RECOVERY OF PURE LITHIUM PHOSPHATE FROM SULFURIC ACID LEACHING SOLUTIONS OF SPENT LiFePO₄ BATTERIES BY SOLVENT EXTRACTION AND CHEMICAL PRECIPITATION

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Abstract

With the increasing use of electric vehicles, the demand for lithium iron phosphate batteries ($LiFePO_4$) has risen sharply. Therefore, the recycling of metals from these batteries at the end of their life is necessary. In this study, a hydrometallurgical process for the recovery of lithium phosphate from spent $LiFePO_4$ batteries was developed. The effects of the parameters on the recovery process, consisting of leaching, solvent extraction, and precipitation were investigated. The addition of H_2O_2 to the H_2SO_4 solution was ineffective for the selective leaching of Li(I) over iron. The results showed that Li(I) and iron were completely dissolved by 1.5 mol/L H_2SO_4, 100 g/L pulp density at 25 °C for 60 min at 300 rpm. After oxidation of Fe(II) in the leaching solution by addition of H_2O_2, Fe(III) was completely separated from the solution by five steps of cross-flow extraction with 1.0 mol/L D2EHPA at room temperature. The loaded Fe(III) was successfully separated by four steps of cross-current stripping with 50% (v/v) aqua regia solution. Finally, most Li(I) was recovered by precipitation of lithium phosphate from the iron-free raffinate by maintaining the pH of the solution at 11 and the temperature at 95 °C for 30 min. The optimum conditions for the complete dissolution of $LiFePO_4$ batteries by sulfuric acid solution and for the separation of iron and lithium ions from the leaching solutions were determined. A hydrometallurgical process was proposed for the recovery of pure lithium phosphate from spent $LiFePO_4$ batteries.

Keywords: Spent LiFePO₄ battery; Recovery, Solvent extraction; Precipitation; Lithium

1. Introduction

Nowadays, the use of lithium iron phosphate (LiFePO₄) batteries in electric vehicles (EVs) has been rapidly increasing [1]. After these batteries approach the end of their lifespan, there is a growing demand for the recycling of spent batteries [2]. From the perspective of the protection of environment and metal resources, the recycling of metals from spent batteries would decrease the processing burden of waste treatment plants and the discharge of waste residues [3].

According to the United States Geological Survey reported in 2024, world resources of lithium is approximately 105 million tons, of which Bolivia has the largest amount of 23 million tons [4]. According to the resource production model, high-quality lithium resources will likely be depleted after 2050, and uneconomical deposits might be needed to develop [5]. Due to the needs of low-carbon economic development, the recycling of lithium from spent batteries as important secondary resources has

attracted much attention. Compared to other types of batteries, such as lithium cobalt oxide batteries ($LiCoO_2$) and lithium nickel cobalt aluminum oxide batteries ($LiNi_xCo_yAl_zO_2$), the recycling of spent LiFePO₄ batteries has a low-cycle value due to the low content of lithium [6]. Another reason is that the structure of LiFePO₄ is an olivine structure, which is relatively stable and not easily damaged [7]. However, the recovery of metals from spent LiFePO₄ batteries is essential for decreasing the pressure on the supply of lithium material and for preventing environmental contamination [8].

In general, pyrometallurgical processes have disadvantages such as high energy consumption and difficulties in the complete recovery of lithium due to its low content [9]. Besides, some studies have shown that about 68% of lithium might be removed during pyrometallurgical processes [10]. In comparison with pyrometallurgy, hydrometallurgy is mostly used for the recovery of lithium from spent batteries as it offers advantages such as smaller scale, minimal energy investment, and minimal CO_2 emissions [11].

Hydrometallurgical processes include dissolution of the components by organic or inorganic acids with or without the addition of oxidants (e.g., sodium persulfate ($Na_2S_2O_8$), hydrogen peroxide (H_2O_2)) and then the separation of metal ions using various methods such as oxidation, extraction, and precipitation [12-14]. Inorganic acids such as sulfuric acid (H_2SO_4), hydrochloric acid (HCl), and phosphoric acid (H_3PO_4) show effective leaching of the metals from the spent batteries [15-17]. The addition of oxidants during the leaching process can oxidize Fe(II) to Fe(III), achieving selective leaching of iron over lithium. Although the use of organic acids such as acetic acid ($C_2H_4O_2$), citric acid ($C_6H_8O_7$), or even lemon juice for the leaching of Li(I) can be achieved with high effectiveness [18-20], their high cost prevents their employment in real operation [21]. After the leaching step, some separation methods, such as solvent extraction, ion exchange, and chemical precipitation, can be applied to the separation and purification of lithium ions from the leaching solution [22,23]. The lithium resources from spent batteries can be recovered as lithium phosphate, carbonate or hydroxide through chemical precipitation. Lithium phosphate is widely used as a solid electrode material [24]. Compared to lithium carbonate and hydroxide, lithium phosphate electrolyte is used in lithium batteries [25]. In addition to improving the diffusion channel and accelerating lithium ion transport, employment of Li_3PO_4 as a coating can also improve interface stability at high temperatures [26].

In this work, H_2SO_4 solution was employed to leach Li(I) and Fe(II) from spent $LiFePO_4$ battery powder. The effect of parameters such as the concentration of H_2SO_4, pulp density, temperature, time, and stirring speed on the leaching effectiveness was investigated. The effect of adding H_2O_2 as an oxidizing agent was also investigated in leaching. Solvent extraction was employed to separate iron ions from Li(I) present in the leaching solution of spent batteries. Li(I) from the iron-free leaching solution was recovered by precipitating Li(I) as lithium phosphate (Li_3PO_4). For these steps, optimum conditions were investigated, and a flowsheet was proposed to recover pure lithium phosphate from spent $LiFePO_4$ battery powders.

