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A green and effective room-temperature recycling process of $LiFePO_4$ cathode materials for lithium-ion batteries

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ABSTRACT

Nowadays $LiFePO_4$ cathode develops rapidly for its advantages of long life span, low cost and non-toxicity, especially in electrical vehicle markets. Because of its stable olivine structure, $LiFePO_4$ is difficult to be recycled by the conventional hydrometallurgical processes as for $LiCoO_2$ or $LiNi_xCo_yMn_2O_2$. Pyrometallurgical processes consume much energy and release toxic gases. Herein, an effective room-temperature process based on the mechanochemical treatment is proposed to extract metals from $LiFePO_4$. Spent $LiFePO_4$ is co-grinded with low-cost citric acid agent in a ball mill. After grinding, the mixture is dissolved in deionized water and filtrated. With addition of H_2O_2, the extraction efficiency of Li reaches as high as 99.35%. Conversely, Fe is hardly extracted with a low extraction efficiency of only 3.86%, indicating a selective recovery of valuable Li element. In addition, when H_2O is used instead of H_2O_2, the mechanochemical reaction changes and the extraction efficiencies of Li and Fe at optimal conditions reach 97.82% and 95.62%, respectively. The Fe impurity is removed as $Fe(OH)_3$ precipitation by adding NaOH, and Li is recycled as Li_2CO_3 after reaction with saturated Na_2CO_3 at 95 °C. This simple and easily-operated process has little negative impact on the environment and has great potential in industrial applications.

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1. Introduction

With the increasing demand for power source, the environmentally friendly lithium-ion batteries (LIBs) have achieved great success in recent decades for their advantages of high energy density, long life span, high capacity, and low self-discharge (Song et al., 2017; Zou et al., 2013). The extensive uses of digital products and electric vehicles (EVs) have promoted the development and constant updating of LIB cathode materials.

Since Goodenough et al. first reported reversible Li intercalation/deintercalation in $LiFePO_4$ (LFP) in 1997, LFP based batteries have rapidly occupied the EV market for the advantages of high safety, long life span, low cost, and non-toxicity (Bian et al., 2016; Göktepe, 2012; Shin et al., 2015). In China, the production of EV cells reached 15.7 GWh in 2015, among which LFP occupied up to approximately 69%. It is predicted by Sociedad Quimica y Minera de Chile S.A. (SQM) research that the annual growth rate of lithium demand from 2016 to 2025 is estimated to be 10%. However, the supply of battery-grade Li salt is limited, and the price of Li_2CO_3 presents a remarkably rising trend, as shown in Fig. 1. Therefore, recycling of Li from spent LIBs becomes increasingly attractive.

In the reported studies, researchers have paid more attention to the recycling of $LiCoO_2$ and $LiNi_xCo_yMn_{1-x-y}O_2$, and have proposed a series of physical and chemical recycling processes (Poyraz et al., 2016; Yang et al., 2016). Generally, the spent batteries are dismantled to separate the cathodes and anodes (Zhang et al., 2016). The cathodes are then dissolved in N-methyl pyrrolidone (NMP) or alkaline solution to separate Al foil and the active cathode materials (Li et al., 2015), which are leached with inorganic or organic acids to extract valuable metals (He et al., 2017a,2017b; Yang et al., 2018a). The leachate can be recovered using various methods. For example, carbonates or hydroxides products can be obtained by chemical precipitation based on the different solubilities (Fan et al., 2016; Yang et al., 2017a). Recently, more studies focus on the regeneration of cathode materials (Nie et al., 2015; Sita et al., 2017; Yang et al., 2018b).

In the recycling of LFP batteries, hydrometallurgical and pyrometallurgical processes have been reported with focus on Li recovery for its high value. Because of the stable structure of LFP, strong acids such as H_3PO_4 (Bian et al., 2016), H_2SO_4 (Zheng

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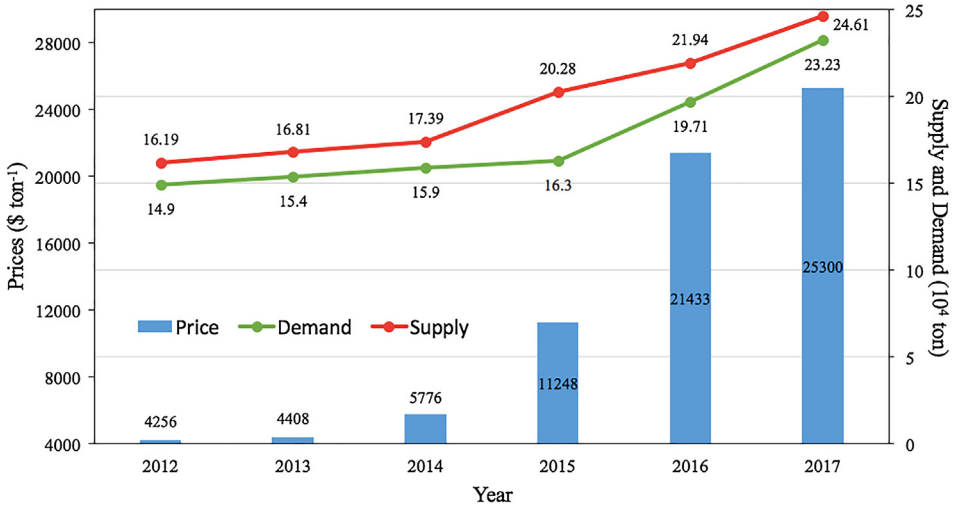

