

Selective Recovery of Lithium Sulfate from Spent LFP(LiFePO₄) Powder

Dae-Keun Kang¹, Min-Yong Shin², Do-Hee Kim³, Jei-Pil Wang⁴

^{1,3}Department of Metallurgical Engineering, Pukyong National University, Busan, Korea

²Department of Marine Convergence Design Engineering(Advanced Materials Engineering), Pukyong National University, Busan, Korea

⁴Department of Metallurgical Engineering, Department of Marine Convergence Design Engineering(Advanced Materials Engineering), Pukyong National University, Busan, Korea

Abstract - This study was conducted to selectively leach and recover lithium from spent LFP (LiFePO₄), an active cathode material of lithium-ion batteries, using a sulfuric acid solution. The lithium recovery rate according to conditions such as the solid-liquid ratio of sulfuric acid solution and LFP powder, the stirring time, and M concentration in sulfuric acid was investigated. Lithium was selectively recovered under each experimental condition, and the following optimal process conditions were derived as a result of the experiment. Under the following experimental conditions: the sulfuric acid solution concentration of 2M H₂SO₄, the stirring time of 60 min, and the weight ratio of 1:5, lithium sulfate excluding impurities was selectively recovered, and the Li content in lithium sulfate solution of 403.19 mg, and the Li recovery rate of 99.79% were achieved.

Keywords - LFP (LiFePO₄), active cathode material, sulfuric acid, lithium sulfate

I. INTRODUCTION

With the development of battery performance, cathode active materials for secondary lithium batteries have been diversely developed. LiCoO₂, which was first used, has continued to develop by adopting technologies such as doping and surface modification to supplement the initial insufficient performance and has recently become applicable even at a charging voltage close to 4.3V. Since the application equipment, on the other hand, became more complex, the required characteristics were further strengthened. Since high capacity and high operating voltage were required, R&D activities for new materials have actively started. In line with the strengthening carbon regulations at home and abroad, development for electric vehicles has become active. As a result, new materials with high output and high safety became necessary, and in line with this demand, materials with excellent safety such as LiMn₂O₄ and LiFePO₄ have been developed.¹⁾

LFP (LiFePO₄)²⁻³⁾ is known as one of the most promising cathode materials for lithium-ion batteries due to its advantages such as²⁻³⁾ high output, cost-effectiveness, low toxicity, excellent thermal stability, and high reversibility.⁴⁾ In particular, LiFePO₄ with low electrochemical potential is a very safe cathode material.⁵⁾ Therefore, in recent years, lithium-ion batteries using LFP as a cathode material have been widely used in electric vehicles (EV) and hybrid electric vehicles (HEV), especially electric buses.⁶⁻⁷⁾ From

2015 till 2020, 401GWh secondary batteries (lithium-ion + LFP) have been used. The demand for LFP batteries in the electric vehicle market in China is a major LFP producing and consuming country, has increased significantly from 2.59GWh in 2019 to 20GWh in 2021.

Currently, the volume of the discarded secondary batteries for EVs that have reached the end of their life cycle (5-10 years) is on the verge of increasing in full scale, and 'Frost & Sullican' predicts that the global spent battery market will grow at a CAGR of 99.8%, reaching \$7.8 billion in 2025. Therefore, it is expected that the disposal of spent LFP batteries will become a problematic issue due to the rapid increase in demand for LFP batteries. In particular, organic electrolytes containing toxic LiPF₆ and metal ions from LFP batteries can cause environmental pollution by penetrating soil and groundwater when disposed of in landfills, so post-treatment processes for recycling and reuse, etc., become important.⁸⁻⁹⁾ In addition, the demand for lithium, the main raw material for LFP batteries, has surged with the development of EVs and HEVs, whereas domestic lithium supply and demand is entirely dependent on imports, indicating that risk to the stability of lithium supply and demand will increase in the future.¹⁰⁻¹¹⁾ Therefore, recycling of spent LFP batteries is expected to contribute to environmental protection and the stability of domestic lithium supply and demand.