2. Experimental
2.1. Chemicals and reagents

Chemicals: All inorganic reagents in this work were purchased from Daejung Chemical & Metals Co., Korea, except for potassium permanganate ($KMnO_4$, >99.3%), which was purchased from Junsei Chemical Co., LTD, Japan. Acidic solutions such as sulfuric acid (H_2SO_4, >95%), hydrochloric acid (HCl,

35%), and nitric acid (HNO_3, 60%) solutions were prepared by diluting their concentrated solutions with doubly distilled water to the desired concentrations. Hydrogen peroxide (H_2O_2, 30%) was employed as an oxidizing agent, whereas sodium hydroxide (NaOH, >97.0) was used to adjust the pH values of aqueous solutions.

A commercial extractant, di-2-ethylhexyl phosphoric acid (D2EHPA, 95%) was supplied from Cytec Industries Inc., New Jersey, USA, whereas commercial grade kerosene (>90%) as a diluent was bought from Daejung Chemical & Metals Co., Korea. All these reagents were employed without any purification.

2.2. Materials

Spent $LiFePO_4$ cathodes used in this study were provided by a company in Korea and were in a powder form with particle size less than 200 μm and their color was black (see Fig. 1). X-ray diffractometer measurement (X'Pert-PRO diffractometer; Malvern Panalytical B.V, Almelo, the Netherlands) confirmed that the materials consisted of Li and Fe which existed as $LiFePO_4$ (see Fig. 2). To determine the contents of each metal in the materials, a certain amount of $LiFePO_4$ was completely dissolved by aqua regia solution, and the concentration of the metal ions in the resulting solution was measured by ICP-OES (Inductively coupled plasma optical emission spectroscopy, Spectro Arcos, Cleve, Germany) analysis. Table 1 shows that the metal component of the materials consisted of 4.94 wt% of Li and 38.09 wt% of Fe. Considering the results in Table 1 and Fig. 2 together, the remaining components in the solution were phosphorus, oxygen and carbon elements, which was consistent with the XRD pattern of $LiFePO_4/C$ in published paper [27].

Table 1. *The chemical composition of the spent $LiFePO_4$ powders*

Metals	Li	Fe	Others
Weight percentage, %	4.94	38.09	56.97

2.3. Experimental procedure and analytical methods

Leaching experiments were done with a desired concentration of H_2SO_4 with or without the addition of H_2O_2 in 50 cm³ two-neck round bottom. The weight ratio of the materials to the volume of the leaching solution (pulp density) was fixed at 100 g/L, except for studying the effect of pulp density on the leaching efficiency. Leaching parameters such as reaction temperature and time, and stirring speed were
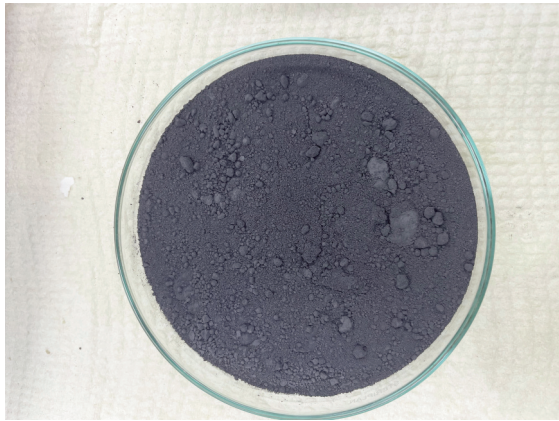
Figure 1. *Spent LiFePO$_4$ powders provided by a company*

Figure 2. *X-ray diffraction (XRD) pattern of the spent LiFePO$_4$ powders*

controlled using a magnetic stirrer (WiseStir MSH-20D, Daihan Scientific Co., Korea) and varied to dissolve these two metals completely. After the required reaction time, residues were separated from the leachate by filtration. The concentration of hydrogen ions and pH value in aqueous solutions before and after the leaching experiments was measured by a pH meter (Orion Star A211; Thermo Fisher Scientific, Waltham, Massachusetts. USA) and the volumetric titration method [28]. The concentration of the metal ions in the leachates was determined by ICP-OES measurement. Besides, the concentration of Fe(II) in the leaching solutions was determined by the permanganate titration method [29]. The leaching percentage of a metal was calculated as follows:

$$\text{Leaching percentage}\left(\%\right) = \frac{m_{M_{aq}}}{m_{M_o}} \times 100\% \qquad (1)$$

where $m_{M_{aq}}$ and m_{M_o} are the mass of a metal in the leaching solution and the initial mass of the metal in the materials.

Extraction and stripping experiments were carried out by mixing equal volumes of aqueous and organic phases (each 20 mL) in a 100 mL plastic bottle. After shaking for 30 min using a wrist action shaker (Burrell model 75, USA), two phases were separated using separatory funnels. The concentration of the metal ions in the loaded organic phase was calculated by using mass balance. The extraction and stripping percentages of the metal ions were calculated by using Eqs. (2) and (3).

$$\text{Extraction percentage}\left(\%\right) = \frac{m_{M_{org}}}{m_{M_{aq}}} \times 100\% \qquad (2)$$

where $m_{M_{org}}$ and $m_{M_{aq}}$ represent the mass of a metal ion in the organic phase after extraction and that in the aqueous phase before extraction, respectively.

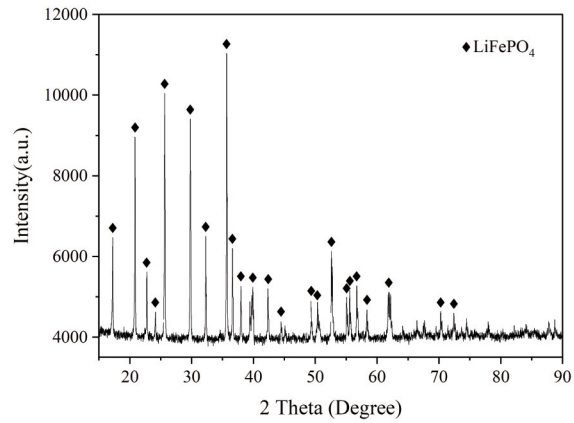$$\text{Stripping percentage}\left(\%\right) = \frac{m^*_{M_{aq}}}{m_{M_{org}}} \times 100\% \qquad (3)$$

where $m_{M_{org}}$ and $m^*_{M_{aq}}$ represent the mass of a metal ion in the organic phase before stripping and that in the aqueous phase after stripping, respectively.