Fig. 1. Global price, supply, and demand of Li_2CO_3 from 2012 to 2017. (Data sources: China Industry Information, https://www.chyxx.com/research/201710/574640.html).

et al., 2016), and HCl (Huang et al., 2016) were used as leaching agents. Xin et al. used the sulfur-oxidizing bacteria and iron (II)-oxidizing bacteria to bioleach the materials and the extraction efficiency of Li reached 98% (Xin et al., 2016). Regeneration methods including electrochemical and chemical lithiation have also been investigated to repair the LFP (Ganter et al., 2014). Due to its simple element composition, thermal treatment has been widely studied to regenerate LFP cathode (Pei et al., 2013; Shin et al., 2015). Chen et al. found that the spent LFP materials can be repaired directly after calcination at 650 °C (Chen et al., 2016). However, the heat treatment consumes much energy and produces greenhouse gases. Meanwhile, the impurity problem of heat treatment remains as a challenge.

Mechanochemical (MC) treatment has been reported to recycle spent batteries in the pretreatment stage, and its application for recovery of metals began in 1990s. MC reaction can decrease the particle size and break the crystal structure, which can facilitate the following treatment (Yang et al., 2017b; Zhang et al., 2000). The relatively low reaction temperature and sealed environment of MC treatment pose less environmental impact compared to thermochemistry (Ou et al., 2015). Moreover, the operation is simple and facile to scale up for industrial application. In addition to particle size reduction, it was also found that chemical reaction can occur with addition of certain aiding agents. For example, PVC and EDTA were used to co-grind with $LiCoO_2$ to form Li/Co-chlorides and Li/Co-EDTA, respectively, which are soluble in water media (Saeki et al., 2004; Wang et al., 2016). $LiCoO_2$ was also co-grinded with PVC and Fe followed by a water leaching process (Wang et al., 2017).

However, the agents such as EDTA and PVC are expensive, and a leaching process is usually necessary after grinding. In this work, a green MC process to selectively recycle Li from spent LFP materials at room-temperature is proposed. The spent LFP materials were co-grinded with citric acid and H_2O_2, which are commonly used chemical agents in practical applications. Moreover, the citric acid is mild and green, which has been widely used to leach spent cathode materials of LIBs. Li was selectively extracted from LFP into the solution and then recovered as Li_2CO_3 precipitate. Most of the Fe remained as $FePO_4$ in the solid residue, and the slight Fe impurity in the solution was removed as $Fe(OH)_3$ precipitation. Compared with previous treatments for LFP, this process is low-cost and consumes less energy. The grinding and leaching were integrated in this recycling process, which is easy to operate and thus possesses great potential for industrial application.

2. Experimental

2.1. Materials and analytical methods

The spent LFP batteries were provided by MTI Corporation. The citric acid and hydrogen peroxide (30%) were purchased from Aladdin. The MC reaction was conducted in a planetary ball mill (XQM-1, Tencan Powder, China) with zirconia beads. Aqua regia was used to completely dissolve the LFP so that the Li and Fe content in the cathode can be determined. The leaching efficiency is defined as the ratio of the amount of Li^+ or Fe^{2+} in the leachate to the total amount of that species in the original cathode. The concentrations of Li^+ and Fe^{2+} were tested by inductively coupled plasma optical emission spectroscopy (ICP–OES; Optima 8300, Perkin Elmer, USA). The concentration values in the study were all tested for three times and the average values were calculated for use. Precipitates after grinding and water treatment were characterized by X-ray diffractometry (XRD; Rigaku, Japan). The data were collected by step scanning with a scanning speed of 8°/min and a scanning angle (2θ) of 10–90°. The analysis of XRD was conducted by MDI Jade 6.0 software.

2.2. Mechanochemical treatment

As shown in Fig. 2. 0.05 g cathode materials were grinded with citric acid powder and H_2O_2 as an aiding agent. After grinding, the mixture was washed out from the ball mill pot using deionized water. Single factor experiments were conducted to preliminarily investigate the effects of the mass ratio of citric acid to LFP (10–80), ball to powder ratio (BPR) (15–55 g/g), the volume of H_2O_2 (0–2 ml), grinding time (0.5–4 h), and rotation speed (100–500 rpm) on the extraction efficiencies of metal ions. The level of these parameters was chosen based on our previous research of acid leaching (Li et al., 2010). The interactions were beyond this study and ignored for simplicity.

As a comparison, grinding experiments without H_2O_2 were also conducted and H_2O was used as an aiding agent. The effects of the mass ratio of citric acid to LFP (10–80), BPR (15–55 g/g), time of water leaching (0–8 h), rotation time (2–10 h), and rotation speed (100–500 rpm) were also investigated.