As presented in Table 1 below, there are a hydrometallurgical method and a direct regeneration method for recycling spent LFP batteries. The hydrometallurgical method is mainly used in recycling spent lithium-ion batteries by leaching the positive electrode active material obtained through pre-treatment, selectively separating the metal from the leaching solution, and then refining it. The hydrometallurgical method intended to recycle spent LFP batteries involves the complex process of leaching all elements of the cathode active materials using inorganic acids such as H₂SO₄, HCl, and H₃PO₄, in leaching process and performing complex chemical precipitation using NaOH or NH₃·H₂O. At this time, since the addition of acid is mostly excessive and the acid concentration is high to leach all metals into solution, a significant amount of alkali is required in the separation process.¹²⁻¹⁴⁾



The direct regeneration method reuses the cathode material recovered from the spent batteries by immersing it in an organic solvent. As an example of a direct regeneration method for spent LFP batteries, there is a method of recovering LFP powder by directly separating it from a positive electrode and heating it at a high temperature or immersing it in an organic solvent. However, the recovered cathode material tends to contain a large amount of impurity, and the structure, in general, tends to be destroyed after a number of charge/discharge cycles, resulting in poor electrochemical performance when reused.¹⁴⁻¹⁶ Therefore, to develop the feasible recycling process of spent LFP batteries from the industrial point of view, it is required to make the process

simpler and more environmentally friendly.

In this study, a process for selectively recovering, Li-excluding impurities was investigated through leaching reaction of LFP (LiFePO_4) powder, which is the cathode material in spent lithium secondary batteries, and sulfuric acid solution (H_2SO_4), unlike the existing process of leaching all elements into a solution and then separating them using an excessive and highly concentrated inorganic acid. The optimal process conditions were established to increase the Li recovery rate by controlling the M concentration in sulfuric acid solution, the stirring time, and the solid-liquid ratio of the sulfuric acid solution and the LFP powder.

Table 1. Reported Methods for the Recycling of Spent LiFePO_4 Batteries

Recycling Method	Reagents/process	products	ref
Hydrometallurgical method	H_2SO_4 and H_2O_2 as leaching agents, NaOH as precipitant, with $\text{LiFePO}_4/\text{H}_2\text{SO}_4/\text{NaOH}$ molar ratio of 1:8:15	$\text{Fe}(\text{OH})_3$, $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$, and Li_3PO_4	14
	6 M HCl as leaching agent, 6.25% $\text{NH}_3 \cdot \text{H}_2\text{O}$ as precipitant	$\text{FePO}_4 \cdot 2\text{H}_2\text{O}$	13
	H_3PO_4 as leaching agent with $\text{LiFePO}_4/\text{H}_3\text{PO}_4$ molar ratio of 1:3.16	$\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ and LiH_2PO_4	6
	2.5 M H_2SO_4 as leaching agent, $\text{NH}_3 \cdot \text{H}_2\text{O}$, and Na_2CO_3 as precipitants	$\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ and Li_2CO_3	12
Direct regeneration	heating cathode scraps at 400–600 °C for 30 min under N_2	LiFePO_4	17
	heating cathode powders at 650 °C for 1h	LiFePO_4	15
	soaking cathode plates in DMAC solvent at 30 °C for 30 min	LiFePO_4	16

II. EXPERIMENTAL MATERIALS AND METHODS

A. Experimental Materials

This study used LFP (LiFePO_4) powder, a cathode active material recovered from spent lithium-ion batteries. The LFP powder used in the study was analyzed by XRD (X-ray Diffraction) and ICP-OES (Inductively Coupled Plasma). The results of XRD and ICP-OES analysis of the LFP powder have been presented in Fig. 1 below. The results of the XRD analysis confirmed that the LFP

powder was in the LiFePO_4 phase, and the results of ICP-OES analysis confirmed that the main element content was Li: 4.04 wt%, Fe: 32.7 wt%, and P: 18.7 wt%, respectively.

In addition, 98.08% H_2SO_4 solution was used as an acid solvent for selectively leaching Li from the spent LFP, and a water purifier prepared distilled water used in this experiment.