To precipitate Li(I) ions as lithium phosphate (Li$_3$PO$_4$) from iron-free raffinate, NaOH solution was added to adjust the pH of the solution to the desired pH values. The reaction was done within 30 min at room temperature (22 ± 1 °C) with 300 rpm stirring speed. The precipitates were filtered from the solution by filter paper, washed several times with doubly distilled water, and dried in an oven for 24 hours. The precipitation percentage of Li(I) was calculated by Eq. (4).

$$\text{Precipitation percentage}\left(\%\right) = \frac{m_{Li} - m^*_{Li}}{m_{Li}} \times 100\% \qquad (4)$$

where m_{Li} and m^*_{Li} are the mass of Li(I) in the aqueous solution before and after the precipitation, respectively.

3. Results and discussion
3.1. Leaching of the battery powders
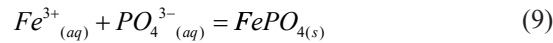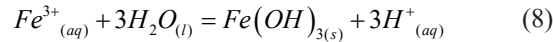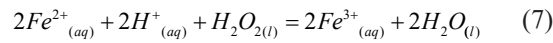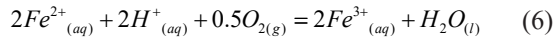#### 3.1.1. Effect of H$_2$SO$_4$ concentration

Since lithium and iron in the materials exist as LiFePO$_4$, complete leaching of the two components could be attained by acidic solutions. The leaching reactions of these two components can be represented by Eq. (5), which showed that iron would be dissolved as ferrous ion during the leaching [30].

$$LiFePO_{4(s)} + 3H^+_{(aq)} = Li^+_{(aq)} + 2Fe^{2+}_{(aq)} + H_3PO_{4(aq)} \qquad (5)$$
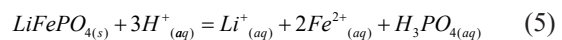
Compared to ferrous ions, the precipitation of ferric ions as ferric hydroxide can occur at around pH 2 [31]. Therefore, it might be possible to selectively

dissolve Li over iron by precipitating the dissolved Fe(II) as either $Fe(OH)_3$ or $FePO_4 \cdot 2H_2O$ in the presence of an oxidizing agent [32]. The following reactions represent the oxidation of Fe(II) by either dissolved oxygen or hydrogen peroxide and subsequent precipitation reactions of Fe(III) [33,34].

$$2Fe^{2+}_{(aq)} + 2H^+_{(aq)} + 0.5O_{2(g)} = 2Fe^{3+}_{(aq)} + H_2O_{(l)} \qquad (6)$$

$$2Fe^{2+}_{(aq)} + 2H^+_{(aq)} + H_2O_{2(l)} = 2Fe^{3+}_{(aq)} + 2H_2O_{(l)} \qquad (7)$$

$$Fe^{3+}_{(aq)} + 3H_2O_{(l)} = Fe(OH)_{3(s)} + 3H^+_{(aq)} \qquad (8)$$

$$Fe^{3+}_{(aq)} + PO_4^{3-}_{(aq)} = FePO_{4(s)} \qquad (9)$$

In this work, H_2SO_4 solution was employed as a leaching agent, and H_2O_2 was added as an oxidizing agent. The effect of H_2SO_4 concentration was investigated from 0.5 to 3.0 mol/L, while the molar ratio of H_2O_2 to Fe(II) was fixed at 2. Leaching experiments were performed at 100 g/L pulp density with 500 rpm stirring speed at 60 °C for 2 hrs. Fig. 3 shows the effect of acid concentration in the presence and absence of H_2O_2 on the leaching of the components. As presented in Fig. 3a, in the absence of H_2O_2, the leaching percentage of both Li and iron increased with rising H_2SO_4 concentration and reached ~100% at 1.5 mol/L acid concentration. Moreover, the leaching percentages of Li and iron were similar in the experimental ranges. This result indicated that the acid concentration played an important role in the dissolution of the components from the batteries. It was noticeable that both Fe(II) and Fe(III) existed in the leaching solution, which can

be ascribed to the oxidation of Fe(II) to Fe(III) by the oxidizing action of the dissolved oxygen. This result agreed well with a decrease in the concentration of hydrogen ions after the leaching in Table 2. Fig. 3b shows that the leaching behavior of Li and iron by H_2SO_4 solution in the presence of H_2O_2. The concentration of H_2SO_4 greatly affected the leaching percentage of iron when H_2SO_4 concentrations were lower than 1.5 M. The leaching percentages of Li and iron were 88 and 12% at 0.5 mol/L H_2SO_4, indicating that the precipitation of Fe(III) might occur under these conditions since the pH of the leaching solution was around 1.24. Moreover, Fig. 3b shows that the mass percentage of Fe(II) to the total mass of iron was nearly constant at 9% in the experimental ranges.

Figs. 3a and 3b show that it is difficult to selectively dissolve Li from the batteries by employing H_2SO_4 solutions in the presence of H_2O_2. Considering the price of H_2O_2, it would be better to completely dissolve Li and iron and then separate the dissolved metal ions. From the obtained results, 1.5 mol/L H_2SO_4 without the addition of H_2O_2 was selected as the optimum condition for the leaching of Li and iron from the materials.