2.3. Precipitation of Fe and Li

After water leaching and filtration, the filtrate was stirred at 60 °C to evaporate most of the water. 10 M and 1 M NaOH

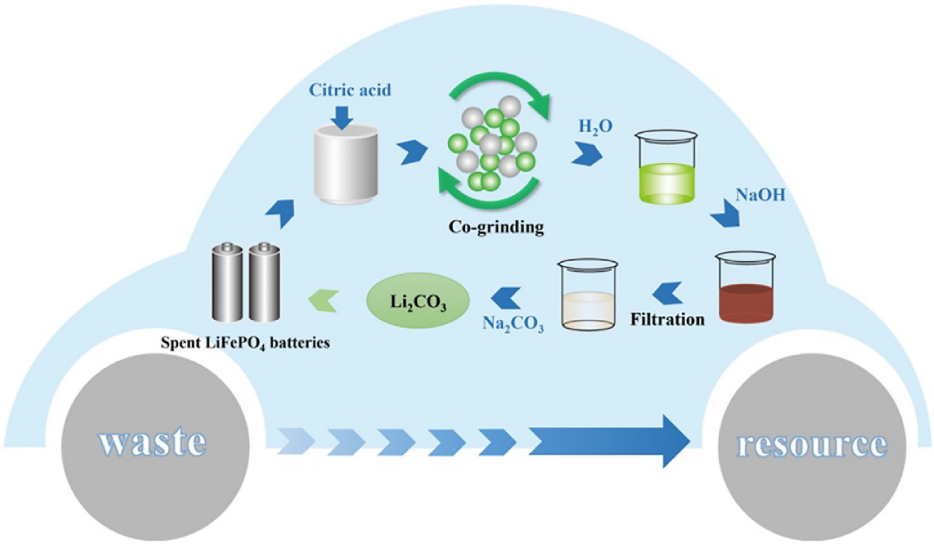

Fig. 2. Scheme of the recycling process.

solutions were added into the condensed solution successively to adjust the pH to precipitate Fe^{3+} as $Fe(OH)_3$. After filtration, saturated Na_2CO_3 was added to the filtrate at 95 °C and Li_2CO_3 precipitate was obtained (Gao et al., 2017).

3. Results and discussion

3.1. Recycling process with H_2O_2

In the process with addition of H_2O_2, the reaction occurs as follows (Li et al., 2017):

$$2H_3Cit + 6LiFePO_4 + 3H_2O_2 \rightarrow 2Li_3Cit + 6FePO_4 + 6H_2O \quad (1)$$

where Fe^{2+} is oxidized to Fe^{3+} by H_2O_2, and $FePO_4$ precipitates from the solution. After water treatment and filtration, Fe remains in the precipitate as $FePO_4$, while Li is extracted into the solution as Li_3Cit. The reaction undergoes a minimization–cleavage–recombination process, as is shown in Fig. 3. The change of activated sites is shown in the left-hand corner of Fig. 3. The particles are subjected to force shocks, which leads to the decreased particle size and increased specific surface areas. The temperature of the system increases at the same time. Then the reaction agents enter into the voids and chemical bonds are broken. Finally, new bonds form and the metals are extracted from LFP.

3.1.1. Effect of ball to powder ratio (BPR)

Fig. 4a shows the effect of BPR when the citric acid to LFP ratio is 40 g/g with 1.0 ml H_2O_2 amount, 300 rpm rotation speed, and 2.0 h grinding time. The highest extraction efficiency of Li is achieved when the BPR is 25. The efficiency of Li decreases when the BPR continues to increase. When the BPR is 35, the extraction efficiency of Fe reaches the maximum value, and the efficiency of Fe changes only a little with further increase of BPR. The higher amount of grinding balls can increase the interface areas and make the force on the materials uniform. However, excessive grinding balls can result in the huddle of balls, which leads to the heterogeneous distribution of materials on the ball surface and blocks the reaction. Therefore, BPR of 25 is chosen as the optimal condition.

3.1.2. Effect of citric acid to LFP mass ratio

The effect of citric acid to LFP mass ratio on the extraction efficiencies is shown in Fig. 4b. The meaning of this ratio is similar to the solid to liquid ratio in the acid leaching process. The extraction efficiency of Li shows a decreasing trend when the ratio is above 20 g/g. For Fe, increasing acid mass results in the decrease of extraction efficiencies. Based on the shrinking-core model, a liquid film of product is formed on the surface of the particles. So, excess acid in the bulk solution might block the diffusion of the produced leaching ions (Li et al., 2018). Considering both the economy and efficiency, the optimal citric acid to LFP mass ratio is determined to be 20 g/g.

3.1.3. Effect of grinding time

Fig. 4c shows the effect of grinding time on the extraction efficiencies of Li and Fe when BPR is 25, citric acid to LFP ratio is 40 g/g, H_2O_2 amount is 1.0 ml, and rotation speed is 300 rpm. The extraction efficiency of Li increases with time until 2.0 h, then the efficiency decreases slightly over time. Different from that of Li, the extraction efficiency of Fe increases with grinding time, which may be explained by the stable structure of LFP cathode. The crystal structure will be destroyed more thoroughly with increasing grinding time, while Li in the structure is much easier to extract, indicating that the grinding time has little impact on the extraction of Li. Therefore, 2.0 h is chosen as the optimal grinding time.

