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Selective recovery of lithium from spent lithium iron phosphate batteries using oxidation pressure sulfuric acid leaching system

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Abstract: Oxidation pressure leaching was proposed to selectively dissolve Li from spent $LiFePO_4$ batteries in a stoichiometric sulfuric acid solution. Using O_2 as an oxidant and stoichiometric sulfuric acid as leaching agent, above 97% of Li was leached into the solution, whereas more than 99% of Fe remained in the leaching residue, enabling a relatively low cost for one-step separation of Li and Fe. And then, by adjusting the pH of leachate, above 95% of Li was recovered in the form of the Li_3PO_4 product through iron removal and chemical precipitation of phosphate.

Key words: spent $LiFePO_4$ batteries; oxidation pressure leaching; separation; Li; Fe; lithium phosphate

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1 Introduction

Lithium-ion batteries (LIBs) are widely used in portable appliances and electric vehicles due to their excellent cycle performance, high discharge voltage and energy density [1−3]. Among various current cathode materials, olivine-structured lithium iron phosphate ($LiFePO_4$) has attracted wide attention for its high theoretical specific capacity (170 mA·h/g), low price, stable structure, high safety, and environment-friendly performance [4]. Therefore, $LiFePO_4$ is considered as the most promising cathode material for power batteries in electric vehicles and hybrid electric vehicles [5]. With an increasing demand for $LiFePO_4$ batteries, it is inevitable to produce a large number of spent $LiFePO_4$ batteries. The direct disposal of these spent batteries will cause serious environmental problems due to some harmful chemical substances in them. Moreover, valuable metals such as Li and Fe are also discarded [6]. Therefore, it is urgent to develop a green and feasible process for the treatment of spent $LiFePO_4$ batteries.

Currently, the direct regeneration of spent $LiFePO_4$ is viewed as a low-cost and relatively simple recycling method [7,8]. Considering the fact that the structure of the $LiFePO_4$ materials has been destroyed after thousands of cycles, regenerated cathode materials are unable to perform perfectly compared with the original materials [9]. Although some studies have been conducted for improving the performance of regenerated $LiFePO_4$ via doping with other materials [10,11], problems with an unstable product quality still remain. Another alternative method is to extract valuable metals from spent materials via hydrometallurgy with mineral acid including H_2SO_4 [12], HCl [13], H_3PO_4 [14,15] or organic acid [16,17] as the leaching agent. As $LiFePO_4$ is rather stable with an

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olivine structure, the amount of acid added must greatly exceed the stoichiometric consumption required, leading to a large amount of wastewater and an elevated recycling cost [18−21]. In order to solve these problems, selective leaching of Li from spent $LiFePO_4$ has been proposed, which is able to simultaneously achieve enriched Li solution and $FePO_4$ precipitate [22]. LI et al [23] adopted near stoichiometric H_2SO_4 to treat spent $LiFePO_4$ cathode materials. The leaching efficiencies of Li and Fe are 96.85% and 0.027%, respectively. Likewise, YANG et al [24] applied acetic acid to achieve 95.05% of Li and 0.93% of Fe in leaching efficiencies from $LiFePO_4$ cathode scrap. The selective leaching presents a huge advantage for separation of Li and Fe; however, the reagents such as organic acids and H_2O_2 are relatively expensive. Moreover, Li recovery within the existing selective leaching methods is not sufficient. Therefore, selective leaching of Li with a high efficiency using certain green, inexpensive, or recyclable reagents should be the objective of future research on the treatment of spent $LiFePO_4$ batteries.

Pressure leaching technology is viewed as a green and strengthening leaching process, which has been successfully applied in the hydrometallurgical extraction of non-ferrous metals [25]. In this study, the technology was proposed to selectively extract Li from spent $LiFePO_4$ batteries by using green and inexpensive O_2 as the oxidant and low concentration of H_2SO_4 as the leaching agent. And then the resulting solution was further purified through a deep iron removal procedure. Finally, the Li in the leaching solution was recovered as Li_3PO_4 product.

2 Experimental

2.1 Materials

The spent $LiFePO_4$ batteries were provided by Guangdong Guanghua Tech. Co., Ltd., China. Before leaching, the material was pretreated to remove impurities including aluminum and copper. All chemical reagents, including H_2SO_4, NaOH, and $Na_3PO_4\cdot 12H_2O$, were of analytical grade. The purity of the oxygen used was above 99%.