3.1.2. Effect of pulp density

A lower pulp density typically indicates a higher liquid-to-solid ratio (L/S ratio), which consequently results in a relatively higher concentration of sulfuric acid in the solution. Some researchers showed that a higher L/S ratio has a significant effect on the leaching of lithium and iron [35]. To investigate the effect of pulp density on the leaching performance of

Table 2. *The change in the concentration of hydrogen ions during the leaching*

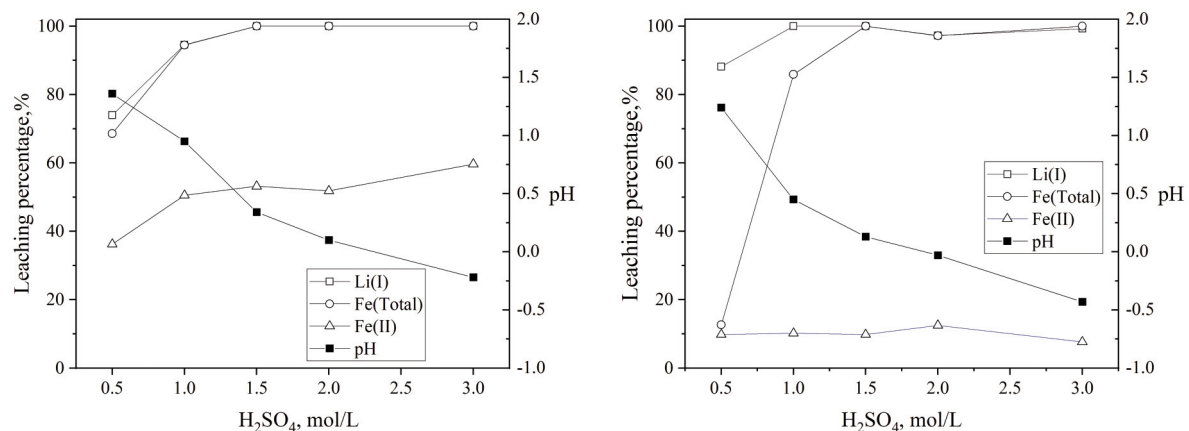| H_2SO_4 concentration, mol/L		0.5	1	1.5	2	3
H^+ concentration, mol/L	After leaching	0.04	0.11	0.46	0.79	1.66

Figure 3. *Effect of H_2SO_4 concentration without (3a) and with (3b) the addition of H_2O_2 on the leaching percentage of lithium and iron. (Leaching conditions: 0.5-3.0 mol/L H_2SO_4, 2 molar ratio of H_2O_2 to Li, 100 g/L pulp density, 60 °C, 2 hrs, 500 rpm)*

Li and iron from the materials, leaching experiments were done by varying pulp density from 80 to 150 g/L at the following conditions: 1.5 mol/L H_2SO_4, 60 °C, 2 h reaction time, and 500 rpm stirring speed. Fig. 4 shows that the leaching percentage of Li decreased from 100 to 92%, while there was little change in the leaching percentage of iron in the investigated ranges of pulp density. According to Fig. 4, the pH of the solution increased rapidly from 0.07 to 0.43 as pulp density increased from 80 to 150 g/L. Therefore, it might be said that a small decrease in the leaching percentage of Li at 150 g/L pulp density might be related to a decrease in the concentration of hydrogen ions, which can participate in the leaching reactions. Thus, 100 g/L pulp density was suitable for the leaching of the components from spent $LiFePO_4$ powders.
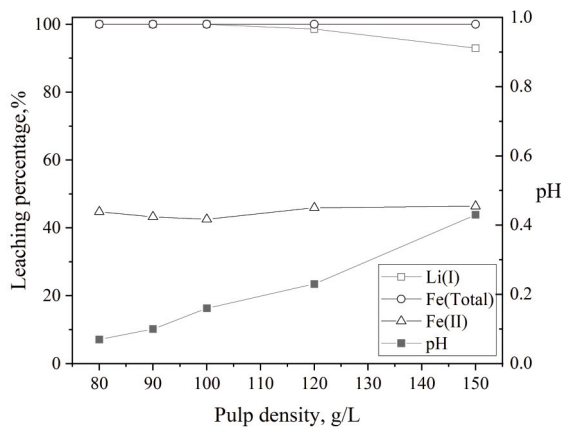

Figure 4. *Effect of pulp density on the leaching percentage of lithium and iron by 1.5 mol/L H_2SO_4 at 60 °C (2 hrs reaction time, 500 rpm stirring speed)*

3.1.3. Effect of reaction temperature

During the leaching process, an increase in temperature enhances the diffusion rate of reactants in the liquid phase, thereby accelerating the mass transfer [36]. The Stokes-Einstein equation indicates that the diffusion coefficient is directly proportional to temperature. To investigate the effect of temperature on the leaching of Li and iron, leaching experiments were conducted at 1.5 mol/L H_2SO_4, 100 g/L pulp density, 2 h reaction time, 500 rpm stirring speed by varying reaction temperature from 25 to 80 °C. Fig. 5 shows that the change in the leaching percentage of Li and iron was negligible in the investigated ranges, indicating that acid concentration is the most important variable in the leaching of the two components. Moreover, the concentration of Fe(II) in the leachate decreased from 46% to 43% as the reaction temperature increased from 40 to 80 °C. Therefore, the reaction temperature was fixed at 25 °C in further experiments.
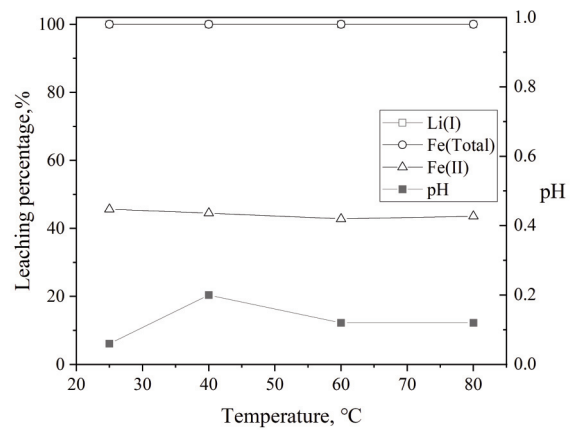

Figure 5. *Effect of temperature on the leaching percentage of lithium and iron by 1.5 mol/L H_2SO_4 (100 g/L pulp density, 2.0 hrs reaction time, 500 rpm stirring speed)*