3.1.4. Effect of rotation speed

The effect of rotation speed on the extraction efficiencies of Li and Fe is shown in Fig. 4d. The experiments were conducted under conditions of BPR of 25, citric acid to LFP ratio of 40 g/g, H_2O_2 amount of 1.0 ml, and grinding time of 2.0 h. The extraction efficiency of Li reaches its maximum value when the rotation speed is 400 rpm. Continuing to increase the speed does not influence much on the extraction of Li. The extraction efficiency of Fe also increases with rotation speed. When the speed is 500 rpm, Fe^{2+} in the solution can reach above 5%. Strenuous mechanical treatment may destroy the structure of $FePO_4$ molecule (Guan et al., 2017). In order to maintain a higher leaching efficiency of Li and lower efficiency of Fe, and considering the energy consumption, a slightly lower speed of 300 rpm is chosen as the optimal rotation speed.

3.1.5. Effect of volume of H_2O_2

For the extraction of Li, the efficiency increases with the increase of H_2O_2 until 1.0 ml, as shown in Fig. 4e. Increase of

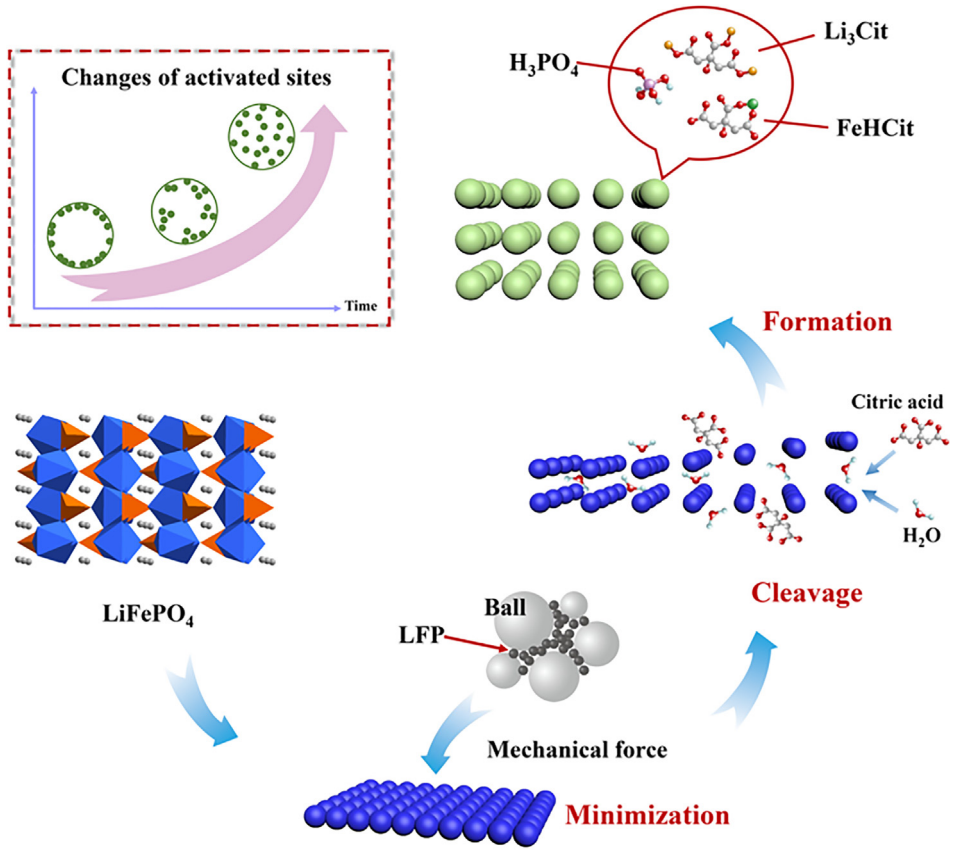

Fig. 3. Mechanism of the mechanochemical treatment.

H_2O_2 promotes the extraction of Li because Fe^{2+} in LFP can be oxidized to form $FePO_4$, releasing Li into the solution. Moreover, the liquid media is beneficial to the MC reaction, which makes the mixing of the reactants more uniform. If the materials are grinded without liquid, the cracks or voids may be squeezed and "close". The design of ball-mill pot has blind corner, which makes the reaction incomplete (Balaz et al., 2013). Therefore, liquid such as water or H_2O_2 are needed to prevent the close of cracks. Besides, without liquid medium, the materials after grinding are easily attached to the surface of the balls and ball-mill pot, which are difficult to wash out by deionized water. For the extraction of Fe, when the H_2O_2 is above 0.5 ml, the extraction efficiency is less than 3%. Considering the leaching efficiencies of both Li and Fe, the H_2O_2 volume is set at 1.0 ml.

In brief, based on the above experimental results, the optimal conditions for high extraction of Li and low extraction of Fe are determined to be at BPR of 25, citric acid to LFP ratio of 20 g/g, grinding time of 2.0 h, rotation speed of 300 rpm, and H_2O_2 amount of 1.0 ml. When the experiment is conducted at optimal conditions, the extraction efficiencies of Li and Fe are 99.35% and 3.86%, respectively.

