instruments Co., China) at 2800 r·min^{-1} for 3 min to obtain a uniformly mixed powder. Samples of mixed powders mentioned above were placed in corundum crucibles with covers and roasted in a tube furnace (MXG1200-80, Shanghai Micro-X Furnace Co., Ltd., China). The detailed procedure was that the air in the tube furnace was replaced by a nitrogen purge of 200 mL·min^{-1} to ensure samples were in an oxygen-free environment. The samples were roasted with the temperature initiated from 30°C to the set temperatures (600, 650, 700, 750, 800, and 850°C) at a rate of 10°C·min^{-1}. After reaching terminal temperature, the samples were roasted isothermally for different intervals (15, 30, 60, 90, and 120 min) and naturally cooled to 30°C in a nitrogen atmosphere. The roasted products were ultrasound crushed (JY92-IIDN, Shanghai Haozhuang Instrument Co., Ltd, China) after being wet ground first to eliminate the possible metal agglomerates. Then it was subjected to water leaching at a solid–liquid ratio of 1:25 g·mL^{-1}, and the Li_2CO_3 product was obtained by heating, evaporating, and crystallizing the lithium-containing aqueous immersion solution at a stirring speed of 500 r·min^{-1} and 80°C.

2.3. Characterization

The weight loss of the mixed samples with temperature was investigated by thermogravimetric analysis (TGA, Mettler Toledo, Switzerland). The physical phases of roasted products were characterized by X-ray diffraction (XRD D8 Advance, Bruker) with operational parameters as 1.5406 Å Cu-K$_\alpha$ radiation, 1°·min^{-1} scanning rate, and 10°–90° range. The elemental states of the roasted products were determined by an X-ray photoelectron spectroscopy (XPS, AXIS Ultra DLD, Kratos, Japan), and the morphologies of the products were scanned by scanning electron microscopy (SEM-EDS, S-4800; Hitachi, Japan). Particle size of the roasted product was carried out using a laser particle sizer (Mastersizer 2000, Malvern, UK). The lithium contents in leachates and purity of Li_2CO_3 were determined by inductively coupled plasma emission spectra (ICP-OES, Agilent 5110, U.S.). The lithium leaching efficiency was calculated using the formula (1):

$$\eta_i = \frac{m_i}{m_{\mathrm{A}}} \times 100\% = \frac{c_i \times V}{m_{\mathrm{A}} \times \omega_i} \times 100\% \tag{1}$$

where η_i represents the leaching efficiency of metal element i, %; m_i means the mass of metal element i in the leaching solution, mg; m_{A} indicates the total mass of the metal element in the sample, mg; ω_i is the mass fraction of metal element i; c_i represents the concentration of metal element i in the leaching solution; V is the volume of the leaching solution, L.

3. Results and discussion

3.1. Thermodynamic and TGA analysis

According to previous studies [38,41–42], LCO cathode material was first pyrolyzed to produce lithium oxide and cobalt oxide in Ar/N_2 atmosphere and above 600°C, and the corresponding reaction equations as follows:

$$6LiCoO_2 = 3Li_2O + 2Co_3O_4 + 1/2O_2(g) \tag{2}$$

$$4LiCoO_2 = 2Li_2O + 4CoO + O_2(g) \tag{3}$$

After thermal decomposition, the generated metal oxide was reduced by carbon. The relationship between $\Delta G^{\ominus}$ and the temperature of metal oxide was calculated, as shown in Fig. 1. The value of $\Delta G^{\ominus}$ for Eqs. (4)–(7) was much less than 0 in the temperature range of 0–1000°C, which indicated that