Table 1 lists the contents of main elements in the spent $LiFePO_4$ cathode material. The scrap contained 34.1% of Fe, 4.5% of Li, and 19.4% of P. X-ray diffraction (XRD) pattern of the cathode material (Fig. 1) shows that $LiFePO_4$ was the only phase existing in the present scrap.

Table 1 Contents of main elements in spent cathode material (wt.%)

Fe	Li	P	C	Others
34.1	4.5	19.4	1.42	40.58

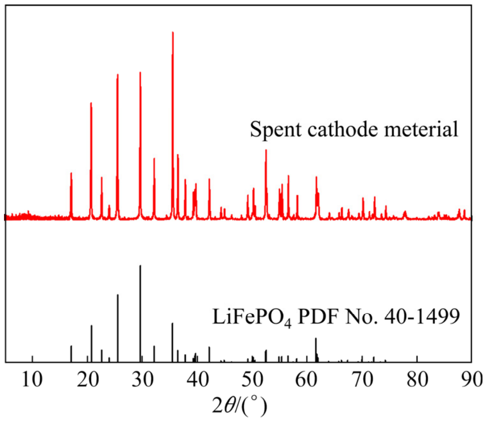

Fig. 1 XRD patterns of spent $LiFePO_4$ cathode material and standard $LiFePO_4$

2.2 Selective leaching of Li from spent cathode materials

The leaching experiments were performed in a 250 mL high-pressure autoclave device (HT−250KC−C, Shanghai Huotong, China). A total of 10 g of the spent cathode material was mixed with a certain amount of H_2SO_4 in the reaction vessel. After installation, the sealed autoclave was heated to the designed temperature. And then, the valve of the O_2 tank was opened to control the pressure inside the autoclave and stirring was conducted at 500 r/min. At certain time intervals, O_2 input and stirring were immediately stopped. Moreover, the autoclave was removed and placed in tap water to cool to 20−30 °C. Finally, the pressure in the autoclave was released through the outlet valve. The solution was separated from the residue by vacuum filtration. The pH of the leaching solution was measured via a pH meter. The residue was washed with ultrapure water several times and dried in a vacuum oven at 80 °C for 12 h and then weighed.

To evaluate the degree of selective Li leaching from the spent $LiFePO_4$ cathode material, a parameter, that is, the "selectivity (S_{Li})" was introduced, which was the Li concentration divided by the sum of the concentrations of Li and Fe in the solution, expressed as follows:

$$S_{\mathrm{Li}}=\frac{\rho_{\mathrm{Li}}}{\rho_{\mathrm{Li}}+\rho_{\mathrm{Fe}}}\times 100\% \tag{1}$$

where ρ_{Li} and ρ_{Fe} were Li and Fe concentrations (g/L) in the solution, respectively.

2.3 Lithium recovery by chemical precipitation

During the oxidation pressure leaching process, a small amount of Fe entered into the leaching solution. To obtain a pure Li-containing solution, the leaching solution was treated by adding a 1 mol/L NaOH solution. The Li recovery was conducted in a stirring water bath. A Na_3PO_4 solution (100 g/L) of the stoichiometric amount was added into the purified leachate at a speed of 3−8 mL/min through a peristaltic pump. The chemical precipitation was controlled at 95 °C for 0.5 h. After completing precipitation, the solution and precipitate were separated via vacuum filtration immediately. The product was subsequently dried in a vacuum oven at 95 °C for 12 h. The obtained mother liquor contained a high concentration of sodium sulfate, which was further treated by means of evaporation crystallization or freezing crystallization for recovering Na_2SO_4 according to its solubility characteristics [26].

2.4 Characterization

The morphology of the solid sample was characterized by scanning electron microscopy (SEM; FEI QUANTA650). The phase of the solid sample was analyzed by X-ray diffraction (XRD; BRUKER QUANTAX) with Cu K_α radiation under an accelerating voltage of 40 kV and a tube current of 30 mA. The data were collected by step scanning with a scanning speed of 10 (°)/min and a scanning angle (2θ) of 5°−90°. The iron valence of the solid sample was detected by X-ray photoelectron spectroscopy (XPS; Thermo Fisher Scientific K_α). The metal contents of the solid sample were analyzed by inductively coupled plasma-atomic emission spectrometer (ICP-AES; SPECTRO ARCOS).