3.1.4. Effect of reaction time

The effect of reaction time on the leaching of lithium and iron from spent $LiFePO_4$ powders was investigated by varying reaction time from 30 to 120 mins at the following conditions: 1.5 mol/L H_2SO_4, 100 g/L pulp density, 500 rpm stirring speed, and 25 °C. In Fig. 6, the leaching percentage of the components reached 100% after 60 mins. The concentration ratio of Fe(II) to that of total iron ions was about 40%. Therefore, 60 minutes of reaction time was selected for the complete dissolution of Li and iron from the batteries.
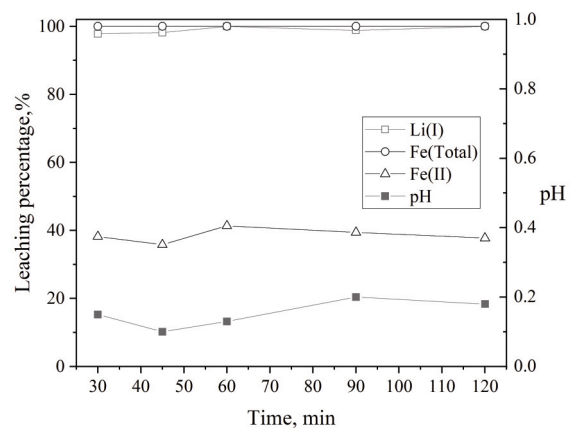

Figure 6. *Effect of time on the leaching percentage of lithium and iron by 1.5 mol/L H_2SO_4 (100 g/L pulp density, 25 °C reaction temperature, 500 rpm stirring speed)*

3.1.5. Effect of stirring speed

The stirring speed is crucial for achieving uniform dispersion of solid particles in the solution, thereby preventing particle aggregation and suspension.

Particularly in cases of larger solution volume, higher stirring speed is essential to ensure uniform distribution of sulfuric acid in the solution and to prevent the formation of local concentration gradients [37]. To investigate the effect of stirring speed on the leaching of the components, the stirring speed was varied from 150 to 900 rpm at the following conditions: 1.5 mol/L H_2SO_4, 100 g/L pulp density, 60 min reaction time, and 25 °C. Fig. 7 indicates that the leaching percentage of both components increased from 87% for Li(I) and 92% for iron to 100% when the stirring speed was higher than 300 rpm. These results indicated that the mass transfer step is important in dissolving both components from the batteries using a sulfuric acid solution. Moreover, the concentration ratio of Fe(II) to the total concentration of iron ions increased from 40 to 50% as the stirring speed increased. This might be ascribed to the decrease in the concentration of dissolved oxygen with stirring speed.
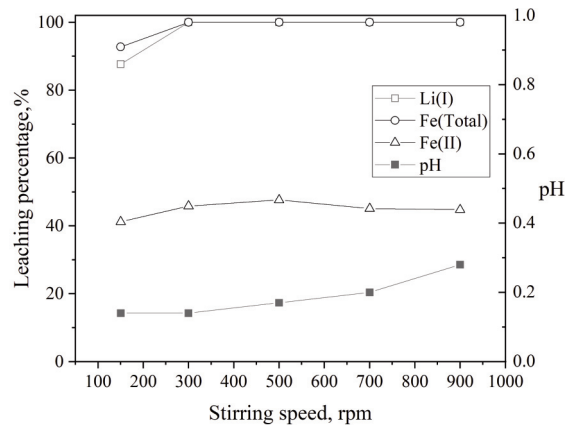

Figure 7. *Effect of stirring speed on the leaching percentage of lithium and iron by 1.5 mol/L H_2SO_4 (100 g/L pulp density, 25 °C reaction temperature, 1 hr reaction time)*

The optimum conditions for the complete dissolution of Li and iron from the spent LiFePO4 powders were 1.5 mol/L of H_2SO_4, 100 g/L pulp density, 60 min reaction time, 300 rpm stirring speed, and 25 °C. Under these conditions, the concentrations of Li(I), Fe(II), Fe(III), and hydrogen ions in the leachate were 4.57, 16.20, and 21.1 g/L, and 0.73 mol/L, respectively.

Therefore, further experiments were performed for the separation of the two metal ions from the leachate. Use of inorganic acids and oxidizing agents during the industrial operation results in the emission of exhaust gases. Therefore, enclosed system for monitoring and detection might be necessary together with exhaust gas treatment systems to achieve the goal of clean production.

3.2. Selective separation of iron over Li(I) from the leachate by solvent extraction

The leaching solution contained Li(I), Fe(II), Fe(III), and sulfate and phosphate ions, and the solution pH was around 0.14. In hydrometallurgy, Fe(III) was separated from the sulfate solutions by solvent extraction with D2EHPA [38-40]. Since Fe(II) is not extracted well by D2EHPA, it is necessary to oxidize Fe(II) to Fe(III) to apply solvent extraction. In this work, H_2O_2 was employed as an oxidizing agent for Fe(II), and the oxidation reaction can be represented as Eq. (7).

To investigate the effect of H_2O_2 concentration on the oxidation of Fe(II) to Fe(III), the molar ratio of H_2O_2 to Fe(II) was varied from 0.5 to 1.5. The reactions were conducted at 25 °C with 400 rpm stirring speed for 30 min. As presented in Fig. 8, Fe(II) ions were completely oxidized to Fe(III) when the molar ratio of H_2O_2 to Fe(II) was unity. According to Eq. (7), one mole of H_2O_2 is necessary to oxidize two moles of Fe(II). Therefore, our data indicate that
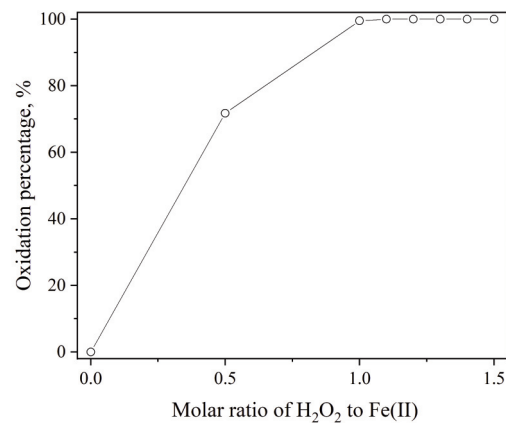