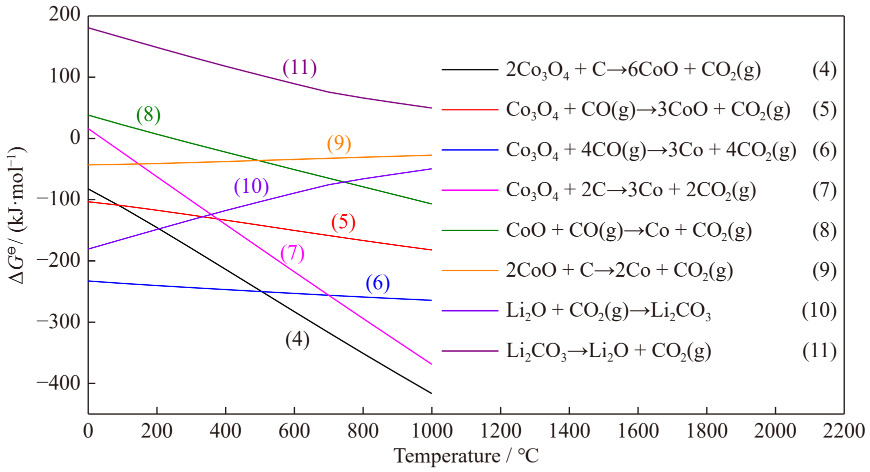

Fig. 1. Relationship between $\Delta G^{\ominus}$ and temperature.

the Co element could undergo a reaction process from Co_3O_4 to CoO [39]. Also, the absolute value of $\Delta G^{\ominus}$ for Eqs. (8)–(9) was less than 0 in this temperature range. It can be inferred that the Co(III) was reduced to Co(II) and Co(0) in the reducing atmosphere. The absolute value of $\Delta G^{\ominus}$ for Eq. (11) decreased with the increase in temperature, indicating the unfavorable to the formation of Li_2CO_3 with the increase in temperature.

The TGA curves of the mixture of spent LCO cathode powder and carbon black within the temperature ranging from 25 to 1000°C were shown in Fig. 2. It was observed that 4 significant weight loss occurred in the nitrogen atmosphere. The 1st weight loss of only 0.554wt% occurred within the temperature ranged from 25 to 400°C, which was attributed to the evaporation of water in the samples. The 2nd significant weight loss of 3.683wt% occurred in the temperature interval between 550 and 700°C (region II). Considering the thermodynamic calculations above, the weight loss at this stage might be ascribed to the oxygen released by the decomposition of spent LCO cathodes. The weight loss of 9.763wt% and 2.455wt% (region III and IV) was explained by the fact that the transition metal oxides were reduced to release CO_2 [41]. In addition, it was accredited to the decomposition and volatilization of Li_2CO_3, since Li_2CO_3 was volatilized and decomposed at 700–900°C) [32,36,43], which was consistent with the predictions of thermodynamic calculations above.

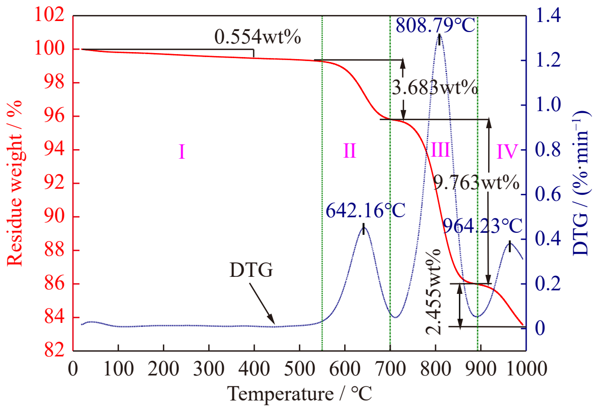

Fig. 2. TGA curve of the mixture of LCO cathode powder and carbon black in reductive roasting.

3.2. XRD analysis

The relationship between the roasting temperature and conversion of LCO at a mass ratio of 1:0.15 for 60 min was shown in Fig. 3. It was found that the diffraction peak of LCO almost was unchanged except for carbon compared to the pristine when the temperature was 600°C (Fig. 3(a)). This indicated that the low calcination temperature was not sufficient to collapse the crystal structure of LCO [41]. When the temperature was 650°C, the LCO peak disappeared, and the diffraction peaks of Li_2CO_3, CoO, and a small amount of Co were observed.