3.2. Recycling process with H_2O

It is worth noting that when H_2O_2 is replaced by an equal amount of H_2O, the extraction efficiency of Fe is nearly 100%, which indicates a totally different reaction (Eq. (2)) (Chen et al., 2015). Without oxidation of H_2O_2, Fe^{2+} remains as ions in the leaching solution. After water treatment and filtration, Fe and Li become citrates in the filtrate.

$$3H_3Cit + 3LiFePO_4 \rightarrow Li_3Cit + Fe_3(Cit)_2 + 3H_3PO_4 \quad (2)$$

3.2.1. Effect of water leaching time

In the previous studies, a leaching step after grinding is generally necessary for better extraction performance of metal ions (Ou et al., 2015). In our experiments, the mixture was washed out from the pot by H_2O after grinding. Experiments were conducted to study the effect of water leaching time when BPR was 25, citric acid to LFP ratio was 40 g/g, grinding time was 6 h, and rotation speed was 300 rpm. As shown in Fig. 5a, the trends of extraction efficiencies of Li and Fe are different. The extraction efficiency of Li decreases with time, because Li_3PO_4 is soluble in acid but almost insoluble in water. The addition of H_2O reduces the acidity of the solution. Therefore, the following reaction may occur.

$$Li_3Cit + H_3PO_4 \rightarrow H_3Cit + Li_3PO_4 \quad (3)$$

The extraction efficiency of Fe increases with time, because the liquid reaction can promote the chelation of Fe^{2+}. Considering the efficiency and economy, 0 h is the optimal water leaching time, which means that this reaction does not need a subsequent water leaching process.

3.2.2. Effect of ball to powder ratio

Fig. 5b shows the effect of BPR on the extraction efficiencies of metal ions when citric acid to LFP ratio is 20 g/g, grinding time is 6 h, and rotation speed is 300 rpm. The leaching efficiencies of both Li and Fe reach the maximum values when the BPR is 45. Higher percentage of milling balls can increase the reaction area and thus is beneficial to the extraction of Li and Fe. Therefore, a BPR of 45 is chosen as the optimal condition.

3.2.3. Effect of citric acid to LFP mass ratio

Fig. 5c shows the effect of citric acid to LFP mass ratio on the leaching efficiencies of Li and Fe. It is shown that the max-