Figure 8. *Effect of molar ratio of H_2O_2 to Fe(II) on the oxidation percentage of Fe(II) at 25 °C (400 rpm stirring speed, 30 mins reaction time)*
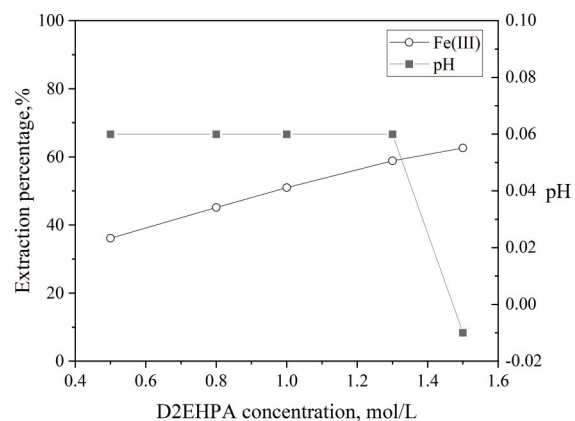

Figure 9. *Effect of D2EHPA concentration on the extraction of Fe(III) from the leaching solution*

the addition of two moles of H_2O_2 was needed to oxidize two moles of Fe(II). After the oxidation of Fe(II) by H_2O_2, the concentrations of Li(I) and Fe(III) in the aqueous solution were 4.30 and 33.30 g/L, respectively, and the concentration of hydrogen ion was around 0.59 mol/L (pH 0.23). The decrease in the concentration of Fe(II), Li(I), and hydrogen ions in the solution was due to the addition of H_2O_2. The hydrogen ions were consumed during the oxidation of Fe(II) to Fe(III) by H_2O_2, resulting in an increase of solution pH and the concentration of Fe(III). The addition of H_2O_2 leads to an increase in solution volume, thereby reducing the concentration of lithium ions.

Considering the concentration of Fe(III) present in the leaching solution after the oxidation of Fe(II), the concentration of D2EHPA was varied from 0.5 to 1.5 mol/L in solvent extraction experiments. Fig. 9 shows that the extraction percentage of Fe(III) increased from 36 to 62% as the concentration of D2EHPA increased, and no Li(I) was extracted at all. Besides, the decrease in pH of the aqueous solution after the extraction was observed, which was attributed to the liberation of hydrogen ions of D2EHPA from the organic phase to the aqueous phase during the extraction. Although the increase in the D2EHPA concentration can increase the extraction percentage of Fe(III), its high viscosity would cause difficulty in the mass transfer of metal ions between two phases, and the liberation of hydrogen ions into the aqueous solution also results in a reduction in the extraction of Fe(III). Therefore, 1 mol/L D2EHPA was selected to extract Fe(III) from the aqueous solution. Since the extraction percentage of Fe(III) by 1 mol/L D2EHPA was 50%, five stages of cross current extraction were applied. Table 3 confirmed that complete and selective extraction of Fe(III) over Li(I) was possible by using 1.0 mol/L D2EHPA after five stages of cross current extraction, and the pH of the raffinate after five stages was zero. The extraction reaction of Fe(III) by D2EHPA can be written as [41]:

$$Fe^{3+}_{(aq)} + 3H_2A_{2(org)} = FeA_3(HA)_{3(org)} + 3H^+_{(aq)} \qquad (10)$$
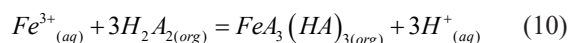
where H_2A_2 is the dimer of D2EHPA. Eq. (10) indicates that three moles of hydrogen ions are released into the aqueous phase during the extraction of one mole of iron ions. Therefore, the equilibrium pH of the raffinate after five stages of cross current extraction was decreased from 0.23 to zero.

In general, it is possible to strip Fe(III) from the loaded D2EHPA by using a reducing agent when the concentration of Fe(III) in D2EHPA is low [42]. Since the concentration of Fe(III) in the loaded D2EHPA of the first stage of cross-current extraction was 24 g/L, aqua regia solution was employed for the stripping [43]. Aqua regia was diluted with distilled water, and the volume percentage of aqua regia was varied from 30 to 80%. Fig. 10 shows that 94% Fe(III) was stripped from the loaded when the concentration of aqua regia was 80%. This result indicates that it was difficult to completely strip Fe(III) from the loaded D2EHPA with one step of stripping.

To reduce equipment corrosion, 50% aqua regia was selected for the stripping of Fe(III) from loaded D2EHPA. Fe(III) was completely stripped by 50% aqua regia after four stages of cross-current stripping (see Table 4).

Our results indicated that complete separation of iron from the leaching solution was possible by extraction with 1.0 mol/L D2EHPA and stripping with 50% aqua regia solution. Further work is necessary on the recovery of iron compounds from the stripping solution.

Table 3. *The variation in the extraction percentage of Fe(III) during five stages of cross-current extraction with 1.0 mol/L D2EHPA. (A/O=1, 25 °C, 30 min)*

Stage	Concentration, ppm			Extraction of Fe(III), %	pH
	Fe(III)	P(IV)	Li(I)		
1	16771	17702	4368	49.6	0.14
2	10648	17436	4368	68	0.1
3	3461	17835	4368	89.6	0.09
4	1650	17569	4332	95.04	0.06
5	0	17668	4352	100	0

Table 4. *The variation in the stripping percentage of Fe(III) during the four stages of cross-current stripping with 50% (v/v) aqua regia solution. (A/O=1, 25 °C, 30 min)*

Stage	Concentration, ppm			Stripping of Fe(III), %
	Fe(III)	P(IV)	Li(I)	
1	7706.49	0	0	74.2
2	2117.59	0	0	94.4
3	461.01	0	0	98.8
4	120.88	0	0	~100