When the temperature continued to increase to 750°C, more CoO was reduced to Co, and the peak intensity of Li_2CO_3 increased, which indicated that more and more Li and Co elements were released. However, when the temperature was raised to 800°C, the peak intensity of Li_2CO_3 decreased while the Co increased further, which indicated that the continued heating was beneficial for the formation of Co metal and unfavorable to Li_2CO_3.

As shown in Fig. 3(b), the reduction roasting process was carried out at 750°C for 60 min with different dosage ratios. The weak characteristic peaks of Li_2CO_3 and Co were observed, with the carbon dosage of 5wt% which was insufficient to make Li completely convert Li_2CO_3. The intensity of the characteristic peak of Li_2CO_3 showed an increasing trend with the increase of carbon dosage, which indicated that the increase of carbon dosage was favorable for the reduction reaction. When the carbon dosage continued to increase, although the formation of Co was favored, the intensity of the characteristic peak of Li_2CO_3 weakened. Therefore, a reasonable range of carbon dosage was 5wt%–25wt%. As shown in Fig. 3(c), XRD results showed that the characteristic peak of Li_2CO_3 appeared when the holding time was 60 min, and it was almost the same when the holding time was extended to 90 min, suggesting that the LCO was converted completely when the holding time was 60 min. The temperature of 750°C, the carbon dosage of 15wt%, and the roasting time of 60 min were the optimal.

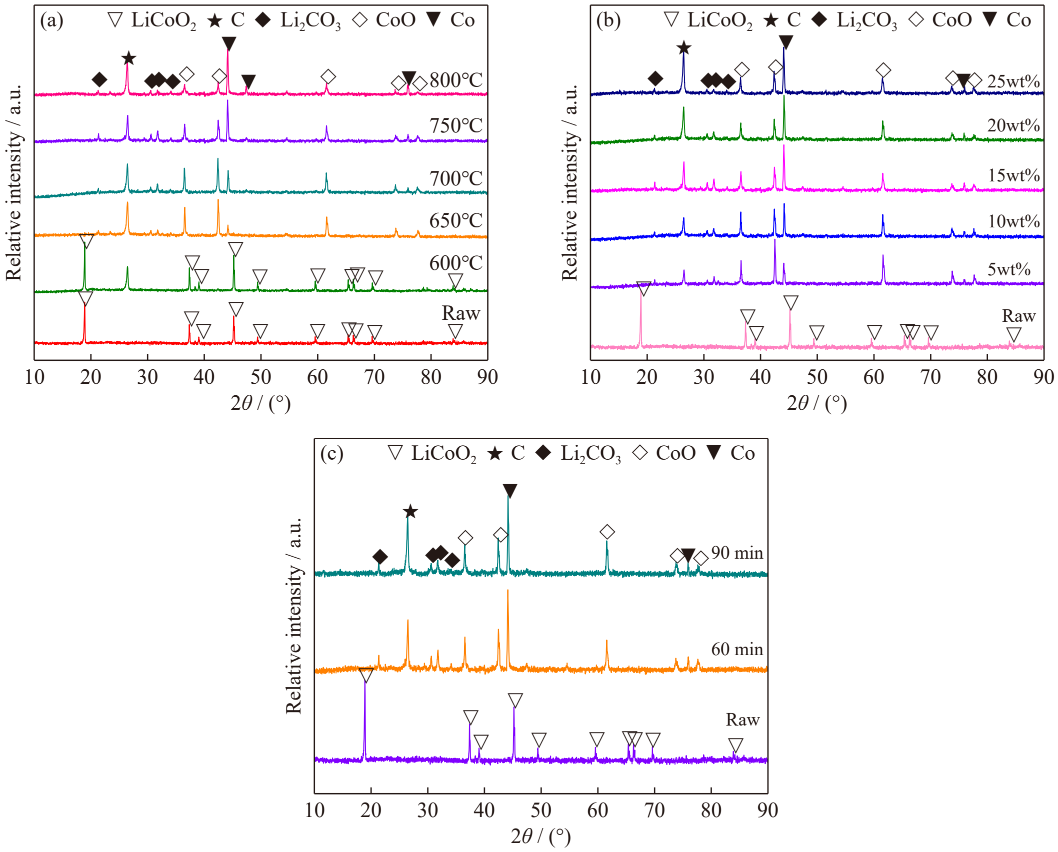

Fig. 3. XRD patterns of roasting products: (a) temperature; (b) carbon dosage; (c) time.