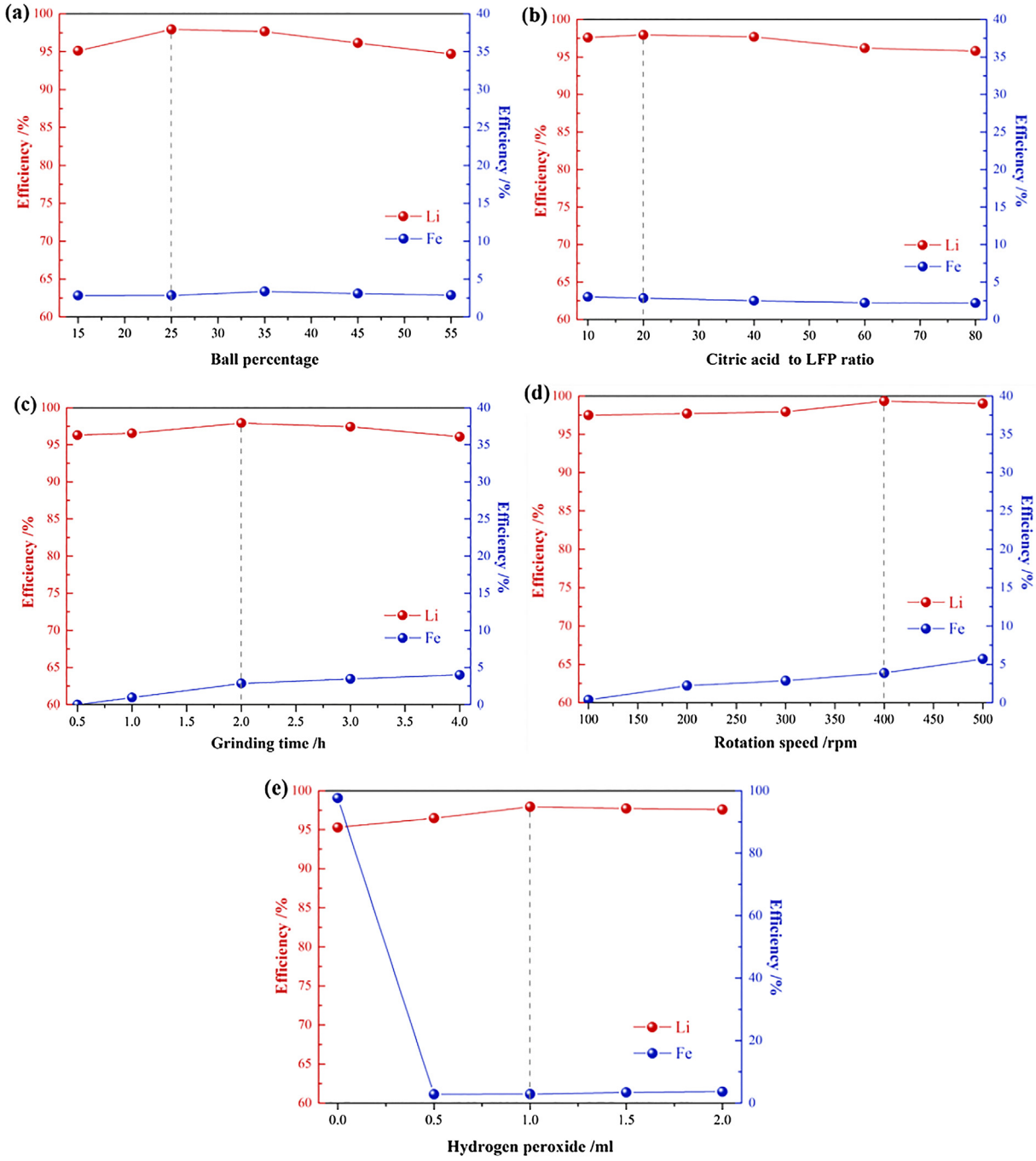

Fig. 4. Effects of BPR (a), citric acid to LFP mass ratio (b), grinding time (c), rotation speed (d), and volume of H_2O_2 (e) on the extraction efficiencies of Li and Fe in the MC process with H_2O_2. (Conducted at BPR of 25, citric acid to LFP ratio of 20 g/g, H_2O_2 amount of 1.0 ml, rotation speed of 300 rpm, and grinding time of 2.0 h).

imum extraction efficiencies of Li and Fe are obtained at 10 g/g and 60 g/g, respectively. The efficiency of Li decreases as the ratio increases. The opposite trends of the two ions result from the different reactions. From the reaction Eq. (2), it can be seen that 1 mol Li reacts with 1/3 mol H_3Cit theoretically. But for Fe, 1 mol Fe needs 2/3 mol H_3Cit to react. This means that citric acid is excess for Li extraction, which may block the diffusion of Li-containing products (Li et al., 2010). Conversely, increasing acid in a suitable range can promote the chelation of Fe because of the chelation activity of citric acid. Considering the efficiency and economy, citric acid to LFP ratio of 20 g/g is chosen as the optimal experimental condition.

3.2.4. Effect of grinding time

Fig. 5d shows the effect of grinding time on the leaching efficiencies of Li and Fe under conditions of a BPR of 45, citric acid to LFP ratio of 20 g/g, and rotation speed of 300 rpm. Due to the stable structure of LFP, longer grinding time (2–10 h) and more energy are needed for the metal extraction. The results show that the extraction efficiencies of Li and Fe increase with time, while the efficiencies change little from 8 to 10 h. Therefore, 8 h is chosen as the optimal condition.

3.2.5. Effect of rotation speed

Fig. 5e shows the effect of rotation speed on the extraction efficiencies of metal ions when BPR is 45, citric acid to LFP ratio is