3 Leaching parameters

3.1 Selective leaching of Li from spent cathode materials

3.1.1 Effect of leaching time

Figure 2 shows the effect of leaching time on the leaching efficiencies of Li and Fe. It can be seen that more than 97.65% of Li was leached into the solution within only 30 min. When the leaching time increased to 90 min, the Li leaching efficiency was enhanced to 98.15%. Continuing to extend the leaching time has little effect on the Li leaching efficiency (only increased to 98.37% in 240 min). The Fe leaching efficiency in each leaching experiment remained stable ranging from 0.032% to 0.044%, suggesting an efficient separation of Li and Fe.

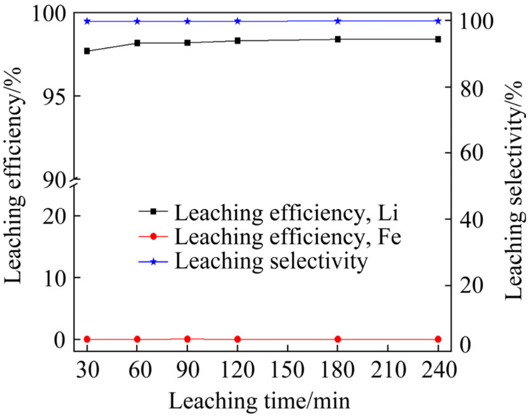

Fig. 2 Effect of leaching time on leaching of metals from spent $LiFePO_4$ cathode material (1.3 MPa O_2 partial pressure, 0.6 mol/L H_2SO_4, H_2SO_4/Li molar ratio of 0.60:1, and 140 °C)

3.1.2 Effects of O_2 partial pressure and temperature

The effect of O_2 partial pressure on the leaching efficiencies of Li and Fe was investigated in detail and the results are shown in Fig. 3. When O_2 partial pressure was 0 (no O_2 input), only 74.7% of Li was leached whereas Fe leaching efficiency was above 23.8%. In the absence of oxidizing atmosphere, soluble Fe^{2+} species were stable in the leaching solution, resulting in a low leaching selectivity. As O_2 was introduced into the autoclave, Fe^{2+} was oxidized into Fe^{3+} and then reacted with PO_4^{3-} or OH^- to form the insoluble substances. Under the condition of 1.3 MPa O_2 partial pressure, Li leaching efficiency reached 97.66% whereas Fe leaching efficiency gradually decreased to 0.005%. The leaching selectivity was as high as 99.96%, indicating a perfect separation efficiency of Li and Fe. However, with an increasing O_2 partial pressure from 1.3 to 1.7 MPa, Li leaching efficiency was reduced from 97.66% to 94.50% instead. The results could be attributed to different Fe precipitation mechanisms under various O_2 partial pressure conditions. Based on XRD analyses,

$FePO_4$ precipitate was observed with the O_2 partial pressure above 1.5 MPa, while $Fe_5(PO_4)_4(OH)_3\cdot 2H_2O$ precipitate was formed below 1.5 MPa.

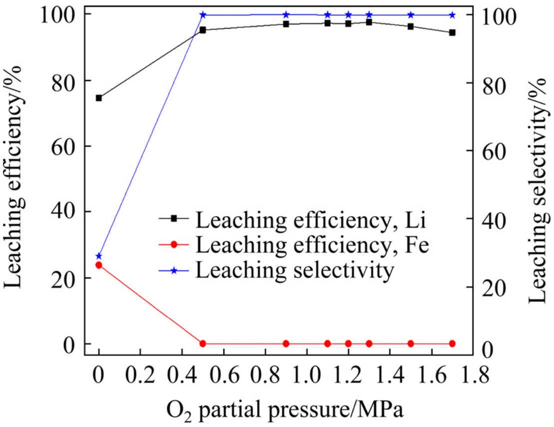

Fig. 3 Effect of O_2 partial pressure on leaching of metals from spent $LiFePO_4$ cathode material (0.3 mol/L H_2SO_4, H_2SO_4/Li molar ratio 0.50:1, 100 °C, and 90 min)

Figure 4 indicates the effect of temperature on the leaching efficiencies of Li and Fe. As observed in Fig. 4, an increasing reaction temperature was beneficial to Li leaching and Fe precipitation. Less than 91.8% of Li was leached into the solution whereas the dissolution of Fe was above 4.7% at 20 °C. The leaching selectivity was as low as 71.58%. When the reaction temperature increased to 100 °C, Li and Fe leaching efficiencies were 97.69% and 0.012%, respectively. An increasing reaction temperature intensified the hydrolysis reaction of Fe^{3+}, which could provide additional H^+ for the dissolution of Li, thus improving the leaching efficiency and selectivity of Li.