3.3. XPS and SEM-EDS analysis

The XPS spectra before and after roasting showed the spectrum of Co 2p (Co $2p_{3/2}$ and Co $2p_{1/2}$) before the reduction roasting were characteristics of Co^{3+} (780.1 and 795.0 eV) [41,44], and the satellite structure was quite weak [45], which might be resulted in Co(II) in the trace amount of Co_3O_4, as shown in Fig. 4(a). The binding energies of Co $2p_{3/2}$ and Co $2p_{1/2}$ of the roasted products changed to 780.8 eV and 796.6 eV, respectively, matching with Co^{2+}, and the characteristic peak at 778.7 eV corresponded Co(0) [16,46], as shown in Fig. 4(b). This suggested that the part of the cobalt oxide octahedron was then destroyed to produce cobalt metal, which was consistent with the XRD results.

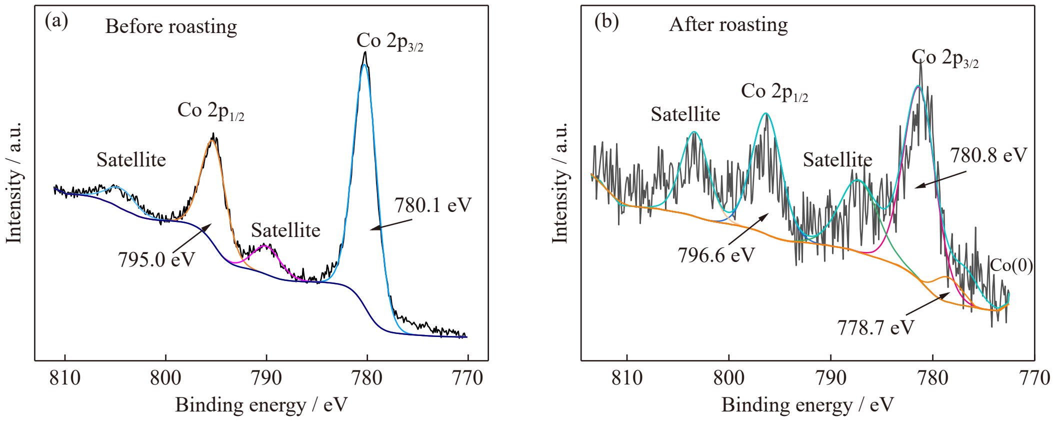

Fig. 4. XPS spectra of spent LCO cathodes (a) before and (b) after carbon reduction roasting.

To further understand the effect of the medium-temperature carbon reduction roasting on the conversion of LCO cathodes, the morphology of the calcined products was investigated by SEM-EDS (Fig. 5). The EDS results indicated that the irregular shape of region 1 was a cobalt-rich phase. There was no doubt that the metal agglomerate structure formed by the disruption of the Li/Co octahedra after medium-temperature carbon reduction roasting. It was preliminarily concluded that the metal agglomerations produced during the medium-temperature carbon reduction roasting might contain a small amount of lithium. To further demonstrate this, the water-leaching residue was dissolved in aqua regia and a small amount of lithium was detected by ICP-OES (Table S2).

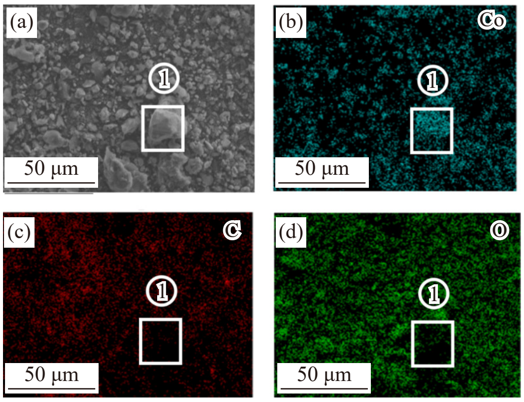

Fig. 5. SEM image and EDS analysis of the roasted products.