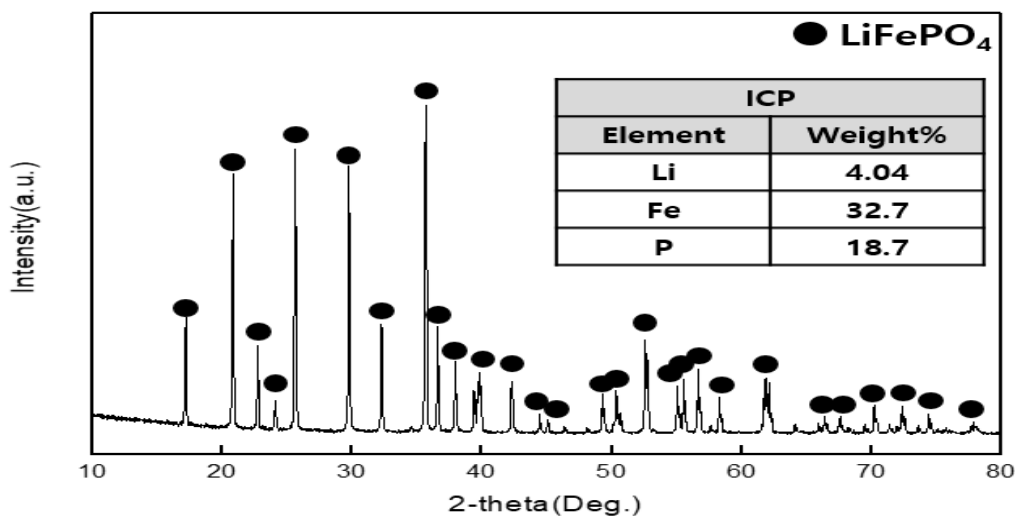


Fig. 1. XRD pattern and ICP analysis results of LiFePO_4 .

B. Experimental Methods

A study was conducted on deriving optimal conditions for selectively leaching Li from LFP (LiFePO₄), a cathode active material, using a sulfuric acid solution. First, the effect on the M concentration in sulfuric acid solution, the stirring time, and the solid-liquid ratio between the sulfuric acid solution and the LFP powder has experimented, and then the lithium sulfate solution filtered by decompression

filtration was dried at 400° C for 24 h. The Li content leached into the filtrate was analyzed by ICP-OES to calculate the Li recovery rate. In addition, to confirm that Li excluding Fe and P was selectively leached, the lithium sulfate powder recovered by drying the lithium sulfate solution was analyzed by XRD. The following is the expected reaction equation between spent LFP powder and sulfuric acid solution.

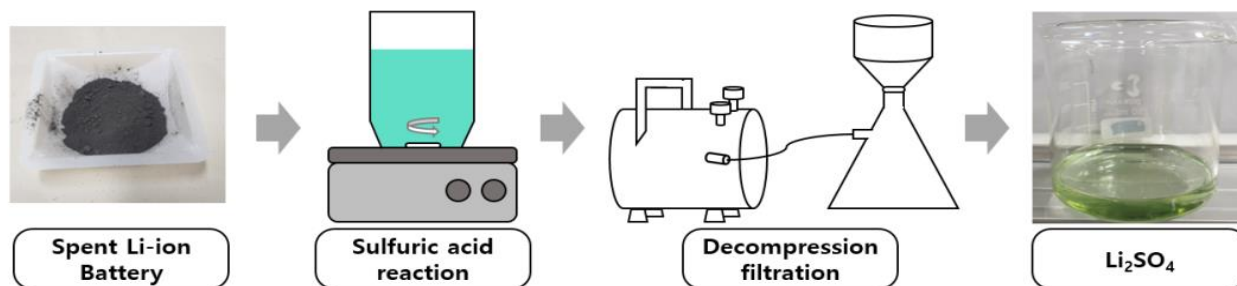
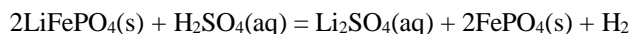


Fig. 2. Schematic diagram of Experimental Process.