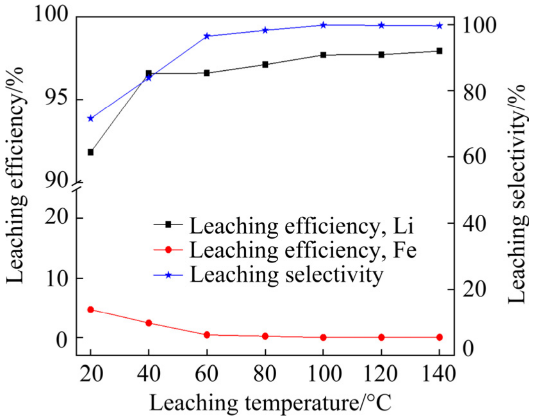

Fig. 4 Effect of leaching temperature on leaching of metals from spent $LiFePO_4$ cathode material (1.3 MPa O_2 partial pressure, 0.6 mol/L H_2SO_4, H_2SO_4/Li molar ratio 0.50:1, and 90 min)

3.1.3 Effects of H_2SO_4 concentration and H_2SO_4/Li molar ratio

To further investigate reagent consumption on the Li and Fe leaching efficiencies, leaching experiments with different H_2SO_4 concentrations and H_2SO_4/Li molar ratios were carried out. As shown in Fig. 5, H_2SO_4 concentration exerted no obvious effect on the Li and Fe leaching efficiencies. Above 96% of Li and less than 0.015% of Fe were leached at the H_2SO_4 concentration ranging from 0.2 to 0.7 mol/L. The leaching selectivity in each experiment was stable in the range from 99.68% to 99.99%. Compared with conventional atmospheric leaching, the consumption of H_2SO_4 was reduced significantly during the oxidation pressure leaching, which was beneficial to the subsequent Li recovery procedure.

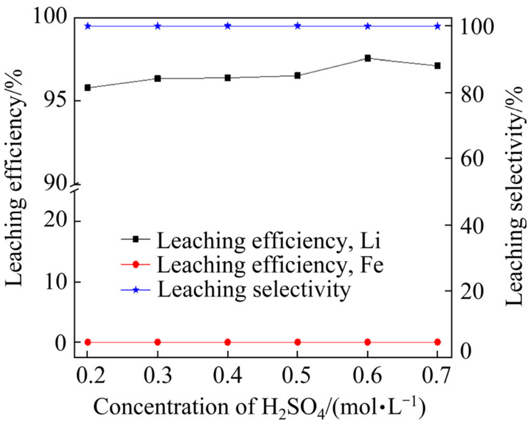

Fig. 5 Effect of H_2SO_4 concentration on leaching of metals from spent $LiFePO_4$ cathode material (1.5 MPa O_2 partial pressure, H_2SO_4/Li molar ratio 0.50:1, 100 °C, and 90 min)

It can be seen from Fig. 6 that H_2SO_4/Li molar ratio played a key role in the leaching process. A relatively high H_2SO_4/Li molar ratio was beneficial to Li leaching. As the H_2SO_4/Li molar ratio increased from 0.45:1 to 0.60:1, Li leaching efficiency also rose from 95.11% to a peak of 98.15%. Fe leaching efficiency in each leaching experiment remained between 0.032% and 0.047%, indicating that an approximately stoichiometric sulfuric consumption could obtain an efficient separation of Li and Fe.

3.2 Characterization of leaching residue

To understand the phase transformation mechanism during the oxidation pressure leaching, XRD, SEM and XPS analyses of the leaching residues collected were performed. Various phases including $FePO_4$, $FePO_4\cdot2H_2O$, and $Fe_5(PO_4)_4(OH)_3\cdot2H_2O$ are shown in Fig. 7. Figure 8 illustrates the relationship among the leaching residue phase and temperature and oxygen partial pressure. There were two main phases in these leaching residues, i.e., $Fe_5(PO_4)_4(OH)_3\cdot2H_2O$ (PDF No. 45-1436) and $FePO_4$ (PDF No. 37-0478). It was easy to form $FePO_4$ precipitate at a lower temperature below 80 °C whereas the occurrence of $Fe_5(PO_4)_4(OH)_3\cdot2H_2O$ required a higher temperature above 100 °C. Moreover, the phase of the leaching residue was independent of the O_2 partial pressure. However, when the temperature was 100 °C, the required O_2 partial pressure for $FePO_4$ formation was above 1.5 MPa. The relatively low O_2 partial pressure below 1.5 MPa promoted the formation of $Fe_5(PO_4)_4(OH)_3\cdot2H_2O$ and $FePO_4\cdot2H_2O$ simultaneously.