3.4. Parameter optimization of water leaching process

The water-leaching treatment was conducted to extract lithium after wet grinding and ultrasonic crushing. The effect of key parameters including particle size, roasting temperature, carbon dosage, and holding time on lithium recovery was investigated, and results were shown in Fig. 6.

3.4.1. Particle size

When the size distribution was 50%, the particle size was 18.86 μm for water leaching, which was larger than that of wet grinding (15.81 μm) and wet grinding+ultrasonic crushing (8.81 μm), respectively (Fig. 6(a)). The Li recovery rate increased from 94.65% before processing to 95.35% and 99.10% for wet grinding and wet grinding+ultrasonic crushing, respectively (Fig. 6(b)). This was because ultrasonic crushing could produce ultrasonic cavitation in the leaching solution, break up the metal agglomerates chemically and mechanically at the solid–liquid interface, and reduce the macroscopic transport resistance, so that the aqueous solution leaching process was enhanced and released the entrapped lithium accordingly.

3.4.2. Roasting temperature

Fig. 6(c) showed the lithium recovery rate at different temperature. As can be seen, the lithium recovery rate increased from 88.72% to 94.65% with the temperature increased from 650 to 750°C. Also, it was observed that the lithium recovery rate was increased to different degrees after two steps of wet grinding and ultrasonic crushing, which was attributed to the release of lithium encapsulated by metal agglomerates. However, when the temperature continued to increase to 800°C, the recovery rate of lithium decreased. Therefore, 750°C was the best the roasting reduction temperature.

3.4.3. Carbon dosage

The effect of carbon dosage on the reduction roasting of LCO was shown in Fig. 6(d). It was found that wet grinding and ultrasonic crushing significantly improved the recovery rate of lithium under different carbon dosage conditions. The recovery rate of lithium was 86.85% when the carbon dosage was 5wt%. It firstly increased and then decreased with the increase of carbon dosage, and it reached 99.10% with the carbon dosage of 15wt%. The recovery rate could decrease when continued increased the carbon dosage due to the excess carbon adsorbing Li_2CO_3 [47–48], which was consistent with the XRD results. Therefore, the optimal carbon dosage was 15wt%.

3.4.4. Holding time

As shown in Fig. 6(e), the holding time of the Li recovery process was optimized at a carbon dosage of 15wt% for 750°C. ICP-OES results showed that the lithium recovery increased from 70.55% to 94.32% when the holding time was increased from 15 to 60 min. When the holding time was extended to 90 min, the final recovery rate of lithium after wet grinding and ultrasonic crushing was basically the same as that at 60 min. This suggested that the carbon reduction roasting reaction was completed when the holding time was 60 min. Therefore, the optimal holding time was 60 min, and the optimal leaching rate of Li was 99.10%.

Finally, the XRD (Fig. 7) confirmed that the white solid after evaporation and crystallization was Li_2CO_3 (PDF #22-