3.3. Precipitation of Li(I) phosphate from the raffinate

After Fe(III) was separated from the leachate by solvent extraction with D2EHPA, the concentration of Li(I) in the raffinate (pH = 0) was 4.30 g/L. The solubility product of Li_3PO_4 at 25 °C is 2.37×10^{-11} [44], and the mole fraction of phosphate ion depends on solution pH because the acidity of phosphoric acid
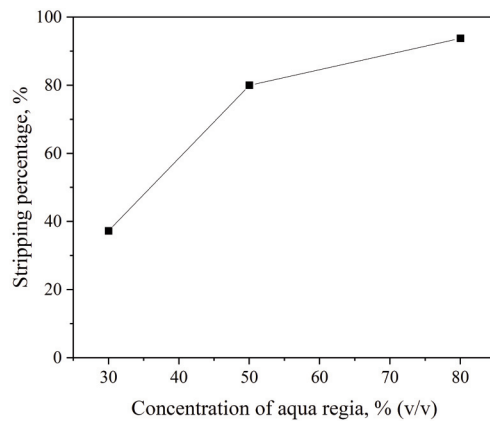
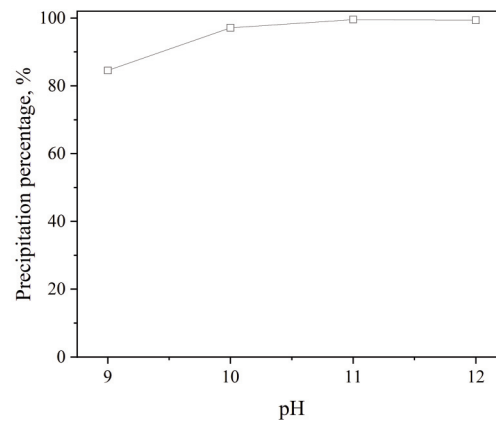**Figure 10.** *Effect of aqua regia concentrations on the stripping of Fe(III) from the loaded D2EHPA*

Figure 11. *Effect of solution pH on the precipitation of Li(I) from the iron free raffinate at 95 °C (300 rpm, 30 mins)*

is weak. Therefore, in order to investigate the possibility of precipitating Li(I) as Li_3PO_4, precipitation experiments were done by varying solution pH. In precipitation experiments, the reaction time and stirring speed were fixed at 30 min and 300 rpm, and the effect of solution pH and reaction temperature was investigated. Fig. 11 shows that the precipitation percentage of Li(I) slightly increased from 85 to 99.6% as the solution pH increased from 9 to 12. Fig. 12 shows that reaction temperature had a favorable effect on the precipitation of Li(I), but the effect was small. The effect of solution pH on the precipitation of Li(I) is related to the increase in the mole fraction of phosphate ion with solution pH [45]. The precipitation reaction of Li(I) phosphate can be represented as

$$3Li^+ + PO_4^{3-} = Li_3PO_{4,solid} \quad (11)$$
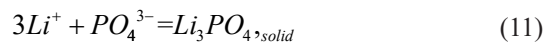
The optimum conditions for the precipitation of Li(I) from the iron-free raffinate were selected as pH 11, 95 °C, and 30 min. The X-ray diffraction pattern
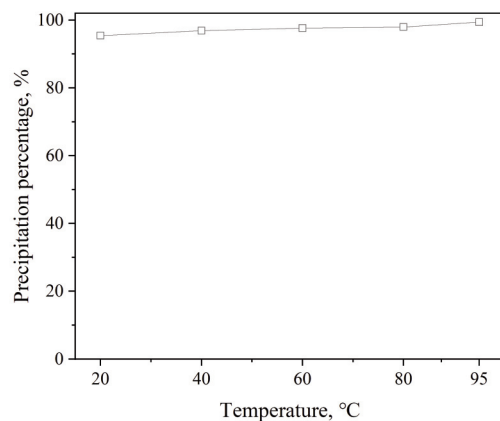
of the obtained Li_3PO_4 precipitates is shown in Fig. 13. In the XRD pattern, the major diffraction peaks correspond closely to the peak positions and relative intensities specified in the standard PDF card for Li_3PO_4 (PDF# 98-001-0257), indicating that the primary component of the sample is Li_3PO_4. No additional impurity peaks were detected, suggesting that the sample has high purity. The remaining ions in the filtrate are sodium, sulfate, and hydroxide ions. Sulfate ions can be eliminated through precipitation or by using an anion-exchange resin. Following the removal of sulfate ions, the alkaline solution can be neutralized and disposed of safely, or it can be utilized for secondary purposes.

3.4. A proposed flow sheet for the recovery of Li(I) from spent LiFePO₄ powder

From the obtained results, a flow sheet for the recovery of lithium from the spent $LiFePO_4$ powders was proposed and is represented in Fig. 14. H_2SO_4

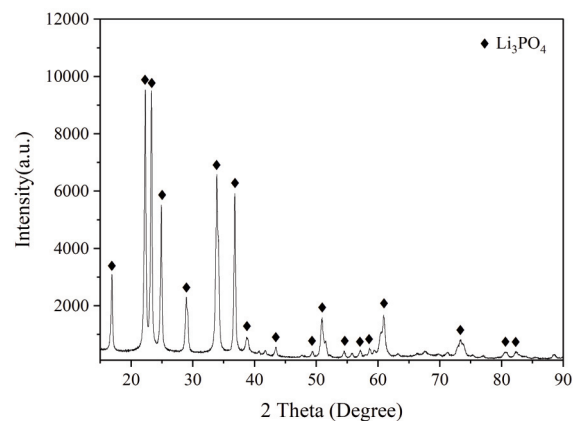**Figure 12.** *Effect of temperature on the precipitation of Li(I) from the iron free raffinate at solution pH 11 (300 rpm, 30 mins)*