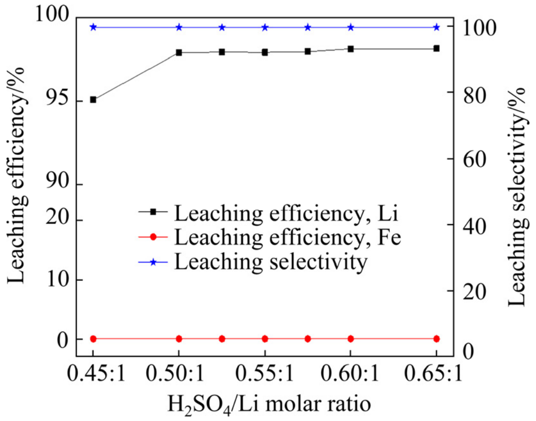

Fig. 6 Effect of H_2SO_4/Li molar ratio on leaching of metals from spent $LiFePO_4$ cathode material (1.3 MPa O_2 partial pressure, 0.6 mol/L H_2SO_4, 140 °C, and 90 min)

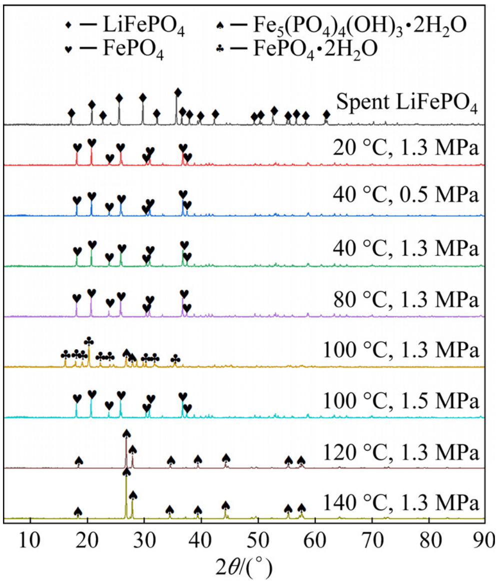

Fig. 7 XRD patterns of raw $LiFePO_4$ cathode scrap and final products at different leaching temperatures and O_2 partial pressures

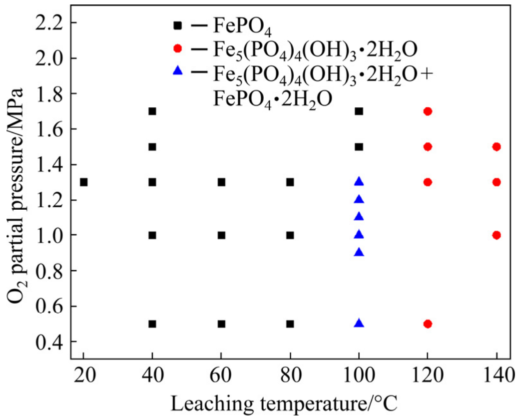

Fig. 8 Relationship among leaching residue phase and temperature and O_2 partial pressure

Figure 9 shows SEM images of the leaching residues obtained under various experimental conditions. The morphology and particle size of $FePO_4$ were similar to the raw $LiFePO_4$ cathode scrap as shown in Figs. 9(a) to (e) and (g). The main reason was that $LiFePO_4$ and $FePO_4$ exhibited an orthorhombic olivine structure [27,28]. It can be seen from Figs. 9(f, h, i) that the leaching residues were composed of many blocky particles. However, the particle size from Fig. 9(f) was smaller compared with that from Fig. 9(h) owing to the presence of $FePO_4\cdot2H_2O$ phase. A higher reaction temperature promoted the formation of $Fe_5(PO_4)_4(OH)_3\cdot2H_2O$ from Fig. 9(i), presenting an entirely different morphology (i.e., an octahedral structure) as well as a larger particle size.