III. RESULTS AND DISCUSSION

A. Effect on the change of M concentration in sulfuric acid solution

10 g of spent LFP powder was put into a beaker containing 50 ml of 0.5, 1, 2, and 3M sulfuric acid solution, respectively, and stirred at a stirring speed of 300 rpm for 60 minutes. After stirring, the solid was separated by decompression filtration. The filtered solution was

analyzed by ICP-OES to measure Li content and to calculate the recovery rate. The solution was dried at 400° C. for 24 h, and the presence of residual impurities and phase ware were analyzed by XRD. The results of the XRD analysis have been presented in Fig 3 below. As shown in Fig. 3 below, only the Li₂SO₄ phase was detected in the 2M sulfuric acid solution, confirming that lithium excluding impurities was selectively leached.

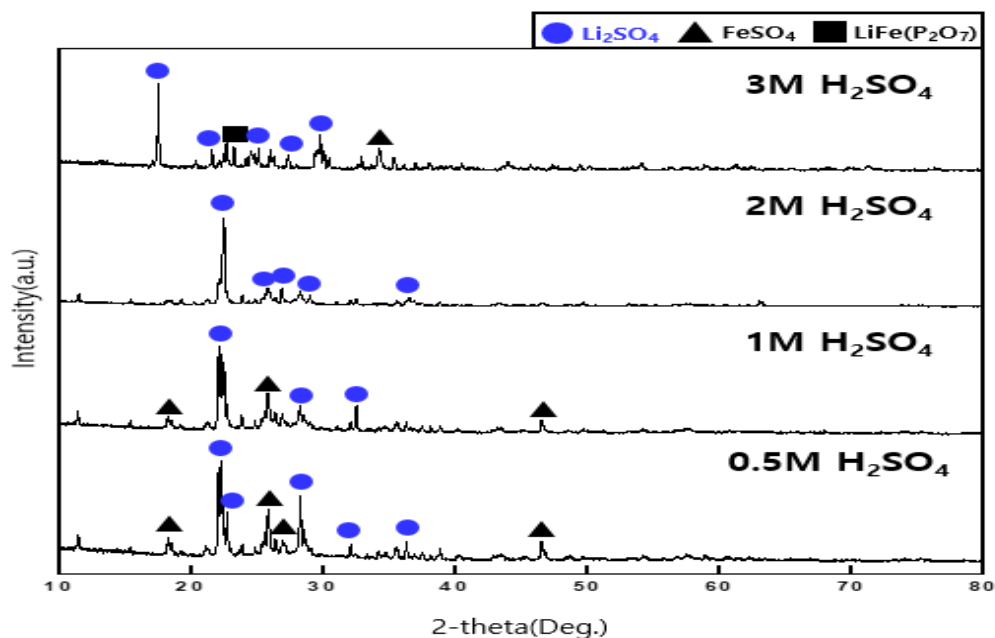


Fig. 3. Results of XRD analysis by the concentration of the sulfuric acid solution.

In Table 2 below, the results of the Li content measured by ICP-OES analysis of the filtered solution after decompression filtration and the Li recovery rate calculated using the following equation have been presented. As a result of calculating the recovery rate, the Li recovery rate was 99.79% when the concentration of the sulfuric acid solution was 2M and 99.87% when the concentration of the sulfuric acid solution was 3M. However, as presented in Fig.3 above, due to XRD analysis, impurities were detected in 3M sulfuric acid solution, whereas only Li₂SO₄ phase was detected in 2M sulfuric acid solution,

confirming that 2M sulfuric acid solution was the optimal condition.

$$\text{Li recovery rate} = \frac{\text{Li content in solution(mg)}}{\text{Li content in experimental sample}} \times 100 \dots\dots\dots (1)$$

Table 2. Li content and Li recovery rate of filtration solution by the concentration of the sulfuric acid solution

Sulfuric acid (M)	Li content (mg)	Recovery rate (%)
0.5	307.85	76.20
1	354.31	87.70
2	403.19	99.79
3	403.48	99.87