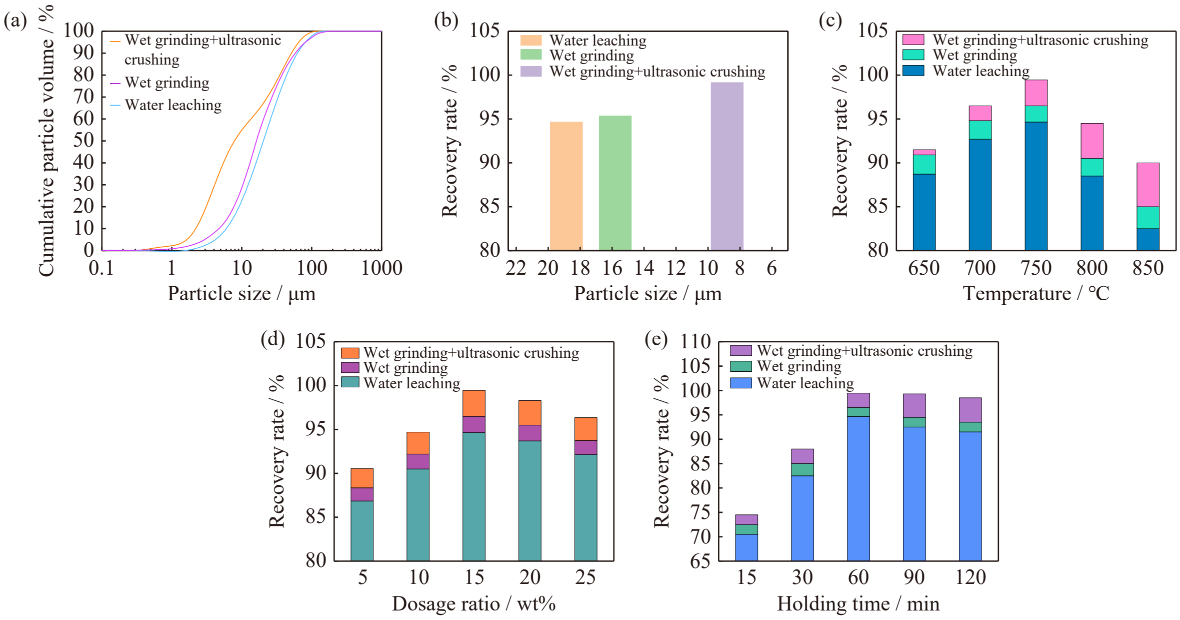

Fig. 6. Effects of (a) and (b) particle size distribution, (c) roasting temperature, (d) dosage ratio, and (e) holding time on lithium recovery rate.

1141). The purity of Li_2CO_3 recovered by aqua regia dissolution and ICP-OES determination reached to 99.55%.

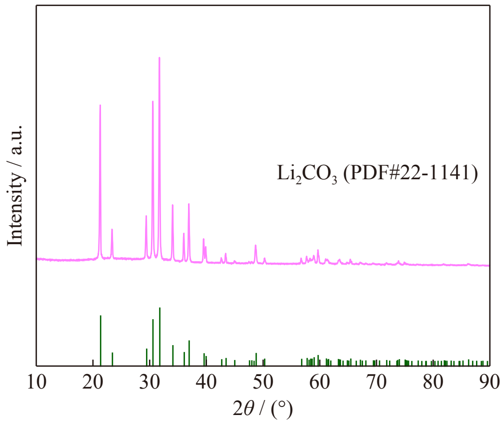

Fig. 7. XRD of the white solid after evaporation and crystallization.

3.5. Mechanism analysis

The possible pathway for lithium release was shown in Fig. 8. After carbon reduction roasting, the laminar structure of LCO began to collapse to release the Li/Co octahedrons. Li octahedrons released oxygen atoms into Li tetrahedrons, which were further collapsed and combined with CO_2 into Li_2CO_3. The partial Co octahedron released oxygen atoms into the cobalt metal with the temperature increase. The electron paramagnetic resonance (EPR) showed that the roasted products exhibited a sharp EPR signal at $g = 2.003$, indicating the formation of more oxygen vacancies on their surface (Fig. S1) [49–50]. It showed that the oxygen ions were removed from the lattice. Although the electrovalent bond energy of Li–O was less than the covalent bond energy of Co–O [38], it did not mean that the Li–O octahedra collapse completely preferentially. This was because the Li/Co octahedral structure did not exist independently, but was alternately filled with Co and Li layers between adjacent O layers [38,51]. It was possible that a part of the Li–O crystals tightly surrounded by Co–O octahedra during the carbon reduction roasting process, resulting in the “intermediate state.” It was speculated that the “intermediate state” could be disrupted for the encapsulated lithium to be completely released when the roasting temperature was not lower than 750°C.