Figure 10 shows the XPS spectra of the $LiFePO_4$ cathode scrap and several leaching residues. In the Fe $2p_{1/2}$ and Fe $2p_{3/2}$ regions, the characteristic peaks of Fe^{2+} from spent $LiFePO_4$ materials occurred at binding energies of 710.31 and 723.78 eV. The characteristic peaks of Fe^{3+} at 712.08 and 725.69 eV were observed in the leaching residues, indicating that nearly all Fe^{2+} in the material was oxidized to Fe^{3+} by the oxidation pressure leaching [29,30].

3.3 Recovery of Li as Li_3PO_4

Compared with conventional $FePO_4$ precipitate, the obtained $Fe_5(PO_4)_4(OH)_3\cdot2H_2O$ precipitate

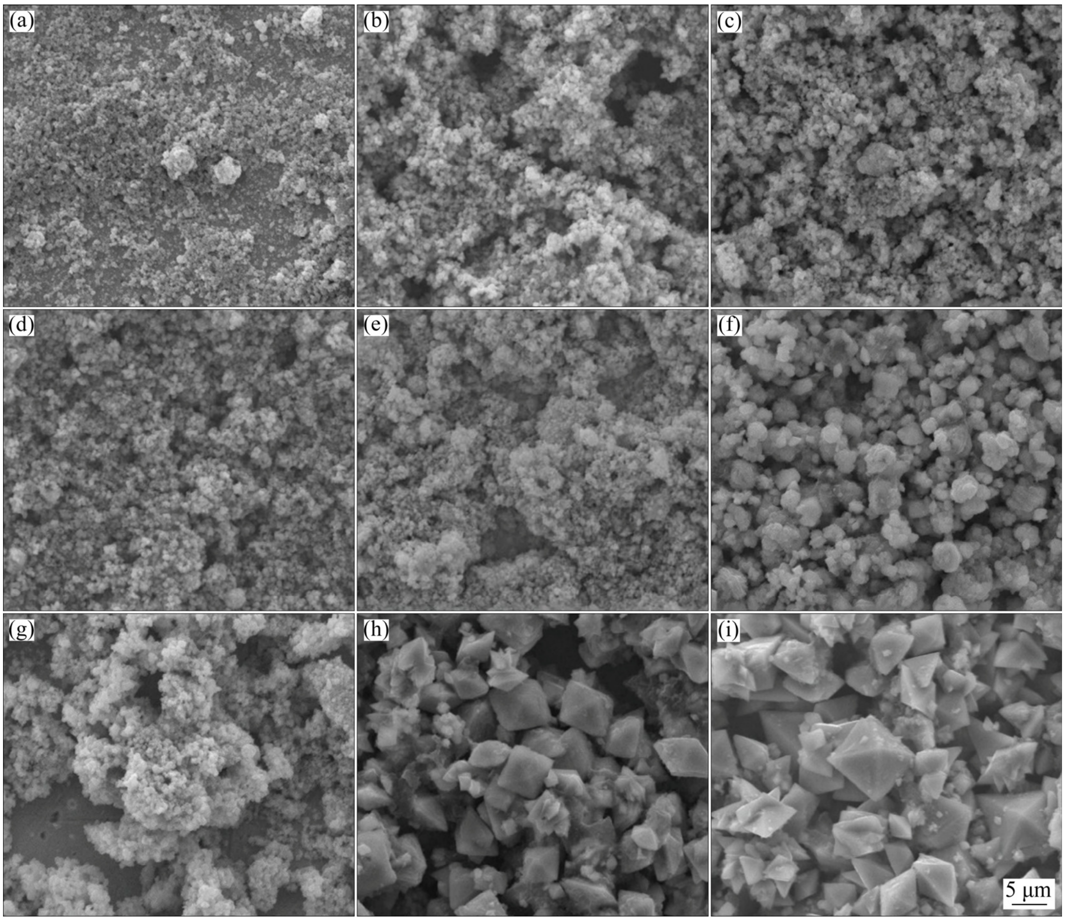

Fig. 9 SEM images of raw $LiFePO_4$ cathode scrap (a) and final products at different leaching temperatures and O_2 partial pressures (b−i), with the same other conditions: (b) 20 °C, 1.3 MPa; (c) 40 °C, 0.5 MPa; (d) 40 °C, 1.3 MPa; (e) 80 °C, 1.3 MPa; (f) 100 °C, 1.3 MPa; (g) 100 °C, 1.5 MPa; (h) 120 °C, 1.3 MPa; (i) 140 °C, 1.3 MPa