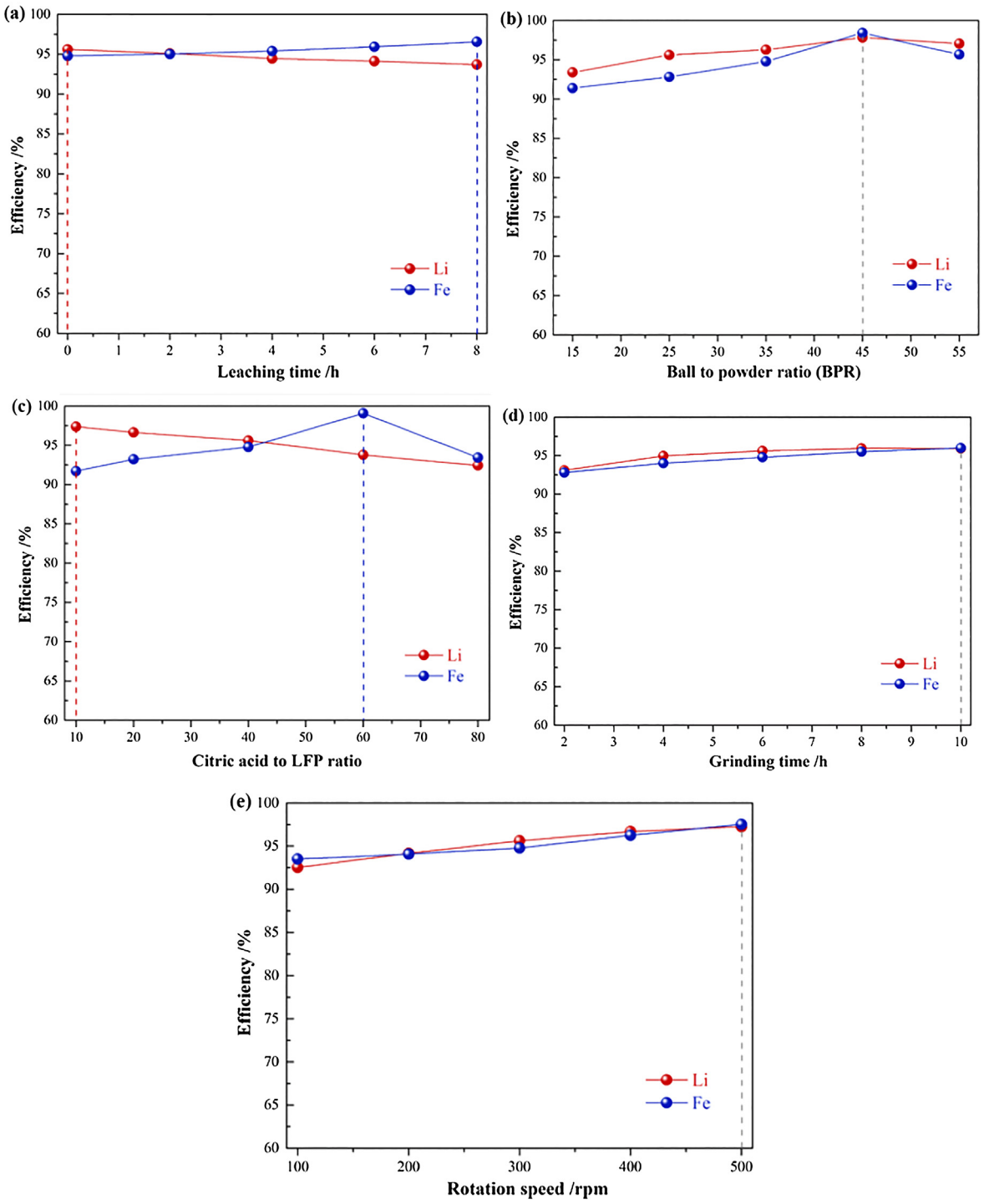

Fig. 5. Effects of BPR (a), citric acid to LFP mass ratio (b), grinding time (c), rotation speed (d), and leaching time (e) on the extraction efficiencies of Li and Fe in the MC process with H_2O. (Conducted at BPR of 45, citric acid to LFP ratio of 20 g/g, grinding time of 8 h, rotation speed of 300 rpm, and leaching time of 0 h).

20 g/g, and grinding time is 6 h. It can be seen that the extraction efficiencies of Li and Fe both increase with the speed, which indicates the positive effect of mechanical energy on the reaction. The size of particles become smaller with the increase of rotation speed, which is expected to promote the extraction reaction. Considering the protection of the equipment, economy, and efficiency, a slightly slower rotation speed of 300 rpm is chosen as the optimal experimental condition.

From the above experiments, the optimal conditions are determined as BPR of 45, citric acid to LFP ratio of 20 g/g, grinding time of 8 h, rotation speed of 300 rpm, and leaching time of 0 h. Fig. 6 shows that the extraction efficiencies of Li and Fe at optimal conditions are 97.82% and 95.62%, respectively.

3.3. Removal of Fe

After grinding and filtration of both processes with and without H_2O_2, the filtrate is evaporated first to increase the concentration of Fe. The temperature needs to be controlled below 70 °C to

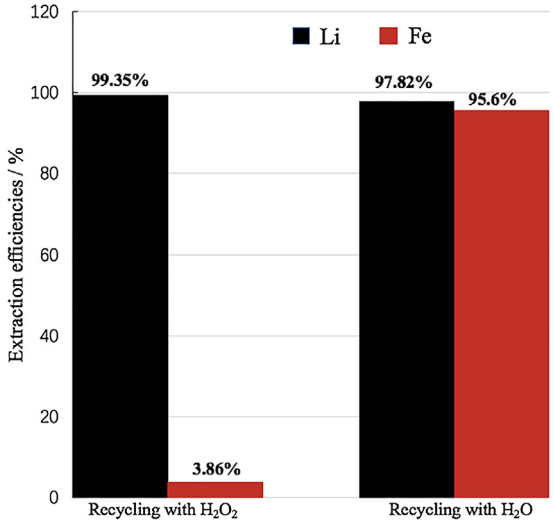

Fig. 6. Extraction efficiencies of Li and Fe at optimal conditions. (Recycling with H_2O_2 was conducted at BPR of 25, citric acid to LFP ratio of 20 g/g, H_2O_2 amount of 1.0 ml, rotation speed of 300 rpm, and grinding time of 2.0 h; Recycling with H_2O was conducted at BPR of 45, citric acid to LFP ratio of 20 g/g, grinding time of 8 h, rotation speed of 300 rpm, and leaching time of 0 h).

prevent side reactions. NaOH is added to precipitate Fe^{2+}. In this process, Fe^{2+} is oxidized to Fe^{3} because of the O_2 in the air.

In our experiments, the citric acid is excess and H_3PO_4 is produced. Therefore, the following reactions may occur when NaOH is added.

$$Fe(OH)_3 + 3H^+ \rightarrow Fe^{3+} + 3H_2O \quad (4)$$

$$3NaOH + H_3Cit \rightarrow Na_3Cit + 3H_2O \quad (5)$$

$$3NaOH + H_3PO_4 \rightarrow Na_3PO_4 + 3H_2O \quad (6)$$

When adjusting the pH, the color of the solution changes from green to yellow, then to transparent brown. The picture of the color change after adjusting pH is shown in Fig. 7a. When the pH increases to 11–12, the color of the solution becomes dark brown and Fe is precipitated. Fig. 7a shows the XRD patterns of materials in different processing stages. It can be seen that $FePO_4$ and some unreacted LFP remains in the residue after grinding, and the extracted Fe in the solution precipitates as non-crystalline $Fe(OH)_3$.