B. Effect on stirring time

10 g of spent LFP powder was mixed with 50 ml of 2M sulfuric acid solution. The stirring speed was maintained at 300 rpm, and then the Li leaching experiment was conducted by changing the stirring time to 5, 10, 30, and 60 minutes. After the experiment, the solid and liquid were separated through decompression filtration, and ICP-OES analysis was performed to analyze the Li content and

phase of the filtered solution. The filtered solution was dried at 400° C for 24 h, and the formation of Li₂SO₄ was confirmed through XRD analysis. The results of XRD analysis according to the stirring time have been presented in Fig. 4 below. As a result of the XRD analysis, only the Li₂SO₄ phase was detected when the stirring time was 60 minutes, confirming that only lithium excluding impurities was selectively leached.

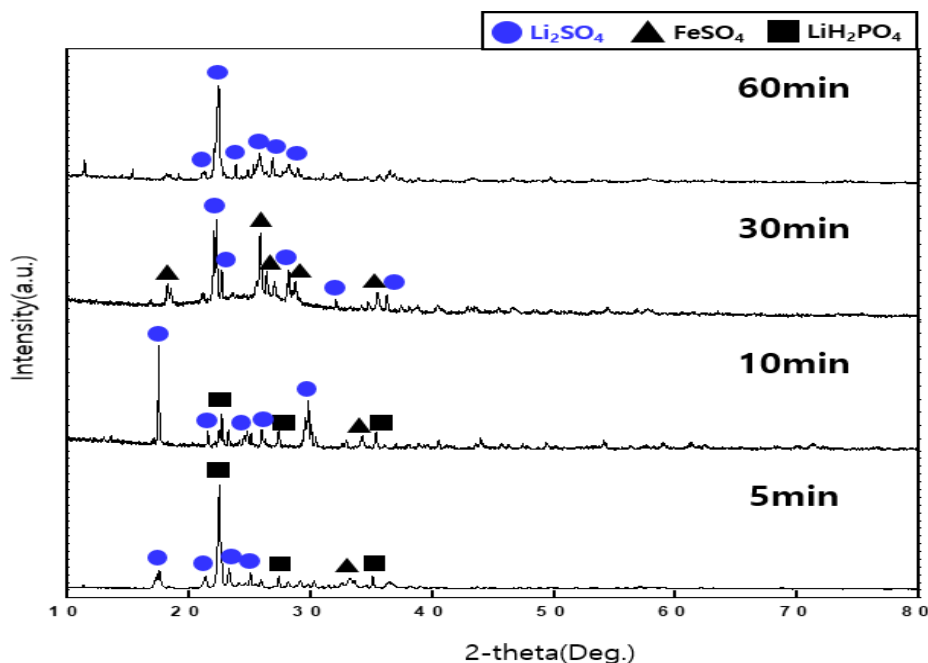


Fig. 4. Results of XRD analysis by stirring time.

Table 3. Li content and Li recovery rate of filtration solution by stirring time

Stirring time (min)	Li content (mg)	Recovery rate (%)
5	239.98	59.40
10	269.06	66.59
30	344.59	85.29
60	402.45	99.61

In Table 3 below, Li content measured by ICP-OES analysis of the filtered solution after decompression filtration and the Li recovery rate calculated through Equation (1) has been presented. When the stirring time was set to 60 minutes, the lithium recovery rate was the highest at 99.61%.

C. Effect on the solid-liquid ratio

10 g of spent LFP powder was put and mixed in a beaker containing 30 ml, 50 ml, and 70 ml of a 2M sulfuric acid solution, respectively. The stirring speed was maintained at 300 rpm, and the stirring was conducted for 60 minutes. After the experiment, the solid and liquid were separated through decompression filtration. ICP-OES analysis was performed to measure the Li content in the filtered

solution; the solution was dried at 400° C for 24 h, and XRD analyzed its phase.

In Fig. 5 below, the results of XRD analysis according to the solid-liquid ratio of sulfuric acid solution and LFP powder have been presented. When the solid-liquid ratio was 1:5, only the Li_2SO_4 phase was detected, indicating that lithium excluding impurities was selectively leached.