Figure 13. *X-ray diffraction (XRD) pattern of the Li₃PO₄ precipitates obtained from the solution with pH 11*
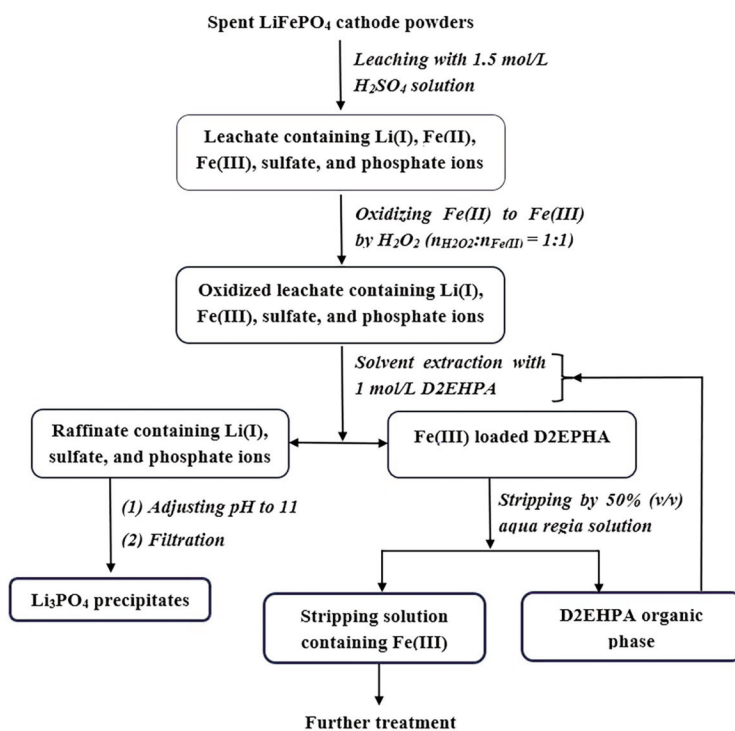
Figure 14. *A flowsheet for the recovery of lithium from spent LiFePO₄ powders*

solution was employed as a leaching agent for the complete dissolution of two components from the batteries. After the dissolution of Li and iron, H_2O_2 solution is added into the leachate to oxidize Fe(II) to Fe(III), which enhances the extraction performance of iron by D2EHPA. After the separation of Fe(III) by solvent extraction with D2EHPA, the Li(I) in the iron-free raffinate can be recovered by precipitation of Li_3PO_4. The Li_3PO_4 precipitates can be employed to produce LiFePO₄ or for other commercial purposes. However, the recovery of iron from the aqua regia stripping solution should be considered.

4. Conclusions

A hydrometallurgical process was proposed for the recovery of pure lithium phosphate from spent LiFePO₄ powder. This process consisted of leaching, solvent extraction, and chemical precipitation. The effect of some variables in each process was investigated. In this work, H_2SO_4 solutions with or without H_2O_2 as an oxidizing agent were used as a leaching solution for battery powders. Selective dissolution of Li(I) from the battery powders was difficult due to the use of sulfuric acid with H_2O_2. Complete dissolution of lithium and iron was achieved in the absence of H_2O_2 under the following leaching conditions: 1.5 mol/L H_2SO_4, 100 g/L pulp density, 60 min reaction time, 300 rpm stirring speed, and 25 °C. The Fe(II) in the leaching solution was

oxidized to Fe(III) by adding H_2O_2 in the molar ratio of Fe(II) to H_2O_2 at room temperature. The Fe(III) ions were then completely separated from Li(I) by five stages of cross-flow extraction with 1.0 mol/L D2EHPA. The loaded Fe(III) in D2EHPA was completely separated by four steps of cross-current stripping with 50% (v/v) aqua regia solution. By adjusting the pH of the solution and the reaction temperature, 99.6% Li(I) was precipitated as pure Li_3PO_4 solid from the iron-free raffinate.

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Author Contributions

Methodology and editing: Man Seung Lee; data support and writing-original draft preparation: Jing Chen and Thanh Tuan Tran. All authors have read and agreed to the published version of the manuscript.

Data availability

The data of this work could be obtained by contacting with the corresponding author by e-mail.

Declarations of competing interest

The authors declare no conflict of interest.

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IZDVAJANJE ČISTOG LITIJUM FOSFATA IZ RASTVORA SUMPORNE KISELINE NAKON LUŽENJA ISKORIŠĆENIH LiFePO₄ BATERIJA PRIMENOM SOLVENTNE EKSTRAKCIJE I HEMIJSKOG TALOŽENJA

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Apstrakt

Sa sve većom upotrebom električnih vozila, potražnja za litijum gvožđe fosfat baterijama (LiFePO₄) naglo je porasla. Stoga, reciklaža metala iz ovih baterija na kraju njihovog životnog veka postaje neophodna. U ovoj studiji, razvijen je hidrometalurški proces za oporavak litijum fosfata iz iskorišćenih LiFePO₄ baterija. Istraživani su efekti parametara na proces izdvajanja, koji se sastoji od luženja, ekstrakcije rastvaračem i taloženja. Dodavanje H₂O₂ u rastvor H₂SO₄ nije bilo efikasno za selektivno luženje litijuma (I) u odnosu na gvožđe. Rezultati su pokazali da su litijum (I) i gvožđe potpuno rastvoreni u 1,5 mol/L H₂SO₄, sa gustinom pulpe od 100 g/L na 25°C tokom 60 minuta pri brzini mešanja od 300 º/min. Nakon oksidacije Fe(II) u rastvoru za luženje dodavanjem H₂O₂, Fe(III) je potpuno odvojen iz rastvora u pet koraka ekstrakcije poprečnim tokom koristeći 1,0 mol/L D2EHPA na sobnoj temperaturi. Učitan Fe(III) je uspešno odvojen u četiri koraka poprečne ekstrakcije sa 50% (v/v) rastvorom carske vode. Na kraju, najveći deo litijuma (I) je izdvojen taloženjem litijum fosfata iz rastvora bez gvožđa održavanjem pH vrednosti rastvora na 11 i temperature na 95 °C tokom 30 minuta. Optimalni uslovi za potpuno rastvaranje LiFePO₄ baterija su određeni u rastvoru sumporne kiseline i za odvajanje jona gvožđa i litijuma iz rastvora za luženje. Predložen je hidrometalurški proces za izdvajanje čistog litijum fosfata iz iskorišćenih LiFePO₄ baterija.

Ključne reči: *Iskorišćena LiFePO₄ baterija; Izdvajanje; Solventna ekstrakcija; Taloženje; Litijum*