3.4. Precipitation of Li

After the removal of Fe, the solution is condensed below 70 °C to make sure the concentration of Li is higher than 5 g L^{-1}. By adding the saturated Na_2CO_3 at 95 °C, the Li_2CO_3 precipitates are obtained. When the concentration of Li increases from 5 to 20 g L^{-1}, the precipitation efficiencies of Li increase from 83.6% to 89.95%.

The XRD patterns in Fig. 7b show that the Li_2CO_3 is well-crystallized with high purity. When the concentration of Li is 20 g L^{-1}, the ratio of the Na_2CO_3 solution volume to the Li-containing solution volume is controlled between 0.25 and 0.30 to avoid further dissolution of Li_2CO_3 as follow.

$$Li_2CO_3 + Na_2CO_3 + 2H_2O \rightarrow 2LiHCO_3 + 2NaOH \quad (7)$$

4. Conclusions

A simple and green mechanochemical process for the recycling of spent LFP materials is proposed in this study. This process is based on the co-grinding of LFP and citric acid with H_2O_2 as an aiding agent. Under the conditions of BPR of 25, citric acid to LFP ratio of 20 g/g, H_2O_2 amount of 1.0 ml, rotation speed of 300 rpm, and grinding time of 2.0 h, the extraction efficiencies of Li and Fe are 99.35% and 3.86%, respectively, indicating a highly selective recovery of valuable Li. As a comparison, when the LFP is co-grinded with H_2O instead of H_2O_2, Li and Fe are both extracted from the cathode materials into the solution because of different mechanochemical reactions. When BPR is 45, citric acid to LFP ratio is 20 g/g, grinding time is 8 h, rotation speed is 300 rpm, and leaching time is 0 h, the extraction efficiencies of Li and Fe are 97.82% and 95.62%, respectively. After grinding, the Fe impurity in the solution is removed by precipitation with NaOH at pH of 11–12. Li is recovered as Li_2CO_3 precipitates by reaction with saturated Na_2CO_3 at 95 °C. The effective separation of Li from spent LFP materials is realized through the two-step process consisting of mechanochemical reaction and water leaching, which consumes less energy and is more environmentally-friendly. The simple operation also indicates a high practical application potential in the future.

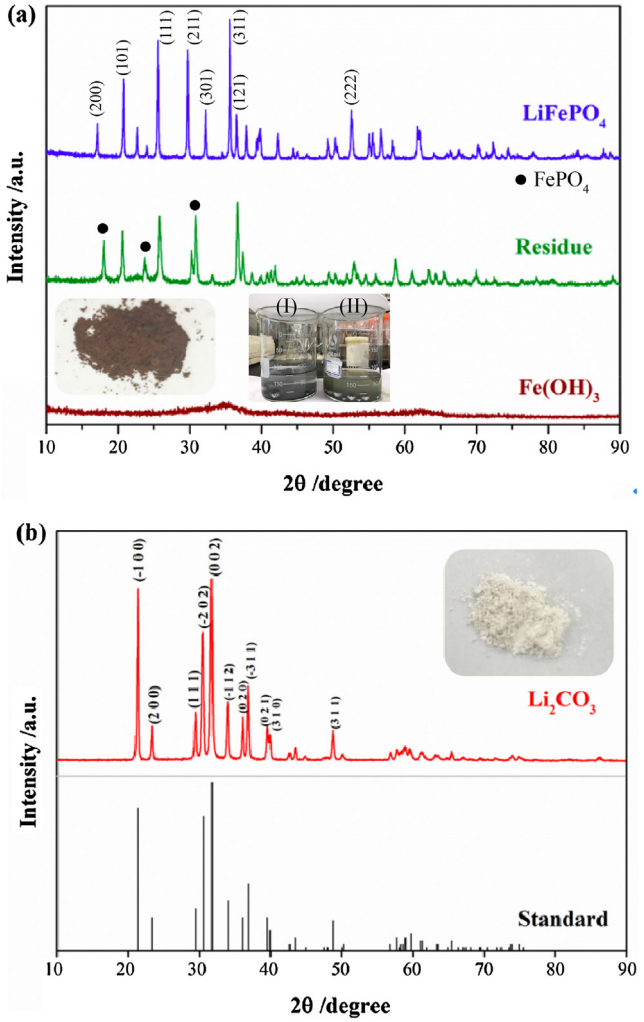

Fig. 7. XRD patterns of spent LFP materials before and after the mechanochemical treatment (a) (Inset: digital photo of precipitated $Fe(OH)_3$ (Left); color change of the precipitation process (I: the precipitation after adjusting pH; II: the beginning of the precipitation); XRD pattern of Li_2CO_3 precipitate (b).

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