To prove the existence of the “intermediate state,” the lithium oxide and cobalt oxide were mixed with carbon powder in the optimal ratio, and then roasted at 650°C far below the temperature of complete lithium conversion in layered LCO, and the XRD and ICP-OES results were shown in Fig. S2 and Table S3. It was found that the cobalt oxide octahedron remained in the original crystallography, but the characteristic peak of Li_2O completely disappeared and the Li_2CO_3 appeared. The ICP-OES results demonstrated that the leaching rate of lithium ions reached approximately 100%. Therefore, it could conclude that Li_2O completely converted into Li_2CO_3 far below 750°C, while the Co–O octahedral structure was not destroyed. Meanwhile, Co metal was prone to polymerization greater than 600°C [52], in which part of lithium was susceptible to being entrapped by Co transition metal agglomerates (Fig. 5), which was solved by the wet grinding coupled with ultrasonic crushing.

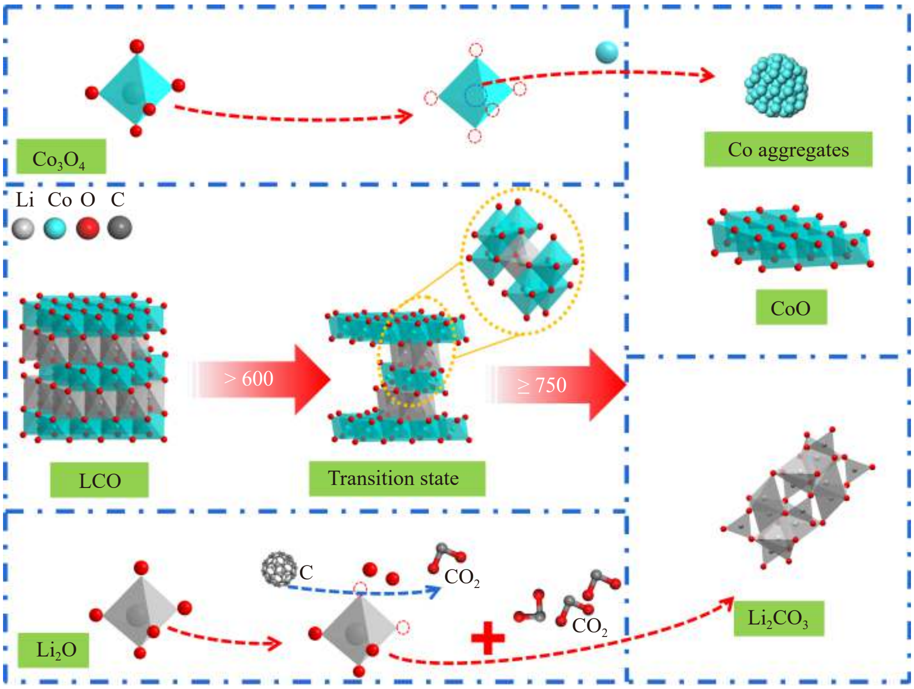

Fig. 8. Collapsing model of spent LCO cathodes at carbon reduction roasting.

4. Conclusions

A medium-temperature carbon reduction roasting was reported in this study, which aimed to preferentially selective lithium extraction to overcome the problem of incomplete recovery of lithium. XRD analysis showed that lithium was completely converted into water-soluble Li_2CO_3 products by adjusting the temperature to control the reduced state of the cobalt oxide during medium-temperature carbon reduction. SEM-EDS showed that part of lithium was encapsulated in Co metal aggregates during that roasting process. The aqueous leaching was intensified through wet grinding coupled with ultrasonic crushing which was decrease the macroscopic transport resistance, which could be verified by particle size distribution analysis. Finally, the battery-grade Li_2CO_3 with a purity of 99.55% was obtained along with the optimal lithium recovery rate of 99.10% at a temperature of 750°C, 60 min, and 15wt% carbon dosage.

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Conflict of Interest

The authors declare no competing financial interest.

Supplementary Information

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