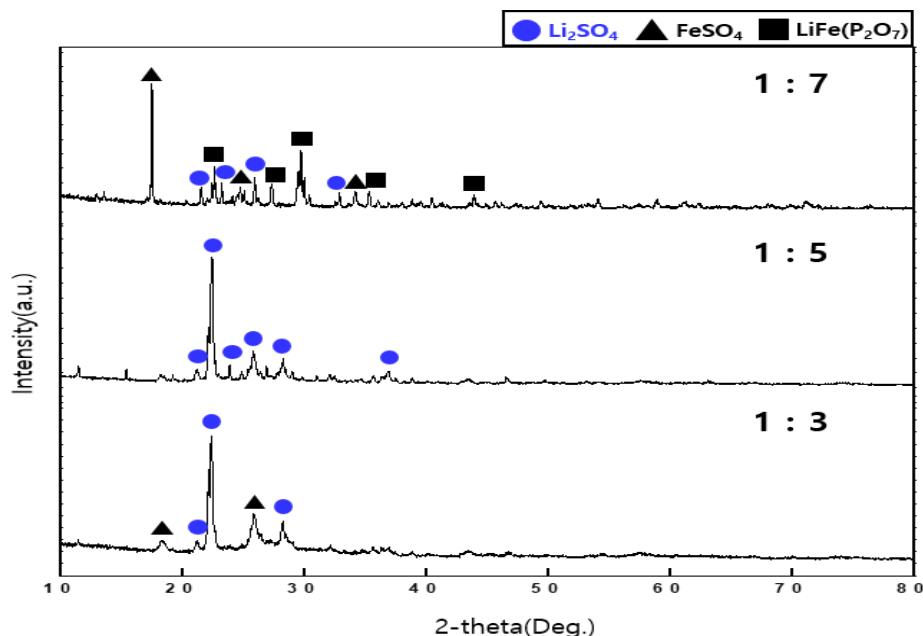


Fig. 5. Results of XRD analysis according to reaction weight ratio of sulfuric acid solution and LFP powder.

Table 4. Li content and Li recovery of the filtration solution according to the reaction weight ratio of sulfuric acid solution and LFP powder

reaction weight ratio (LFP : sulfuric acid solution)	Li content (mg)	Recovery Rate (%)
1 : 3	310.06	76.74
1 : 5	402.98	99.74
1 : 7	403.2	99.80

In Table 4 below, the Li content measured by ICP-OES analysis of the filtered solution after decompression filtration has been presented. As a result of calculating the recovery rate through the ICP-OES analysis results and Equation (1), the recovery rate was more than 99.7% in both 1:5 and 1:7 conditions. However, as a result of XRD analysis and as presented in Fig.5, impurities were detected at the solid-liquid ratio of 1:7, whereas only the Li_2SO_4 phase was detected at the solid-liquid ratio of 1:5, confirming that the solid-liquid ratio of 1:5 was the optimal condition.

IV. CONCLUSION

In this study, a method for selectively recovering Li excluding impurities through a leaching reaction between LFP (LiFePO_4) powder, an active cathode material in spent lithium secondary batteries, and a sulfuric acid solution (H_2SO_4) was investigated. To increase the Li recovery rate,

the optimal conditions were derived for each M concentration in sulfuric acid solution, the stirring time, and the solid-liquid ratio of the sulfuric acid solution and the LFP powder. After the experiment, the filtered solution was analyzed by ICP-OES to measure the Li content and to calculate the recovery rate, and the solution was dried at 400° C for 24 hrs, and XRD analyzed the presence of residual impurities and phase. As a result of the experiment, the optimal process conditions for selectively recovering Li from spent LFP powder were derived as 2M H_2SO_4 , the stirring time of 60 minutes, and the solid-liquid ratio of sulfuric acid solution and LFP powder of 1:5, and at this time a lithium content of 403.19mg and lithium recovery rate of 99.79% was achieved.

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