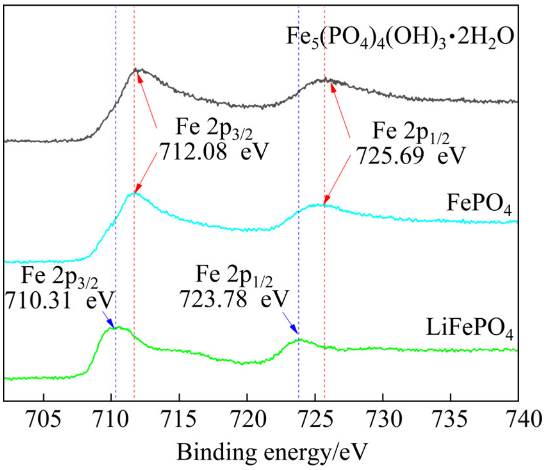

Fig. 10 XPS spectra of raw $LiFePO_4$ cathode scrap and $FePO_4$ and $Fe_5(PO_4)_4(OH)_3\cdot 2H_2O$ leaching residues

presented broad application prospects owing to its unique catalytic property and ion exchange capacity, which was widely used in high-tech fields [31−33], including catalysis, biology, and sewage treatment. Therefore, O_2 partial pressure of 1.3 MPa, H_2SO_4 concentration of 0.6 mol/L, H_2SO_4/Li molar ratio of 0.525:1, reaction temperature of 120 °C, and reaction time of 90 min were selected as the optimized leaching conditions. Under these conditions, the leaching efficiencies of Li and Fe were 97.82% and 0.022%, respectively.

In order to produce the Li_3PO_4 product with a high purity, a small proportion of Fe impurity should be removed preferentially. Therefore, the pH of the leaching solution was adjusted to 5.0 through adding 1 mol/L NaOH solution. As a result, Fe concentration in the resulting solution dropped from 95.4 to 0.327 mg/L owing to the formation of $FePO_4\cdot 2H_2O$ precipitate, as shown in Fig. 11. During the Fe removal procedure, the loss rate of Li was about 0.1%.

The Li_3PO_4 product was prepared via adding a 100 g/L Na_3PO_4 solution. About 60% of Li in the leaching solution could precipitate as the Li_3PO_4

product due to the presence of a large amount of PO_4^{3-} in the solution. Therefore, only 50% of the required theoretical amount of Na_3PO_4 was added to the purified solution to precipitate Li. The reaction was performed in a water bath at 95 °C for 30 min. After completing the process, Li concentration in the mother liquor was decreased from 5.3 g/L to 89 mg/L, indicating that about 97.97% of Li in the solution was recovered as the Li_3PO_4 product. The XRD pattern, shown in Fig. 12, demonstrated an exact match of the standard diffraction peaks for Li_3PO_4. The resulting mother liquor contained a higher concentration of Na_2SO_4, which was further treated to recover the $Na_2SO_4·10H_2O$ byproduct via evaporation crystallization or freezing crystallization.

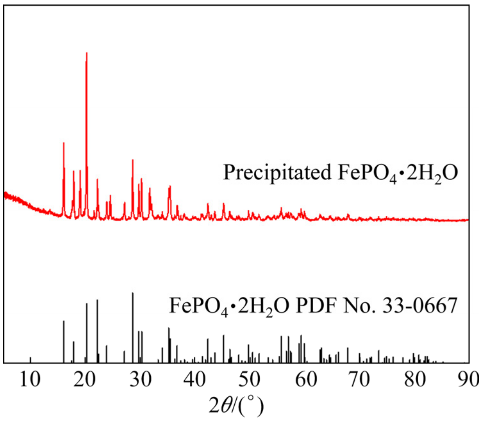

Fig. 11 XRD patterns of precipitated $FePO_4·2H_2O$ and standard $FePO_4·2H_2O$

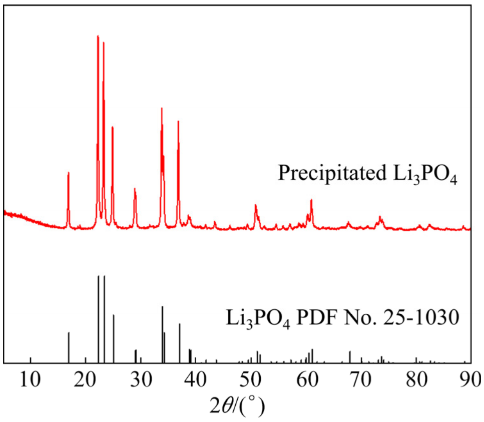

Fig. 12 XRD patterns of recovered Li_3PO_4 product and standard Li_2PO_4

3.4 Development of new green spent LiFePO4 recycling process

Based on the above-mentioned analysis results, a novel and green recycling process, including leaching, purification, and precipitation, was presented in Fig. 13. During the oxidation pressure leaching, more than 97% of Li was dissolved into the solution, whereas more than 99% of Fe precipitated in the leaching residue, indicating an efficient Li−Fe separation. And then, a thorough Fe removal procedure was conducted with a total loss rate of Li below 0.1%. Finally, more than 95% of Li was recovered through chemical precipitation for producing the Li_3PO_4 product with a high purity. The proposed process presented a significant potential of the effective treatment of spent $LiFePO_4$ batteries, contributing to environmental protection, sustainable economy, and social development.

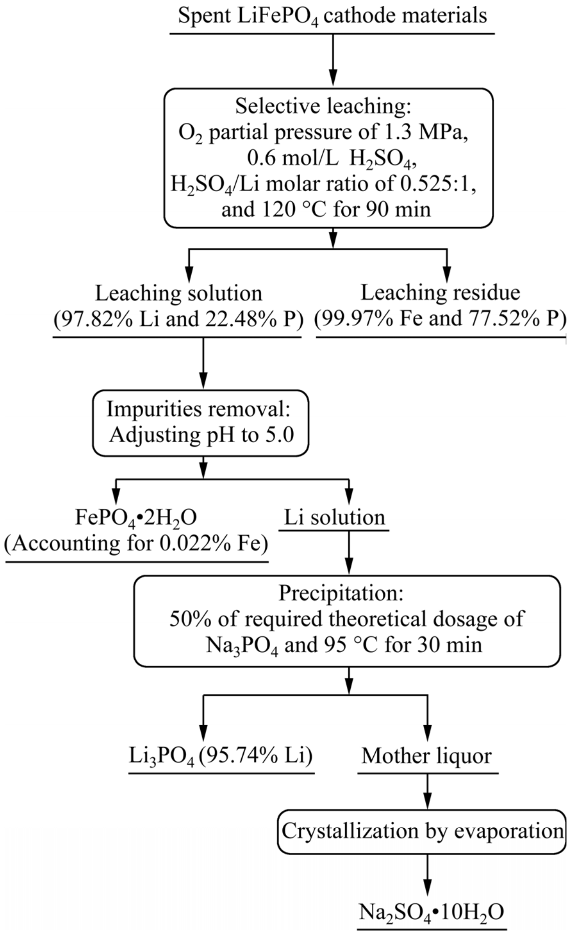

Fig. 13 New and green recycling process for treatment of spent $LiFePO_4$ batteries

4 Conclusions

(1) More than 97% of Li was selectively dissolved into the solution with a H_2SO_4 concentration of 0.6 mol/L, a H_2SO_4/Li molar ratio of 0.525:1 and O_2 partial pressure of 1.3 MPa at 120 °C for 90 min.

(2) More than 99% of Fe remained in the leaching residue in the form of $FePO_4$ (below 80 °C) or $Fe_5(PO_4)_4(OH)_3\cdot 2H_2O$ (above 100 °C) precipitate.

(3) The remaining Fe impurity was thoroughly removed through adjusting pH to 5.0 with a total Li loss rate of 0.1%.

(4) The high purity Li_3PO_4 was successfully produced with a total Li recovery of 95.74%.

Acknowledgments

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氧压硫酸浸出废旧磷酸铁锂电池选择性回收锂

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摘　要：采用氧压浸出法在化学计量硫酸溶液中从废旧磷酸铁锂电池中选择性浸出锂。以氧气作为氧化剂，化学计量硫酸作为浸出剂，97%以上的 Li 浸出至溶液中，而 99%以上的 Fe 保留在浸出渣中，从而实现 Li 和 Fe 的低成本一步分离。通过调节浸出溶液 pH 深度除铁和磷酸盐沉锂，制备 Li_3PO_4 产品，锂回收率高于 95%。

关键词：废旧磷酸铁锂电池；氧压浸出；分离；锂；铁；磷酸锂

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